INTERNATIONAL CLAY CONFERENCES

aipea

XVIII ICC

Dublin, Ireland

13–18 July 2025

PROGRAMME AND ABSTRACTS

Mineralogical Society of the UK and Ireland

Est. 1947

Trinity College Dublin

The University of Dublin

COMMITTEES

Local organising committee

Steve Hillier (Clay Minerals Group)
David Chew (Trinity College Dublin)
Emma Tomlinson (Trinity College Dublin)
Kevin Murphy (Mineralogical Society of the UK and Ireland)
Russell Rajendra (Mineralogical Society of the UK and Ireland)

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Helen Pendlowski
Peter Ryan

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WELCOME

We are delighted to welcome all delegates, in-person and remote, to Dublin for this the eighteenth edition of the International Clay Conference (ICC). Thanks to your enthusiasm and willingness to participate, we have a jam-packed programme for you to enjoy. We have sessions numbering up to 47 and we have five plenary lectures, four pre-conference workshops and two mid-week field trips.

The theme of the conference is 'Sustaining Clays' to emphasise the myriad roles played by clays, clay minerals, and the closely allied layered double hydroxides and natural zeolites in sustainable development, the use and management of very many resources, and their bright future in tomorrow's world.

Our key aim with this conference is to integrate our diverse industrial, technological, and academic worlds of clays and clay minerals with a blend of sessions, workshops and field trips assembled under three sub themes where clay research and applications flourish namely "Materials and technologies", "Food, Water and Environment", and "Terra and extra-Terra".

You should have received a copy of the 'Joining Instructions'. If not, the document is available from the Conference Staff at registration/help desk. This should answer most if not all of the questions you may have. If it does not, please let conference staff/convenors know.

Our international team of volunteers will be identifiable by their T-shirts. They will be mostly responsible for running the hybrid aspect of our meeting ensuring that our remote participants have a rewarding conference experience.

The Chair of the Clay Minerals Group (Helen Pendlowski) and the President of the Mineralogical Society of the UK and Ireland (Sam Saw) will be present at the conference. Say hi!

We encourage all delegates to visit the booths of our sponsors/exhibitors and engage with their representatives. Our conference could not run without their support and attendance.

Below is a QR code and a url. Both of these will take you to our online form for assessing student presentations at the conference. Please do review student work; your assessments will be a big help to the 120+ students that are presenting their research as talks and posters. We have prizes coordinated across the various awarding societies for ten students.

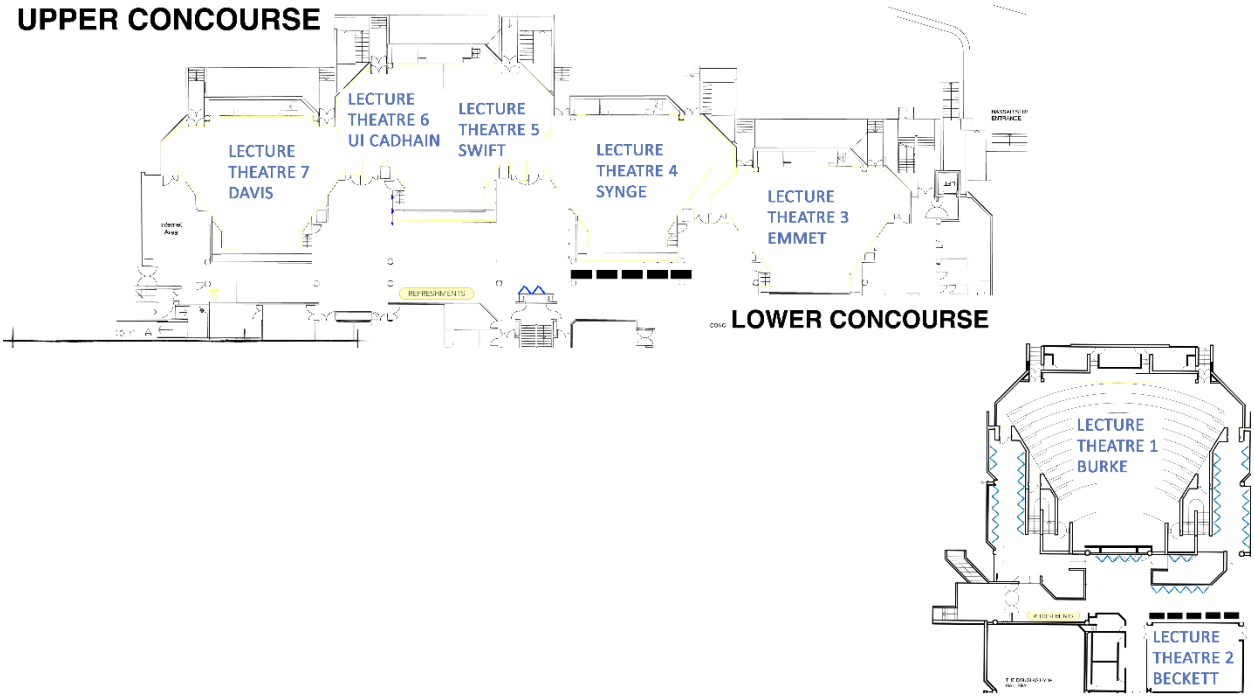
Lastly, but perhaps most importantly, we hope you enjoy this conference, first and foremost, for the opportunities it presents to network and discuss clays and their related phases, with old colleagues you have met before but especially with new colleagues you have yet to meet and forge new friendships.

Steve Hillier
The James Hutton Institute, Aberdeen
David Chew, Emma Tomlinson
Trinity College, Dublin
Russell Rajendra, Kevin Murphy
Mineralogical Society

Scan this QR code or follow the link to the online form to assess student presentations

https://icc.aipea.org/students/

PROGRAMME



AT A GLANCE 1 – PLENARY LECTURES

All lectures below will take place in the Burke Lecture theatre. In case of lack of seating, the lecture will also be broadcast in the Emmet Lecture theatre.

Monday 08:40 — *Plenary - George Brown Lecture, Clay Minerals Group*
About comparison of claystones as potential host rocks for radioactive waste
Kaufhold, S.

Monday 17:05 — *Plenary - Marion L. and Chrystie M. Jackson Mid-career Clay Scientist Award Lecture, Clay Minerals Society*
Small Minerals, Big Impacts: A Geochemist's Approach for Resource Recovery
Tang, Yuanzhi

Tuesday 08:30 — *Plenary - Marilyn and Sturges W. Bailey Distinguished Member Award Lecture, Clay Minerals Society*
Clay mineral-microbe interactions and applications
Dong, H., Zeng, Q., Sheng Y. and X. Liu

Thursday 08:30 — *Plenary - Pioneer Lecture – Clay Minerals Society*
Understanding the structure and dynamics of clay and other layered minerals and their interfaces using molecular modelling – a perspective
H. Chris Greenwell

Friday, 08:30 — *Plenary - Bradley Award Lecture, AIPEA*
Clay minerals formation in MgO-SiO_2-H_2O low temperature system by hydrothermal synthesis: A study in function of Mg/Si molar ratio and pH
Jourdain, A., Dutournié, P., Michelin, L., Le Meins, J.-M., Brendlé, J., Michau, N., Martin, C., and Dzene, L.

AT A GLANCE 2

	Lecture theatre 1-Burke	Lecture theatre 2-Beckett	Lecture theatre 3-Emmettt	Lecture theatre 4-Synge	Lecture theatre 5-Swift	Lecture theatre 6-Ui-Cadhain	Lecture theatre 7-Davis
Monday	Nuclear #20		Calcined #31	Ceramic #13	Zeolites #10	Synthesis #34	Tube #25
			Di-Tri-Smec #4	Photon #28	Catalysts #23	Teaching #5	Jackson #7
Tuesday	Nuclear #20 cont.	Iron-rich #47	Mod-Rem #44	Health #35	Origin #6	Universal #1a	1D-nano #26
	Layered #12	Universal #1b			Mining #40	Mars #2+11	
Thursday	Smart #29	Carbon-Soil #39+42	Mech-Activ #33	Geotech #30	38+43-Chem-Rem	Layer-charge #19	Compute #27
		Industrial #17			Diagenetic #18	Rad-Temp #21	Layer-Life #3+16
Friday	Eco Clay #32		Panel led discussion	Ordered #14	Critical #8+9		Health tech #36
				Green #24			

Session	Session Title	Day	Room
#1a	Universal Session	Tue	6-Ui Cadhain
#1b	Universal Session	Tue	2-Beckett
#3+16	Sorption and intercalation in layered materials: from origins of life to material science	Thu	7-Davis
#4	From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis	Mon	3-Emmet
#5	Teaching, History, and Future of Clay Mineralogy (in honor of Dewey Moore and Bruce Velde)	Mon	6-Ui Cadhain
#6	Origin and Age of Clay Minerals in Soil and Sediment	Tue	5-Swift
#7	Soil and Clay Chemical Analysis – Symposium Honoring M.L. Jackson (Short title: Jackson Symposium)	Mon	7-Davis
#8+9	Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential	Fri	5-Swift
#10	Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges	Mon	5-Swift
#2+11	Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies	Tue	6-Ui Cadhain
#12	Advances in structural characterization of layered compounds	Tue	1-Burke
#13	Clay Applications in Ceramics	Mon	4-Synge
#14	Materials via Ordered Interstratifications	Fri	4-Synge
#17	Industrial Applications of Clays	Thu	2-Beckett
#18	Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development	Thu	5-Swift
#19	Smectite Layer Charge and Interlayer Environment: Structure, Alteration, and Environmental and Technological Significance	Thu	6-Ui Cadhain
#20	Science and Engineering of Clays for Nuclear Waste Disposal	Mon Tue	1-Burke
#21	Impact of temperature on bentonite barrier systems based on findings from in situ experiments in the context of radioactive waste disposal	Thu	6-Ui Cadhain
#23	Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes	Mon	5-Swift
#24	Greenhouse Gas Remediation	Fri	4-Synge

#25	Fundamentals of Tubular Nanoclays	Mon	7-Davis
#26	1D Nanoporous Clay Materials and Their Industrial Applications	Tue	7-Davis
#27	Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces	Thu	7-Davis
#28	Nanoelectronic and Nanophotonic Applications	Mon	4-Synge
#29	Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials	Thu	1-Burke
#30	Clays in Geotechnics – Problems and Applications	Thu	4-Synge
#31	Advances in Calcined Clays as Supplementary Cementitious Materials in Blended Cements	Mon	3-Emmet
#32	Sustainable and eco-friendly clay-based materials	Fri	1-Burke
#33	Mechanical and Mechano-chemical Activation of Clays	Thu	3-Emmet
#34	Synthesis of geo-inspired clay minerals and associated hybrids	Mon	6-Ui Cadhain
#35	The Role of Clays in Human Health and Biomedical Sciences	Tue	4-Synge
#36	Clay Materials in Healthcare Technologies	Fri	7-Davis
#38+43	Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies	Thu	5-Swift
#39+42	Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils	Thu	2-Beckett
#40	Clays in Mining	Tue	5-Swift
#44	Synthesis and Applications of Modified Clays in Environmental Remediation	Tue	3-Emmet
#47	Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling	Tue	2-Beckett
	Panel-led discussion: Questions concerning clay minerals in radioactive waste disposal	Fri	3-Emmet

AT A GLANCE 3

MONDAY, 14TH JULY 2025

Session Number	Session Title	Room
#20a	Science and Engineering of Clays for Nuclear Waste Disposal	1-Burke
#31	Advances in Calcined Clays as Supplementary Cementitious Materials in Blended Cements	3-Emmet
#4	From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis	3-Emmet
#13	Clay Applications in Ceramics	4-Synge
#28	Nanoelectronic and Nanophotonic Applications	4-Synge
#10	Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges	5-Swift
#23	Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes	5-Swift
#34	Synthesis of geo-inspired clay minerals and associated hybrids	6-Ui Cadhain
#5	Teaching, History, and Future of Clay Mineralogy (in honor of D. Moore and B. Velde)	6-Ui Cadhain
#25	Fundamentals of Tubular Nanoclays	7-Davis
#7	Soil and Clay Chemical Analysis – Symposium Honoring M.L. Jackson	7-Davis

TUESDAY, 15TH JULY 2025

Session Number	Session Title	Room
#20b	Science and Engineering of Clays for Nuclear Waste Disposal	1-Burke
#12	Advances in structural characterization of layered compounds	1-Burke
#47	Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling	2-Beckett
#1b	Universal Session	2-Beckett
#44	Synthesis and Applications of Modified Clays in Environmental Remediation	3-Emmet
#35	The Role of Clays in Human Health and Biomedical Sciences	4-Synge
#6	Origin and Age of Clay Minerals in Soil and Sediment	5-Swift
#40	Clays in Mining	5-Swift
#1a	Universal Session	6-Ui Cadhain
#2+11	Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies	6-Ui Cadhain
#26	1D Nanoporous Clay Materials and Their Industrial Applications	7-Davis

THURSDAY, 17TH JULY

Session Number	Session Title	Room
#29	Smart Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials	1-Burke
#39+42	Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils	2-Beckett
#17	Industrial Applications of Clays	2-Beckett
#33	Mechanical and Mechano-chemical Activation of Clays	3-Emmet
#30	Clays in Geotechnics – Problems and Applications	4-Synge
#38+43	Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies	5-Swift
#18	Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development	5-Swift
#19	Smectite Layer Charge and Interlayer Environment: Structure, Alteration, and Environmental and Technological Significance	6-Ui Cadhain
#21	Impact of temperature on bentonite barrier systems based on findings from in situ experiments in the context of radioactive waste disposal	6-Ui Cadhain
#27	Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces	7-Davis
#3+16	Sorption and intercalation in layered materials: from origins of life to material science	7-Davis

FRIDAY, 18TH JULY

Session Number	Session Title	Room
#32	Sustainable and eco-friendly clay-based materials	1-Burke
	Panel-led discussion: Questions concerning clay minerals in radioactive waste disposal	3-Emmet
#14	Materials via Ordered Interstratifications	4-Synge
#24	Greenhouse Gas Remediation	4-Synge
#8+9	Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential	5-Swift
#36	Clay Materials in Healthcare Technologies	7-Davis

Detailed Programme

MONDAY 14th July

Lecture theatre 1-Burke

08:30 — *Opening Ceremony*
08:40 — *Plenary George Brown Lecture*
About comparison of claystones as potential host rocks for radioactive waste
Kaufhold, S.

09:25 — *Sponsor's Presentation*
09:30 — *Break*

Science and Engineering of Clays for Nuclear Waste Disposal (session #20)

Marcelo Javier Sanchez Castilla, Texas A&M University, USA, msanchez@civil.tamu.edu
Youjun Deng, Texas A&M University, USA, yjd@tamu.edu
Ian C. Bourg, Princeton University, USA, bourg@princeton.edu
Maria Victoria Villar Galicia, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain, mv.villar@ciemat.es
David Schofield, Nuclear Waste Services, UK, david.i.schofield@nuclearwasteservices.uk

09:35 — *Keynote*
Clay in the Context of the Swiss Geological Repository
Leupin O.X.

10:05
The Sandwich shaft sealing experiment at Mont Terri Rock Laboratory – Selected aspects of clay science
Emmerich, K., Hinze, M. and Nagel, T.

10:25
Student
Effect of boundary conditions and heterogeneities on the hydromechanical behaviour of two Calcium bentonites
Nitsch, A., Asaad, A., Emmerich, K., Wichtmann, T. and Baille, W.

10:45
The Effect of High Temperatures on the Swelling Pressure of Expansive clays
Sanchez, M., Al-Masri, R., Sanchez, C., Deng, Y., Greathouse, J. and Matteo, E.

11:05 — *BREAK*

11:25
Student Remote
Effect of high temperature and exchange cations on the layer charge and swelling pressure of compacted bentonite
Sanchez-Avellaneda, C., Deng, Y. Greathouse, J. Al-Masri, R. Matteo, E. and Sanchez M.

11:45
Remote
Applications of Thermo-Hydro-Mechanical-Chemical and Gas Transport (THMC-G) Material Models in Engineered Barrier Systems (EBS) Using CODE_BRIGHT
Erdem Toprak and Sebastia Olievlla

12:05
Student
Investigating the effect of NaCl on the volumetric behaviour of bentonite
Parisa Samadi, Matteo Pedrotti and Rebecca Lunn

12:25 — *Keynote*
Evidence of an alkaline reaction in a 15-year iron powder–compacted bentonite interaction
Cuevas, J.F., Mota, C., Torres, E., Fernandez, R., Martín, P.L., Ruiz, A.I., Ortega, A., Garralón, A., Turrero, M.J.

12:55 — *LUNCH*

14:00
Student
An XAS study on the effect of ionizing radiation on the redox state of the structural iron in hydrated clay minerals
Lavauzelle, N., Jonsson, M., Holmboe, M.

14:20
Influence of salinity gradients on the diffusion of water and ionic species in dual porosity clay samples
Emmanuel Tertre, Thomas Dabat, Jingyi Wang, Sébastien Savoye, Fabien Hubert, Baptiste Dazas, Christophe Tournassat, Carl I. Steefel and Eric Ferrage

14:40
Effects of Alkaline and Saline Conditions on Bentonite Alteration, Cesium and Iodine Retention, and Key Performance Parameters
Ja-Young Goo, Seonyi Namgung, Sang-Ho Lee, Jang-Soon Kwon and Ho Young Jo

15:00
Student Remote
Cs sorption onto clays from different deposits: what controls the process?
Menshikova-Tonyan I., Semenkova A., Svitelman V., Krupskaya V., Romanchuk A., Kalmykov S.

15:20
A generic kaolinite sorption model for a consistent radionuclide sorption database
Marinich, O., Miron, G.D., Baeyens, B., Marques Fernandes M., Zechel, S., Bok, F. and Brendler, V.

15:40
CEC as quality proof for quantification of smectitic phases in lower Cretaceous clay rocks – illite-smectite ± pure smectite?
Dohrmann, R., Ufer, K.

16:00 — *BREAK*

16:00 — *Early Career Clay Scientist Meet and Mingle Coffee (lower concourse)*

17:05 — *Plenary Jackson Lecture*
Small Minerals, Big Impacts: A Geochemist's Approach for Resource Recovery
Tang, Yuanzhi

Lecture theatre 3-Emmet

Advances in Calcined clays as supplementary cementitious materials in blended cements (session #31)

Karen Scrivener, EPFL, Switzerland. karen.scrivener@epfl.ch
Shashank Bishnoi, IIT Delhi, India. shashank.bishnoi@civil.iitd.ac.in
Alastair Marsh, EPFL, Switzerland. alastair.marsh@epfl.ch

09:35
Student
Characterization of the local Al environment in calcined clays using transmission electron microscopy
Mouro, E., Paris, M., Gaillot, A.C., and Deneele, D.

09:55
Student
The Potential of Co-calcining Bentonite and Calcite for SCM Production: Insights into Ca2SiO5 Stabilization
Mohammad Mobasheri, Alastair T.M. Marsh and Karen L. Scrivener

10:15
Enhancing the rheology, reaction kinetics and early-age strength of limestone calcined clay cement (LC3) with sodium silicate addition
Xiaodi Dai, Marcus Yio, Haoming Wu, Susan A. Bernal, Chris Cheeseman, Hong S. Wong

10:35 — *Keynote*
Understanding Reactivity: From Nanoscale Layer Thinning to a 5-minute UR2 Test
Nishant Garg

11:05 — *BREAK*

11:25
Remote
Enhanced performance of blended cements with high levels of calcined clay
Sharma, P.K., Rehman M.UL., Babatola, O., MacLeod, A.J.N., **Gates, W.P.**

11:45
Characterisation, activation, reactivity and performance of heterogenous natural clays
Arezou Baba Ahmadi

12:05
Performance of cements blended with limestone and calcined 2:1 clays with focus on early hydration, sulfate demand, setting and workability
Maier, M., Schaller, V., Shams, T., Panzer, M., Scherb, S. and Beuntner, N.

12:25
Student
Thermal Performance of Calcined Clay Supplementary Cementitious Materials in Mass Concrete Applications
Sristi Das Gupta, Christopher Ferraro, Oscar Cardenas, Kejin Wang, Maria Juenger, Kimberly Kurtis, Kyle Riding

12:45
Automatic control of raw clay quality and clay calcination in the cement industry through XRPD
Negrão, L. B. A., Pernechele, M., Olmeda G., **O'Meara P.**

13:05 — *LUNCH*

Lecture theatre 3-Emmet

From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis (session #4)

George E. Christidis, Technical University of Crete, Greece, gchristidis@tuc.gr
Manuel Pozo, Universidad Autónoma de Madrid, Spain, manuel.pozo@uam.es
Telma Musso, Universidad Nacional del Comahue, Argentina, telma.musso@probien.gob.ar

14:15
Student
Natural 1-layer and 2-layer hydrated montmorillonites are resilient to changes in basal spacing despite major cation substitution
Zabala, A.B., Cuevas, J. and Villar, M.V.

14:35
Characterization of trioctahedral smectite-sepiolite assemblages in the Neogene Madrid Basin (Spain): Genetic considerations
Pozo, M., Villa, L. and Pérez-Abad, A.

14:55
Student
Predicting cis- and trans-vacant configurations in smectites using X-Ray Diffraction
Lorenzo, A., García-Romero, E.-, Suárez, M. and Hillier, S.

15:15
Influence of Detrital Input on Saponite Authigenesis in the Pre-Salt Barra Velha Formation, Santos Basin
Silva, L.A.C., **Mexias, A.S.**, Da Silva, M.D., Gomes, M.E.B., Rossoni, R.B., Sobiesiak, J.R.S., Bongiolo, E., Semeler, A.R., Jantsch, L.C.

15:35
Remote
Geochemical constraints of Upper Cretaceous Na-bentonite beds from Pellegrini Lake deposit, Argentina
Musso, T.B., Christidis, G. and Pozo, M.

15:55 — *BREAK*

Lecture theatre 4-Synge

Clay Applications in Ceramics (session #13)

Fernanda Andreola, University of Modena and Reggio Emilia, Italy. andreola.fernanda@unimore.it
Fakher Jamoussi, Water Research and Technologies Center, Tunisia. fakher.jamoussi@certe.rnrt.tn
Sonia Conte, Istituto di Scienza, Tecnologia e Sostenibilità per lo Sviluppo dei Materiali Ceramici-ISSMC, Italy, sonia.conte@issmc.cnr.it

09:35
Student Remote
Influence of diatomite addition to two types of clay on the hydrothermal synthesis of zeopolymer materials
Cotón, N., Morita, A.K.M., Sánchez-Arcos, O., Alonso-Azcárate, J., Fernández, R., Ruiz, A.I., Conde-Sánchez, A., Martínez-Rodríguez, A.M., Jamoussi, F. and Moreno-Maroto, J.M.

09:55 — *Keynote*
Case Study of Spanish, Italian and Portuguese Clays as Raw Material for Lightweight Workable Aggregates (LWAs)
Cotes-Palomino, M.T, López-García, A.B., Iglesias-Godino, F.J., Alonso-Acárate, J., Moreno-Maroto, J.M., Barbieri, L., Lancellotti, I., Andreola, F., Labrincha, J., **Martínez-García, C.**, Cobo-Ceacero, C.J.

10:25
Student
Influence of Sewage Sludge Ash on Brick Properties Using Diverse Clay Types
Feldthus, F.B., Ottosen, L.M., Bertelsen, I.M.G. and Kirkelund G.M.

10:45 — *Keynote*
From Design to Valorization: Circular and Innovative Practices for the Use of Clay Products in Construction
Díaz Rubio, **Roberto**, Millanes Sánchez, Marta, Peces Martín, Celia, Rodriguez Chirico, Caterina

11:15 — *BREAK*

11:35
Student
Relationship between the presence of iron and the sintering atmosphere on the final properties of kaolin-based ceramics
Guillemin, F., Lecomte-Nana, G., El Hafiane, Y., Duttine, M., Peyratout, C. and Smith, A.

11:55
Energy savings in silicate ceramics through Optimization of the raw material mix
Piribauer, C.J., Haeusser, S., Friedrich, H. and Stepanyan, M.

12:15
Zeolites as ceramic raw materials for feldspar substitution in porcelain stoneware tiles production
Chiara Molinari, Sossio Fabio Graziano, Guia Guarini, Sonia Conte, Michele Dondi, Concetta Rispoli, Piergiulio Cappelletti, Chiara Zanelli

12:35
Student
Mineralogical, physico-chemical and geotechnical characterization of Yagoua clays (Far North Cameroon) for application in traditional ceramics
Moongon Obam, B.I., Mache, J.R., Balo Madi, A., Manjia, M.B. and Fagel, N.

12:55
Brazing of ceramics with reactive metallic alloys and oxide glasses
Hodaj F.

13:15 — *LUNCH*

Lecture theatre 4-Synge

Nanoelectronic and Nanophotonic Applications (session #28)

Jon Otto Fossum, Norwegian University of Science and Technology, Norway, jon.fossum@ntnu.no
Raphaela de Oliveira Gonçalves, LNLS/CNPEM, Brazil, raphaela.goncalves@lnls.br
Ingrid David Barcelos, LNLS/CNPEM, Brazil, ingrid.barcelos@lnls.br
Alisson Ronieri Cadore, LNNano - CNPEM, Campinas, Brazil, alisson.cadore@lnnano.cnpem.br

14:05 — *Keynote*
Naturally occurring 2D semiconductor with antiferromagnetic ground state
Pacakova, B., Lachtingen-Dahl, B., Kirch, A., Demchenko, H., Osmundsen, V., Fuller, Ch.A., Chernyshov, D., Zakutna, D., Miranda, C.R., Raaen, S., Fossum, J.O.

14:35
Remote
Ultra-confined plasmons reveal moiré patterns in a twisted bilayer graphene-talc heterostructure
Barbosa, T. C., Chaves, A. J., Freitas, R. O., Campos, L. C., Barcelos, I. D.

14:55
Student
Ionic Transport in 2D Slits with Angstrom Precise Confinement Control
Stevenson, D. M. and Breu, J.

15:15 — *BREAK*

15:35
Remote
Ultrathin natural biotite as a layered dielectric for van der Waals heterostructure and device applications
de Oliveira, R, Rodrigues, G. L., de Oliveira, R. C., Malachias, A., Teixeira, V. C., de Oliveira, A. J. A., Gobato, Y. G., Barcelos, I. D. and **Cadore, A. C.**

15:55
Towards a delamination of iron(II)-rich synthetic mica
Jourdain, A., Thanner J. and Breu, J.

16:15
Remote
Defects in Natural 2D Materials
Thamires C. Soares, Raphaela de Oliveira, Verônica C Teixeira, Yara Galvão Gobato, Luiz Fernando Zagonel, and Ingrid D. Barcelos

16:35
Manipulating heterogeneities of clay minerals at the nanoscale to tune their properties for nanodevice applications
De Oliveira, Raphaela, Gobato, Y. G., Freitas, R. O., Teixeira, V. C., Malachias, A., Krambrock, K., Cadore, A. R. and Barcelos, I. D.

Lecture theatre 5-Swift

Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges (session #10)

Hossein Kazemian, University of Northern British Columbia, Canada, hossein.kazemian@unbc.ca
Fernando Borsatto, Zeogroup and Conquer Business School, Brazil, fb.faria82@gmail.com
Bruno Azevedo, Università di Pisa, Italy, bruno.piodeazevedo@phd.unipi.it

09:35
Geological value of the Si/Al ratio in natural zeolites: critical assessment of selected precursor reactions
Campbell, L.S., and Bish, D.L.

09:55
Student Remote
Hydronium exchange in ion exchange and dissolution of feldspathoids sodalite and cancrinite
Lin, C.W., Graefe, M., Howe, J.A., and Deng, Y.

10:15
Remote
Characterization of Natural Zeolites from the Republic of Argentina
Vigna, Belen, Cozzi, Guillermo, Sapag, Karim, Lamas, Diego

10:35
Student
Natural Zeolite Modified with MnOx Coating: Treatment of Mn^{2+} and Fe^{2+} contamination
de Azevedo, B.F.P., Mugnaioli,E. Petrini, R., Perchiazzi, N., Ghezzi, L.

10:55 — *BREAK*
11:15
Remote
Challenges of Scaling Resilience: A Critical Review of Pettit et al. (2010) in the Natural Zeolites Sector
Cruz, J.C.

11:35 — *Keynote*
Actual and expected application of zeolite for remediation and waste management of radioactively contaminated nuclear site
Koyama, T., Hijikata, T. and Uozumi, K.

12:05
Modified Zeolite for Groundwater Treatment: A Brazilian Plant Study
Maronezi, V., Borsatto, F., Silva, L.B., Silva L.M. and Sousa, A.B.M.

12:25
Synthesis of Zr^{4+}/Ag^{+} Modified Zeolite for Fluoride and Pathogen Removal
Mudzielwana, R., and Nemakanga, S

12:45 — *LUNCH*

13:05

Student

Zeolitic Tuff for Ammonium Recovery from Anaerobic Digestates: Efficiency, Optimization, and Large-Scale Potential Application

Alberghini, M., Ferretti, G., Galamini, G., Botezatu, C. and Coltorti, M.

13:25

Assessment of the Potential Role of Zeolites in Biological Electro Molecular Mechanisms

Cortés Hernández, F.A., Insignares-Carrione, E., and Bolaños Gómez, B.

13:45

Evaluation of Philippine natural zeolite-based particle film for pest management in cacao

Olegario, E.M., Barrion, A., Santos, K.L., Esguerra, J.M. and Amalin, D.

14:05 — *BREAK*

Lecture theatre 5-Swift

Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes (session #23)

Ambra Maria Fiore, Università degli studi di Bari, Italy. ambra.fiore@uniba.it
Alfin Kurniawan, Zhejiang University of Technology, Hangzhou 310032, China. alfin_kur@yahoo.com
Chun Hui Zhou, Zhejiang University of Technology, Hangzhou 310032, China. clay@zjut.edu.cn

14:25

Designing Montmorillonite-Supported Metal Oxide Catalysts for Efficient Gas-Phase Glycerol Oxydehydration

Kurniawan, **Alfin**, Roy, Tania, and Zhou, Chun Hui

14:45

Design of clay-based catalysts assisted by machine-learning

Lo Dico, G., Esteban Cubillo, A., Haranczyk M.

15:05

Construction strategies of the organic-inorganic interface structures in phyllosilicates-based nanozymes and their environmental applications

Shiyong Sun, Ke Wang, Jin Liu, Yifan Zeng, Yan Liu

15:25

Remote

Silica/clay based Composites used in the Adsorption of FFA, Optimizing the Process by RSM

Kepdieu J. M., Djangang C.N., Tchanang G., Njimou J.R., Maicaneanu S.A. and Tizaoui C.

15:45

Amino-functionalized porous nanosilica modulates Pt nanoparticle morphology for low-temperature toluene catalytic combustion

Zhang, **X**, Chen, Q., and Zhu, R.

16:05 — *Keynote*
Acidified Montmorillonite and Site-Specific V-Doping Keggin-Type NH4PM Catalysts for Sequential Conversion of Glycerol to Acrylic Acid and Allyl Alcohol
Tania Roy, Alfin Kurniawan, Jin Wang, **Chun Hui Zhou**

Lecture theatre 6-Ui Cadhain

Synthesis of geo-inspired clay minerals and associated hybrids (session #34)

Pierre Picot, CEA Paris-Saclay, France. pierre.picot@cea.fr
Sabine Petit, Université de Poitiers, France. sabine.petit@univ-poitiers.fr
Liva Dzene, Université de Haute-Alsace, France. liva.dzene@uha.fr
Vanessa Prévot, Institut de Chimie de Clermont-Ferrand, France. vanessa.prevot@uca.fr
Chun-Hui Zhou, Zhejiang University of Technology, China. clay@zjut.edu.cn
Hongping He, Chinese Academy of Sciences, China. hehp@gig.ac.cn
Makoto Ogawa, VISTEC, Thailand. waseda.ogawa@gmail.com
Antoine Thill, University Paris-Saclay, France. antoine.thill@cea.fr
Kirill Shafran, BYK Additives Ltd., Widnes, UK, kirill.shafran@altana.com
Jocelyne Brendlé, Université Haute-Alsace, France, jocelyne.brendle@uha.fr

09:35
Diameter and chirality of natural and synthetic imogolite
Picot, Pierre, Gobeaux, Frédéric, Charpentier, Thibault, Belloni, Luc, Takahara, Atsushi, Wada, Shin-Ichiro and **Thill**, **Antoine**

09:55
From molecular precursors to allophane and imogolite: evidence and importance of intermediate nanostructures
Pierre Picot, Fabienne Testart, Frederic Gobeaux, Luc Belloni and Antoine Thill

10:15
Student
Experimental assessment of pH dependent allophane formation rates at low temperatures
Kayla R. Russo, Nicole M. Fernandez

10:35 — *Keynote*
Strategy in host-guest assembly for organic light emitter interleaved into layered double hydroxide: to retain or release, that is the question
Leroux, F.

11:05 — *BREAK*

11:25
Student Remote
The influence of reaction conditions on kaolinite synthesis
Koroleva T.A., Pokidko B.V., Nesterenko A.A., Morozov I.A. and Krupskaya V.V.

11:45
Formation of iron-rich phyllosilicates in the $FeO–SiO_2–H_2O$ system during hydrothermal synthesis as a function of pH
Dzene, L., Doggaz, A., Dutournié, P., Inoué, S., Abdelmoula, M., Jourdain, A., Le Meins, J.-M., Brendlé, J., Martin, C. and Michau, N.

12:05
Student
Synergistic chemical evolution of Fe-smectite and glycine during mineral crystallization
Fkiri, R., Gregoire, B., Baron, F., Geffroy, C., and Petit. S.

12:25 — *LUNCH*

13:25
Experimental evidence for the evolution of crystal chemistry and morphology during saponite growth
Zhang, C.Q., Decarreau, A., Baron, F., Tao, Q., Gregoire, B., Zhu, J.X., He, H.P., **Petit, S.**

13:45
Electrophoretic Mobility Characteristics Resulted from Varying Layer Charge of Smectite
Zhou Chun Hui, Wang Guo Ya, Chen Xiao Lan, Kurniawan Alfin, and Roy Tania

14:05
Student
On the all-inorganic protection of lead halide perovskite nanocrystals from the environment
Clasen, E.B. and Hill, E.H.

14:25
Remote
A straightforward, one-step synthesis of a layered alkylammoniumsiloxane without additives
Fujii, K., Wakahara, T., Iwanade, A., Hattori, M., Higuchi M. and Hayashi, S.

14:45 — *BREAK*

Lecture theatre 6-Ui Cadhain

Teaching, History, and Future of Clay Mineralogy (in honor of Dewey Moore and Bruce Velde) (session #5)

Georg Grathoff, University of Greifswald, Germany, Grathoff@uni-greifswald.de
Bruno Lanson, ISTerre, CNRS, France, bruno.lanson@univ-grenoble-alpes.fr
Paul Schroeder, University of Georgia, USA, schroe@uga.edu

15:05
Dewey Moore: Teacher, Mentor, and Visionary
Grathoff, G.H.

15:25
Teaching Clay Mineralogy: A survey of who, what, where, and how it is being taught
Schroeder, P.A., Grathoff G.H. and Lanson B.

15:45
An update on the multidisciplinary science of applied clay research: A 2023–2025 bibliographic analysis
Biswas, B., Warr L.N. and Naidu R.

16:05
Remote
The future of clay mineralogy: Soil Forensic Examinations Using Advanced Laboratory Source and Synchrotron XRD Techniques
Fitzpatrick R.W., Raven M.D. and Self P.G.

16:25 — *Break*

Lecture theatre 7-Davis

Fundamentals of Tubular Nanoclays (session #25)

Nia Gray-Wannell, The James Hutton Institute, UK. Nia.Gray-Wannell@hutton.ac.uk
Giuseppe Cavallaro, The University of Palermo, Italy. giuseppe.cavallaro@unipa.it
Eirini Siranidi, National Hellenic Research Foundation, Greece. esiranidi@eie.gr
Aasim Shaffi, University College London, UK. aasim.shaffi.17@ucl.ac.uk
Milan Pšenička, Charles University, Czech Republic. milan.psenicka@centrum.cz
Pooria Pasbakhsh, University of Melbourne, Australia. pooria.pasbakhsh@unimelb.edu.au
Yafei Zhao, Zhengzhou University, China, zhaoyafei007@zzu.edu.cn
Mingxian Liu, Jinan University, China, liumx@jnu.edu.cn

09:35
Student
Structure and Dynamics of Water Confined in Halloysite Nanotubes
Pšenička, M. and Pospíšil, M.

09:55
Integrated Computational and Experimental Approach for the Design of Halloysite Clay based Multifunctional Catalysts
Lisuzzo, L., Lazzara, G., Guercio, L., Ferlito, F., Ferrante, F., Bertini, M., Palella, A., Aho, A., Spadaro, L., Murzin, D.Y. and Duca, D.

10:15
Student
Toward Green Catalysis with Halloysite–Gold Nanocomposites Materials
Guercio, L., Ferrante F., Bertini M., Lisuzzo L., Ferlito C., Cavallaro G., Lazzara G., Duca D.

10:35
Filling halloysite nanotubes with functional materials
Liu, M.X., Zhao, P.X., Feng, Y., Chen, X.Y. and Zhou, S.Q.

10:55 — *BREAK*

11:15
Patch halloysite as a clay precursor for hydrogel and multifunctional inorganic films
Calvino, M.M., Lo Bianco, A., Cavallaro, G., Pasbakhsh, P., Lisuzzo, L., Milioto, S., Lvov Y., Lazzara, G.

11:35
Halloysite Nanotubes Under the Microscope: Potential Occupational Risks and Toxicity Indicators
Fantini, R., Glossop, L., Malferrari, D., Castellini, E., Lassinantti Gualtieri, M., Hanuskova, M., Nodari, L., Ogor, J. and Gualtieri, A.F.

11:55 — *Keynote*
Fundamentals of powder XRD data in relation to hydration state, particle morphologies, and nomenclature: a short review of key features
Hillier, S.

12:25
N-methyl formamide (NMF) intercalation in Halloysites
Siranidi, E., Kouseri, A.A., Chryssikos, G.D. and Hillier, S.

12:45 — *Lunch*

Lecture theatre 7-Davis

Soil and Clay Chemical Analysis – Symposium Honoring M.L. Jackson (session #7)

Joseph W. Stucki, University of Illinois at Urbana-Champaign, USA, jstucki@illinois.edu
Janice L. Bishop. SETI Institute, USA, jbishop@seti.org

14:00
Introduction
Stucki, J.W.

14:05
Family Reflections
Conlon, T.

14:15
Reflections of a former student (live remote)
Roth, C.

14:22 — *Keynote*
How M.L. Jackson paved the way for our understanding of the mineralogy of soil clays: the case of the complex nature of interstratified clay minerals
Hubert, F.

14:29
Oxidation-reduction Mechanism of Structural Fe in Clay Minerals
Stucki, J.W.

14:36
Interlayers and Interconnections: The Influence of M.L. Jackson on a Scientific Career
Johnston, C.T.

14:43
Updating life at the edge: Clay mineralogy and the Kamchatka microbial observatory
Schroeder, P.A., and Karpov, G.

14:50
Coupled redox cycling of iron in clay minerals and organic matter transformation across redox interfaces
Dong, H., Zeng, Q. and Sheng, Y.Z.

14:57
Lithium extraction methods influence Li-isotope measurements of clays
Williams, L.B., Bose, M. and Vierling, S.A.

15:04
Remote
The pink book: A useful resource for mineralogical research
Gates, W.P.

15:11
Association of organic carbon with different forms of metal oxides in Australian soils
Bright E. Amenkhienan, Feike A. Dijkstra, Charles Warren, and **Balwant Singh**

15:18
Remote
Career Research: Inorganic Contaminant Interactions at the Mineral-Water Interface and in Soils
Arai, Y.

15:25 — *BREAK*
15:45
Clays on Mars: Their Identification from Orbit and Implications for the Martian Environment
Bishop, J.L.

15:52
Modulation of Sorption and Transformation of Organic Contaminants in Clay Minerals
Li, H., Boyd, S.A., and Teppen, B.J.

15:59
Digital Soil Mineralogy – Some recent advances and future horizons
Hillier, S.

16:06
Mineralogical Controls over Environmental Fate and Behavior of Contaminants and Nutrients
Qafoku, N.P.

16:13
Tracking Mineral and Chemical Changes in Fertilized Soils: Combining Synchrotron X-Ray Techniques and Wet Chemical Methods Reveal Key Insights
Hettiarachchi, G.M.

16:20
Remote
Photochemically-induced abiotic Mn oxide nanoparticle formation
Jun, Y.-S., Gao, Z., Chou, P.-I., and Jung, H.

16:27
An isotope approach to identify biologically mediated reactions and fingerprinting of sources of phosphorus
Jaisi, D.P.

16:34
On the interaction between clays and fungi: an alternative interpretation of the role of medicinal clays
Milling, S., Izaz U.Z., Venieri, D., **Christidis, G.E.**, Rattray, N.J.W., Gounaki, I., Andrusaite A., Hareendran A., Knapp, C.W., Jones, A.X. and Photos-Jones E.

TUESDAY 15th July

Lecture theatre 1-Burke

08:30 — *Plenary Bailey Lecture*
Clay mineral-microbe interactions and applications
Dong, H., Zeng, Q., Sheng Y. and X. Liu

09:15 — *Sponsor's Presentation*
09:20 — *Break*

Science and Engineering of Clays for Nuclear Waste Disposal (session #20b)

Marcelo Javier Sanchez Castilla, Texas A&M University, USA, msanchez@civil.tamu.edu
Youjun Deng, Texas A&M University, USA, yjd@tamu.edu
Ian C. Bourg, Princeton University, USA, bourg@princeton.edu
Maria Victoria Villar Galicia, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain, mv.villar@ciemat.es
David Schofield, Nuclear Waste Services, UK, david.i.schofield@nuclearwasteservices.uk

09:25 — *Keynote*
Granular buffer material after 12 years heating under early repository conditions
Villar, M.V., Gutiérrez-Rodrigo, V., Melón, A.M., Cuevas, J., Mäder, U. and Kober, F.

09:55
Student
Experimental Characterisation of Water Affinity in a Colloidal Silica-Bentonite System
Mutahi, N.S., Pagano, A.G. and Lunn R.J.

10:15
Time-dependent rheology of charge and shape anisotropic clay gels: Role of electric double layer repulsive force in structural rejuvenation process, layer and face charge effects
Leong, Y.K.

10:35
Student
Microstructure observation of cemented bentonite under the swelling state using electron microscopy
Tobimaru Ishiwata, Ryosuke Kikuchi and Tsubasa Otake

10:55 — *BREAK*

11:15
Full pore size distribution of shale by combination of innovative gas adsorption isotherms, mercury intrusion porosimetry and laboratory nano-X ray tomography
Pret, D., Rogers Evarist S., Mazurier A., Faivre M., and Giot R.

11:35
Geochemical characterisation of porewater from poorly indurated Neogene and Paleogene clays in the Netherlands
Fernández, A.M., Nieto, P., de Jong, T., Toshniwal, V., Broere, W., Vardon, P.J., Dieudonne, A-C.

11:55
Remote
The rationale for choosing bentonite in the the engineered barrier system of the Russian deep geological nuclear waste disposal concept
Krupskaya V.V., Zakusin S.V., Koroleva T.A. and Morozov I.A.

12:15
Ion migration under gravitational fields for nuclear waste disposal
Im, J. and Santamarina, J.C.

12:35 — *Lunch*

Lecture theatre 1-Burke

Advances in structural characterization of layered compounds (session #12)

Bruno Lanson, Université Grenoble Alpes - CNRS, France, bruno.lanson@univ-grenoble-alpes.fr
Toshihiro Kogure, University of Tokyo, Japan, kogure@eps.s.u-tokyo.ac.jp

13:45
Thermogravimetric Characterization of Trans- and Cis-Vacant Dioctahedral Smectite Structures Reveals Acid Leaching and Interior Acid Storage
Bickmore, B.R., Villafane-Barajas, S. and Sahai N.

14:05
Confirmation of dehydroxylation of dioctahedral 2:1 layers in TEM by oxygen imaging using OBF-STEM
Kogure, T., Miura, H., Murayama, H., Aoyama, Y., Sato, H., Okumura, T. and Ohnishi, I.

14:25
Atomic-resolution OBF-STEM imaging for beam-sensitive clay minerals
Miura, H., Kogure, T., Okumura, T. and Ohnishi, I.

14:45
Local Surface Charge, Ion Adsorption, and Water Structuring at Layered Mineral–Electrolyte Interfaces: Insights from Atomic Force Microscopy
A. Klaassen, F. Mugele and **I. Siretanu**

15:05
Student
Specific Cr(VI) Removal through Colloidal Nanoparticles: Unraveling the Complex Interactions in Mg/Al LDH Anionic Exchange
Fezraoui A., Cornu D., Steciuk G., Ghanbaja J. and Hebrant M.

15:25
Exchange of interlayer K in mica and implications for mineral identification
Jelavić, S., **Lanson, B.**

Lecture theatre 2-Beckett

Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling (session #47)

Thomas L. Gout, Peking University, China, tlg29@cantab.ac.uk
Yandi Hu, Peking University, China, huyandi@pku.edu.cn
Hailiang Dong, China University of Geosciences, China, dongh@cugb.edu.cn

09:25 — *Keynote*
Ferrihydrite transformation in soils: The impact of organic carbon
ThomasArrigo, L.

09:55
Remote
Schwertmannite formation and properties as an indicator of biogeochemical processes at low pH in acid sulfate weathering environments
Fitzpatrick R.W., Burton E.D., Mosley L.M., Raven M.D. and Self P.G.

10:15 — *Keynote*
Coprecipitation and phase transformation OF Fe(III)/metal hydroxides with organics
Hu, **Yandi**

10:45 — *Break*

11:05
Student
Microbially-mediated ferrihydrite transformation for controlling the mobility of Mo
Jing Zhang

11:25
Photochemical Alterations of Fe-Organic Matter Coprecipitates Promoted the Organic Matter Preservation or Degradation: Role of Organic Matter Functional Groups
Dawei Cai, Yandi Hu, Suona Zhang

11:45
Clay Minerals Regulating the Fe(II)-Catalyzed Ferrihydrite Transformation under Anoxic Conditions
Chen, Q.Z., Zhu, R.L., Wei, H.Y., Wei, S.S., Liu, J., Zhu, J.X., and He, H.P.

12:05
Fe(II)-Catalysed Transformation of Ferrihydrite: Effects of Organic-Functionalised Solid-Liquid Interfaces
Goût, **Thomas L.**, Zhang, J. and Hu, Y.

12:25 — *LUNCH*

Lecture theatre 2-Beckett

Universal (Session #1b)

Simon Kemp, BGS, UK, sjk@bgs.ac.uk
Helen Pendlowski, The James Hutton Institute, UK, helen.pendlowski@hutton.ac.uk
Dave Wray, University of Greenwich, UK, D.Wray@greenwich.ac.uk
Francis Clegg, University of Shefield, UK, f.clegg@shu.ac.uk
Mohamed Mouafon, Institut Clément Ader, FRANCE, mohamed.mouafon@mines-albi.fr
Javier Garcia Rivas, Complutense University of Madrid, SPAIN javier.garcia.rivas@ucm.es

13:35
Ni- and Cr- bearing clays in green siliceous gemstones: a LA-ICP-MS study
Gilg, H.A., Dussubieux, L., Thoresen, L., and Allen, R.

13:55
Student
GALOPER 2: Simulating and Analyzing Crystal Growth Processes in MATLAB
Nye, J.G., Vest, D., Bickmore, B.R., Evans, E.J. and Eberl D.D.

14:15
Remote
Stimuli-induced excimer formation in confined space
Matejdes, M., Škorňa, P., Slaný, M., Klement, R., Kawamata, J., Breu, J.

14:35 — *BREAK*

14:55
Student Remote
Mineralogical Properties of Two Hydrothermal Illite from Yeongdong County, South Korea
Lee, N., Koo, T.-h., Park, H.†, Jeong, H., Son, W., Lee, S., Kogure, T., and Kim, J.

15:15
Student
Characterization of Illite Clay Mineral in Norwegian Quick Clay
Tammen, R.,, Eiser, E., Li, G., de Wijn, A., Zablocka, K., and de Weerdt, K.

15:35
High oxygen barrier coating using non-toxic nanosheet dispersions for flexible food packaging film
Yu, J., Ruengkajorn, K., Crivoi, D.G., Chen, C., Buffet, J.C., O'Hare, D.

15:55
Effect of Al powder and CTAB addition on the properties of porous metakaolin based geopolymers
Mohamed M., Elodie P., Gilles D., Thierry C. and Pascal R.

Lecture theatre 3-Emmet

Synthesis and Applications of Modified Clays in Environmental Remediation (session #44)

Bhabananda Biswas, University of Newcastle, Australia, Bhaba.Biswas@newcastle.edu.au
Bénédicte Prelot, Institut Charles Gerhardt Montpelier, France, benedicte.prelot@umontpellier.fr
Laurence N. Warr, University of Greifswald, Germany, warr@uni-greifswald.de
Himanshu Yadav, Indian Institute of Technology, India, yadav18b@iitg.ac.in

09:25
Student Remote
Exploring Polycaprolactone, Halloysite Nanotubes, Diatomaceous Earth, and their composites for Acetic Acid Mitigation in Museum Display Cases
Carotenuto, M.R., Strlič, M., Kraševec, I., Deraz, R., Cavallaro, G., Chinnici, I., Lazzara, G., Milioto S.

09:45
Nonionic Organoclay: a versatile material for the sorption of organic contaminants
Guégan, R.

10:05
Remote
Elaboration of glyphosate pesticide electrochemical sensor based on synthesized organophilic saponite
Tagne, A.J., Dzene, L., Michelin, L., Josien, L., Rigolet, S., Dedzo, G.K. and Ngameni E.

10:25
Enhanced VOC removal from natural rubber emissions using combined water scrubbing and surface-modified Philippine natural zeolites
Olegario, E.M., Arellano, F.J.T., Lauzon, M.J.A., and Vasquez, M.R.

10:45 — *BREAK*

11:05 — *Keynote*
Organo-modification of clay minerals for remediation, and a focus on bentonite-chitosan adsorbents for heavy metals
Clegg, F., Sammon, C. and Majiya, H.

11:35
Student
Development and evaluation of non-expansible pillared Quick Clay for pollutant removal in water
Coulombe, A., Soubaneh, Y.D., Pelletier, É., Lu, Z., L'Heureux, J.S. and Bardeau, J.F.

11:55
Preparation of calcium-aluminum layered bimetallic hydroxide and study on their adsorption properties for U (VI)
Faqin Dong, Siyi Liao and Jing Bai

12:15
Student
Computational Insights into Styrene Adsorption by Pristine and Modified Smectites
Asbat, A., Scholtzova, E.

12:35 — *LUNCH*

13:45
Student
Targeting zearalenone and deoxynivalenol: Two distinct mycotoxin elimination strategies using kaolin group-based mineral materials
Klaudia Dziewiątka, Jakub Matusik

14:05
Remote
Effective removal of lead (II) ions from aqueous solutions using modified waste mica
Navya, M. and Sandeep, S.

14:25
Use of layered double hydroxides (LDHs) for short chain PFAS removal in water treatment: impact of structure and surface properties
Darracq, G., **Jakob, A.**, Gabas, C., Carême, C.

14:45
Student
Rapid removal of chromium (VI) and diuron from aqueous solution by novel Sepiolite-based nanocomposite: Material characterizations, enhanced performance and mechanism
Zhang, **Chenhao**, Hou, Kai

Lecture theatre 4-Synge

The Role of Clays in Human Health and Biomedical Sciences (session #35)

Cesar Viseras, University of Granada, Spain. cviseras@ugr.es
Saverio Fiore, Italian National Research Council, IMAA, Italy. saverio.fiore@cnr.it
Serena Riela, University of Catania, Italy. serena.riela@unict.it

09:20 — *Keynote*
Modification of clay minerals for biomedical applications
Massaro, M., Cinà, G., de Melo Barbosa, R., Leone, F., Sanchez-Espejo, R., Viseras, C., Riela, S.

09:50 — *Keynote*
Halloysite nanotube-based shuttle for intracellular transport of Peptide Nucleic Acids (Ps) in Gene Therapy
Falanga, A.P., Oliviero, G., Borbone, N., Riela, S.

10:20
Student
The Influence of Clay Pores Volume and Surface Charge on Isoniazid Adsorption and Release
Arjona, J.C., Ulsen, C., Samara, M., Valenzuela-Diaz, F.R., and Demarquette, N.R.

10:40
Student
Exploring Halloysite Nanomaterials for potential theranostic applications
Leone, F., Bagherpour, S., de Melo Barbosa, R., Massaro, M., Noto, R, Pérez-Garcia, L., Raymo, F.M., Sánchez-Espejo, R., Viseras, C., and Riela S.

11:00 — *Break*
11:20
Student
A Perspective of Halloysite and Carbon Dots-Based Nanomaterials
Cinà, G., Massaro, M., Cavallaro, G., de Melo Barbosa, R., Lazzara, G., Sanchez-Espejo, R., Viseras, C., and Riela, S.

11:40
Development of a nanoemulgel system based on Opuntia ficus-indica seed oil and nanoclays: a promising approach for skin biocompatibility and antimicrobial performance
Anna Imbriano, Maria Mendico, Sara Primavilla, Luana Perioli, Alberto López Galindo, Maurizio Ricci, Alessandro Di Michele, **César Viseras**, Cinzia Pagano, Fátima García Villén, Raquel de Melo Barbosa

12:00
Surface Characteristics of Geologically Ancient Occluded Quartz from Bentonite and Their Toxicological Implications: A Case of Guilt by Association?
Brown, R. K., Hochella, M. F., Murayama, M., Berti, D. and Cantando, E.

12:20 — *Keynote*
Remote
Clays in Epoxy composites: a new tool against healthcare associated infections
R. Bertani, P. Sgarbossa, A. Pontefisso, F. Tateo, A. Mansi, A.R. Proietto, A. Chiominto, F. Boccuni, A. Bargellini, I. Marchesi, C. Cermelli, A. Rossini

12:50 — *LUNCH*

14:10 — *Keynote*
Photoactive Clay/Polymer Nanocomposite Surfaces: A Promising Strategy for Combatting Pathogenic Biofilms
Bujdák J., Skoura E., Bugyna L., Bilská K., Bujdáková H.

14:40
Remote
Study of anti pathogens activity of zeolite, activated by silver ions (Ag+)
Purevtsogt Dorgjoo, Tsogtbaatar Lkhagvajav, Banzragch Sukhbat, Ulzii-Uchral Davaasuren, Tumenjargal Bazarragchaa, Demberel Shirchin, **Zolzaya Majigsuren**

15:00
Geophagy and cultural practices among the Businenge of western Guyana: a physico-chemical and mineralogical characterization of ingested pemba clays
Joussein, E., Soubrand, M., Schreck, E., Maurice, L., Paineau, E., Courtin, A., Reguer, S., Vantelon, D., Tareau, M.A.,, Ansoe-Tareau, C. and Odonne, G.

15:20
Covalent functionalisation of natural clays for environment remediation
Puglisi, R., Massaro, M., Pappalardo, A., Trusso, G., Nicosia, A., Mineo, P. G., Viseras, C.,, Sánchez-Espejo, R., Riela S.

Lecture theatre 5-Swift

Origin and Age of Clay Minerals in Soil and Sediment (session #6)

Thierry Allard, Sorbonne Université, France, thierry.allard@upmc.fr
Thomas Munier, University of Burgundy, France, thomas.munier@sorbonne-universite.fr
Pierre Pellenard, University of Burgundy, France, Pierre.Pellenard@u-bourgogne.fr
Pauline Corentin, Université de Montepellier, France, pauline.corentin@u-bourgogne.fr

09:25
Reconstructing kaolinite formation conditions and ages in lateritic profiles from central Amazonia: Insights from EPR Spectroscopy
Ataytür, Ö., Allard,T., Gautheron, C., Balan, E., Messias, R., Calmels, D. Guinoiseau, D., Bouchez, J., Fekiacova, Z., Genezini, F., Somogyi, A., Horbe, A.

09:45
Dating the polytypes of illite to decipher the successive hydrothermal events leading to uranium mineralization in the Athabasca basin, Canada
Gerardin, M., Bartier, D., Hueck, M., Cathelineau, M., Milesi, G. and Mercadier, J.

10:05
Soil clay minerals on Byers Peninsula (South Shetland Islands, Antarctica) "R.A. Howie Memorial Lecture"
Pelayo M., Schmid T., Melón A.M. and López-Martínez J.

10:25
Evidence of massive authigenic kaolinite proportions in Early Cretaceous silico-clastic deposits: the impact of marine weathering on paleoclimate interpretation
Munier, T., Abouassi, P. and Riquier, L.

10:45 — *BREAK*

11:05
Student
Origin of smectite and influence of volcaniclastic material on a Paleocene-Eocene Thermal Maximum clay assemblage record from the Norwegian-Greenland Sea (IODP Expedition 396)
Turton, N.A., Pellenard, P., and Xu, W.

11:25
Clay Mineralogy coupled to Hf-Nd Isotopes: deciphering chemical weathering and mechanical erosion in the Late Cretaceous climate evolution
Pauline Corentin, Camillo Esteban Gaitan, **Pierre Pellenard**, Emmanuelle Pucéat, Michel Guiraud

11:45
Student
Clay mineral response to hyperthermal events in coastal settings: new insights from Eocene deposits in the Paris Basin
Talon, J., Pellenard, P., Baele, J.-M., Quesnel, F., Iakovleva, A., Bruneau, L., Santoni, A.-L. and Dupuis, C.

12:05 — *LUNCH*

13:05
Student
Early diagenetic overprint on Eocene-Miocene lacustrine clay minerals: Influence of phreatomagmatism and microbial activity in the Limagne Basin, France
Lawnizack G., Pellenard P., Vennin E., Bosse V., Olivier N., Pucéat E.

13:25
Varve-like sediments in caves from the northern rim of the Dachstein Massif (Austria)
Franziska Holzer, **Susanne Gier**, Lukas Plan

13:45 — *Keynote*
Clay Minerals Markers of Paleo-conditions
Abderrazzak El Albani

14:15 — *Keynote*
Climatic significance of clay minerals in Cenozoic sediments
Fagel, N.

14:45 — *BREAK*

Lecture theatre 5-Swift

Clays in Mining (session #40)

Heather Kaminsky, Northern Alberta Institute of Technology, Canada. hkaminsky@nait.ca
Andrew Vietti, Vietti Slurrytec, South Africa. AVietti@VSlurrytec.com
Daniel Dodoo, University of Melbourne, Australia. ddodoo@student.unimelb.edu.au

15:05
A new exploration in surrounding of Michaľany-Lastovce bentonite deposit, East Slovakia – mineralogical, geochemical and petrological characterization
Uhlík, P., Gread, F.A., Biroň, A. Osacký, M., Šurka, J., Kureková, V., Majdan, M., Pálková, H. and Lintnerová, O.

15:25
Clay Characterization Challenges: Insights from Methylene Blue Index and X-Ray Diffraction Analyses of Coal Mine Wastes from Alberta
Luu, V., Khatun, M., Ng, J., Knudson, C. and Kaminsky H.

15:45
Student
Characterising and predicting the flotability of gangue minerals from X-ray diffraction patterns: A case study of talc
Daniel Dodoo, Liza Forbes, Nathan A.S. Webster, Nick Owen, Shane P. Usher, Peter J. Scales, and Anthony D. Stickland

16:05
The Role of Water Chemistry on Clay Behavior in Mine Process and Tailings Circuits
Vietti, A.J.

16:25
Remote
Impact of Clay Activity and Surface Chemistry on Polymer-Assisted Dewatering of Oil Sands Fluid Fine Tailings
Ghuzi, M., Patel, A., Tacas, J., Kaminsky, H., Wong, P., Tizzotti, M., and Whitham, L.

16:45
Lime Treatment Impact of In-Line Flocculation Polymer Performance and Strength Development of Deposited Tailings
Heather Kaminsky, Yunhui Li, Catalina Romero, Joel Tacas and Nikolas Romaniuk

Lecture theatre 6-Ui Cadhain

Universal (session #1a)

Simon Kemp, BGS, UK, sjk@bgs.ac.uk
Helen Pendlowski, The James Hutton Institute, UK, helen.pendlowski@hutton.ac.uk
Dave Wray, University of Greenwich, UK, D.Wray@greenwich.ac.uk
Francis Clegg, University of Shefield, UK, f.clegg@shu.ac.uk
Mohamed Mouafon, Institut Clément Ader, FRANCE, mohamed.mouafon@mines-albi.fr
Javier Garcia Rivas, Complutense University of Madrid, SPAIN javier.garcia.rivas@ucm.es

09:25
Student
A Deep Learning Approach for Mineral Identification With X-Ray Powder Diffraction Patterns
Spencer Chandler, Barry Bickmore, and Emily Evans

09:45
Data quality of low angle X-ray powder diffraction
Ectors, D.

10:05
Identifying clay minerals based on oxide compositions using MinMatch
Warr, L.N., Thombare, B.R, Sudheer Kumar, R., and Grathoff G.H.

10:25
RockJockML: An updated version of RockJock for the modern geologist
Evans, E.J., and Bickmore B.R.

10:45
Student
A comparison of ATR and transmission FTIR spectroscopic methods as tools for qualitative and quantitative analysis of clay mineral identities and properties
Chipman, A.J., Bickmore, B.R., LeMonte J.J.

11:05
VNIR-SWIR spectroradiometric study of ground samples from the Tajo Basin
García-Rivas, J., García-Romero, E., and Suárez, M.

11:25 — *BREAK*

Lecture theatre 6-Ui Cadhain

Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies (sessions #2+11)

Janice Bishop, SETI Institute, USA, jbishop@seti.org
Slávka Andrejkovičová, University of Aveiro, Portugal, slavka@ua.pt
Marco Ferrari, Istituto di Astrofisica e Planetologia Spaziali, INAF, Italy, marco.ferrari@inaf.it

11:45
Clay minerals survey along the Martian Crustal Dichotomy to Assess Aqueous Conditions on Early Mars
J. Brossier, F. Altieri, M.C. De Sanctis, A. Frigeri, M. Ferrari, S. De Angelis, E. Bruschini, A. Apuzzo, M. Rasmussen, and J. Trisic Ponce

12:05
Student
Distinguishing detrital from authigenic phases in a subaqueously altered basaltic sandstone: A Mars analog remote sensing study
Yanez, K.L., Milliken, R.E., Meyer, M.J. and Robertson, K.M.

12:25
Characterizing Phyllosilicate-Sulfate Assemblages at Mawrth Vallis as Indicators of Environmental Change on Mars
Bishop, J.L., Gross, C., Gruendler, K.E.W., Tjan, G., Huang, R., Parente, M., Gruendler, M.R.D., Saranathan, A.M., Itoh, Y., and Gulick, V.C.

12:45 — *LUNCH*

13:45
Remote
Formation of jarosite in a nontronite bearing deposit on Mawrth Vallis, Mars
Mukherjee, A., Gupta, S.

14:05
Student
Cation-Exchange Reactions in Nontronite − Indicator for Water Reservoir and Active Geochemical Processes on Mars
Trung Nguyen, Amanda Ekman, Nicolas Boulanger, Michael Holmboe, Merve Yesilbas

14:25
Formation mechanisms of hematite in Gale crater, Mars: insight from hematite crystallite sizes
Peretyazhko, T., Szczerba, M., Rampe, E., Bristow, T., Tutolo, B., Ming, D., Vaniman, D., Morris, R., Ralston, S.J., Haney, N., Blake, D., Chipera, S., Downs, R., Hazen, R., Morrison, S., Treiman, A., Yen, A., Tu, V., Thorpe, M., Achilles, C., Des Marais, D, Grotzinger, J., Castle, N., Craig, P., Hausrath, E. and Simpson, S.

14:45
Student
Mineral mapping in Uzon Caldera for classifying surficial alteration terrains over time and implications for similar studies of Mars
Bradley T.W., Schroeder P.A., Crowe D.E., and Karpov G.

15:05 — *BREAK*

15:25
New model for NIR band assignment in 2:1 dioctahedral Fe-rich phyllosilicates
Cuadros, J., López-Quirós, A., Nieto, F., Marco, J.F. and Montgomery, W.

15:45
Remote
Exploring serpentinization: Insights from Cabeço de Vide (Portugal) as an analog for Mars
Rebelo, R., Andrejkovičová, S., Carrizo, D. and Macário, I. P. E., Rocha, F.

16:05
Remote
Amorphous constituent of sialic/silicate rust in nakhlites
Velbel, M.A.

16:25
Phengite textures in Precambrian impact spherules reveal extreme shock disintegration mechanisms
Percival, J.A., Percival, J.B., and Shalchi Amirkhiz, B.

Lecture theatre 7-Davis

1D Nanoporous Clay Materials and Their Industrial Applications (session #26)

Peng Yuan, Guangdong University of Technology, China. yuanpeng@gdut.edu.cn
Pilar Aranda, Materials Science Institute of Madrid (ICMM), Spain. pilar.aranda@csic.es
Antoine Thill, CEA Saclay, France. antoine.thill@cea.fr
Giuseppe Lazzara, University of Palermo, Italy. giuseppe.lazzara@unipa.it
Lala Setti Belaroui, University of Oran 1, Ahmed Ben Bella, Algeria. belaroui.lalasetti@univ-oran1.dz
Pooria Pasbakhsh, University of Melbourne, Australia. pooria.pasbakhsh@unimelb.edu.au
Yanfu Wei, Macau University of Science and Technology, China. yfwei@must.edu.mo
Guanzheng Zhuang, Guangdong University of Technology, China. zhuangguanzheng@gdut.edu.cn

09:25 — *Keynote*
Designing Functional Nanoarchitectures through Cross-Assembly of 1D Clay Minerals
Ruiz-Hitzky, E.

09:55
Sustainable fibrous clay-based bionanocomposites as additive for the improvement of high strength art papers
Aguilar-Briceño, R., Darder, M., Martín-Sampedro, R., Eugenio, M.E., Tomás-Miralles, A. and **Aranda, P.**

10:15
Bioinspired superhydrophobic coatings based on palygorskite
Junping Zhang

10:35
Sepiolite modification with phosphatidylcholine to improve adsorption and controlled release of amphotericin B
Misol, A., Hernández Ponz, S., Saez, E., Colom, M.F., **Darder, M.** and Aranda, P.

10:55
Molecular simulation study of the adsorption of Cu(Ⅱ) on palygorskite
Jinhong Zhou, Xiancai Lu and Xueyuan Gu

11:15 — *BREAK*

11:35
Beneficiation and application of β-sepiolite in the field of environment and energy
Hou Kai, Feng Guorui and Xi Yunfei

11:55
Injectable halloysite-based nanocomposite hydrogel for antibacterial and hemostatic wound management.
Wong, L.W., Lau, C.S.S., Teow, S-Y., Chai, W.Y., Tan, J.B.L., **Pasbakhsh, P.**

12:15
Biohybrid Xerogels with Halloysite clay nanotubes and Chitosan for sustainable applications
Caruso, M.R., Calvino, M.M., Šiler, P., Cába, V., Milioto, S., Lisuzzo, L., Cavallaro, G. and Lazzara, G.

12:35
Student
Hydrophobically modified Halloysite nanotubes for the formulation of a water in oil Pickering emulsion gel
D'Agostino, G., Caruso, M.R., Joseph, E., Cavallaro, G., Milioto, S., and Lazzara, G.

12:55
Preliminary Investigation on the Role of Halloysite Nanotubes in Methane Hydrate Formation
Li, Y.

13:15 — *LUNCH*

14:15 — *Keynote*
From imogolite to Imogolite-Like-Structures family years of exciting discoveries
Thill A.

14:45
Student
Tailoring Functional Properties in Hybrid Composites through Geopolymerization: From Fire Resistance to Pollutant Capture
Lo Bianco A., Calvino M.M., Cavallaro G., Šiler P., Milioto S., Lazzara G.

15:05
A Comparative Study on Geopolymerization of Nanotubular Halloysite and Platy Kaolinite
Zhang, B. F., Yuan, P. and Yu, T.

15:25
How does the geological deposit affect the properties and applications of halloysite clay?
Cavallaro, G., Lo Bianco, A., Calvino, M.M., Milioto, S., Pasbakhsh, P., and Lazzara G.

15:45
Remote
Fabrication of Porous Adsorbents from Eco-friendly Aqueous Foam for High-Efficient Removal of Organic Pollutants and Sustainable Utilization
Yongfeng Zhu, Fangzhi Duan, Jiang Xu, Bin Mu, Aiqin Wang

THURSDAY 17th July

Lecture theatre 1-Burke

08:30 — *Plenary Pioneer Lecture*
Understanding the structure and dynamics of clay and other layered minerals and their interfaces using molecular modelling – a perspective
H. Chris Greenwell

09:15 — *Sponsor's Presentation*
09:20 — *BREAK*

Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials (session #29)

Erwan Paineau, CNRS/UPSaclay, France. erwan-nicolas.paineau-lanone@cnrs.fr
Yusuke Ide, Yokohama National University, Japan. IDE.Yusuke@nims.go.jp
Nobuyoshi Miyamoto, Fukuoka Institute of Technology, Japan. miyamoto@fit.ac.jp
Vanessa Prévôt, Université Clermont Auvergne, France. vanessa.prevot@uca.fr

09:25
Organic-inorganic hybrids having a talc-like structure for light-driven applications
Dullin, T., **Brendlé, J.,** Schuller, A.-S, and Ley, C.

09:45 — *Keynote*
Photochemistry of 2D Molecular Assemblies on Clay Mineral Nanosheets
Yohei Ishida

10:15
Student
Insight on the photocatalytic properties of ZnAl-Cl LDH derived mixed oxide toward degradation of persistent herbicide in water
Hao Wang, Claude Forano, Monier Guillaume, Réveret François, Mohamed Sarakha, Vanessa Prévot

10:35
Proton conductivity of montmorillonite nanosheet membranes and their application as electrolytes in fuel cells
Ida, S., Tsugawa, T. and Hatakeyama, K.

10:55 — *BREAK*

11:15
Clay mineral-based separators and solid-state electrolytes for advanced lithium metal batteries
Yang, Y.F., Zhang, J.P.

11:35
Aggregation behaviour of colloidal clay-organic hybrids observed by utilizing fluorescence correlation spectroscopy
Kawamata, J., Tsubone, M., Hosoi, T., Ishii, K., Kinjo, M.

11:55 — *Keynote*
Materials Design of Bentonite by Purification and Organic Modification
Hayakawa, T., Minase, M., **Ogawa, M.**

12:25
Self-Assembly of Monodisperse Nanosheets Into Columnar Nanofibers
Miyamoto, N., Hiroyuki Iwano, Hiroyuki Nonaka

12:45
Columnar brucite-type layered metal hydroxides with tunable shape and surface properties associated with edges
Muramatsu, K., Watanabe, A. and Sugimoto W.

13:05 — *LUNCH*

14:05
Bridging the gap between osmotic and crystalline swelling in smectites clay minerals using levitated droplets
Hotton, C., Bizien, T., Hamon, C., Ferrage, E. and **Paineau, E.**

14:25
Sub-nanometer thickness engineering of amorphous silica nanosheets
Yamamoto, E., Takezaki, Y., Kobayashi, M. and Osada, M.

14:45
Remote
From Quenching to Fluorescence Enhancement: Central Metal Effects in Porphyrin–Smectite Hybrids
Boháč, P., Budzák, Š., Sasai, R., Planetová, V., and Bujdák, J.

15:05
Stabilisation of iron-oxo dimers in a natural layered clay for photocatalysts comparable to TiO2
El-Hosainy, H., Ezz-Elregal, E.M., **Ide, Y.**, and Okada, T.

15:25 — *Keynote*
Characterization of Polymer Hybrids from Imogolite and Halloysite
Takahara, **Atsushi**

Lecture theatre 2-Beckett

Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils (sessions #39+42)

Balwant Singh, University of Sydney, Australia, balwant.singh@sydney.edu.au
Georg Guggenberger, Leibniz Universität Hannover, Germany, guggenberger@ifbk.uni-hannover.de
Ines Mulder, Ruhr-Universität Bochum, Germany, ines.mulder@ruhr-uni-bochum.de
Robert Mikutta, Martin-Luther-Universität Halle-Wittenberg, Germany, robert.mikutta@landw.uni-halle.de
Katharina Lenhardt, Martin-Luther-Universität Halle-Wittenberg, Germany, katharina.lenhardt@landw.uni-halle.de
Ranjan Paul, ICAR-National Bureau of Soil Survey and Land Use Planning, India, rajan.reliance@gmail.com
Raj Mukhopadhyay, ICAR-Central Soil Salinity Research Institute, India; Present address: Carnegie Mellon University, Pittsburgh, USA, rajssaciari@gmail.com
D.K. Pal, ICAR-National Bureau of Soil Survey and Land Use Planning, India, paldilip2001@yahoo.com

09:25 — *Keynote*
Essential role of minerals in modulating the dynamics of soil organic carbon
Thompson, **A.**

09:55

Probing the chemical environment of Al and Si in secondary silicates by X-ray photoelectron spectroscopy
Lenhardt, K.R., Rennert, T., and Mikutta, R.

10:15
Student
An investigation into chemical interactions between dissolved organic matter and clay minerals
Yang, Z., Dijkstra, F.A., Guggenberger, G. and Singh, B.

10:35
Soil minerals as boundary condition of microbial carbon use of sorbed organic model compounds
Ines Mulder, Alexander Konrad, Diana Hofmann, Kenton P. Stutz, Friederike Lang, Jan Siemens

10:55
Clay interactions with amino acids in marine sediments: Evidence for mineral-modulated organic matter stabilization
Blattmann, T.M.

11:15 — *BREAK*

11:35
Exploring soil mineralogy as an indicator of soil functioning and health.
Ghosh, U., Gray-Wannell, N., Afriyie, E., Baggaley, N., Paterson, E., Stephen Hillier

11:55
Multiple K-bearing minerals in soil distinctively react with two non-exchangeable potassium extraction tests
Kurokawa, K., Nakao, A., Suzuki, A., Wakabayashi, S., Fujimura, S., Eguchi, T., Shinano, T. and Yanai, J.

12:15
Stepwise expansion of micaceous interlayer space changes affinity to cesium
Nakao, A., Uno K., Kitayama, R., Ogasawara, S. and Yanai, J.

12:35 — *LUNCH*

13:35
Remote
Role of nanoscale soil minerals in stabilization of organic carbon in acidic Ultisols of humid tropical India
Ranjan Paul, Duraisamy Vasu, Pramod Tiwary and P. Chandran

13:55
Student
Tropical climates, soil clays and landslide susceptibility
Ryan, Peter C., Parkinson, T., Pérez-Martín, I., and **Reyes Collovati, J.**

14:15 — *Keynote*
Clays in the Critical Zone: How fast and how long do they hang around?
Schroeder. P.A., Richter, D.D., and Allard, T.

14:45 — *Break*

Lecture theatre 2-Beckett

Industrial Applications of Clays (session #17)

George E. Christidis, Technical University of Crete, Greece, gchristidis@tuc.gr
Stephan Kaufhold, BRG, Germany, s.kaufhold@bgr.de
Jon Phipps, IMERYS, United Kingdom, jon.phipps@imerys.com
Prakash Malla, United States, pbmalla10@gmail.com
Matthias Schellhorn, Stephan Schmidt Gruppe, Germany, Matthias.Schellhorn@schmidt-tone.de

15:05 — *Keynote*
How can the use of pre-consumer wastes from industrial minerals production help meet future customer demand?
Mariani, E., Ansari, D.

15:35
Redefining the terminology of bentonites based on geological and mineralogical criteria and the industrial practice
Christidis, G.E.

15:55
The importance of particle aspect ratio in industrial applications of clay minerals and its measurement
Phipps, J.S., Righton, O., Staples, M. and Rowe, N.B.

16:15
Student Remote
Investigation of Thermal and Mechanical Properties of Pyrophyllite-Impregnated Natural Fiber Fabrics
Aykasım, D. and Toksoy Köksal, F.

16:35
LAPONITE® 7007 – Introducing powerful new 'special agent' for rheological applications and beyond
Shafran, K.L., Potter C., Grant N. and Kelly, O.

16:55
Student
Potential of kaolin clay in reducing methanogenic microbial activity in cattle
Zubaer Hosen, Md. Rashidul Islam, Ravi Naidu, Bhabananda Biswas

17:15
Dry processed Westerwald Saprolithe Clays as a new filler for waterborne adhesives and further applications
Piribauer, C.J., Akbasak, T. and **Schellhorn, M.**

Lecture theatre 3-Emmet

Mechanical and Mechano-chemical Activation of Clays (session #33)

Ilda Tole, University of Bath, UK. it509@bath.ac.uk
Susan Bernal, University of Bath, UK. sbl30@bath.ac.uk
Alastair Marsh, EPFL, Switzerland. alastair.marsh@epfl.ch
Xinyuan Ke, University of Bath, UK. xk221@bath.ac.uk
Matej Balaz, SAS, Slovak Republic, balazm@saske.sk

09:25
Remote
Mechanochemical activation of kaolin with abrasive pozzolans and its effect on the pozzolanic reactivity
Makó, É. and Őze, Cs.

09:45
Characterisation of Iron-rich clay soils subjected to intense grinding
Juvenal Giogetti, **Deutou Nenaleu** and Takafumi Noguchi

10:05
Mechanical activation of halloysite-rich kaolin for slow-release phosphate fertiliser
Biswas, B., Amiri, A. and Warr L.N.

10:25 — *BREAK*

10:45 — *Keynote*
Mechanochemistry: A unique tool to boost the potential of natural minerals
Baláž, M.

11:15
Student
Mechanochemical Activation of Mine Tailings as Alternative Secondary Cementitious Materials
Papadopoulou, K., Cwirzen, A. and Alakangas, L.

11:35
Student
Mechanochemical Activation of Phyllosilicates: Efficient utilization of Agitator Ball Mills
Ruckes, L., Maier, M.

11:55
Comparative study of mechanochemical and thermal activation of clays in low-carbon binder
Tetiana Gutsalenko, Roberta Alfani, Laurent Frouin, Thomas Wattez, Mohend Chaouche, Martin Cyr

12:15 — *LUNCH*

13:15 — *Keynote*
Bridging the Gap: Meca-clay - Scaling Up Mechanochemical Clay Activation from Lab to industry
Hendrik Möller

13:45
Remote
Evaluation of different process conditions for mechanochemical activation of clays
Brito, B. L. F., Danieli, S. and Longhi, M. A.

14:05
Relationships between milling input energy and chemical reactivity
Marsh, A.T.M., Krishnan, S., Rahmon, S., Bernal, S.A., Ke, X.

14:25
Performance of thermo-mechanically activated Finnish clay
Asaam, N., Adediran, A., and **Perumal, P.**

14:45 — *BREAK*

15:05 — *Keynote*
Mechano-Chemical Activation of Low-Purity Clays
Susan A. Bernal

15:35
Student Remote
Mechanochemical activation of low-kaolinitic clays and basaltic fines
Amroun, S. and Suraneni, P.

15:55
Student
Reactivity, dissolution, and hydration of mechanochemically activated clay minerals as supplementary cementitious materials
Wu, H., Cheeseman, C.R., Wong H.S.

16:15
Student
Under the microscope: How mechanochemically activated shale behaves in hydrated blended cement systems
Pengfei Zhao, Alexander Ozersky, Alexander Khomyakov, Wisdom Okoh, and Karl Peterson

16:35
Enhancing the Reactivity of Low Purity UK Clays
Tole, I., Dhandapani, Y., Kemp S., Mitchell C., Wong H., and Bernal S.A

Lecture theatre 4-Synge

Clays in Geotechnics – Problems and Applications (session #30)

Michael Plötze, ETH, Zurich, Switzerland. ploetzel@ethz.ch
Claudia Vitone, DICATECh, Politecnico di Bari, Italy. claudia.vitone@poliba.it
Bharat Venkata Tadikonda, Indian Institute of Technology Guwahati, India. tvb@iitg.ac.in
Rossella Petti, DICATECh, Politecnico di Bari, Italy. rosella.petti@poliba.it

09:25
Micro- and Nano-scale investigation into the origins of sensitivity in clay
Casarella, A., Saaedifar, D. and Dijkstra, J.

09:45
Coupled geotechnical and electrical investigations to assess marsh soil variability: a case study at Poiré-sur-Velluire marsh (France)
Cosenza, **Ph.**, Caner, L., Pavageau, C., Salim I., and Decoene D.

10:05
Wetting-Induced Collapse Behaviour of Loosely Compacted Kaolin Soil: A Microstructural Study
Das, D. S., and Bharat, T. V.

10:25
Student
Impact of Substrate Friction on Internal Non-uniform Deformation and Desiccation Crack Formation in Drying Fine Sediments: An X-ray CT Study
Li, L.D., Tang, A.M. and Zhao, B.D.

10:45
Studies of electrochemical properties of compacted clays by concentration potential method
Andriy Yaroshchuk, Martin A. Glaus and Luc R. Van Loon

11:05 — *BREAK*

11:25
Novel perspectives on the transport and mechanical properties of pollutant containment systems comprising enhanced bentonites
Guarena, N., Dominijanni, A. and Manassero, M.

11:45
Student
Polymer-modified bentonite-silt composites to improve the hydro-mechanical properties of landfill mineral sealings
Kallerhoff, N., **Sellinghoff, R.**, Lieske, W., Baille, W. and Wichtmann, T.

12:05
Montmorillonite and kaolinite as a novel bio-inspired material for the attenuation of viral pathogens and salt leachates
Das, P. and Bharat, TV.

12:25
Student
Modified Clay Precursors for their Evaluation as Alkaline Binders for the Stabilization of Marine Sediments
Girardi, G., Petti, R., Pinto, D. and Vitone, C.

12:45
Student
Fix clay with clay
Sadasivan, V., Casarella, A., Baba Ahmadi, A., and Dijkstra J.

13:05 — *LUNCH*

14:05
Student
Stability and Solubility of Mg-Hydroxy-Interlayered Smectite (Mg-HIS)
Zucha, W.J., Bernard, E., Plötze, M. and Puzrin A

14:25
Student
Soft Calcite from mussel shells: a bio-derived additive for the geotechnical enhancement of marine clays.
Carcagni,M., Petti,R., Vitone,C., Giotta,L., Ploetze,M., Puzrin,A., Pinzon, G., Viggiani, G.

14:45 — *Keynote*
Remote
Soil-Contaminant Interaction: Influence of Elevated Temperatures
Singh, D.N.

Lecture theatre 5-Swift

Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies (sessions #38+43)

Emmanuel Tertre, Université de Poitiers, France, emmanuel.tertre@univ-poitiers.fr
Valentin Robin, Université de Limoges, France, valentin.robin@unilim.fr
Thorsten Schaefer, Friedrich Schiller University Jena, Germany, thorsten.schaefer@uni-jena.de
Anke Neumann, PSI, Switzerland, anke.neumann-jenal@psi.ch
Binoy Sarkar, University of South Australia, Australia, Binoy.Sarkar@unisa.edu.au
Jonathan Suazo Hernandez, Universidad de la Frontera, Chile, jonathan.suazo@ufrontera.cl

09:25
Microwave-Assisted Synthesis of advanced NiFe Layered Double Hydroxides from MOFs for Environmental Remediation
Prévot, V., M. Li., and Forano, C.

09:45
Mineral-based advanced oxidation processes for enhancing the removal of antibiotic resistance genes from domestic wastewater
Adamou, P., Entwistle, J., Graham, D.W. and **Neumann, A.**

10:05
Student
Exploring oxidative pathways in iron redox-mediated chlorinated contaminant degradation
Malvika Patial, Lucia Rodriguez Freire, Shannon Flynn, Anke Neumann

10:25 — *Keynote*
Coarse-grained simulation of colloidal self-assembly, cation exchange, and rheology in Na/Ca smectite clay gels
Zheng, X., Shen, X., and **Bourg, I.C.**

10:55 — *BREAK*

11:15
Student
Osmotic swelling mechanism of clay soils from marsh: the spectacular case of 'mottureaux'
E. Le Gouguec, F. Hubert, E. Tertre, S. Hillier, A. Beaudoin, P. de Bouët du Portal, P. Lagrange & G. Rousseaux

11:35
Competitive adsorption of Cs and Sr onto a soil clay fraction
Latrille, C., Latrille, J., and Léonhardt, N.

11:55
Student
Source of metals (Mn, Fe) in fresh and altered basalts
Olivia Terry, Tianxiao Shen, Lucas Abernathy, Quin Miller, Nabajit Lahiri, James Leong, Todd Schaef, and Shaina Kelly

12:15
Student
Probing the Surface Bridging Hydroxyl sites of aluminum oxide by 19F Solid-State NMR Spectroscopy
Jinhui Li, Wei Li

12:35 — *LUNCH*

13:35
Stability of FeII-FeIII hydroxyphosphate formed by anionic exchange of a hydroxychloride green rust precursor
Sdiri W., Coustel R., Ounacer M., Ona-Nguema G., Cornu D., Despas C., Mallet M., Truong C., Nitschke W., Duval S., Abdelmoula M., Bergaoui L., **Ruby, C.**

13:55
Enhanced H_2S removal in greenhouse gases using copper-modified naturally occurring zeolite from Mangatarem, Philippines for waste to energy applications
Olegario, E.M.

14:15
Adsorption of chromate pollutants with polyethyleneimine- and poly(N-butylethyleneimine)-modified montmorillonite using combined theoretical and experimental approaches
Škorňa, P., Jankovič, L., Scholtzová, E. and Tunega D.

14:35
Remote
Clay-based amendments reduce PFAS bioavailability in soil: Dynamics of soil-pore water-lettuce system
Raj Mukhopadhyay, Carrie A. McDonough

14:55
Remote
Clay-based formulation of azoxystrobin to control corn late wilt disease and cotton coal rot disease
Rytwo, G., Hadad, A., Abramovici, A., Levi-Lion, A., Dimant, E., Hadari, P., Steckler, R. and Degani, O.

15:15 — *BREAK*

Lecture theatre 5-Swift

Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development (session #18)

Branimir Segvic, Texas Tech University, USA, branimir.segvic@ttu.edu
Rafael Ferreiro Mählmann, TU Darmstadt, Germany, ferreiro@geo.tu-darmstadt.de

15:35
Paragenetic and non-paragenetic clay mineral assemblages in geothermal prospection
Rafael Ferreiro Mählmann

15:55
Mid-Cretaceous Alpine metamorphism of the Tisza Mega-Unit (Inner Carpathians) constrained by illite K-Ar dating and mineral metamorphic indicators
Iuliu Bobos, Jan Środoń, Alexandre Kounov, Juliano Senna, Marek Szczerba, Zuzanna Ciesielska and Ionel Nicolae

16:15
Mutual influence of clay diagenesis and bacterially-induced siderite cementation in Carboniferous strata, Anadarko Basin, U.S.A.
Branimir Šegvić, Evans Akouko Ansah, Owen Smith and Dustin Sweet

16:35
Student
A new depositional and diagenetic hypothesis for Mg-clay minerals in the Pre-salt Tupi Field, Barra Velha Formation, Santos Basin (Southeastern Brazil)
Santana, F.L., Salgado-Campos, V.M.J., Santos, H., Diaz, N., Santos, J. and Ribeiro, A.

16:55
Student
Partitioning behavior of rare earth elements in hydrothermal chlorite
Oluwaseye Oyetade, Branimir Šegvić, Kevin Byerly, Kevin Werts, Damir Slovenec, and Matthew Siebecker

Lecture theatre 6-Ui Cadhain

Smectite Layer Charge and Interlayer Environment: Structure, Alteration, and Environmental and Technological Significance (session #19)

Arkadiusz Derkowski, Instytut Nauk Geologicznych Polskiej Akademii Nauk, Poland, ndderkow@cyf-kr.edu.pl
Eric Ferrage, CNRS Poitiers, France, eric.ferrage@univ-poitiers.fr
Liva Dzene, Ecole Nationale Supérieure de Chimie de Mulhouse, France, liva.dzene@uha.fr

09:25
Application of the vO-D probe to vermiculites
Kuligiewicz, A., Skiba, M., Kisiel M., Ferrage, E., Dzene, L. and Derkowski, A.

09:45
Inferring the position of interlayer cations and their effect on smectite properties from spectroscopic measurements of a D2O-saturated interlayer
Derkowski, A., Kuligiewicz, A., Rybka K., Siranidi, E. and Chryssikos G.D.

10:05
Layer Charge measurements for the industrial characterization of bentonite: The past and future of the OD method
Chryssikos, G.D. and Siranidi, E.

10:25 — *Keynote*
A Molecular View on the Effects of Smectite layer charge
Michael Holmboe

10:55 — *Break*
11:15
Homoionic trans-vacant and cis-vacant montmorillonites: A density functional theory study
Emmerich, K., Nugraha, I., Liu, Y.-Y., Asaad, A. and Thissen, P.

11:35
Determination of the presence and magnitude of tetrahedral layer charge of swelling clay minerals by intercalation of glycerol
Jelavić, S., Lanson, B., Lanson, M., Gverić, Z., Tibljaš, D., Fryer, B., and Violay, M.

11:55
Thermal effects on smectite's interlayer water stability under constant relative humidity conditions
Rybka K., Skiba M. and Derkowski A.

12:15 — *LUNCH*

Lecture theatre 6-Ui Cadhain

Impact of temperature on bentonite barrier systems based on findings from in situ experiments in the context of radioactive waste disposal (session #21)

Nadine Kanik, Institute of Geological Sciences Polish Academy of Sciences in Krakow, Poland, ndkanik@cyf-kr.edu.pl
Reiner Dohrmann, BGR/LBEG, Hannover, Germany, reiner.dohrmann@lbeg.niedersachsen.de
Patrik Sellin, SKB, Stockholm, Sweden, patrik.sellin@skb.se
Daniel Svensson, SKB, Oskarshamn, Sweden, Daniel.Svensson@skb.se

13:15 — *Keynote*
Results from field experiments covering the temperature-related clay mineralogy and pore water processes below and above 100°C on bentonite buffer materials.
Fernández, A.M.

13:45
Iron reduction in bentonite in field experiments
Sellin, P. and Svensson, D.

14:05
Bentonite Erosion and Piping Test (BEPT) Preparation considering Heating Effect in KAERI Underground Research Tunnel (KURT) in South Korea
Hong, C.H., Choi, S., Kim, J.S. and Hong, E.S.

14:25
Student
First H-and O-stable isotope results from the Alternative Buffer Materials experiments: Tracking structural isotope exchange in smectite during bentonite-water interactions from 70-250°C
Kanik, N.J., Longstaffe, F.J., Kuligiewicz, A., Gilg, H.A., and Derkowski, A.

14:45
What can we learn from cation exchange studies of buffer materials in in-situ tests' (ABM-1, -2 and -5) after heating from 140 °C to 250 °C?
Dohrmann, R., Gröger-Trampe, J., Kaufhold, S.

15:05
Mineralogical and Chemical Transformation of Ca-Bentonite at High Temperatures: A Long-Term Evaluation
SeEun Chang, Deuk-Hwan Lee, Changsoo Lee, and Dong Keun Cho

Lecture theatre 7-Davis

Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces (session #27)

Xiandong Liu, Nanjing University, China, xiandongliu@gmail.com
Andrey G. Kalinichev, Subatech, France, kalinich@subatech.in2p3.fr
Chris Greenwell, Durham University, UK, chris.greenwell@durham.ac.uk

09:25 — *Keynote*
Element partitioning between clay minerals and fluids: a molecular dynamics simulation approach
Xiancai Lu, Qin Li, Mengzi Zhou, Jinhong Zhou, Meng Chen, Xiandong Liu

09:55
Student
Hydrogen-Induced Swelling in Clay Minerals: Molecular Insights into Caprock Integrity for Subsurface Hydrogen Storage
Ghasemi, M., Erastova, V. and Babaei, M.

10:15
Molecular dynamics to resolve mechanistic ambiguities in Cs adsorption on todorokite
Juhyeok Kim and **Kideok D. Kwon**

10:35
Atomistic computational modelling of thaumasite and its aqueous interfaces
Tararushkin, E.V., Smirnov, G.S., Kondratyuk, N.D., and **Kalinichev, A.G.**

10:55
Student
Atomistic insight into the effects of actinyl-ligand interactions on the actinyl retention by clay minerals
Ličko, J. and Kalinichev, A.G.

11:15 — *BREAK*

11:35 — *Keynote*
Frontiers of multiscale modelling of retention and transport in clays: Surface reactivity to chemical thermodynamics
Churakov, S.V.

12:05
Bridging the Gap between Molecular Simulations and Surface Complexation Modeling for Heterogeneous Surfaces: A Case Study with Uranium and Arsenic Adsorption on Clay Minerals
Gao, P., Liu, X., Guo, Z., and Tournassat C.

12:25
Remote
Harnessing Machine Learning Models for Predicting Pore Size Distribution in Clays
Saranya, N., Valliappan Raman, Sudha, K., Keerthana, S., Haripriya, V., Nivetha, S. S., Pavithra, G.

12:45 — *LUNCH*

13:45
Multi-scale simulations of the retention and aggregation of organophosphate esters (OPEs) with clay-organic complexes
Chi Zhang, Zhiyu Zhou, and Hanzhong Jia

14:05
Surface complexation of rare earth elements on clay minerals and iron (oxyhydr)oxides: Insight from first principles simulations
Yingchun Zhang, Xiandong Liu, Xiancai Lu and Rucheng Wang

14:25 — **Warren Huff Clay Science Pathway Award**
Unravelling smectite clay nanoparticle aggregation: microstructure, dynamics, and coupled material properties
Zheng, **Xiaojin**, Bourg, Ian C.

14:45 — *BREAK*

Lecture theatre 7-Davis

Sorption and intercalation in layered materials: from origins of life to material science (sessions #3+16)

Valentina Erastova, University of Edinburgh, UK, valentina.erastova@ed.ac.uk
Chris Greenwell, Durham University, UK, chris.greenwell@durham.ac.uk
Sarah V Stewart, University of Edinburgh, UK, s.v.stewart@sms.ed.ac.uk
Daniel Santamaria Gonzales, University College London, d.santamaria@ucl.ac.uk
Stanislav Jelavic, ISTerre, CNRS, France, stanislav.jelavic@univ-grenoble-alpes.fr
Bruno Lanson, ISTerre, CNRS, France, bruno.lanson@univ-grenoble-alpes.fr

15:05Role of Layered Minerals in the Emergence and Preservation of Proto-Proteins and Detection of Extraterrestrial Biosignatures

Valentina Erastova, Hannah Pollak and Sarah V Stewart

Student
15:25
Understanding the adsorption of amino acids onto montmorillonite clays through molecular simulations
Stewart, S.V., McMahon, S., Cockell, C.S. and Erastova, V.

15:45
Mineral-mediated RNA Revolution
Santamaria, D. and Attwater, J.

16:05
Competitive Sorption of H_2O and CO_2 in Clay Mineral Interlayers
Johnston, C.T. and Bish, D.L.

16:25
Student
Hybrid clay pigments: the influence of lamellar clays and intercalation on structural properties
Guillot, M., Rochut, S. Lambert, J.F. and Jaber, M.

16:45
Luminescent pigments based on organically modified smectites: structural and spectroscopic characterization
Pálková, H., Barlog, M. and Bujdák, J.

FRIDAY July 18th

Lecture theatre 1-Burke

08:30 — *Plenary Bradley Lecture*
Clay minerals formation in MgO-SiO2-H2O low temperature system by hydrothermal synthesis: A study in function of Mg/Si molar ratio and pH
Jourdain, A., Dutournié, P., Michelin, L., Le Meins, J.-M., Brendlé, J., Michau, N., Martin, C., and Dzene, L.

09:00 — *Sponsor's Presentation*

09:05 — *BREAK*

Sustainable and eco-friendly clay-based materials (session #32)

Nathalie Fagel, University of Liège, Belgium. nathalie.fagel@uliege.be
Meriam El Ouahabi, Ecole Supérieure des Arts Saint-Lu, Belgium. elouahabi.meriam@saint-luc.be

09:10 — *Keynote*
Eco-friendly clay-based bricks using Construction and Demolition Waste
Andreola, F., Pozzi, P. and Barbieri, L.

09:40
Student
Remote
Recycling Aggregate Washing Sludge into Ceramic Applications: A Case Study of the Marrakech Region, Morocco
Zahir, S., Daoudi, L., El Ouahabi M. and Fagel, N.

10:00
Hydrothermally treated sewage sludge as a substitute for clay in the synthesis of ceramic bricks
Tarantino, S.C., Fernández-Jiménez, A., Marian, N.M., Riccardi, M.P., Sturini, M., and Zema, M.

10:20
Student
Thermophysical and mechanical performances of eco-friendly clay bricks from northeastern Morocco
Miri, H., Rezqi, H., Nasri, H., Fagel, N.

10:40 — *BREAK*

11:00
Remote
Hydrothermal synthesis of zeopolymers from kaolin and construction wastes
Morita, A.K.M, Cotón, N., Afonso, A.J., Fernández, K., Alonso-Azcárate, J., Regadío, M., Mota-Heredia, C. and Moreno-Maroto, J.M.

11:20
Low T fired clays with dolomite addition: sustainability in ceramic industry
Pérez-Monserrat, E.M., Capela, M., Oliveira, M. and Labrincha, J.

11:40
Remote
Behaviour of calcined and uncalcined Tunisian clay in the cold consolidation process by alkali activation

Jrad, Z., Genua, F., Lancellotti, I., Andreola, F., Leonelli, C., Mahmoudi, S.

12:00
Clay influence on compaction and strength of unfired sediment bricks
Ndahirwa, D., Shimpo, T., Levacher, D., Hussain, M., Zmamou, H., Leblanc, N., Karamian, P. and Katsumi, T.

12:20 — *LUNCH*

13:20
Remote
Student
Effect of prolonged curing of compressed lime-stabilized clays from the Far North Region of Cameroon on their physical, mechanical and mineralogical characteristics
Njimboum, A.S., **Balo, M.A.**, Mache, J.R., Fagel, N., Nchare, M.

13:40
Sediments as renewable raw earth for producing unfired bricks and mortars
Levacher, D., Hussain, M., Leblanc, N., Zmamou, H., Ndahirwa, D., Martellotta A.M.N. and Piccinni A.F.

14:00
Reusing excavated Finnish clays in sustainable construction: A laboratory study on compressed earth blocks
Thomas Kronberg, Jan-Erik Eriksson, Topias Mannisto, Leena Hupa

14:20
Remote
Improvement of characteristics of subbase layer materials in rigid pavement using natural aggregate and cement
Nzeukou, N.A., Adjindjibe, B., Tsozué, D. and Fagel, N.

14:40
Recycling marble waste clay powder for cement mixes
Martellotta, A.M.N., Petrella, A., Levacher, D. and Scarascia Mugnozza, G.

15:00
Durability and Resilience of Geopolymers Incorporating Iron Mine Tailings
Santos A., Pinho T., Andrejkovičová S., Rocha F., Almeida F.

15:20 — *BREAK*

15:30 — *AIPEA General Assembly, Awards and Closing Ceremony*

Lecture theatre 3-Emmet

10:30 — *Panel led discussion: Questions concerning clay minerals in radioactive waste disposal*

12:30 — *LUNCH*

14:00 — *Early Career Clay Scientist session: "How to Be a Good Reviewer"*

15:00 — *BREAK*

Lecture theatre 4-Synge

Materials via Ordered Interstratifications (session #14)

Josef Breu, University of Bayreuth, Germany, josef.breu@uni-bayreuth.de
Jon-Otto Fossum, Norwegian University of Science and Technology, Norway, jon.fossum@ntnu.no

09:10 — *Keynote*
Colloidal system of dye-sandwiching clay bilayers: liquid crystallinity and photonic applications
Nakato, T., Watanabe, T., Mouri, E., Harada, T., Shintaku M., Suzuki, Y., Kawamata, J., Miyata, H., Yamauchi, Y., and Breu, J.

09:40
The Multiple Ways to Break Symmetry during Partial Ion Exchange for Making Ordered Interstratifications
Felix Uhlig, **Josef Breu**

10:00
Student
Orderly Interstratified Layered Ruthenic Acid as a Precursor of Ruthenium Oxide Nanosheets with Double-Layer Structure
Eda, T., Muramatsu, K., and Sugimoto, W.

10:20
Bright, Non-Iridescent Structural Colors from delaminated Ordered Interstratified Clay Nanosheets
Fossum, J.O., Breu, J., Michels-Brito, P.H., Dudko, V., Trigueiro-Neto, O., Rosenfeldt, S.

10:40 — *BREAK*

Lecture theatre 4-Synge

Greenhouse Gas Remediation (session #24)

11:00 — *Keynote*
Functionalized Smectites for CH_4-CO_2 Gas Separation in Biogas Upgrading
N. Mendel, I. Siretanu, D.W.F. Brilman, and **F. Mugele**

11:30
Hybrid mineral composites obtained by heterocoagulation, as effective nanomaterials for CO2 capture
Małgorzata Zimowska, Jerzy Podobiński, Robert Kosydar, Jerzy Datka

11:50
A permselective membrane for size-sieving based H2/CO2 separation
Lukas Federer, Ingmar Pietsch, Felix Uhlig, Max Stevenson, Daniel Friedrich, **Josef Breu**

12:10
Remote
Natural kaolin minerals with varying iron contents reduced cattle's enteric methane generation
Md. Rashidul Islam, Ravi Naidu, Bhabananda Biswas

12:30 — *LUNCH*
13:30 — *BREA*

Lecture theatre 5-Swift

Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential (sessions #8+9)

Crawford Elliott, Georgia State University, USA, wcelliott@gsu.edu
Anthony Boxleiter, Georgia State University, USA, aboxleiter1@student.gsu.edu
Yuanzhi Tang, Georgia Institute of Technology, USA, yuanzhi.tang@eas.gatech.edu
Paul Schroeder, University of Georgia, USA, schroe@uga.edu
Rona Donahoe, University of Alabama, USA, rdonahoe@ua.edu
Martin Li, University of Brighton, UK, martinyhli@gmail.com

09:10
Experimental Investigation of Li+ Adsorption by Chlorite
Yu, W., Deng, Z., and Wan Q.

09:30
Student
Distribution, mineralogy, and formation environment of lithium- rich clays in the Salar de Pastos Grandes
Owen McCaffrey, Kristina Butler, Tom Benson

09:50 — *Keynote*
Utilizing stable isotopes to identify the formation processes responsible for lithium enrichment in clay deposits of the Western United States
Gagnon, C.A., Butler K.L., Robertson K., Emproto C., Gans, P., Eden R., Ibarra D.E., Benson, T.R.

10:20
Student
Mineralogical Insights in the Recovery of Lithium from Clays of the Thacker Pass Deposit (Nevada, USA) by Acid Leaching
Arias-Quintero, C.A., Muchez, P., Deferm, C. and Binnemans, K.

10:40
Using airborne and orbital imaging spectroscopy to differentiate lithium bearing hectorite from spectrally similar phyllosilicates - results and on-going difficulties
Meyer, John M., Swayze, Gregg A., Kokaly, Raymond F., Pfaff, Katharina, Key, Erica L., Wesoloski, Catherine E., Stillings, Lisa L., Hoefen, Todd M., and Cox, Evan.

11:00 — *BREAK*

11:20
Critical Mineral Potential of Clays and Clay-Rich Materials, Southeastern USA.
Donahoe, R.J., Okunlola, I.G. and Tew, K.J.

11:40
REE elements geochemistry in the present-day acid-sulfate types alteration from the active hydrothermal systems, São Miguel island, Azores Archipelago
Iuliu Bobos

12:00
Controls on cold-climate critical minerals: Rare earth elements in supra-permafrost sediments of three brine ponds in Wright Valley, Antarctica
Burton, Z.F.M., Koeberl, C., Bishop, J., Englert, P., Smith, M., Foerder, A., and Gibson, E.

12:20
Effect of clay mineralogy on REE recovery from regolith-hosted REE deposits
Martin Li

12:40 — *LUNCH*

13:40 — *Keynote*
Ion-sorbed Rare Earth Elements in Kaolins and Bauxite ore deposits, Western Georgia, Upper Coastal Plain, USA
W. Crawford Elliott, Yuanzhi Tang, Yinghao Wen, Anthony Boxleiter, Joell Ashcraft, Geoffrey Hooper, Prakash Malla

14:10
Student Remote
Clay mineralogical and geochemical characteristics of a lateritic profile within the Karakaya Complex, Biga Peninsula, NW Türkiye
Abdelnasser, A., **Kaya, M.**

14:30
Concentration and distribution of critical metals in laterites, bauxites and red muds
Laita, E., Bauluz, B., Yuste, A, Subirana, M.A., Schaumlöffel, D.

14:50
An uncommon occurrence of Ni-Co-Mn-Fe-rich nodules hosted in Plio-Pleistocene palygorskite and palygorskite-smectite continental deposits of west Macedonia, Greece
Stamatakis M., Vythoulkas K., Argyraki A., Pozo E., and Calvo J.P.

15:10 — *BREAK*

Lecture theatre 7-Davis

Clay Materials in Healthcare Technologies (session #36)

Huaming Yang, China University of Geosciences, Wuhan, China. hm.yang@cug.edu.cn
Menghan Yu, China University of Geosciences, Wuhan, China. yumenghan@cug.edu.cn
Hao Wang, China University of Geosciences, Wuhan, China. wanghao13@cug.edu.cn

09:10
Nanoclay-Mediated Crystal Engineering in Biofunctions to Balance Antibacteriality and Cytotoxicity
Menghan Yu

09:30
Student
Effect of Montmorillonite Modification on Its Antibacterial Mechanism
N. Ben Haj Yahia, J. Labille and A.R Schneider

09:50
Layered Clay Minerals in Cancer Therapy
Ying Chen, Huaming Yang

10:10 — *Keynote*
Biosafety of clay materials as biomedical nanocarriers
Huaming Yang, Juan Liao, Meng Zheng, Hao Wang, and Ying Chen

10:40 — *BREAK*

11:00
RENOVITE®: A Novel Injectable Clinical-Grade Nanoclay for Targeted Biomedical Applications
Himanshi Mishra, Allison Shaw, Roxanna Ramnarine-Sanchez, Mohamed Mousa, Richard OC Orefffo[1,2], Agnieszka Janeczek[2], Jonathan I Dawson[1,2]

11:20
Preparation and performance modulation of kaolin-based antimicrobial materials
Hao Wang, Huaming Yang

11:40
Facet engineering modulates d-π* hybridization for boosting antimicrobial activity
Xiongbo Dong, Huaming Yang

12:00 — *LUNCH*

13:00
Clay-based nanostructured systems for the controlled delivery of chlorhexidine
Martín-Morales, C., Aranda, P., Raquel Martin-Sampedro, David Ibarra, María E. Eugenio, Francisco Sánchez del Valle and Ruiz-Hitzky, E.

13:20
Deep detoxification of secondary aluminum dross treated by carbide slag
Lei Liu, Xiubao Lv, Rui Wang and Huaming Yang

13:40
Student Remote
Effect of montmorillonite and sepiolite on the production of virulence factors, eDrelease, and biofilm formation in Pseudomonas aeruginosa culture medium
Md Wasek Foysal, Youjun Deng, Terry J. Gentry, Carolyn L. Cannon

14:00
Kaolinite Interface Engineering for Biomedical Applications
Dongyue Wang, Huaming Yang

14:20 — *BREAK*

Go back to Sessions at a glance listing

POSTERS

All posters displayed from Monday–Friday, with two dedicated poster sessions (including refreshments) on Tuesday and Thursday afternoons.

Universal Session (session #1a,b)

Student

1. Clay-based systems for stimuli-controlled release of active molecules
   Dumont, A., Dhaini, A., Brendlé, J., Maillard, A., Arkoun, M., and Pluchon, S.
2. Clay minerals in the underpainting layers of northwestern European paintings (16th–19th century)
   El Ouahabi, M., and Broers, N., Fagel, N.
3. Mineralogy and Geochemistry of the Kaolinite-Alunite Deposit of Madriguera (Segovia, Spain)
   San-Cipriano, A., Santamaría-López, A., Suárez, M, **García-Romero, E.**

Student

4. Spectral and Geochemical Discrimination Between Different Slovak Bentonites
   Faisal A. Gread, Peter Uhlík
5. Determination of KGa-1b and SHCa-1 Δ'17O and δ18O via Laser Fluorination of Lithium Fluoride Clay Pellets
   Gagnon, C.A., Havel R., Chen J., Piccione G., Ibarra, D.E.
6. Utilization of infrared spectroscopy to study LBL films based on smectite and quaternized chitosan
   Kureková, V., Kováčik, D., Bilská, K., Bujdáková, H., Gread, F., Osacký, M. and Pribus, M.
7. Characterization and settling behavior of Alberta oil sands mature fine tailings (MFT)
   Osacký, M., Bai, Y. and Pálková H.

Student

8. Hydrothermal alteration and clay minerals in Palomares fault zone in Neogene volcanic province of the SE Iberian Peninsula (Spain)
   Real Fernández, E., Pozo Rodríguez, M., de Ignacio San José, C. and Sanz Rubio, E.
9. EvalOpt – Increasing the reliability of quantitative phase analysis by optimising Rietveld refinement results with alternative analytical methods
   Ufer, K., Ohmann, S., Dohrmann, R., Sitnikova, M., Ranneberg, M., Fell, H., Kernbach, C.

Sorption and intercalation in layered materials: from origins of life to material science (sessions #3+16)

Student

10. The role of layered double hydroxide minerals in the origin of prebiotic peptides
    Stewart, S.V., McMahon, S., Cockell, C.S. and Erastova, V.
11. Structural and spectroscopic characterization of montmorillonite modified with poly(2-n-alkyl-2-oxazolines)
    Pribus, M., **Jankovič, L.**, Kureková, V., Barlog, M. and Madejová, J.
12. Preparation and Characterisation of Montmorillonite/Polyquaternium-2 Nanocomposites
    Pribus, M., Bizovská Kureková, V., Matejdes, M., Jankovič, Ľ. and Madejová, J.

Student

13. Infrared spectroscopic analysis of smectite-chitosan nanocomposites
    Labib Shotorban, P. and Pálková, H.

From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis (session #4)

14. Diagenetic and hydrothermal assemblages at Izu-Bonin rear arc (International Ocean Discovery Program – IODP Site U1437)
    Bongiolo, E.M., Nascimento, L.S., Mexias, A.S., Neumann, R., Gomes, M.E.B.

Student

15. Use of Electron Probe Microanalysis in the Quantitative Analysis of Magnesium Clay Minerals from the Pre-Salt (Brazil): Microsite Evaluation and WDS Compositional Mapping
    Da Silva M. D., Gomes M. E. B., Pozo M., Mexias A. S., Bongiolo E. M., Ramnani C. W., Semeler, A.R., Jantsch, L.C.

16. Zircon U-Pb geochronology of Sarmatian (Serravallian) bentonite clay from the southern margin of the Pannonian Basin System
    Grizelj, A., Lukács, R., Mišur, I., Mandic, O., Milošević, M., Bakrač, K., Hajek-Tadesse, V., Ćorić, S. and Šegvić, B.

17. The Universe of Clay Minerals in Basalts – a petrographic approach of some Paraná-Etendeka flows in South Brazil
    Gomes, M.E.B., Toloti, C.K., Mexias, A., Bongiolo, E.M., and Da Silva, M.D.

Teaching, History, and Future of Clay Mineralogy (in honor of Dewey Moore and Bruce Velde) (session #5)

18. Combined 3D printing and computer models for teaching clay mineralogy: symmetry, rotation, shifting, and stacking of layer structures
    Deng, Y. and Sanchez-Avellaneda, C.

Origin and Age of Clay Minerals in Soil and Sediment (session #6)

Student

19. Mineralogical and geochemical evolution of Fe- and Al-rich phyllosilicates during the formation of the Baniaka Archean-age iron deposit in South-Eastern Gabon
    Aupissy, **Christian Pierrick**, Fontaine, Claude, Abderrazzak, El Albani

20. The crucial role of textural characteristics in sepiolite crystallinity and rheological properties
    Esteban Cubillo, A., Lo Dico, G., and Pozo Rodríguez, M.

21. A new method for measuring the K-Ar age of diagenetic illite
    Shahbazi-Asl, A., **Elliott, W.C.**, Wampler J.M., and McIntosh, J.A.

22. Investigating 40Ar* loss from hydrothermal illite crystals of different size
    Szczerba, M., Środoń, J. and Ciesielska, Z.

23. Formation of laterites through the alteration of basalts
    Bauluz, B., Do Campo, Yuste, A., Laita, E. M., Arranz E.

Student

24. Clay mineralogy in transitional-continental environments of the Late Triassic: an indicator of the paleoenvironmental impact of the Carnian Pluvial Episode in southeastern Iberia
Boullosa, I., Barrenechea, J.F., and López-Gómez, J.

25. Mineralogical analysis of egg-bearing palaeosols (External Sierras, Pyrenees, Spain): Insights into Late Cretaceous paleoenvironmental conditions
Laita, E., Ezquerro, L., Sanz-Acaso, C., Bauluz, B, Moreno-Azanza, M.

Student

26. Interstratified Kaolinite-Smectite in the Paris Basin: A new perspective on enhanced chemical weathering during the PETM
Talon, J., Pellenard, P., Baele, J.-M., Quesnel, F., Iakovleva, A., Bruneau, L., Rusch, C. and Dupuis, C.

Student

27. Intensified hydrological conditions and environmental changes during the Paleocene-Eocene Thermal Maximum at Modgunn Hydrothermal Vent Complex (IODP Expedition 396)
Turton, N.A., Xu, W., Varela, N., and Pellenard, P.

Student

28. Assessing the role of clay mineralogy in Blue Carbon storage and stability in Ireland's Offshore Continental Shelf Sediments
Ní Mhaoldomhnaigh, C.B., Grey, A., Chatting, M., Walsh, P., Coughlan, M. and Kelleher, B.

Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential (sessions #8+9)

29. Boron, lithium and strontium in the Late Miocene saline-alkaline lake deposits of Karlovassi Basin, Samos Island, Greece
Stamatakis M.

Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges (session #10)

Student

30. Sustainable Alternative to Copper-Based Pesticides in Agriculture: The LIFE MICROFIGHTER Approach
Alberghini, M., Ferretti,G., Galamini,G., Faccini, B. and Coltorti, M.

31. Obtention of Clinoptilolite Nanoparticles via Ultrasonic Cavitation Dispersion
Cortés Hernández, F.A., Insignares-Carrione, E., and Bolaños Gómez, B.

Student

32. Sodalite and cancrinite for safe entrapment of As and Se
Khait, L., Dähn, R. and Churakov, S. V.,.

33. Origins of compositional diversity in natural zeolites within the Antrim Lava Group, Northern Ireland, UK
Moles, N.R., Adair, B.J.I., Tindle, A.G. and Green, D.I.

34. Synthesizing zeolites from granite cutting sludge
Iglesias-Godino, F.J., Cotes-Palomino, M.T, López-García, A.B., Alonso-Acárate, J., Fakher Jamoussi, Martínez-García, C., Guerrero-Quirós, A.

Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies (#11)

35. Assessing the Spectral Response of Secondary Martian Minerals
Santamaría-López, A., **Suárez, M.**

Remote

36. Spatially resolved analysis of habitability-related phenomena: Talc-like and associated minerals at different scales
Velbel, M.A., and Steele, A.

Advances in structural characterization of layered compounds (session #12)

37. Electron diffraction mapping and DFTEM imaging as potential tools to probe layered materials superstuctures and structural defects
Gaillot, A.-C.

38. Computational study of 1-Phenanthroline trapping by smectites
Scholtzova, E. and Mičejová, E.

39. Assessment of basic properties of nanostructured anionic layered double hydroxide derived nanocomposites by in-situ CO2 FTIR sorption
Małgorzata Zimowska, Jerzy Podobiński, Robert Kosydar, Jerzy Datka

Clay Applications in Ceramics (session #13)

Student

40. Shear stability of ceramic slips in solid casting product
Alessandro Fontanari, Maurizio Bellotto and Gilberto Artioli

Student

41. Physicochemical Characterization of Altered Clays from the Ankaratra Volcanic Massif (Madagascar) for Ceramic Applications
V.S. Randresiarison, N. Fagel & A.J. Mandimbiharison

Student

42. Monitoring the quality of a kaolin mine over time: Piloni di Torniella (Tuscany, Italy)
Zatti, G., Musa, M., Tarantino, S.C., Zucca, F. and Riccardi, M.P.

43. Preliminary development of a composite Circularity Indicator applied to the Construction and Demolition Waste Sector.
Torres-Fernández, Fco. de A., Cotes-Palomino, M.T, López-García, A.B., Revelo Rodríguez, A.C., Troyano-Pérez, F.J., **Martínez-García, C.**, Cobo-Ceacero, C.J.

44. Development of a strategy for obtaining lightweight artificial aggregates (LWAs)from CDW
Troyano-Pérez, F.J., Alonso Azcárate, J., Andreola, F., Barbieri, L., Conde Sánchez, A., **Cotes-Palomino, M.T.**, López, A.B., Labrincha, J., Lancellotti, I., Martínez-García, C. Martínez Rodríguez, A. M. and Cobo-Ceacero, C.J.

45. Circular Engineering: effect of adding different organic wastes on the development of lightweight artificial aggregates (LWAs) from mining waste
Cobo-Ceacero, C.J., Alonso Azcárate, J., Conde Sánchez, A., López, A.B., Martínez-García, C., Martínez Rodríguez, A.M., Troyano-Pérez, F.J. and **Cotes-Palomino, M.T.**

Remote

46. Manufacture of geopolymers for the sustainable recovery of CDW
López, **Ana. B.,** Revelo- Rodriguez A.C., Cotes-Palomino, M.T., Martínez-García C., Jimenez-Moreno, J.M., Cobo-Ceacero C.J. and Troyano-Pérez, F.J.

47. Sustainable Ceramics: Extractive Waste for Porcelain Stoneware Tiles
Fantini, R., Conte, S., Arletti, R., Molinari, C., Zanelli, C., Dondi, M., Bernini, M. and Gualtieri, A.F.

48. Porcelain Stoneware and Sustainability: Innovation through Local Resources and Recycling
Andreola, F., Conte, S., Sisti, M., Colombo, F., Fantini, R., Barbieri, L., Gualtieri, A.F. and Arletti, R.

49. Hydrothermal Synthesis of Mn- and Ni-Doped Talc and Its Effect on the Microstructure and Thermomechanical Properties of Clay-Based Stoneware
Bloise, A., Parisi, F., La Russa, M. F., Godbert, N., Aiello, I., Giorno, E., Croce, A., Filicetti, S., Vespasiano, G., Fuoco, I., Apollaro, C.

50. Influence of red muds in the properties of alumina ceramics
Laita, E., Yuste, A. Salazar, M., **Bauluz, B.**

Materials via Ordered Interstratifications (session #14)

52. Engineered Clays for CO_2 Capture and Biogas Separation: Influence of Layer Charge and Interlayer Cations
Fossum, J.O., Breu, J., Hunvik, K.W.B., Loch, P., Bordallo, H.N., Pacakova, B., Cavalcanti, L.P., Kirch, A., Miranda, C.R.

Industrial Applications of Clays (session #17)

53. Deep learning methods for quantitative characterization of bentonite clays via X-ray diffraction
Owen, N.D., Li, R., and Huang, S., Fan, R., Gomez-Camacho, R., Roccisano, J., Webster, N.A.S., Self, P.G., Raven, M.D.

Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development (session #18)

54. Clay (trans)-formation in sediment-hosted mineral systems: examples from world-class Zn and Cu districts
Schleicher, A.M., Magnall, J.M., Mohammedyasin, M.S., Gleeson, S.A.

Science and Engineering of Clays for Nuclear Waste Disposal (session #20)

55. Multiscale simulation of thermal-hydraulic-mechanical-chemical (THMC) coupled processes in compacted bentonite clay
Zheng, X. and **Bourg, I.C.**

56. Mineralogy and geochemical processes in the Upper Eocene volcanic ash and bentonite deposits in East Central Texas, USA
Deng, Y. a, Barrientos-Velazquez, A. L., Yancey, T. and Berti D. and Smith, C.

57. In-situ experiment Engineered Barrier 200C – Preliminary results of a mineralogical study of the bentonite barrier
Magdaléna Koubová, František Laufek, Jiří Svoboda, Markéta Kučerová, Radek Vašíček and Marek Szczerba

Student Remote

58. Behaviour of engineered safety barrier materials under deep geological repository model conditions
Morozov I.A., Koroleva T.A. and Krupskaya V.V.

Impact of temperature on bentonite barrier systems based on findings from in situ experiments in the context of radioactive waste disposal (session #21)

Student

59. Impact of a long-term thermal pulse on bentonite erosion rates in lab scale experiments: First results from samples of the LOT/ABM experiments
Van Overloop, L., Brandt, F., Klinkenberg, M, Schäfer, T.

60. What limits the temperature at canister surface in clay-based HLRW concepts? – Discussion in an international context
Dohrmann, R., Chaudry, S., Lippmann, R.

Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes (session #23)

Student

61. Optimization and molecular insights into the adsorptive efficiency of Cu-Al layered double hydroxides derived from aluminum saline slags
Boulahbal, A.I., Santamaría, L., Bourzami, R., Bendrihem, A.S., Boutahala, M., Korili, S.A. and Gil, A.

62. Design of clay-based catalysts assisted by machine-learning
Lo Dico, G., Esteban Cubillo, A., Haranczyk M.

63. Advanced and sustainable piperazine functionalized clay catalyst for aldol production in water-acetone mixture
Muhammad Kashif, Alireza Pourvahabi Anbari, Fatimah Algarni, Jeroen Lauwaert, Joris W. Thybaut, **Philippe M. Heynderickx**

Fundamentals of Tubular Nanoclays (session #25)

Remote

64. Halloysite nanotubes as stable support materials for gold/silver-nanotags
Gray-Wannell, N., Kershaw, C., Aslam, Z., McGettrick, J., Hillier, S., Greenwell, C., Brydson, R. and Holliman, P.J.

65. Halloysite nanotubes dispersions in chitosan for archaeological wood conservation
M.R. Caruso, M. Romani, G. Cavallaro, O. Gómez-Laserna, M. Maguregui, **G. Lazzara**

1D Nanoporous Clay Materials and Their Industrial Applications (sessions #26)

66. Sepiolite-carbon based bionanocomposites: a green approach to corrosion protection
Barra A., García-Galván F.R., Nunes C., Ferreira P., Galván J.C., **Ruiz-Hitzky E.**

67. Kinetics and isotherms evaluation of Albumin protein adsorption on Algerian Clays
Abderraouf Boudahri, **Lala Setti Belaroui**

68. Application of tubular halloysite in low-carbon building materials: geopolymers and limestone calcined clay cement
Yuan, P., Zhang, B. F. and Yu, T.

Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces (session #27)

69. Multiscale simulation of thermal-hydraulic-mechanical-chemical (THMC) coupled processes in compacted bentonite clay
Zheng, X. and **Bourg, I.C.**

70. A comparison study between halloysite interactions with mono-cationic and di-cationic form of irinotecan
Gianni, E., Avgoustakis, K., Scholtzova, E., Panagiotaras, D., Papoulis, D. and Pospíšil, M.

Student

71. A classical forcefield for selenium oxyanions in aqueous solutions and minerals
Glushak, A.A., Tararushkin, E.V. and Smirnov G.S.

Student

72. ClayCode: A software tool for modelling realistic clay systems
Pollak, H., Degiacomi, M. T., and Erastova, V.

73. Physical adsorption of OH- ions at mineral-water interface
Xiandong Liu, Yingchun Zhang, Pengyuan Gao

74. Various concentrations of atorvastatin intercalated into Mg-Al layered double hydroxides
Pospíšil, M., Novotný, R. and Kovanda, F.

Nanoelectronic and Nanophotonic Applications (session #28)

Remote

75. Memory Effects in Ultrathin $MoSe_2$/Clinochlore Devices
Ames, A., Sousa, F. B., Souza, G. A. D., de Oliveira, R., Barcelos, I. D., Cadore, A. R., Lopez-Richard, V. and Teodoro, M. D.

76. Nitrogen-doped graphene in the interlayers of a nanolayered silicate for sustainable upscaled energy applications
Pacakova, B., Matejdes, M., Thanganian, K., Demchenko, H., Wagner, D., Michels, L., Brito, P., Blanco, M.V., Araki, K., Raaen, S., Breu, J., Fossum, J.O.

Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials (session #29)

77. Aspect Ratio Control of Layered Double Hydroxide Nanosheets and Their Application for High Oxygen Barrier Coating in Flexible Food Packaging
Fan, S., Yu, J.

Student

78. Durable radially polarized tubular nanoreactors for catalysis
Lucile Hamm, Antoine Thill, Sophie Le Caër and Pierre Picot

Student

79. Tuning the interlayer space of Li-Al LDHs as adsorbents with application in the direct lithium extraction (DLE) technology
Kaźmierczak, M., Matusik, J., Seftel, E.M., Cool, P.

Student

80. Synthesis and Characterization of BODIPY with different meso groups for the study of hybrid materials
Leonardo K. Santos, Peter Boháč, Juraj Bujdák

81. Efficiency Enhancement of Circularly Polarized Luminescence from a Binaphthyl Compound via Interlayer Confinement in Clay
Hiroki Moritomo, Ryo Moriguchi, Daichi Yamashita, Ren Nishiyama

Student

82. Unlocking Fluorescence Enhancement in Benzothiazole-based Dyes in Hybrid Silicate Dispersions
Planetová, V., Boháč, P., Hrobárik, P. and Bujdák, J.

Student

83. Synthesis of transition metal-doped Li-Al layered double hydroxides and their application for selective lithium extraction from brines
Siwek, K., Matusik, J., Seftel, E.M., Cool, P.

84. Ionic Conductivity of Ion Defect Introduced Layered Double Hydroxide and its Mechanism
Sonoyama, N, Uchimura, S. and Yamaguchi G.

85. Analysis of the abrasive and micro-impact wear of hydrotalcite-like coatings on zinc alloy
S. Zimowski, D. Kharytonau, K. Skowron, G. Mordarski, J. Krupa, M. Zimowska

Clays in Geotechnics – Problems and Applications (session #30)

86. An appraisal on the characteristics of organically modified clays for applications as engineered barriers
Vandana Sreedharan, Sivapullaiah, P.V

Student

87. Experimental method for testing thixotropic properties of clays
Alicja Bożek, Łucja Kordaszewska .

88. Strength and Liquidity Index Correlation in Transitional Oil Sands Tailings
Kaheshi, P., Kaminsky, H. and Wilson G.W.

89. The role of vermiculite in the geotechnical behaviour of Plioquaternary clayey soils from the Zagreb Podsljeme hilly area
Martinčević Lazar, J., Durn, G., Mihalić Arbanas, S., Grizelj, A., Peh, Z.

90. Experimental Study on Biogenic $CaCO_3$ for Sustainable Stabilisation of Dredged Fine Sediments
Petti, R., **Vitone, C.**, Plötze, M. and Puzrin, A.

Student

91. Clay materials identified within construction and demolition waste
Tijero-Martín, M., Ruiz, A.I., Cuevas, J. and Regadío, M.

Advances in Calcined Clays as Supplementary Cementitious Materials in Blended Cements (session #31)

92. Calcined Clay interaction with superplasticizers: adsorption behaviour and ion release kinetics
Hellmann, S., Jara Heredia, D., Link, J., Strybny, B., Hoffmann, C., Sowoidnich, T., Rößler, C., Gil-Díaz, T., Lützenkirchen, J., Heberling, F., Ludwig, H.M., Haist, M. and **Schäfer, T.**

93. The role of accessory minerals in the activation of natural bentonites
Aguilar Guimaraes, P., Paris, M. and **Deneele, D.**

Student

94. Hydration Mechanisms and Phase Assemblage Of Very-Low Clinker Cement Blends Comprising Non-Kaolinitic Calcined Clays
Menezes, D.C., Vanhee, L., Arnout, L. and Snellings, R.

95. Sedimentation as a low-cost alternative to laser diffraction for particle size measurement of calcined clays – limitations and opportunities
Marsh, A.T.M., Massonnet, G., Scrivener, K.L.

Sustainable and eco-friendly clay-based materials (session #32)

Remote

96. Experimental Design-Based Optimization of Clay Bricks from Rissani for Enhanced Mechanical and Thermal Performance
Mahdi Lechheb, Kamal Essifi, Soukaina El Bourachdi, Hassan Ouallal, M'barek Azdouz, Mohamed Azrour, Meriam El Ouahabi and Gharibi El Khadir

Remote
Student

97. From fired clay bricks to an accessible eco-material in the Sudano-Sahelian zone of Cameroon: what local appropriation for sustainable development?
Mounpe Chare, I., Pirotte, G., Mache, J.R., Fagel, N.

Remote

98. Potential reuse of Steel Slag and Phosphogypsum in Bentonite-Lime Composites
Harrou, A., Jouini M., Elghali A., El Ouahabi M., Fagel N., Gharibi E.

99. Porosity in sustainable bricks: merging tradition with environmental innovation
Zema, M., Lica, J., Marian, N.M., Bonou, S., Idjiwole, F., Agbahoungbata, M., Fernández-Jiménez, A., A. Monno, Riccardi, M.P., and Tarantino, S.C.

Student

100. Clay minerals in earthen binders for Earth Additive Manufacturing (EAM) applications
Tsiotou, S., Maier, M. and Machner, A.

101. Addition of stevensite to a magnesium potassium phosphate cement formulation with application for 3D printing
Padilla-Encinas, P., Guerrero, A., Cuevas, J. and Fernández, R.

Remote

102. Compressed lime-stabilized clay from Benoue valley (North, Cameroon) for sustainable construction: Evolution of their properties
Mache, J.R, Moongon Obam, B.I., Balo Madi, A and Fagel, N.

103. Promoting green compressed earth bricks towards net zero emissions commitment of Vietnam
Hieu, N.T., Tuan, N.V, **Dinh, N.Q.**, and Fagel, N.

104. High strength eco-cement from alkali-activated gravel wash mud and quartzite dust
Kukemilks, K., Wagner J.-F. and Baeza Urrea, O.

Remote
Student

105. Physico-mechanical and mineralogical properties of lime-treated clay materials from Northern Cameroon (Pitoa and Gaschiga)
Njimboum, A.S., Mache, J.R., Balo, M.A., Fagel, N., Nchare, M.

Mechanical and Mechano-chemical Activation of Clays (session #33)

Student

106. Impact of metakaolin characteristics on properties of alkali-activated materials
Launai, D., Robin, V. and Joussein, E.

The Role of Clays in Human Health and Biomedical Sciences (#35)

Student

107. A Novel Nanomaterial Based on Halloysite and Laccase: A Sustainable Approach for Dyes Degradation
Riela, S., **Cinà, G.**, Cardullo, N., Mancari, G.G., Massaro, M., Mineo, P.G., Nicosia, A., Sanchez-Espejo, R., Sciacca, C., Viseras-Iborra, C., and Muccilli, V.

Student

108. Photosensitizer-Loaded Nanocomposite Hydrogels with Functional Photoactive Surfaces for Photodynamic Applications
Vinny George, Peter Bohac and Juraj Bujdak,.

109. Application of Ukrainian Kaolins for the Development of Novel Hemostatic Agents
Zatovsky, I.V., Prokopenko, V.A., **Panko, A.V.**, Tsyganovich O.A., Dybkova S.M. and Rieznichenko L.S.

110. Interactions of cyclic peptides with montmorillonite surface for a natural drug delivery system
Sainz-Díaz, C.I., Nogueira de Sousa, L.H., Viseras, C.

Clay Materials in Healthcare Technologies (session #36)

Remote

111. Monitoring the cellular internalization of Eu^{3+}-Laponite using combined Raman imaging and fluorescence microscopy
Perdigón, A.C., Iturrioz-Rodríguez, N., Martín-Rodríguez, R., Aguado, F.

Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils (sessions #39+42)

112. Changes in Clay Mineral Composition in Pit-Mound Profiles Resulting from Tree Uprooting in the Žofín Forest, Czech Republic
Magdaléna Koubová, Pavel Šamonil, Filip Oulehle, Jan Dietel

113. Quantifying N_2 and H_2O isotherm-based mineral surface area and cation exchange capacity: Revisiting basic properties related to mineral reactivity
Blattmann, T.M., Galili, N.N., Yoshimura, T., Usman, M.O., Eglinton, T.I. and Plötze, M.

Student

114. Impact of Clay on Soil Organic Carbon in Response to Agricultural Management in Central Kansas
Nelson, I., Presley, D. R. and Tomlinson, P. J.

115. Redox-Driven Interactions of Fe^{2+} with Imogolite Nanotubes in the Presence of Ca^{2+} and As(III) under Anoxic and Oxic Conditions.
Cuevas R.D., Orozco L., Fabris, José D., Pizarro, C., Manquián-Cerda, K. and Arancibia-Miranda N.

Student

116. Modeling cohesive fine-grained sediment erosion using a computational fluid dynamics framework
Jans, M.D., Yang, J.Q., Soulaine C., and Bourg I.C.

Student

117. Long-Term Agricultural Inputs and Clay Mineral Weathering, Plus Potential Evidence of Shallow Mixed-Layer Silicates
Correira, A. L., LaCroix, B., Arnall, B., and Presley, D. R.

118. Mapping organic carbon species in soils with contrasting clay minerals
Mia, S., Dijkstra, F.A., Guggenberger, G. and **Singh, B.**

119. Potential of Clays from the Nahuelbuta Mountain Range in Chile for Agricultural Crop Applications
Castro, E., Pinto, A., Mora, S., Jarpa, M., Sanhueza, V.

Clays in Mining (session #40)

Student

120. Portable VNIR-SWIR spectroradiometry for material classification in clay mineral deposit exploitation works
García-Vicente, A., **Lorenzo, A.**, San-Cipriano, A., García-Romero, E.-, Suárez, M.

Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies (sessions #38+43)

121. Adsorption of short-chain perfluoroalkyl acids (PFAAs) on montmorillonite clay using density functional theory
Bashir, S., Scholtzova, E.

Student

122. Adsorption performance of Eu(III) on natural clays and high-charge synthetic micas: Isotherm and kinetic studies comparison
López-Marín, A., Martín-Rodríguez, R., Perdigón, A.C., and Aguado, F.

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Synthesis and Applications of Modified Clays in Environmental Remediation (#44)

123. Monitoring drug adsorption by smectite composites
Plevova, E., Vallova, S., Vaculikova, L., Vytiskova, K., Duraczynska, D., Ocwieja, M. and Hlavacek, P.

124. Adsorption of Cs-137 and Co-60 by metabentonite and metakaolin-based geopolymer composites
Slaný, M., Juriček, A., Struhárová, G.A., Rezbárik, Š.J., Vavrincová, L. and Horník, M.

125. Multifunctional smectite composites
Vaculikova, L., Plevova, E., Valovicova, V., Vallova, S., Duraczynska, D., Kosydar, R., Krzan, M. and Mahdi Niktabar, S. M.

Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling (session #47)

126. Structural Fe promotes allophane reactivity towards model organic compounds
Zelano, I.O., Emmanuelle-Montarges-Pelletier, Ralf Kaegi, Laurel ThomasArrigo

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PLENARIES

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About comparison of claystones as potential host rocks for radioactive waste

Kaufhold, S.[1]

[1]Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany

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Claystones are currently being investigated as potential host rocks for the storage of high-level radioactive waste (HLRW). In France and in Switzerland the decision was already taken to built a repository in claystone (Callovo-Oxfordian claystone, COX, France and Opalinusclay, OPA, Switzerland). While other countries such as Finland and Sweden decided to select crystalline rocks as host rock, some countries are still searching for the optimum host rock. In Germany, several regions containing salt, crystalline, and claystone formations remain under investigation. In order to assess the suitability of different sites, however, the different host rock formations have to be compared with respect to their suitability as host rock, which is particularly challenging in the case of claystone formations. The desired material properties of a claystone host rock (apart from thickness of the geological formation) are: low permeability, high mechanical stability, self sealing ability (incl. ductility), temperature stability (high paleo-temperature), high heat conductivity, and retention capacity (for radionuclides). For the identification of the most suitable claystone it is required to rank the parameters according to their importance with respect to the overall performance of the barrier. As an example, claystone A has a 20°C higher paleo-temperature (and hence higher thermal stability) than claystone B which, however, contains 10 % more smectite (probably affecting self sealing, retention capacity, and mechanical behaviour) with equal permeability of A and B. Without knowing the quantitative effect of such differences on the overall performance of a barrier it will be difficult to accurately determine the optimum claystone. Moreover, these data are often incomplete or entirely missing for many of the German claystones under consideration. On the other hand, for most claystones geological models exist predicting their maximum burial depth. This parameter is particularly valuable for a qualitative comparison of claystones because the desired properties mentioned above all change with burial depth. It is important to note that some properties (e.g. porosity and mechanical strength) do not change significantly anymore below a burial depths of about 2000 m.

In the present study 17 different claystones (including German claystones as well as COX and OPA) with different maximum burial depths are characterised with particular focus on maturity indexes such as vitrinite reflectance, Kübler index, porosity, RockEval, and pore size. The vitrinite reflectance representing the thermal history does not reflect the burial history in case of thermal anomalies and illitization (Kübler index) is known to be affected by the geochemical conditions of a basin. The porosity, however, is systematically reduced upon compaction (burial) along with the average pore size in turn reflecting the average distance of particles which decreases upon burial. The porosity, however, can also be reduced by cementation and hence low porosity does not necessarily reflect deep burial. The average pore size, on the other hand, neither is affected by the thermal nor geochemical environment and can be used to define a limit representing a maximum burial depth (e.g. 40 nm corresponding to about 2000 m). Claystones which reached at least this burial depth can be considered less permeable and mechanically more stable and hence considered more suitable than others. Additional parameters such as paleo-temperature and smectite content could be used for further differentiation, as an example. This study demonstrates how burial depth-related parameters can support the structured comparison of claystones for repository site selection. The framework can be adapted based on the weighting of individual properties, which remains a key task in future assessments.

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Small Minerals, Big Impacts: A Geochemist's Approach for Resource Recovery

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Building on the scientific legacy of Professor Marion L. Jackson, whose pioneering contributions to soil and clay chemical analysis laid the groundwork for generations of clay and soil scientists, this presentation explores the molecular-scale interfacial processes that govern element behaviour in clay-rich environments. Over the past decade, my group has investigated the molecular scale geochemical mechanisms of element retention, release, and transformation in natural and engineered systems, with a focus on clay and clay minerals as reactive surfaces. We employ advanced spectroscopic and microscopic tools, coupled with thermodynamic modeling, to bridge atomic-scale observations with field-scale relevance.

To illustrate the importance of fundamental molecular understanding, this talk will present our recent work on critical mineral recovery from waste streams. Rare earth elements (REEs), essential to clean energy and high-tech applications, face increasing demand and potential supply risk. REE recovery from alternative or waste feedstocks offers a strategic path to sustainable resource development and waste valorization. Our research combines detailed speciation analysis of REEs in a variety of industrial residues with rational system design for their selective extraction, achieving both environmental remediation and resource recovery goals.

As a recipient of the Jackson Award, I am honored to contribute to this symposium in celebration of Professor Jackson's enduring influence. His commitment to analytical rigor continues to shape and inspire the advancement of environmental geochemistry and clay science.

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Clay mineral-microbe interactions and applications

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Clay minerals and microbes co-exist in natural environments, their interactions influence energy flow and elemental cycling. Clay minerals provide protection, nutrients, and energy to support their growth and metabolism. In return, microbes can alter the chemistry and structure of clay minerals through dissolution, transformation and secondary mineralization. Structural iron in clay minerals is redox active and can serve as an important electron acceptor and donor for various functional microbial groups. In redox-active environments, many iron-reducing and oxidizing bacteria can reduce or oxidize structural Fe(III)/Fe(II) in clay minerals and they gain energy from these processes [1-2`. As a result, these microbially-mediated redox processes alter the physicochemical properties of clay minerals and soils.

Clay mineral-microbe interaction plays an important role in geochemical cycling of carbon, nitrogen, silicon and phosphorus. For example, adsorption of organic matter on clay minerals decreases the bioavailability of organic matter and its mineralization rate, thus offering some protection. However, under redox-fluctuating environments, clay minerals can activate molecular oxygen to produce reactive oxygen species (ROS), which can degrade organic matter and increase its bioavailability [3]. Clay minerals adsorb extracellular enzymes to decrease their activity in organic matter transformation [4]. Microbes can also couple iron oxidation in clay minerals with nitrate reduction [5] and Fe reduction with ammonia oxidation to affect nitrogen cycling [6]. Because of these roles, clay mineral-microbe interaction has a wide range of applications in heavy metal remediation [7], organic pollutant degradation [8], and development of antibacterial materials [9-10].

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Understanding the structure and dynamics of clay and other layered minerals and their interfaces using molecular modelling – a perspective

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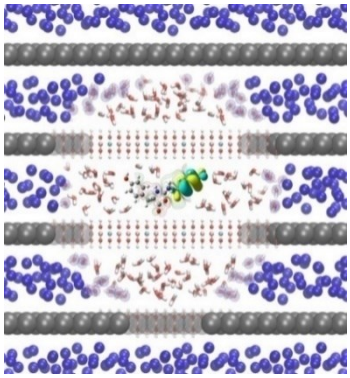

Layered minerals are implicated in governing a number of natural biogeochemical cycles, as well as controlling the transport and fate of xenobiotic molecules in the natural and built environment. In industry, layered minerals find numerous technological applications. The properties of layered minerals are embedded at an atomic scale, with the identity and location of isomorphic substitutions and structural defects influencing ion exchange and acid/base reactions, as well as the interlayer spacing. As such, even macroscopic phenomena, such as swelling and shrinkage in clay rich soils are determined by the initial atomic structure of the minerals. Layered minerals are, therefore, excellent examples with which to illustrate structure-activity relationships.

Owing to their low crystallinity, and layered nature, understanding the structure of clay and other layered minerals presents a number of challenges. Experimental techniques give insights into bulk mineral crystal structure and reactivity, and advanced microscopy methods are increasingly able to address external surface structure and phenomena. However, the interfacial region, and especially the interlayer region of layered minerals is difficult to characterise by experimental methods. Early studies inferred interlayer structure based on molecular size and packing for simple interlayer guests, however the dynamics and reactivity of the interlayer region, especially with either low numbers or mixtures of guest molecules, or for those with complex guest molecule structures remain a challenge.

Computational chemistry methods applied to layered minerals have given exceptional insight into the “hidden” world of interlayer structure, dynamics and reactivity (as in the schematic shown [1]). Over the last 25 years, these techniques have moved from studying small and idealised model structures of fragments of clay minerals on very small time scales (10s of ps) through to aggregates of multiple clay crystals with accurate composition, while maintaining atomic resolution, at timescales in the order of 10’s of ns. Different computational techniques have allowed new understanding of experimental data and observed phenomena, including electron movement in redox active layered minerals, Lewis and Brønsted acidity at basal and edge sites, hydration of ions at isomorphic substitutions, *inter alia*.

Drawing on case-studies from electronic structure and classical molecular modelling studies of layered double hydroxides and clay minerals over a 25-year career, this lecture looks at why computational chemistry methods have become fundamental to studying these fascinating materials, looking at the motivation for the studies, engagement with industry applications, and how computational and experimental approaches have converged to give new insights. As the length scales accessible by modern laboratory and computational experiments converges, it seems certain that computational chemistry techniques will continue to be a large part of layered mineral science in the future.

[1]Schematic by V. Erastova and T. Underwood

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Clay minerals formation in $MgO\text{-}SiO_2\text{-}H_2O$ low temperature system by hydrothermal synthesis: A study in function of Mg/Si molar ratio and pH

Jourdain, A.[1], Dutournié, P.[1], Michelin, L.[1], Le Meins, J.-M.[1], Brendlé, J.[1], Michau, N.[2], Martin, C.[2], and Dzene, L.[1]

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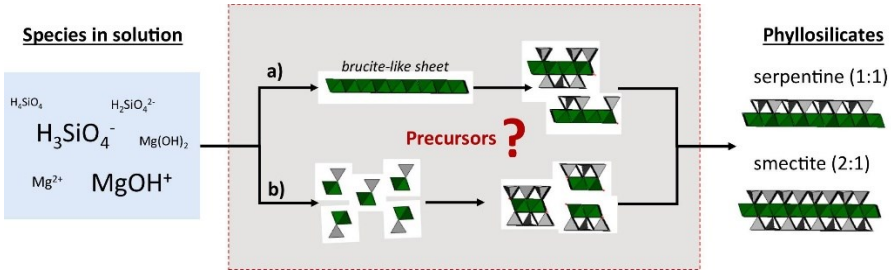
Magnesium phyllosilicates such as serpentines (1:1) and stevensite (2:1) do exist in nature but are not abundant in pure form, whereas synthesized materials can ensure higher purity. Clay mineral hydrothermal synthesis is quite easy to perform, however, the condensation reactions leading to the formation of these phyllosilicates and their precursors are not well understood. Such knowledge would allow to predict the synthesis outcome in case of variation of experimental parameters. Previous studies found that in the case of $FeO\text{-}SiO_2\text{-}H_2O$ systems, the type of clay mineral, i.e. 1:1 or 2:1 would strongly depend on pH, and could be related to the element speciation in aqueous solution, and in particular, silica speciation [1,2].



Schematic representation of possible pathways for phyllosilicate formation at basic pH [3].

This study reports a chemical reaction mechanism explaining the parameters that are determining the type of the formed clay mineral. After a detailed characterization of each obtained phase, it is shown that, for these $MgO\text{-}SiO_2\text{-}H_2O$ systems, pH has a lower effect compared to Mg/ Si molar ratio. Our results show that above pH 10 the mechanisms of lizardite and stevensite formation are similar with the same elementary units, but that the type of material obtained depends on the excess availability of magnesium (formation of lizardite) or of silicon (formation of stevensite).

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MONDAY

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LECTURE THEATRE 1 – SESSION 20

Science and Engineering of Clays for Nuclear Waste Disposal

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Clay in the Context of the Swiss Geological Repository

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In November 2024, Nagra—the Swiss National Cooperative for the Disposal of Radioactive Waste—submitted its application for a general license to construct a deep geological repository at the Nördlich Lägern site in northern Switzerland (Nagra 2025). This milestone reflects more than four decades of intensive site investigations and focused research, development, and demonstration (RD&D) activities, particularly in the use of clay as a natural and engineered barrier for the safe disposal of radioactive waste.

The post-closure safety (Nagra 2024) of the repository is founded on a system of multiple, passive barriers. The most importnat among these is the geological barrier formed by the Opalinus Clay and its surrounding clay-rich confining rock zone, which together isolate the repository from regional aquifers above and below. In Nagra's provisional design, bentonite plays a critical role—providing protection of the canisters and sealing construction tunnels and shafts.

Demonstrating the long-term safety of the repository involves more than positive results from safety assessments. It requires a robust, defensible safety case, built on the principle of "defense in depth." This means supporting safety-relevant claims through multiple, independent lines of evidence—an approach made possible only by a comprehensive and high-quality assessment basis. For many years, Nagra has developed detailed RD&D roadmaps, built internal and external competence, and structured its work to ensure the availability of the necessary information, when and where it is needed.

This presentation will trace the journey from field data collection to the conceptualization of relevant processes and phenomena, the formulation of representative scenarios, and ultimately, the assessment of barrier evolution over the post-closure timescale. A key focus thereby of safety assessment is understanding how thermo-hydraulic and chemical transients—induced by the repository itself—affect the performance of these clay-based barriers over time.

Finally, the presentation will provide a forward-looking perspective on how the current provisional design will evolve—transitioning from a standardized concept to a site-optimized deep geological repository tailored to the site characteristics of Nördlich Lägern.

Nagra (2024): Post-Closure Safety Report. Nagra Technical Report NTB 24-10 Rev. 1.
Nagra (2025): Rahmenbewilligungsgesuch für das geologische Tiefenlager – Sicherheitsbericht. Nagra Technischer Bericht NTB 24-01.

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The Sandwich shaft sealing experiment at Mont Terri Rock Laboratory – Selected aspects of clay science

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Shaft and drift seals are part of the engineered barrier system of geological repositories for high-level radioactive waste. Thereby the Sandwich sealing system acts as a hydraulic sealing in seals [1,2]. It consists of of sealings segments (DS) sandwiched by equipotential segments (ES). DS are built of a binary mixture of bentonite pillows and bentonite granular material (BGM). The ES are characterized by a higher hydraulic conductivity than the DS and preferential flow paths of fluid during hydration are interrupted in ES. Fluid is evenly distributed over the cross section of the seal in the ES and available for hydration of adjacent DS resulting in homogenous hydration, swelling and sealing.

The international Sandwich project investigates the behaviour of the Sandwich sealing system by experiments on multiple scales and numerical hydro-mechanical(-chemical) simulations [3,4]. Experiments range from swelling pressure measurements and MiniSandwich experiments to semi-technical scale tests and a large-scale experiment, that consists of two experimental shafts with Sandwich sealing systems installed in each, has been conducted at the Mont Terri rock laboratory (MTRL) since July 2019. Both shaft seals are hydrated from the bottom with artificial pore water and closely monitored, alongside the surrounding rock.

This contribution is particularly related to the laboratory experiments, parametrization of material models for numerical simulations (interpretive and predictive) and the structure-functionality-relation of swellable clays that relates fundamental smectite and bentonite properties to the hydration and swelling of DS.

The Sandwich shaft sealing experiment at the MTRL is a joint project of KIT, GRS, TUBAF together with Swisstopo, ENSI, BetterDataSystems (CH), BGR, ISU mbH Karlsruhe, IFG Leipzig, IBeWa Freiberg, SSKG Langendernbach (all D), CIEMAT, UPC, Amphos 21 (all Spain). Many thanks for their valuable contributions. The authors thank the German Federal Ministry BMUV for funding the projects (contracts 02E11587A+B, 02E11799A to C, 02E12163A to C) and the project management agency of Karlsruhe. The authors also thank the Mont Terri partners ENRESA (Spain), NWS(GB) and NWMO (Canada) for their constant support in the project.

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[2] Schuhmann R et al. (2009) https://doi.org/10.2314/GBV:637752392
[3] Emmerich K et al. (2019) https://doi.org/10.2314/KXP:1692488228
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Effect of boundary conditions and heterogeneities on the hydromechanical behaviour of two Calcium bentonites

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Bentonite clays are planned to be used within backfills, plugs and buffer elements in the Engineered Barrier System (EBS) in the context of underground waste disposals for high-level radioactive waste as they show substantial swelling upon hydration together with an ability for self-sealing of gaps or cracks and a very low permeability [1] [2]. Heterogeneities with respect to dry density are present in the EBS either by the initial design or are a result of the installation process [3] [4]. Their influence on the safety of the EBS is currently under investigation.

In the present study, the effect of boundary conditions and initial heterogeneities on the hydromechanical behaviour of two German calcium bentonite granules (Securisol UHP and Calcigel with 80% and 61% smectite content, respectively) is investigated. The experimental program includes high stress oedometer compression tests on compacted (un)saturated samples, constant volume swelling pressure tests on homogeneous and heterogeneous samples and unconfined swelling strain tests as well as measurement of the soil-water characteristic curve during hydration under confined condition. At selected sample states, microstructural investigations using mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) are performed.

The time evolution of swelling pressure is influenced by heterogeneities in the sample, but the equilibrium magnitude is within measuring tolerances for all presented configurations compared to homogeneous samples as heterogenous samples homogenize upon saturation. Technical voids must not exceed the achievable swelling expansion of the surrounding material in absolute terms. Securisol UHP exhibits higher swelling pressures over the wide dry density range tested, which is in line with its higher smectite content. However, swelling strains measured at unconfined conditions were found to be larger for Calcigel bentonite for the whole density range considered, which is explained by the inherited rock structure of Securisol UHP hindering expansion upon hydration to some extent.

In the present study, a consistent method for the dimensioning of heterogeneous samples was demonstrated and tested on German calcium bentonites. Overall, the sealing and healing ability of the material remains for application in the EBS.

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The Effect of High Temperatures on the Swelling Pressure of Expansive clays

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Geological Disposal Facilities (GDFs) for high-level radioactive waste (HLW) and spent nuclear fuel (SNF) are based on a multi-barrier system comprising a metallic canister, an engineered barrier system (EBS), and the host rock, such as granite, claystone, or rock salt. Compacted unsaturated bentonite is widely employed in the EBS due to its low permeability, high swelling capacity, and strong radionuclide retention. Recent research has increasingly focused on the behaviour of EBS materials under elevated temperatures. However, the effects of high temperatures (e.g., up to ~200 °C) on the swelling pressure of compacted bentonites—and their implications for the long-term safety functions of the EBS—remain insufficiently understood. Furthermore, it has been suggested that the swelling pressure of Ca-bentonite (i.e., bentonite saturated with divalent cations) tends to decrease with increasing temperature, as observed in the FEBEX bentonite [1]. In contrast, the swelling pressure of Na-bentonite (i.e., saturated with monovalent cations) may increase with temperature [2].

Two main swelling mechanisms control the expansion of compacted clays, namely, crystalline swelling and osmotic (or double layer) swelling. In Na-dominated clays, both **osmotic** and **crystalline** swelling mechanisms significantly contribute to the overall swelling pressure. Conversely, in Ca-bentonite, swelling is predominantly governed by **crystalline swelling**. This distinction arises from the structural differences between the two clay types: Ca-montmorillonite generally has a greater number of layers per stack compared to Na-montmorillonite, which leads to a lower density of electrical double layers (per unit volume and, consequently, a weaker diffuse double layer (DDL) effect.

This study aims to advance the current understanding of the behaviour of clays intended for use in EBS when subjected to elevated temperatures, up to approximately 200 °C. A combination of fundamental, experimental, and numerical approaches is employed. The experimental program includes: (i) **macroscale investigations** using single-element tests to evaluate the swelling pressure of compacted clays as a function of temperature; and (ii) **microscale investigations** to examine structural changes in clay minerals, thereby supporting interpretation of the macroscopic responses.

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" *CIEMAT Report*. https://www.osti.gov/etdeweb/biblio/22134576

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Effect of high temperature and exchange cations on the layer charge and swelling pressure of compacted bentonite

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The current concept of isolating high-level nuclear waste considers compacted bentonite as a buffer material for deep geological repositories. Ongoing research on optimizing waste repositories tries to understand the behavior of buffer material at high temperature (exceeding 100 ˚C) to develop more efficient and economic solutions [1]. Experimental observations on the swelling properties of smectites suggest that their initial swelling capacity can reduce when samples are subjected to high temperature for a long time. Changes to the crystal structures of expansive clays occur at high temperature, depending on the type of exchangeable cation. The presence of K^+ can cause the collapse of the smectite interlayer at high temperature due to dehydration and fixation of K^+ in the ditrigonal holes (illitization). Collapse in smectite d_{001} has been reported due to migration of Mg^{2+} into the vacant sites of dioctahedral smectite after heating [2]. However, the impacts of these structural changes on the swelling pressure (SWP) developed by the compacted clay are not well understood. This study is aimed at analysing the role of the initial exchange cation composition on the expansive clays' swelling properties when the temperature of the buffer material is expected to be close to or greater than 200 ˚C. We focus on the crystalline swelling and swelling pressures of monoionic smectites, particularly Mg-smectite (Mg-Sm), after being subjected to various heating treatments.

The clay fraction (<2 µm) of a Texas bentonite was extracted. Montmorillonite is the dominant mineral as indicated by XRD analysis. Monoionic montmorillonites saturated with Na^+, K^+, Ca^{2+}, and Mg^{2+} ions, respectively, were prepared. A swelling pressure device for thin samples (~2mm thickness) was developed. Mineralogical analysis and spectroscopic analysis were conducted for the heated samples. The experimental campaign consists of SWP tests of compacted smectites (before and after heating), X-ray diffraction (XRD), cation exchange capacity (CEC) and infrared spectroscopy (IR). Three different heating treatments in the range of 200 ˚C to 250 ˚C are adopted and the samples are exposed to the target temperature for ten days inside a muffle furnace.

The chemical composition of the clay fraction was checked with SEM-EDS, showing that the exchanging cation peaks were enhanced after ion saturation. Preliminary results on the sample exposed to 200 ˚C showed that the CEC of Mg-Sm decreased after the heating treatment. No apparent effect on the basal spacing (d_{001}) from XRD or changes in the IR pattern were observed, but a reduction in swelling was observed when the Mg-Sm was exposed to higher-T heating. The reduction in the CEC value can be an indicator of the counterion fixation into the vacant sites in the octahedral sheet of the smectite. Additional mineralogical and chemical analyses and SWP tests on thin samples are currently being conducted.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

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[2] Kaufhold, S., et al. (2016). Clays and Clay Minerals, 64(6), 743-752.

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Applications of Thermo-Hydro-Mechanical-Chemical and Gas Transport (THMC-G) Material Models in Engineered Barrier Systems (EBS) Using CODE_BRIGHT

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This paper explores the applications and challenges in modeling the long-term performance of EBS within the framework of coupled THMC-G processes. The study primarily focuses on the modeling of the Finnish nuclear [1] waste repository using CODE_BRIGHT [2], incorporating key thermal, hydraulic, mechanical, chemical, and gas transport interactions.

The thermal process is primarily governed by the initial canister power and the thermal conductivity of EBS components. The spacing between canisters and tunnels plays a critical role in repository thermal dimensioning. Initially, thermal conductivity value is lower in unsaturated conditions compared to fully saturated states, necessitating a degree-of-saturation-dependent thermal conductivity function. The presence of a technological gap between the canister and buffer blocks introduces additional heat transfer mechanisms, such as thermal radiation, which must be accounted for alongside conduction. The hydraulic process is characterized by water uptake dynamics, as EBS components begin in an unsaturated state and gradually saturate due to water migration from the host rock or fractures toward the canister. Key hydraulic modeling parameters include the water retention curve (WRC), intrinsic permeability, and relative permeability. Sensitivity analyses of fracture networks are crucial for accurate hydraulic modeling. Furthermore, porosity-dependent WRC and permeability functions are required to realistically simulate the hydration of bentonite-based materials, including pellets and mixtures. During heating phases, water vapor advection plays a significant role in desaturation, with tortuosity influencing vapor transport mechanisms. The mechanical process is predominantly associated with the development of swelling pressure during saturation. The Barcelona Basic Model (BBM) is typically applied to compacted clays, whereas a double-structure model is proposed for bentonite pellets and granular mixtures. Thermo-mechanical coupling is observed during cooling periods when thermal strains lead to a reduction in mean total stresses. Additionally, porosity changes directly affect permeability, exemplifying hydro-mechanical coupling effects. The gas transport process in the repository is critical due to the potential buildup of gas pressure over extended timescales, which may compromise barrier integrity. High gas pressures can induce the formation of microcracks or macrocracks within EBS materials. The geochemical process is strongly influenced by groundwater chemistry, particularly salinity. The reduction in swelling pressure and the consequent increase in permeability pose significant challenges, necessitating specialized material formulations and modeling approaches to ensure long-term EBS stability.

Overall, this study highlights the necessity of integrating multiphysical and multiphase modeling approaches to accurately predict the long-term evolution of EBS performance. The findings contribute to the optimization of nuclear waste repository designs, ensuring enhanced safety and reliability in geological disposal systems.

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Investigating the effect of NaCl on the volumetric behaviour of bentonite

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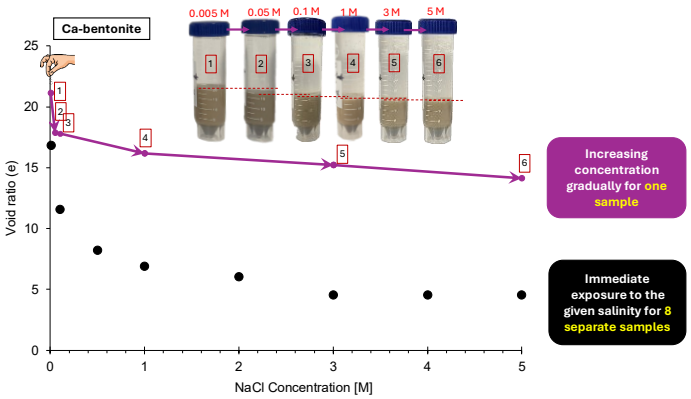
Bentonite, primarily composed of montmorillonite, is a clay commonly utilised in Geological Disposal Facilities (GDF) as a critical component of the Engineered Barrier System (EBS). Bentonite is currently considered as a buffer or backfill material for the repository programme for the UK geological disposal facility. Unlike GDF considered in other countries (the only exception is Canada), the UK concept of deep geological disposal takes into account ground water at high salt concentration because of the high content of the evaporites within the host repository rock [1]. Bentonite is selected as a barrier material because of its low hydraulic conductivity, high swelling pressure. the presence of ground water with high salt concentration might preclude such benefits.

This study investigates the impact of high salinity on both Na- and Ca-bentonite in compacted and non-compacted forms, employing sedimentation, dilution, free swelling tests, and consolidation tests from slurry to evaluate the swelling potential of bentonite.

Sedimentation tests were conducted on non-compacted bentonite to examine behaviour under varying concentrations of sodium chloride (NaCl) solution, ranging from low (0.01 M) to high (5 M) molarity. Dilution tests assessed the chemical reversibility of both Na- and Ca- bentonite types after saline exposure. Free swelling tests were performed on compacted samples with dry densities of 1.4 and 2 g/cm^3, exposed to lowest, highest NaCl concentration, and cored halite. 1-D consolidation tests were conducted on Na-bentonite starting from slurry samples prepared at different initial water content and NaCl concentration.

Results indicate that at low concentrations, Na-bentonite final volume is greater than Ca-bentonite. In high salt concentration, both Na- and Ca-bentonite reach the same final volume. Dilution tests reveal that upon decreasing NaCl concentration, both Na- and Ca-bentonite volumes were similar to the final volume obtained at low salinity for Na-bentonite. Therefore, upon increasing and decreasing the NaCl concentration, Ca-bentonite shows volumetric behaviour similar to the Na-bentonite. Free swelling tests demonstrate that Na-bentonite consistently swells more than Ca-bentonite, with swelling potential increasing as dry density rises and decreasing as NaCl molarity increases. The swelling potential of bentonite during halite exposure test was higher than expected, suggesting that the swelling mechanism might be chemical-path dependent.

[1] Lennart Börgesson(2020) RWM report RWM/Contr/20/029



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Evidence of an alkaline reaction in a 15-year iron powder–compacted bentonite interaction

Cuevas, J.F.[1], Mota, C.[1], Torres, E.[2], Fernandez, R.[1], Martín, P.L.[2], 2, Ruiz, A.I.[1], Ortega, A.[2], Garralón, A.[2], Turrero, M.J.[2]

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The chemical interaction between the carbon-steel container (CSC) and the bentonite is one of the aspects to investigate regarding the long-term safety of a Deep Geological Repository (DGR), since failure of the container and alteration of the bentonite could compromise the safety of the site concerning radionuclide migration. In the context of the NF-PRO project [1], a single iron-bentonite interaction experiment was implemented at CIEMAT (Madrid) with the aim of evaluating the iron mobility (FeMo) and the bentonite alteration considering a conservative scenario: (i) saturated conditions, (ii) aerobic initial conditions, (iii) high corrosion rates, and (iv) room temperature.

The FeMo experimental set-up was performed in a 120 x 120 mm square container 16 mm-high, made of methacrylate and stainless steel 316L. FEBEX bentonite (Ca-Mg-Na-montmorillonite from Cabo de Gata (Spain) was compacted to a dry density 1.6 g/cm^3 and placed into the cell with its hygroscopic water content (14 wt.%). Six holes were drilled into the bentonite and a 0.45 µm porous sintered steel tube was introduced inside. The gap between the sintered tube and the bentonite was filled with powdered iron. Hydration was done through the sinters using syringes fitted with O-rings to the system. The syringes were filled with Ca-Na-HCO_3-granite-type water from the Grimsel Test Site (Switzerland). The test was in operation for 15 years at room temperature until its dismantling in the context of the European EURAD-ACED project [2]. The experiment was dismantled inside a chamber with a poor oxygen (sub-oxic environment) atmosphere (<1% vol.). The sample was divided into six sections, each of which included bentonite-iron powder sintered with its black to brown and ochre corrosion halo. One of the sections was sealed with Araldite 2020 resin and cut under anoxic conditions to check the extent of the black and brown halo surrounding the iron powder between the bentonite and the sintered steel cylinder. Polished sections were studied by SEM-EDX. Detailed chemical maps were acquired from the porous sintered steel along 2 cm longitudinal paths. The diffusion of the iron halo reached up to 1-2mm in the bentonite. This halo was segmented by a zone of Mg concentration between 0.1 and 0.3 mm and a zone of Ca concentration between 0.2 and 0.3 mm measured from the interface with the iron powder. X-ray diffraction (XRD) was used to study the mineralogical changes of very small samples (< 0.5 g) associated to this zonation along the bentonite at the interface with iron powder. The small samples were gently pressed in a zero-background silicon plate to obtain a XRD powder profile. Small samples taken in this area were also dispersed in water to obtain information about the mineralogy of the clay fraction. The mineralogical composition of the iron powder showed the predominance of magnetite (50%) accompanied by goethite (25%) and siderite (5%), with metallic iron remaining in a proportion of around 20 wt.%. The brown-stained bentonite contact contained, in addition to bentonite minerals (montmorillonite, cristobalite, feldspars and quartz), magnetite, and oxyhydroxides such as goethite and lepidocrocite, with minor siderite. The bentonite near this contact had the same composition as in the original mineralogy. Clay fraction was virtually absent in the iron powder contact. However, the brown bentonite within the Ca-Mg zone exhibited evidence of a broad reflection at 0.7 nm and of the presence of a trioctahedral clay component mixed with montmorillonite. Carbonates and Mg-rich clays precipitation are characteristics of an alkaline reactivity contact, presumably promoted by a transient oxic to anoxic environment.

[1] NF-PRO UE Project final Report (2008) N Sci Tech EUR 23730
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An XAS study on the effect of ionizing radiation on the redox state of the structural iron in hydrated clay minerals

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The Swedish KBS-3 concept, among other nuclear waste disposal projects, involves a Bentonite clay buffer surrounding copper canisters containing nuclear waste. Smectite-rich Bentonites, like Wyoming Bentonite MX80, have elaborate chemical, hydraulic, and mechanical properties due to the surface chemistry and layer charge of their main component, Montmorillonite. This research examines the effects of ionizing radiation on Fe(II)/Fe(III) cycling, mineral transformations, and redox interactions with interlayer Cu(II) in smectite-rich Bentonite clays, crucial for nuclear waste repository safety.

Previous studies using γ-radiation have demonstrated a substantial reduction of structural Fe(III) to Fe(II) in dilute montmorillonite suspensions [1] or hydrated smectite-rich Bentonite [2][3]. However, most findings relied on wet chemistry techniques post-irradiation, highlighting the need for *in-situ* irradiation combined with simultaneous X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD).

It is well known that ionizing radiation at high doses can induce defects in clay minerals and adjacent geochemical environments [4]. While prior studies found no interlayer changes upon radiation exposure [5], a varying Fe(II)/Fe(III) ratio may cause lattice strain and structural charge defects over time, as elevated Fe(II) in the octahedral sheet is unstable.

This study examines Fe(III) to Fe(II) cycling due to interactions with primary radicals from radiolysis of clay pore water (Figure 1). Using the synchrotron beamline Balder at MAX IV, a multi-modal XRD and XAS approach to analyze crystal and unit cell changes (XRD), interatomic distances and local symmetry (EXAFS), and oxidation state and coordination environment.

In addition to Wyoming Bentonite MX80, Fe-rich (Nau-1, Nau-2) and Fe-free (Syn-1) clays were investigated to explore 1) effects of physical conditions relevant to nuclear waste repositories (anoxic, varying water content), 2) structure in highly reduced clays (radical scavengers, Na-dithionite), and 3) redox states of Cu/Fe in Cu-exchanged smectite.

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SSM2023:14, (2023), Strålsäkerhetsmyndigheten.
P. D. Svensson and S. Hansen, *Clays Clay Miner*. 61, 566–579.
Th. Allard, E. Balan, G. Calas, C. Fourdrin, E. Morichon, and S. Sorieul (2012), *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* 27, 112–120.
D. Gournis, A. E. Mantaka-Marketou, M. A. Karakassides, and D. Petridis (2000), *Phys. Chem. Miner*. 27, 514– 521.

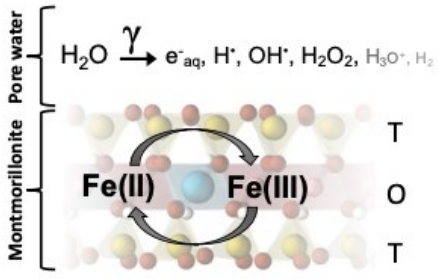

Figure 1: Schematic process of Fe(II)/Fe(III) cycling (flip-flopping) due to reactions with reactive species formed by water radiolysis.

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Influence of salinity gradients on the diffusion of water and ionic species in dual porosity clay samples

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Diffusion is the main transport process of chemical species in natural clayey rocks. Most of the published data, especially in the context of nuclear wastes storage [1], consider tracer diffusion under constant salinity gradients. However, although salinity gradients can occur in environmental conditions, the diffusion of ions in charged clayey porous material under such gradients have rarely been studied. Under salinity gradients, the few existing studies evidenced that diffusion of salt are primarily governed by anion mobilities due to anionic exclusion, with effective diffusion coefficients of cations being equal to those of anions [2]. Furthermore, studies have been carried out considering porous materials made of smectite displaying osmotic swelling under water-saturated conditions, resulting in an ill-defined interlayer volume. In order to assess (i) the role played by interparticle and interlayer porosities and (ii) the effect of salinity gradient on diffusion of water and ions in dual porous media rich in swelling clays, diffusion experiments were carried out with vermiculite, a mineral that does not present any osmotic swelling under water-saturated conditions. Water and ions diffusion experiments were performed using a through-diffusion setup previously used [3]. The experiments were performed using samples prepared with a 0.1-0.2 µm size fraction of vermiculite with a known particle morphology and an interparticle porosity of 25% (total porosity of 50 %). Diffusion data were collected by considering two experimental conditions: (i) with salinity gradient between upstream and downstream reservoirs (10^{-2} or 1 mol/L NaCl in the upstream, using HDO, Na^+ and Cl^- as tracers; systematic osmosed water in the downstream reservoir), and (ii) without a salinity gradient (NaCl solution fixed at 10^{-2} or 1 mol/L in both reservoirs, using HTO, $^{22}Na^+$ and $^{36}Cl^-$ as tracers at ultra-trace concentrations). The experimental data were interpreted using both a classical Fickian diffusion model and with a reactive transport code, CrunchClay [4] that can handle multi-porosity diffusion processes in the presence of charged surfaces.

The effective diffusion coefficients (D_e) of water (HDO and HTO) interpreting the experimental data are found to be independent of the presence or absence of a salinity gradient, while the diffusion of anions and cations are highly impacted by this parameter. Under no salinity gradient, with an increase of salinity, D_e values for $^{36}Cl^-$ and $^{22}Na^+$ increase and decrease, respectively. Such behavior is in agreement with the reduction of anionic exclusion and increase of adsorption of cations with an increase of salinity. Under salinity gradient, the same behavior is observed for Cl^-, while that of Na^+ contrasts drastically because in this case, Na^+ diffusion is totally controlled by that of Cl^-. In this presentation, by combining experimental and simulated data obtained with Crunchclay, we will show that (i) the flux of water diffusing through the interlayer porosity of vermiculite is minor compared to that diffusing through the interparticle porosity, and (ii) a model considering at least three types of porous volumes (interlayer, diffuse layer interparticle, and bulk interparticle) is necessary to consistently reproduce the variations of neutral and charged species diffusion as a function of salinity gradient conditions.

[1] Bourg I.C. et al. (2003). J. Contam. Hydrol., 61, 293-302.
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[3] Tertre E. et al. (2018). Environ. Sci. Technol., 52, 1899-1907.
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Effects of Alkaline and Saline Conditions on Bentonite Alteration, Cesium and Iodine Retention, and Key Performance Parameters

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Bentonite is a key engineered barrier material in deep geological repositories for high-level radioactive waste (HLW) due to its low hydraulic conductivity, high swelling capacity, and radionuclide retention properties. However, long-term geochemical evolution, induced by hyperalkaline conditions from cement degradation or saline conditions from seawater intrusion, may alter its physicochemical characteristics and affect its long-term performance. This study investigates the alteration behavior of bentonite and the retention of cesium (Cs) and iodine (I) under simulated repository conditions. A 90-day batch sorption experiments under alkaline and saline conditions were conducted to evaluate physicochemical changes and Cs and I retention. Pre- and post-experimental measurements of the free swelling index and cation exchange capacity (CEC) were conducted to evaluate physicochemical alterations. Montmorillonite interlayer cations were replaced by dominant cations in solution, and notably, partial montmorillonite dissolution and the formation of secondary minerals (e.g., zeolites) were observed under alkaline conditions. While Cs retention remained consistently high over 90 days, I retention was minimal under most conditions, with slight retention observed only under saline conditions. Swelling capacity and CEC varied depending on solution conditions, primarily influenced by cation exchange processes.

Acknowledgement

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Cs sorption onto clays from different deposits: what controls the process?

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Ensuring long-term safety of high-level radioactive waste (HLW) disposal requires effective engineered barriers. Bentonite clays, with their low permeability and strong radionuclide sorption capacity, are a critical component. Special attention must be given to Cs isotopes — fission products with high mobility and toxicity. Reliable geomigration models must account for sorption processes and site-specific conditions to predict long-term containment.

In this work, we compare the behavior of Cs in its interaction with 11 different bentonite clays to determine the dependence of sorption on their individual characteristics such as CEC, SSA, and mineral composition. Samples of bentonite clays from all over the world were used: lesser-studied deposits were represented by samples from Dash-Salakhly (Republic of Azerbaijan), Taganskoye (Kazakhstan), Kutch (India), Zyryanskoe, 10 Khutor and Dashkovskoe (Russia) and widely studied clays included samples MX-80 (USA), FEBEX (Spain), Kunipia-F (Japan), NAu-1 (Australia), ISCz-1 (Slovakia).

Study of Cs^+ sorption isotherms across a wide concentration range revealed two distinct plateaus for nearly all samples, suggesting the presence of multiple sorption site types. This multi-site sorption behavior was found to be independent of clay mineral composition.

Existing approaches to the description of cesium sorption include models with different types of sites. The results of simulation with 6 literature approaches showed the best correlation with experimental data for approaches using two types of sites. However, these approaches did not accurately describe all dependencies, and obtained concentrations of sorbed sites did not correspond to their individual characteristics.

To enhance modeling accuracy, new approaches were developed based on optimizing reaction constants and sorption site concentrations. The parameters were optimized for each specific isotherm, as well as for all dependencies together. Based on the optimization results, the values of the constants $\log K_1 = 6.48$ for highly and $\log K_2 = 1.35$ for low-selective sites with separate optimization and $\log K_1 = 6.00$ and $\log K_2 = 1.61$ for joint optimization, respectively, were proposed.

This work was supported by the Russian Science Foundation (project 25-13-00221).

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A generic kaolinite sorption model for a consistent radionuclide sorption database

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The development of a unified sorption model for radionuclide uptake on kaolinite is a key objective of the SOREDA (Sorption Reference Database) joint project, which aims at creating a quality-assured reference database for sorption processes. SOREDA supports the safety assessment of deep geological repositories for radioactive waste.

Kaolinite, a non-swelling 1:1 clay mineral with a lower sorption capacity than 2:1 clay minerals such as illite and montmorillonite, is widely studied as an adsorbent in natural and engineered barriers of deep geological repositories. Given that kaolinite can constitute a significant fraction of the mineralogical composition of argillaceous rocks (e.g., up to 25 wt.% in Opalinus Clay), incorporating kaolinite sorption into retention modelling is crucial for improving the accuracy of safety assessments.

Moreover, sorption experiments on natural clay minerals often show high variability due to factors such as mineral origin, reactive impurities, mineral crystallization, chemical pre-treatment and laboratory-specific experimental conditions. Consequently, developing a robust generic sorption model requires a critical evaluation of existing sorption data and their acquisition conditions, complemented by a fundamental understanding of kaolinite's surface chemistry and uptake mechanisms.

In this study, titration and sorption data for kaolinite, obtained from both in-house experiments and open literature, were rigorously analysed. The quasi-mechanistic two-site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model, initially developed for montmorillonite (Baeyens and Bradbury, 1997 [1] and Bradbury and Baeyens, 1997 [2]), was adapted for kaolinite using carefully selected experimental data and incorporating the latest advancements from surface chemistry. The kaolinite sorption model developed in this study includes elements such as Cs(I), Sr(II), Ra(II), Ni(II), Am(III), Cm(III), Np(III-VI), Pu(III-VI), Sn(IV), Th(IV) and U(IV-VI). Where applicable, data gaps for certain elements were addressed using data derived from their chemical analogues. Additionally, sorption parameters were derived for naturally occurring cations to account for competitive interactions in natural waters.

The sorption model will be expanded in future work to encompass a broader range of (radioactive) contaminants, thus ensuring a comprehensive safety assessment of natural barriers in deep geological repositories. Additionally, the model can be applied to simulate radionuclide migration in natural environments impacted by near-surface radioactive waste repositories.

Funding for this research was provided by the Federal Company for Radioactive Waste Disposal (BGE, Germany) within the framework of the SOREDA project.

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CEC as quality proof for quantification of smectitic phases in lower Cretaceous clay rocks – illite-smectite ± pure smectite?

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Crystallographic clay mineralogical tools combined with cation exchange capacity (CEC) allowed deeper insight in the geochemical variability and sequence stratigraphic interpretation of the mudstone-dominated Lower Cretaceous succession in the eastern Lower Saxony Basin, Northern Germany, described by Thöle et al. (2020) [1].

Instead of operationally describing the development of interstratified illite-smectite minerals in diagenesis studies of clayey sediments using e.g. broadening of XRD intensities of illite, we studied the crystallographic features of interstratified illite-smectite using the Rietveld method [2, 3]. After qualitative analyses of the < 2 µm fraction based on established diagnosis tools, Rietveld refinement allows for a full quantitative phase analysis of complex clay mineral admixtures [4, 5], however the results have to be checked for plausibility using parameters such as the chemical composition. This check validated the mineralogical composition, however, an even more detailed quality check was performed based on CEC analyses using the Cu-triethylentetramin method. Smectitic 2:1 (TOT) layers within an interstratified phase have much larger CECs than corresponding 2:1 layers of illite, chlorite, and 1:1 (TO) layers of kaolinite, accordingly CEC differences in principle correlate with different amounts of smectitic layers [6].

CEC data of a ≈ 200 m depth borehole (1 sample/m) were correlated with proportions of smectitic layers in illite-smectite and indicated that in some parts presence of smectite-rich illite-smectite minerals alone cannot explain the CEC values. In those parts up to half of the CEC was not explained quantitatively indicating that a high-CEC clay mineral may be present but formerly not detected by characterisation of the < 2 µm fractions.

In-depth analyses of very fine clay fractions < 0.2 µm allowed detection of additional pure smectite (physical mixture) along with the well-known illite-smectite minerals. The quantitative amounts of the improved qualitative and updated (Rietveld refinements) quantitative clay mineral composition now also correlated well with the CEC in those parts with the observed misfit.

This clay mineralogical tools improved our understanding of i) the development of the Lower Cretaceous succession, specifically the Valanginian Weissert Event, and ii) how to detect high sorption capacity lithologies.

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[3] Ufer K et al. (2012b). Clays Clay Miner. 60:535–552
[4] Ufer K and Kleeberg R (2015) Clay Miner. 50:287-295
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LECTURE THEATRE 3, Emmet – SESSION 31

Advances in Calcined Clays as Supplementary Cementitious Materials in Blended Cements

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Characterization of the local Al environment in calcined clays using transmission electron microscopy

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The use of calcinated clays as supplementary cementitious materials (SCM) has increased over the past decades in an effort to reduce the carbon footprint of the cement industry. Like other SCMs, metakaolin can indeed partially replace the clinker, and then reduce the CO_2 emission upon calcination. The formation of 4- and 5-fold Al ($^{[IV]/[V]}$Al) during the calcination process was shown to be one of the key elements explaining the increase of their reactivity in cementitious media [1]. The understanding of the reaction mechanisms leading to the formation of $^{[IV]/[V]}$Al is thus fundamental to optimize the calcination temperature of the clay and later optimize their contribution in cement reactivity. Nuclear Magnetic Resonance (NMR) spectroscopy is the master technique for the characterization of the local Al environment in calcinated clays, it is however limited by some factors. It is for instance unsuitable for Fe-containing samples, or when other Al-containing minerals are present in the same sample. Electron Energy-Loss Spectroscopy (EELS) in a transmission electron microscope is able to overcome these challenges and is therefore a promising technique for the characterization of Al in clays. We performed therefore an in-depth EELS characterization of raw and calcinated kaolinites, in order to develop an alternative characterization methodology when NMR cannot be employed.

We investigated the spectral features associated with the 4-fold and 6-fold coordination at the Al-L edge in kaolinite and other Al-containing minerals, in order to propose a quantitative determination of the proportion of $^{[IV]}$Al in the structure of individual particles. In agreement with a previous NMR study [1], we observed a gradual formation of $^{[IV]}$Al in calcined samples (Figure 1-a). In addition to that, we could determine that the amount of $^{[IV]}$Al in the kaolinite particles of the sample calcined at 525°C content varied greatly between particles (Figure 1-b). Some clay particles have completely reacted to form $^{[IV]}$Al at this temperature, whereas others stayed in their original state. Such difference between the individual spectra was not observed at other temperatures.

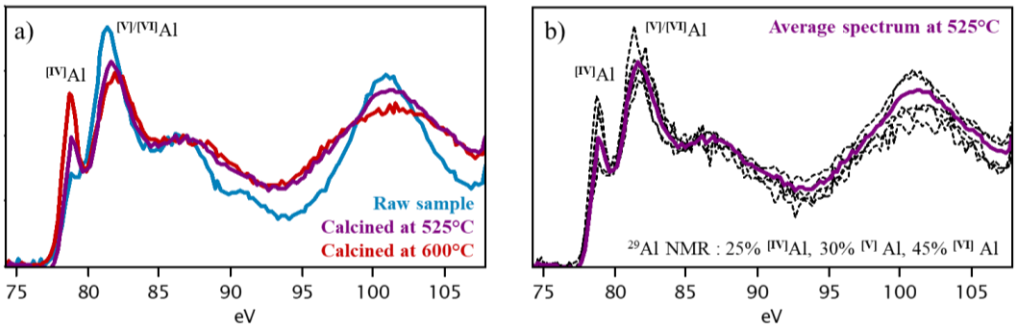

Figure 1 : a) EEL spectra at the Al-L edge of kaolinites calcined at different temperatures. Spectra are averaged over 5-10 particles for each temperature. b) Spectra of individual particles (dashed) and average spectrum (purple) at 525°C. The proportion of Al coordination determined by ^{27}Al NMR is given for reference [1].

[1] Poussardin V. et al., Construction and Building Materials, 416, 135180.

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The Potential of Co-calcining Bentonite and Calcite for SCM Production: Insights into Ca_2SiO_5 Stabilization

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Partially substituting cement clinker with supplementary cementitious materials (SCMs) is a highly effective strategy for reducing the carbon footprint of the cement industry and mitigating climate change. However, the availability of many conventional SCMs is limited, highlighting the need for alternative sources. The potential of 2:1 clay minerals to produce calcined clay SCMs has been explored in various studies [1]. Amongst the associated minerals that commonly occur in clays alongside 2:1 clay minerals, calcite is generally regarded as undesirable as it releases CO_2 upon thermal decomposition to form free lime [2], [3]. However, the possibility of selecting clay composition and calcination conditions (within the typical range of 700 – 900°C) to form reactive calcium silicate and/or calcium aluminosilicate phases has not been investigated in detail. Ca_2SiO_5 (C_2S in cement chemists' notation) is a reactive phase found in Portland cement clinker; higher temperature polymorphs (including α'_H- and β-C_2S, considered to be more reactive) can be stabilised through the incorporation of dopants including potassium. Co-calcination of 2:1 clay minerals and calcite to form reactive polymorphs of C_2S may offer a useful valorization for clays which are typically considered as undesirable for calcined clay production.

This study investigated the co-calcination of bentonite, a 2:1 clay mineral from the smectite group, with calcite at 900°C. C_2S and C_2AS (Gehlenite) were the main reaction products. The addition of minor quantities of potassium carbonate as a dopant source was also investigated. Increasing potassium content promoted the formation of β-C_2S and facilitated the production of α'_H-C_2S. Microstructural analysis also revealed the presence of compositional gradients within particles, indicating the direction of diffusion processes which led to C_2S and CS (wollastonite) formation. The R^3 test was conducted to assess the reactivity of the samples. The majority of samples had chemical reactivity comparable to those of fly ashes. These findings offer insights into new routes for utilizing clays for SCM production which contain higher quantities of calcite alongside 2:1 clay minerals.

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[2] M. P. Riccardi, et al. (1999) Appl Clay Sci, vol. 15, no. 3–4, pp. 393–409.
[3] M. J. Trindade, et al., (2009) Appl Clay Sci, vol. 42, no. 3–4, pp. 345–355

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Enhancing the rheology, reaction kinetics and early-age strength of limestone calcined clay cement (LC3) with sodium silicate addition

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Calcined clays are well stablished supplementary cementitious materials (SCMs), and when combined with limestone fines to produce Limestone Calcined Clay Cements (LC3) a synergetic reaction takes place enabling significant reductions of clinker content in concrete. LC3 based construction products can develop comparable mechanical properties, enhanced durability (in some environments), and lower carbon intensity compared to those produced with CEM I [1]. However, despite the numerous advantages of LC3, several challenges need to be addressed. For example, studies on LC3 have centred on the use of high kaolinite content clays (>40 wt.%), and these binders can have complex rheology and high-water demand [2]. This makes their mixing, handling, and casting more difficult in the absence of admixtures. Another significant challenge when using LC3 is its low early-age strength development. This being dependent on the characteristics of the calcined clay and binder mix design. From a practical perspective this can delay formwork removal and construction schedules, as well as increase the risk of early-age cracking.

The application of alkali solutions is known to enhance the reactivity of SCMs. Although several studies [3] have investigated the effect of alkali solutions such as NaOH and Na_2SO_4, on early hydration enhancement of CEM I and blast furnace slag/fly ash cementitious systems, few have explored the role of alkaline solutions in systems blended with calcined clay. Furthermore, the potential of sodium silicate, another commonly used alkali solution in alkali-activated materials, remains largely unexplored.

In this study, it was investigated the effect of adding small quantities (~1.5 wt%) of sodium silicates (SS), with bespoke compositions, on the rheology, reaction kinetics, and early-age strength of LC3 systems. Rheology and reaction kinetics were evaluated using a rotational rheometer and isothermal calorimetry respectively. The chemical and structural effects of sodium silicate were determined using in-situ X-ray diffraction, thermogravimetry coupled with mass spectrometry and scanning electron microscopy. The pore structure was evaluated by the mercury intrusion porosimetry. Compressive strength evolution was also determined, to infer the correlation between the microstructure development of the sodium-silicate added LC3s with their mechanical performance.

Sodium silicate addition reduced the colloidal interaction between particles in LC3, and depending on the SS composition a significant reduction in yield stress and viscosity was observed. A SS solution with 1% Na_2O and silicate modulus of 0.4 significantly accelerated the silicate and aluminate reactions of cement clinker, and the synergetic reactions between calcined clay and limestone, resulting in 120% and 13% increase in 1 day strength compared to the reference LC3 and CEM I mixes, respectively. A denser microstructure with refined pore size was observed at 1 day of curing, consistent with higher reaction and phase assemblage evolution. The improved rheology and early-age strength of optimised sodium silicate-added LC3s demonstrate that bespoke sodium silicate solutions can be effective accelerators in LC3 systems.

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[2] L. Lei, M. Palacios, J. Plank, A.A. Jeknavorian (2022), Cem Concr Res 154.
[3] B. Mota, T. Matschei, K. Scrivener (2015), Cem Concr Res 75 53–65

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Understanding Reactivity: From Nanoscale Layer Thinning to a 5-minute UR2 Test

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Clays, upon calcination, can turn into reactive pozzolans that can partially replace cement, enabling a concrete that is more sustainable, lower-cost, and durable. However, the reactivity of the final calcined clay can vary widely depending on the intrinsic clay mineralogy, fineness, and calcination conditions such as temperature and residence time. Thus, understanding and predicting clay reactivity has been of significant interest to the cement community. In this keynote talk, I will highlight two recent efforts to improve our understanding of clay reactivity – specifically in the context of dissolution [1]. Firstly, I'll introduce a quantitative imaging approach where calcined clay particles subject to dissolution are imaged in a statistical manner to understand their disintegration and dissolution behavior. Specifically, we find that highly reactive metakaolin undergoes *nanoscale* layer thinning (of ~20 nm) upon dissolution [2]. Secondly, I'll introduce a newly developed Ultra-Rapid Reactivity (UR2) test that can predict reactivity of calcined clays within 5 minutes [3]. This new 5-minute test, validated on ~50 unique clay samples from across the world, is a significant improvement over the state-of-the-art R3 test (ASTM C1879), which takes 7 days to complete. This 5-minute UR2 test can enable quick screening of new clay sources and help calcined clay producers in online QC/QA during production. Overall, these new advances in understanding and predicting clay reactivity take us one step closer to large-scale, commercial deployment of calcined clays as SCMs in concrete.

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[2] Romero P and Garg N (2022) Apl Clay Sci 222:106486
[3] Min Y et al. (2024) Cem Concr Res 191:107806

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Enhanced performance of blended cements with high levels of calcined clay

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Improving the sustainability of infrastructure materials has become an important aspect of major projects in Australia and key to this is the use of calcined clays to (i) replace a portion of cement, (ii) reduce the embodied carbon content of the resulting material and (iii) lower the reliance on traditional supplementary cementitious materials that are often imported. Cement replacement levels above 30 wt% with calcined clays often result in excessive consumption of portlandite which slows or halts strength development. Pozzolana require portlandite, formed during hydration of clinker, to form calcium silicate hydrates and calcium aluminate silicate hydrates. Lower clinker contents necessarily reduce the amount of portlandite formed, and highly reactive pozzolana rapidly consume available portlandite; thus portlandite is a limiting factor in strength development of these blends. To enable higher cement replacement levels using local resources (bentonite or gravel washed fines of mixed clay mineralogy) for calcined clays, and to achieve required strength and other performance attributes from blended cements, we studied the effect of additional hydrated lime on calcined clay-limestone-cement pastes and mixed-mineralogy calcined gravel wash fines-cement mortars at, respectively 0.45 and 0.5 water to binder contents. A carboxylate-based water reducer was used to control workability as measured by slump-flow diameter. The influence of available early lime on phase development was examined by thermogravimetric analysis, Fourier transform infrared spectroscopy and energy dispersive X-ray spectroscopy.

In general, hydrated lime improved early (7- and 28-day) strength development. Addition of hydrated lime enabled cement replacement levels of 60 wt% in limestone-calcined clay-cement blends, attaining acceptable 7- and 28-day compressive strengths relative to reference cement pastes. The 7-day strengths for in limestone-calcined clay-cement pastes with 4 wt% hydrated lime were greater at lower limestone (5 wt%) and higher calcined clay (50 wt%) ratios. At cement replacement levels of 40 wt% with the reactive fines from calcined gravel wash fines, mortars achieved exceptional 7-, 28- and 56-day strengths relative to a control mortar. In the latter case, a calcined gravel wash fines dominated by 2:1 smectite clay mineralogy (59% of <2 μm fraction) achieved compressive strengths for mortars approaching 100 MPa (130% that of the control) at 4 wt% additional hydrated lime. Hydrated lime addition increased the proportion of hydrated phase development as observed in the 100-150 °C weight loss relative to that of the <100 C in calcined bentonite mixes relative to the control and a residual level of portlandite was maintained that was equivalent to the amount observed in the reference pastes (after accounting for dilution). Infrared spectroscopy confirmed an increase in the amount of residual portlandite in all gravel wash fines mixes containing additional hydrated lime as well as growth of cementitious hydrate phases. While a considerable range in chemistries was observed the addition of hydrated lime shifted the aluminium/calcium and silicon/calcium ratios of cementitious phases toward chemistries of calcium aluminate silicate hydrates with lower aluminate contents.

The addition of hydrated lime to compensate for portlandite consumption by pozzolan reactions proved to be an effective means to replace as much as 60 wt% cement in ternary limestone-calcined clay-cement pastes and 40 wt% cement in binary calcined clay-cement mortars. In addition to positively impacting the embodied carbon balance, use of local resources for calcined clays can help shift the cement, concrete and construction industries toward fit-for-purpose and sustainable infrastructure.

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Characterisation, activation, reactivity and performance of heterogenous natural clays

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The use of calcined clays as supplementary cementitious materials (SCMs) presents a promising pathway for reducing clinker content in cement and, consequently, lowering its embodied carbon. In Sweden, however, regulatory hurdles around clay extraction have historically limited interest in exploring local clay sources. While the southern regions contain kaolinitic clays, the west and east coasts are richer in illite- and smectite-bearing clays, which remain underutilized. To work within these constraints and promote sustainable practice, our group within two PhD projects [1,2], employed a construction waste-derived clay, using its availability and performance as a means to demonstrate feasibility and encourage renewed interest in resource mapping and future extraction possibilities.

The clay, characterized by Hazarika et al. [3], exhibits a heterogeneous mineralogy with low kaolinite and higher proportions of smectite and illite. A hybrid activation approach combining thermal treatment followed by a mechanochemical activation was applied, enabling clay replacement levels of up to 40% while maintaining a comparable 56-day strength as ordinary Portland cement (OPC) system. Despite the clay's aluminate content (~19%), synergy with limestone was limited—likely due to restricted formation of AFm phases or preferential aluminium uptake into the C-A-S-H gel, both currently under further investigation. The expected filler effect of limestone was also minimal. Given that admixtures were used, and rheology was satisfactory, this limited interaction is unlikely to stem from workability issues. Instead, it may result from the finer particle size distribution of the clay, which could dominate the packing structure and reduce the space-filling benefits provided by coarser limestone particles.

Carbonation resistance was also evaluated. Samples cured for 28 days were notably vulnerable to carbonation, whereas those cured for 100 days (with 30% clay replacement) showed significantly improved resistance. This improvement is attributed to progressive pore refinement, which hinders CO_2 ingress. However, pore coarsening in the gel pore range was still observed, possibly due to ongoing changes in the C-(A)-S-H structure, such as decalcification or polymerization. Current investigations are examining the sensitivity of these binders to carbonation under varying relative humidities, particularly around 70%, as preliminary findings suggest that drying alone may be driving changes in the gel pore structure. Preliminary data on chloride binding indicate that the use of these mixed-layered clays does not significantly increase chemical binding via AFm phases, unlike systems with high-reactivity metakaolin. As a result, the differences total chloride binding capacity compared to OPC system appears to be governed more by modifications in the C-A-S-H (or C-S-H) nanostructure, rather than by additional formation of Friedel's salt.

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[2] https://research.chalmers.se/en/project/11047
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Performance of cements blended with limestone and calcined 2:1 clays with focus on early hydration, sulfate demand, setting and workability

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The ongoing search for suitable clay resources with regard to the production of calcined clays as SCMs unfolds clays with complex mineralogical composition, that open up new questions regarding their behaviour during and their performance after calcination. In this context, a special focus is laid on 2:1 clay minerals, that show, despite their lower reactivity compared to kaolinitic clays, a great potential due to their abundant availability in many regions [1]. In previous studies, a significant impact of the composition of the multi-component mixture consisting of calcined clay, limestone powder and sulfate carrier on the hydration kinetics in cementitious systems was found [2].

In the present study, the suitability of different 2:1 dominated clay as supplementary cementitious materials (SCMs) in combination with limestone is investigated with regards to early hydration, sulfate demand and setting behaviour in binder systems as well as workability and strength development in mortar systems.

To correlate mineralogical properties of the raw clays with their performance in cementitious systems after calcination, an extensive characterization is carried out using XRD on texture and powder specimen, TG-DSC analysis and FTIR spectroscopy while the chemical composition is determined by ICP-OES. The reactivity in dependence of calcination temperature is determined by R^3-test and solubility experiments in alkaline solution.

After sulfate adjustment carried out by isothermal calorimetry, the impact of the calcined clays on the early hydration, setting and workability in binder and mortar systems is systematically investigated using isothermal calorimetry, in-situ XRD, Vicat needle apparatus and spread flow measurements over time.

The minor impact of calcined smectite in comparison to calcined kaolinite on the early hydration and sulfate demand as recently proved by da Silva et al. [3] is confirmed. The behaviour of calcined smectitic clays with regards to setting, superplasticizer demand and slump retention in comparison to kaolinitic clays is discussed and correlated to the early hydrate phase development.

The suitability and challenges of the investigated clay-types as SCMs in composite cement or cement replacement in concrete are outlined.

[1] Maier M et al.(2021) Appl. Clay Sc. 202: 105990
[2] Scherb S et al. (2024) Cem. Con. Res. 175: 107356.
[3] Da Silva, M R C (2024), Mater. Struct. 57: 1–19.

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Thermal Performance of Calcined Clay Supplementary Cementitious Materials in Mass Concrete Applications

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The integration of calcined clays as supplementary cementitious materials (SCMs) in blended cement formulations has emerged as a promising approach to improve both sustainability and durability in concrete applications [1]. When calcined clays are combined with ASTM C595 Type IL cement in a system called CCIL, the use of calcined clays further lowers the clinker content, contributing to a reduced environmental footprint. This study measured the temperature sensitivity of CCIL and the adiabatic heat evolution in cementitious mixtures incorporating four commercial calcined clays with different reactivity levels [2], [3]. These clays were evaluated with three different Type IL cements sourced from Florida, Iowa, and Tennessee. Hydration kinetics were examined using isothermal calorimetry at 15, 23, 30, 40, and 50°C, with the Arrhenius model applied to determine the apparent activation energy of each system. In parallel, semi-adiabatic calorimetry was employed to assess the concrete's adiabatic temperature rise, a crucial parameter for developing effective thermal management strategies in mass concrete structures and modeling strength and stress development in young concrete.

The results indicate that both the type of calcined clay and the source of the Type IL cement significantly impact hydration kinetics, peak heat evolution, and overall heat release. Mixtures with calcined clay demonstrated higher **temperature rise** than cement-only mixtures at a low replacement level (<30% by mass), independent of their reactivity level. Notably, the lowest reactivity clay mixture with a higher cement replacement level (40%) displayed a lower temperature rise and a more extended hydration period compared to the control mixture, suggesting the improved thermal performance with increasing cement replacement. Additionally, cementitious mixtures combining calcined clay with limestone were evaluated in this study to further reduce clinker content to 50% and assess the effectiveness of limestone (15 μm) in mitigating concrete heat rise in mass concrete structures. Results indicate that higher replacement levels of calcined clay with limestone further reduce the concrete temperature rise, independent of the clay reactivity level. Conversely, mixtures with lower calcined clay substitution (<30%) exhibited a slightly elevated temperature rise after 7 days relative to the control. However the rate of heat gain was lower. This suggests that the impact of calcined clay on structural mass concrete may be dependent on the structural concrete member size and ability to dissipate the heat. Overall, these findings highlight that even though calcined clays are often associated with increasing durability and sustainability, they can **increase the total heat evolution**, underscoring the importance of careful mix design for the structure of interest that includes optimizing calcined clay replacement levels or supplementing with additional SCMs and temperature monitoring for mass concrete applications.

[1] Scrivener K et al. (2018) Cem Concr Res 114:49-36
[2] Dhandapani Y and Santhanam M (2017) Cem Concr Res 84:36-47
[3] Zaribaf B H and Kurtis K E (2018) RILEM Bookseries 16:500-506

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Automatic control of raw clay quality and clay calcination in the cement industry through XRPD

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The mineralogical characterization of clays is important in several research areas and essential for different industrial sectors such as oil and gas, mining and cement industry. The control of clays and calcined clays is crucial for the cement industry due to clays significant impact on the final properties of cementitious materials. Natural clays contain phyllosilicate minerals from the clay groups of kaolinite, smectite, and illite, which, upon calcination, control the pozzolanic reactions of calcined clays in the cement mixture [1]. Depending on the clay type and its order, effective calcination occurs at different temperatures to induce clay mineral decomposition and amorphization. X-ray powder diffraction (XRPD) is a powerful analytical technique for precise characterization of the mineralogical composition of raw and processed clays that provides critical insight into these phase transitions, helping to optimize calcination conditions and assess the purity of the final product. Moreover, it easily aids the detection of crystalline phases considered impurities as quartz or unreacted clay minerals, which may affect the performance of blended cement. Aeris x-ray diffractometer, from Malvern Panalytical, was used to automatically control the quality of raw clays by monitoring optimal concentrations of kaolinite in kaolinitic clays, contents of iron oxy-hydroxides hematite and goethite due to their effect on lowering calcination temperature, and all the other mineral species present in the clays. The clay calcination process, including raw material residence time and kiln target temperature, was optimized by avoiding non-reacted kaolinite after calcination and, avoiding moderate to high contents of cristobalite and mullite observed on over-calcined clays. The latter was particularly important to avoid kiln clogging and excess energy expenditure. Online XRPD information on mineralogical and amorphous content during the calcination enhanced the quality of the calcined clay, contributing to performed cement mixtures, and sustainable cement production by ultimately reducing the clinker factor and lowering CO_2 emissions.

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LECTURE THEATRE 3, EMMET – SESSION 4

From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis

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Natural 1-layer and 2-layer hydrated montmorillonites are resilient to changes in basal spacing despite major cation substitution

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Determination of the distribution of exchangeable cations in smectite, which make up bentonites, is important for tracking the transport and exchange of cations when bentonites are used in compacted form. Understanding how these properties evolve over time is essential to assess the behaviour of a given bentonite as an engineered barrier for waste isolation and other sealing applications. This study discusses the feasibility of determining the cation distribution in originally divalent and monovalent montmorillonites exchanged with sodium and calcium in their clay fractions, and subsequently mixed wet in different proportions.

Two natural bentonites composed of montmorillonite were used as starting materials. FEBEX bentonite (Serrata de Níjar, Cabo de Gata, Almería, Spain) contains Ca^{2+}, Mg^{2+}, and Na^{+} as exchangeable cations. MX-80, of Wyoming type, contains Na^{+} as the main exchangeable cation. The <2 μm fractions of both clays were converted into homoionic Na^{+} and Ca^{2+} forms and mixed in proportions ranging from 0 to 1 for each component and each clay. Powder diffraction profiles were collected using a zero-background silicon sample holder. The corresponding Ca^{2+} and Na^{+} components were quantified using the Profex©-BGMN software [1]. Two crystallographic structures were used for the refinement of the dioctahedral smectite: Na^{+}, 1-layer hydrated and Ca^{2+}, 2-layer hydrated, based on calcium smectite [2]. The refinements are consistent with the presence of a mixture of two discrete structures, with basal spacings of 1.5 nm (calcium montmorillonite in both bentonites) and 1.25 nm (sodium montmorillonite FEBEX) or 1.25–1.10 nm (sodium montmorillonite MX-80). The calcium montmorillonites refine as pure phases in both cases, showing narrower reflections, while sodium incorporation induces markedly different disorder effects in the two montmorillonites. FEBEX montmorillonite maintains the 1.5 nm basal spacing as the dominant reflection up to a Na^{+} proportion of 0.5, with a significant contribution even up to 0.75 in Na^{+}. Quantification does not match the theoretical composition. In the case of MX-80 montmorillonite, the 1.25 nm reflection is already dominant at 0.25 Na^{+}, and this reflection contracts toward 1.1 nm as the Na^{+} proportion increases.

The XRD profiles of the mixed samples show two disorder effects: the appearance of a broad band between 0.6 and 0.5 nm (corresponding to the (002) Na^{+} and (003) Ca^{2+} spacings), and a narrower band at 0.30–0.31 nm, which was modeled by introducing an amorphous structure. This prevents accurate quantification of the exchangeable cation distribution unless improved structural models are introduced to account for the disorder. Nevertheless, the analysis reveals distinct performance comparing the two montmorillonites, such as a tendency in FEBEX to maintain larger hydrated spacings (2-layer hydrates), versus a contraction toward unusually low spacings in MX-80 (<1.1 nm; 1-layer hydrates). This could be considered a memory effect of the natural original conformation. Further study of other natural montmorillonites is planned to confirm these effects.

[1] Doebelin N and Kleeberg R. (2015) J Appl Cryst 48: 1573-1580
[2] Ufer K et al. (2008) Clays Clay Miner 56: 272-282

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Characterization of trioctahedral smectite-sepiolite assemblages in the Neogene Madrid Basin (Spain): Genetic considerations

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Magnesian clay deposits are common in the Madrid Basin, consisting of both fibrous (sepiolite, palygorskite) and non-fibrous (kerolite, stevensite, saponite) clay minerals [1]. Especially interesting are the Mg-smectite and sepiolite deposits that can reach several metres in thickness and excellent quality. Two types of deposits can be distinguished: the first type is associated with mud-flat deposits in a lacustrine-palustrine context; the second type occurs between detrital facies corresponding to middle and distal deposits of alluvial fans of predominantly arkosic composition. The aim of this work is to evaluate the influence of the sedimentary environment on the Mg-smectite and sepiolite formation process in an alluvial type deposit. A total of 20 samples were collected in two lithostratigraphic sections located near the town of Illescas in Toledo (Spain). Sepiolite and bentonite beds are respectively white and brown-green in color, inserted between detrital facies of sands, silts and clays which show darker colours. The samples have been analysed by X-ray diffraction and studied petrographically both in thin sections and in selected fragments by scanning electron microscopy (SEM-EDS). The results obtained show several mineralogical assemblages in which Mg-smectite or sepiolite can be the predominant clay mineral. The analysis of the bulk sample shows the predominance of phyllosilicates (>95%) with subordinated quartz, potassium feldspar, plagioclase, calcite and dolomite. In minor content heavy minerals (zircon, rutile, ilmenite, monazite, xenotime, apatite, tourmaline), barite and celestine. In the clay fraction mineralogy, three mineralogical assemblages have been observed: Assemblage 1. Trioctahedral smectite (>90%)-illite (≥5%). Assemblage 2. Trioctahedral smectite (15-72%)-sepiolite (26-85%)-illite (1-15%). Assemblage 3. Sepiolite (>90%)-trioctahedral smectite (≤10%)-illite (<5%). The highest variety and proportion of inherited minerals has been observed in laminated to granular samples with the highest content of trioctahedral smectite (assemblages 1 and 2) and in sepiolite samples with evidence of bioturbation. In massive sepiolites with evidence of desiccation, the lowest contents of inherited minerals have been detected, which may even be absent. The trioctahedral smectite is mostly of saponite composition, which would have formed as a result of the transformation of aluminous smectites associated with distal alluvial deposits of clayey character. The results allow us to propose the existence of two genetic types of sepiolite. One of them is linked to replacement phenomena (transformation) of a previous smectite phase, responsible for the presence and variety of the identified inherited minerals, a process that has been observed petrographically. The lower contents and variety of inherited minerals would correspond to sepiolite formed by direct precipitation (neoformation) under evaporitic conditions which would justify the existence of desiccation features and the formation of authigenic sulphates such as barite and celestine, during early diagenesis.

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Predicting cis- and trans-vacant configurations in smectites using X-Ray Diffraction

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The configuration of the octahedral sheet is one of the most relevant structural parameters in dioctahedral smectites, as it significantly influences their thermal behaviour. Depending on this configuration, smectites exhibit distinct thermal responses: when the octahedral vacancy is adjacent to OH^- groups (cis- vacant (cv) configuration), dehydroxylation occurs at higher temperatures compared to those with a trans-vacant (tv) configuration, where the vacancy is arranged longitudinally relative to the OH^- groups. Drits [1] proposed 600°C as the threshold temperature to differentiate between these two configurations.

The most widely used technique to determine the octahedral configuration type is thermogravimetric analysis (TGA). However, alternative analytical methods have also been explored, such as multiple quantum (MQ) magic angle spinning nuclear magnetic resonance (MAS NMR) or X-ray diffraction (XRD).

This study aims to predict the type of octahedral sheet configuration in smectites using XRD analysis. To this end, a statistical analysis of 21 high-purity smectite samples was performed in R [2] using two types of variables. The first set of variables was extracted from the derivative thermogravimetric (DTG) curve and is associated with the octahedral configuration. The second set includes indices derived from the peak height intensity ratios of the 02, $\bar{1}3$, and 06 reflections ($I_{02}/I_{\bar{1}3}$, I_{02}/I_{06}, and $I_{06}/I_{\bar{1}3}$), obtained from random-powder diffraction patterns prepared using the spray drier technique [3].

The results from the Pearson correlation matrix between the $I_{02}/I_{\bar{1}3}$ and I_{02}/I_{06} and the DTG-derived variables were satisfactory, revealing statistically significant correlations with absolute coefficients above 0.71 and p-values near 0.000. The strongest correlation was found between the percentage of cv configuration (%cv) and the $I_{02}/I_{\bar{1}3}$ index, with a coefficient of 0.88. Furthermore, the optimized PLS-DA model effectively discriminated between cv and tv samples using the indices, achieving near-perfect classification. These findings demonstrate that the structural differences between tv and cv octahedral occupancies are clearly detectable through XRD analysis of random powder specimens.

Additionally, by plotting the $I_{02}/I_{\bar{1}3}$ index values versus %cv on a scatter plot, an exponential-type regression function was obtained. The equation of this function allows a direct estimation of the octahedral configuration based on XRD data alone.

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Influence of Detrital Input on Saponite Authigenesis in the Pre-Salt Barra Velha Formation, Santos Basin

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Saponite, a clay mineral from the smectite group, is a key indicator of the geochemical characteristics of its environment. This is mainly because its formation is associated with authigenic processes involving the transformation of pre-existing minerals [1], allowing the incorporation of various ions into its structure. In the Barra Velha Formation (BVF), located in the sag section of the post-rift sequence of the Santos Basin within the pre-salt interval, rocks are predominantly composed of magnesium-rich smectites (saponite, stevensite), kerolite, stevensite-kerolite as mixed-layers, and carbonates [2]. Additionally, there is a contribution of detrital sediments, with mica and feldspar being the most significant components.

This study aims to present evidence of the authigenic formation of saponite in the Barra Velha Formation (BVF), based on the ionic contribution derived from extrabasinal detrital sediments. A total of 26 samples from a drill core collected in the pre-salt Santos Basin were analyzed. To characterize the saponite, X-ray diffraction (XRD) was employed, along with a modified version of the Christidis [3] test for the distinction of magnesium-rich smectites. Scanning electron microscopy (SEM) was used to capture the various morphologies, while electron microprobe analysis (EMPA) provided point chemical data. Trace element analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS).

Unlike reported by Da Silva [2], where the presence of detrital sediments is considered volumetrically insignificant and stevensite is the most abundant smectite, the drill core analyzed in this study shows a predominance of saponite, with a calculated structural formula of $K_{0.01–0.09}$ $Ca_{0.04–0.1}$ $Na_{0.02–0.9}$ $(Mg_{2.5–2.9}$ $Al_{0.14–0.31}$ $Fe_{0.01–0.04})$ $(Si_{3.65–3.92}$ $Al_{0.35–0.08})$ O_{10} $(OH, F)_2$, while stevensite occurs only in subordinate amounts. Based on the evidence, this is attributed to a higher influx of sediments into this sector of the basin and the dissolution of feldspars [Fig. 1], which releases Al^{3+} into the system, promoting the authigenesis of saponite incorporating both tetrahedral and octahedral aluminum. Additionally, the trace element signature—with elevated concentrations of Ba (95.38 ppm) and Sr (71.68 ppm) in the saponite—further supports the occurrence of extrabasinal detrital sediment dissolution as a contributing factor in the formation of this clay mineral.

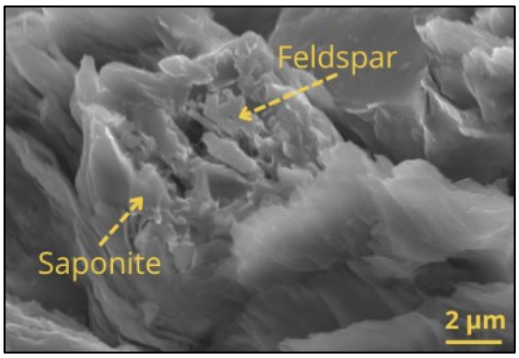

Figure 1. Secondary electron microscopy (SEM) image of the studied samples. Partially dissolved feldspar surrounded by saponite.

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Geochemical constraints of Upper Cretaceous Na-bentonite beds from Pellegrini Lake deposit, Argentina

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The Upper Cretaceous Na-bentonite deposit from Pellegrini Lake is located in the eastern region of Neuquén basin, one of the richest areas in Argentina for this type of clays. The bentonites occur in the middle section of Allen Formation (Malargüe group) interpreted as an estuarine environment with a mixing of freshwater and marine influence. Two bentonite beds are mined, each of 0.60 m average thickness, which stand out by their lighter colours compared to the darker intercalated siliclastic facies. Twenty samples were collected from four profiles (PL1, PL2, PL3 and PL4) for mineralogical and geochemical characterization. The minerals identified in the bentonite samples include Al-smectite, plagioclase, K-feldspar, quartz and clinoptilolite, subordinate pyrite, barite, kaolinite, illite and muscovite and trace (<1%) anatase, gypsum, halite and calcite. Other phases identified by petrographic analysis are biotite, zircon, chlorite, monazite, rutile and tourmaline. The lower bentonite bed (green) has a higher smectite content and lesser amount of detrital minerals highlighting the common occurrence of biotite. In contrast, clinoptilolite, zircon and anatase are almost exclusively present in the upper bentonite bed (white). The major chemical element abundances are in accord with the mineralogical assemblages. Green bentonite samples have on average a SiO2/Al2O3 ratio of 3.1 and a (Na + K)/Ca ratio of 9.45, while, white bentonite has a slightly higher SiO2/Al2O3 ratio (3.2) and a lower (Na + K)/Ca ratio (around 3) due to a higher Ca-content. The samples have moderate iron contents (3.1-5.4% Fe2O3), with two samples having higher iron contents (6.5 and 7.8%) related to the presence of pyrite. The MgO content is slightly higher in green bentonites compared to their white counterparts (2.96 vs 2.30%) and Na2O contents are comparable (2.83 vs 3.07%). The high Na+ content of the bentonites compared to K+ and Ca2+ corroborates that this raw clay is Na-bentonite. A higher TiO2 content is observed for white bentonites (0.15 vs 0.52%) in accordance with the presence of anatase in these samples. Regarding the trace elements the green bentonite samples have higher Ba, Nb and Ta contents and lower Rb and Zr contents than the white bentonite samples. Most of the green bentonite samples have higher B content being highest in samples from PL4 profile. The B/Ga ratios are indicative mostly of freshwater salinities (< 2.39) and to a lesser extent brackish and marine waters. There is generally a light REE (LREE; La to Sm) enrichment relative to the heavy REE (HREE) throughout the dataset. The REE content is much higher in white bentonites which, on adding Y, reaches 330 µg/g compared to 181.75 µg/g for the green bentonite. When plotted in the Winchester and Floyd [1] diagram, the green bentonites plot in the trachyandesite field, whereas white bentonite plot in the rhyodacite/dacite area suggesting a derivation from a more felsic magma. In the diagram Rb vs Y + Nb all samples are projected in the volcanic arc granite field [2]. The chemical composition of the bentonites suggests a more felsic provenance for white bentonites, which could be the result of a different composition of the source rock and/or a higher detrital input in the sedimentary environment.

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LECTURE THEATRE 4, SYNGE – SESSION 13

Clay Applications in Ceramics

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Influence of diatomite addition to two types of clay on the hydrothermal synthesis of zeopolymer materials

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The addition of different proportions of diatomite wastes (DW) from brewery industry (Heineken, Madrid factory, Spain) to two different clays – kaolin (Caobar, Taracena, Spain) and a ceramic brown clay (BC; Asociación Notio, Toledo, Spain) – has been investigated to obtain innovative zeolite/geopolymer composites, here called zeopolymers. Samples were prepared using the method developed by Moreno-Maroto *et al.* [1]: wet rounded specimens of 10.3 ± 0.5 mm were manually shaped from mixtures covering each clay and 0, 5, 10, 20 and 40 wt.% of DW. After drying at 105 °C for 24 h, the specimens were fired in a muffle at 600 °C for 1 h (except those of kaolin with 20 and 40% of DW, which were fired at 800 °C to ensure their structural integrity in liquid media). The fired material was hydrothermally treated with 4 ml/g NaOH 4M at 90 °C for 24 h. The supernatant was removed and the samples were dried for 24 h at 105 °C. The resulting zeopolymers were characterized by Rietveld-refinement XRD to study the mineralogical changes, while the most relevant technological properties, such as mechanical strength, were also determined.

The results show that, in general, hydrothermally treated samples with BC are stronger than those with kaolin and that the mechanical strength decreases while increasing the content in DW for both clays: from 8.45 to 1.05 MPa for BC, and from 5.70 to 0.95 MPa for kaolin. In the case of BC, there are signs of some zeolite formation, although its contribution is much lower than in the kaolin mixtures, reaching values between 16% (with 20% DW) and 34% (with 40% DW), with contents in Zeolite A between 8 and 25.4%, except for the samples with 40% DW, showing instead 26.8% of Zeolite NaY as the dominant phase.

In conclusion, the hydrothermal method for the fabrication of structural ceramics provides a more sustainable alternative to the conventional methods, where higher temperatures are involved. The clays and the diatomite waste investigated have potential for zeopolymerization, paving the way for further investigation.

Acknowledgments:

This work is associated to the ZEUS project (ref. PID2023-146912OA-I00), funded by ICIU/AEI/10.13039/501100011033 and FEDER funds from the European Union. Special thanks to Caobar, Asociación Notio and Heineken-Madrid for providing the samples.

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Case Study of Spanish, Italian and Portuguese Clays as Raw Material for Lightweight Workable Aggregates (LWAs)

Cotes-Palomino, M.T[1]; López-García, A.B.[1]; Iglesias-Godino, F.J.[1]; Alonso-Acárate, J.[2]; Moreno-Maroto, J.M.[3]; Barbieri, L.[4]; Lancellotti, I.[4]; Andreola, F.[4]; Labrincha, J[5].; Martínez-García, C.[1]; Cobo-Ceacero, C.J.[1]

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This work investigated the potential of clays from Spain, Italy, and Portugal, as well as various wastes, as raw materials for the production of lightweight artificial aggregates (LWAs). The swelling behaviour of the clays, the effect of the addition of organic wastes, and the role of iron (Fe) phases in the expansion process were studied.

Different types of clays were characterized, including those from the Bailén area (Spain), Italian red clay, and others of Portuguese origin. Their chemical composition, mineralogical characteristics, and thermal properties were analyzed. The Italian red clay exhibited a bulk density of 0.47 g/cm³ due to its high porosity, suggesting an intrinsic potential for expansion during heat treatment. A high proportion of phyllosilicates was also found to favour aggregate bursting [1].

The incorporation of organic wastes into clays with low expansive capacity was also evaluated. Wastewater treatment plant sludge, paper industry wastes, and cork dust were used. The addition of up to 15% of these wastes did not compromise the properties of the final material, while higher amounts increased open porosity due to the combustion of organic matter and the decomposition of calcite. In particular, cork dust, combined with kaolin and metal residues, acted as a source of organic carbon and a gas-generating agent during sintering, thus favouring expansion [2].

Additionally, the influence of iron phases on the expansion of LWAs was analyzed. Seven iron-rich residues were used in addition to native iron phases. The results showed that a high Fe content is essential to achieve the appropriate reduction and viscosity conditions for expansion. The reduction of oxides such as hematite and magnetite, together with the presence of wüstite (FeO) as a flux, promoted the formation of a viscous matrix capable of retaining the released gases, generating closed porosity. The optimization of the mixtures, through statistical design, considered both the proportion and the oxidation state of iron. High-quality lightweight aggregates were obtained from residues of the iron oxide extraction process and from screenings, demonstrating the strong potential for the valorisation of these materials [3].

In conclusion, while some clays have a naturally expansive character, the addition of organic waste can induce porosity in those that do not. However, iron phases are essential to the expansion process for obtaining LWAs, as they facilitate the formation of a viscous matrix capable of trapping the gases generated during sintering.

Acknowledgements: This research was conducted as a part of the ECO-MET-AL Project, PID2019-109520RB-I00 / AEI / 10.13039/501100011033,

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Influence of Sewage Sludge Ash on Brick Properties Using Diverse Clay Types

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The brick industry is actively seeking sustainable solutions that will contribute to resource conservation and reduce its dependence on natural clay reserves. At the same time, the generation of sewage sludge ash (SSA) is increasing due to expanding incineration of sewage sludge at wastewater treatment plants. Previous studies [1] have concluded that SSA is a viable option for a partial substitute for clay in brick manufacturing. Supplement ratio and firing temperature have been the most considered variables when evaluating SSAs influence on brick properties. Brick properties vary greatly from country to country, even within one brick factory. Brick properties depend on the firing temperature, admixtures, and especially the chemical composition of the raw material. In general, clay with a high content of the clay minerals illite, chlorite, and vermiculite has a large firing shrinkage and low porosity due to increased sintering [2]. The carbonate content in clay also largely influences the fluxing behaviour of the clays, as fluxing (lowering the melting point of clay minerals) tends to decrease when carbonates are present [3].

This study evaluates the influence of SSA on brick properties, with three significantly different clay types. One clay type has high carbonate content and low clay mineral content (C1), the second has low carbonate and low clay mineral content (C2), and the third has low carbonate and high clay mineral content (C3).

The mineralogy and chemical composition of the materials were investigated with X-ray diffraction (XRD) and X-ray fluorescence (XRF). Bricks were produced at a brick factory in the southern part of Denmark. Bricks with 0% and 24% (dry weight) SSA were hand-moulded using wooden moulds and pistons. The bricks were dried and fired at the factory in their drying chambers and tunnel gas oven. Firing of the bricks took 4.5 days, with maximum firing temperatures reaching 1035°C and 1060°C. Porosity, initial rate of absorption (IRA), water absorption and compressive strength of the fired bricks were investigated.

Bricks with SSA had higher porosity, water absorption and initial rate of absorption compared to reference bricks. The brick strength was significantly improved with SSA. The incorporation of SSA led to a reduction in the workability for all clay and SSA mixtures compared to pure clay, which made it difficult to achieve a smooth surface on the bricks. The overall brick properties for bricks with clay and SSA compared to their reference bricks were in the order of C3>C1>C2.

This research underlines the importance of considering different clay types when assessing the potential use of waste materials as alternative raw materials in brick manufacturing. This study contributes to research on resource conservation and more sustainable construction practices.

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From Design to Valorization: Circular and Innovative Practices for the Use of Clay Products in Construction

Díaz Rubio, Roberto[1]; Millanes Sánchez, Marta; Peces Martín, Celia;. Rodriguez Chirico, Caterina

[1] NOTIO – CENTRO TECNOLÓGICO DE ACTIVIDADES DE LA CONSTRUCCIÓN – C/ Río Cabriel s/n (Toledo-Spain)

The construction sector, and especially construction using fired clay products, is currently facing several challenges in terms of economic, social, and environmental sustainability. A key issue is the need to evolve from a linear production model to a circular one. This change is essential to mitigate impacts and comply with European regulations [1], which demand greater efficiency in resource use and waste reduction. Actions are presented that address the sector's specific challenges, such as the valorization of ceramic and other industrial waste to create new, more efficient and sustainable construction systems, as well as the integration of renewable energy into urban environments.

The methodology followed focuses on applied research and the development of innovative solutions to advance sustainability, with the key focus on the use of clay and ceramic product waste. Through waste valorization, the adoption of renewable energy, and the design of industrialized ceramic construction systems, the aim is not only to reduce the environmental impact but also to improve the competitiveness of the ceramic construction industry. Specifically, the presentation will address four innovative projects developing new clay-based construction materials.

The CERAFROST project proposes the adaptation of ceramic façade products to new frost regulations [2] by incorporating a percentage of glass from recycled solar panels into the ceramic mass. SUSTAINFLOOR, on the other hand, proposes an innovative paving system, obtained by 3D printing, that generates clean energy, as it transforms the kinetic energy of pedestrians into electrical energy for lighting urban environments, using CDW, clays, and other ceramic waste from industry as its main raw material. The CECOM4PV project proposes a unique construction material that integrates photovoltaic elements into standard ceramic-based products, making traditional ceramic products compatible with new technologies. Finally, NEXT-CER seeks to design an industrialized façade construction system that improves energy efficiency and sustainability through the use of lightweight ceramic materials and rapid assembly systems, providing added value to ceramic construction products.

The results of the projects, currently in the validation phase, demonstrate the viability of using clays and ceramic products and their waste within the scope of the circular economy in the construction sector, with the aim of scaling up the results and adapting them to real construction solutions.

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Relationship between the presence of iron and the sintering atmosphere on the final properties of kaolin-based ceramics

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The ceramic industry must evolve in line with environmental objectives, particularly the transition toward a "competitive low-carbon economy by 2050" [1]. Among the various stages in ceramic manufacturing, sintering plays is a critical step to achieve the desired final properties of the product. To reduce environmental impact, alternative thermal treatment methods—such as the use of biogas, green hydrogen, or electric furnaces—are being explored.

These changes in the sintering environment can significantly affect the transformation kinetics, and thus the final properties, by changing the surrounding atmosphere and heat transfer patterns.

Clay, more precisely phyllosilicates are naturally occurring and widely distributed across the globe. In particular, kaolins are widely use to manufacture materials for traditional and advanced functional applications. These kaolins are mainly constitute with kaolinite mineral ($Al_2Si_2O_5(OH)_4$). Kaolinite is a 1:1 layer-type clay mineral, composed of a tetrahedral silica sheet bonded to an octahedral alumina sheet [2]. In their natural state, many secondary phases can be present in kaolins, in particular ferric oxides, which can significantly impact the behavior and properties of the final ceramic product. A comprehensive understanding of the interactions between kaolinite and secondary phases—especially iron oxides—is crucial for controlling the chemical and physical characteristics of kaolin-based materials.

One model clay was chosen for this study: a kaolin known as "CR" provided by Imerys company. To investigate the effects of iron content, the kaolin was enriched with iron through both chemical and physical additions, reaching concentrations of up to 10 wt%. Using Ellingham diagrams and data on oxygen partial pressures, two sintering environments were compared: a reducing atmosphere (argon) and an oxidizing atmosphere (synthetic air).

To track the phase transformations, in situ differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were employed, complemented by ex situ X-ray diffraction (XRD). Additionally, Mössbauer spectroscopy and solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) provided detailed insights into the iron coordination environment and its interaction with the kaolinite structure. Scanning electron microscopy (SEM) was used to observe microstructural changes induced by atmospheric conditions and iron content. Finally, mechanical compression tests and porosity measurements were conducted to evaluate the final performance of the iron-enriched kaolin-based ceramic products.

The results revealed the emergence of a distinct reaction pathway in the presence of iron under a reducing atmosphere, notably leading to the formation of hercynite. This modified transformation sequence had a significant impact on the physical properties of the material. The two iron addition methods—chemical and physical—produced complementary results, offering valuable insights and enabling meaningful comparisons with naturally occurring systems.

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Energy savings in silicate ceramics through Optimization of the raw material mix

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Silicate ceramics manufacturing is one of the most energy intensive industries. The firing process is almost exclusively based on fossil fuels. Raw material preparation and drying are also energy intensive production steps. Composition, preparation, drying and heat treatment are closely linked. The production units (kilns, etc.) operate for several decades, so changes can only be expected in the long term. Optimisation of process parameters is therefore of particular importance in the medium term. As the raw materials have a decisive influence on the behaviour in the manufacturing process and the properties of the end product, there is much more room for manoeuvre than if manufacturing technologies were considered in isolation. Targeted modification of raw material composition to improve drying behaviour therefore plays a key role in improving energy efficiency in ceramic production. The presented data and work was funded as part of the SuSiDry project (FKZ: 03EN2096A-D) by the German Federal Ministry for Economic Affairs and Climate Action (BMWK).

The research project pursues the overall goal of significantly improving the sustainability of silicate ceramic products. This is to be achieved primarily by reducing the energy required for production by 20% across the entire production chain. A major goal for the Stephan Schmidt group includes the classification of clays and the testing of process additives with regard to processing properties, homogeneity, mixing water content and microstructure optimization.

Therefor several raw clays have been tested regarding their chemical and mineralogical composition, grain size distribution, specific surface area, homogeneity and plasticity. To investigate the influence of initial raw material variations on process parameters and product properties, a comprehensive DoE test plan was established using computer-aided experimental design. For six different types of raw materials, more than 20 different mixtures have been prepared and systematically varied. The mixtures were examined with regard to their suitability for the plastic production process. The target value for the mixing water requirement was established as a compression height of 25 mm, as outlined by Pfefferkorn. In addition, oscillation rheology was employed to determine the visco-elastic properties, with the objective of describing the plasticity of the mixtures. The storage and loss modulus were measured under increasing shear stress, where the storage modulus G' (G prime, in Pa) represents the elastic portion of the viscoelastic behaviour, which quasi describes the solid-state behaviour of the sample, and the loss modulus G'' (G double prime, in Pa) characterises the viscous portion of the viscoelastic behaviour, which can be seen as the liquid-state behaviour of the sample [1]. These measurements were accompanied by shrinkage measurements using thermo-optical dilatometry (TOM).

The successful completion of the SuSiDry project is expected to yield significant benefits for the silicate ceramics industry, including a substantial reduction in energy consumption, as well as improvements in product quality and durability. The developed methods and tools will contribute to a more efficient use of resources and a decreased environmental footprint of silicate ceramic production, aligning with national and European energy and climate goals. Furthermore, the transferability of the project's findings to other sectors within the ceramic industry is also anticipated.

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Zeolites as ceramic raw materials for feldspar substitution in porcelain stoneware tiles production

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In recent years, there has been a growing trend in the demand for white-firing clay materials for ceramic tile production, following a continued shift towards porcelain stoneware bodies. The sourcing of raw materials by industries on the global scene has been challenged by the current geopolitical scenario, consequently requiring a rethink of the well-established European supply chain, and there is an urgent need to evaluate the possibility of using Italian raw materials to produce porcelain stoneware. With this in mind, zeolite-containing waste generated from extraction and processing tuffs (ZT) from two active quarries in Sorano (Tuscany, Italy) were studied. The experimental work was carried out to characterize and test ZT as feldspars substitute in porcelain stoneware formulation. Collected samples were physically and chemically characterized and the most promising material was defined on the base of thermal stability (lower bloating). Two different amounts were tested (10-20 wt%) for feldspars substitution in comparison with a reference porcelain stoneware batch and tile-making process was replicated at the laboratory scale. Samples were characterized in terms of technological properties throughout the process. Waste addition led to a limited reduction of green and dry bulk density, not followed by a decrease in mechanical properties. All the studied batches show a maximum in linear shrinkage and bulk density at 1200 °C, reaching the standard requirement for water absorption and mechanical properties. For mixture with 20 wt% waste addition, the desired values are reached already at 1180 °C leading to reduce thermal energy demand. On the basis of the achieved results, the use of ZT is suitable in the whole evaluated range selected for porcelain stoneware production and to be screened for a potential industrial scale up.

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Mineralogical, physico-chemical and geotechnical characterization of Yagoua clays (Far North Cameroon) for application in traditional ceramics

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The raw clay materials of the locality of Yagoua (Far North of Cameroon) have been studied for their use in traditional ceramic (fired bricks). The analytical methods such as X-Ray diffraction (XRD), X-Ray fluorescence (XRF), Fourier Transform Infrared spectrometry (FTIR), Scanning Electron Microscopy (SEM), simultaneous thermal analysis (TG/DSC), Particle Size Distribution (PSD) and Atterberg limits were investigated on raw clay materials. Water absorption, porosity, bulk density, linear shrinkage, compressive and flexural strengths and microstructural phases evolution were investigated on specimens fired at 750°C, 800°C, 900°C, 1000°C and 1100°C.

Quartz, k-feldspars, plagioclases, goethite, smectite, kaolinite and illite were detected on raw clay. The plasticity indices ranged between 4.5 to 18.4% suggesting weak to moderate plasticity with a relatively high proportion of sand (51-74%). The ratio SiO_2/Al_2O_3 is greater than 3.0 indicating the abundance of quartz whose expansion during the alpha/beta quartz transformation with rise of temperature would cause changes of dimension of the bricks and possibly deleterious microcracking if cooling is too rapid [1].The evaluation of the technological properties of fired specimens revealed that, the bulk density does not vary significantly and remain in the recommended range (<2g/cm^3) for fired bricks. The linear shrinkage increased with firing temperature but remained below 2%, meanwhile water absorption (10-21%) and porosity (26-32%) decreased with increasing firing temperature. The flexural (1.0 -6.6Mpa) and compressive (6.0 -28Mpa) strengths increased due to the formation of the new phase detected by XRD (mullite)during densification [2] particularly observed in Bakara clay material. The overall technological properties have shown that Bakara clay material above 1000°C can be used for the production of fired bricks (according to the NF EN 771-1.2011 standard) unlike the Zoulla material which requires an appropriate amendment.

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Brazing of ceramics with reactive metallic alloys and oxide glasses

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Brazing is a joining process in which two or more solids are joined by melting and flowing a filler material into the joint having a lower melting point than the solids being joined. The brazing process is of particular interest in the design of complex, thin or very small ceramic parts, at manufacturing costs lower than other processes.

Good wetting of solids to be joined by the liquid filler is a necessary condition for a good adhesion to the interfaces. However, most of ceramic materials are not wetted by liquid metallic alloys, the contact angle being higher than 90°. A way to improve wettability is to add specific solutes to the metallic matrix which react with the ceramic substrate and form wettable continuous layers of reactive compounds at the interface. Such reactions can in turn affect the physicochemical and mechanical properties of the brazed joints. Thus the control of physicochemical interactions at liquid filler/ceramic interface is a crucial issue.

Brazing ceramics with metallic alloys is carried out in a controlled atmosphere or under vacuum to avoid oxidation of the metal fillers and/or ceramic substrates. On the other hand, the use of oxide glasses, a versatile joining material for high-temperature applications, allows brazing and/or repair of brazed parts in air, as they are not susceptible to oxidation.

The purpose of this presentation is to focus on the fundamental issues of wetting and interfacial reactions in liquid metal/ceramic and liquid glass/ceramic systems and to analyse the main thermodynamic and kinetic factors governing them. Some examples of wetting and brazing of ceramic materials such as alumina by active liquid metallic alloys and silicon carbide by liquid calcium aluminosilicate glasses will be presented and discussed. In particular, the confinement and size effect as well as the role of atmosphere on the microstructural evolution of the interfacial system in both wetting and brazing configurations will be discussed in detail.

The wetting experiments are performed under high vacuum or in air by using either the classical sessile drop or the deposited drop method and the spreading process is followed in situ by a camera. The brazing experiments are performed in sandwich configuration under high vacuum or in air. Reactive interfaces for wetting and brazing samples are characterized by SEM, DRX and TEM.

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LECTURE THEATRE 4, SYNGE – SESSION 28

Nanoelectronic and Nanophotonic Applications

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Naturally occurring 2D semiconductor with antiferromagnetic ground state

Pacakova, B.[1], Lachtingen-Dahl, B.[1,] Kirch, A.[2], Demchenko, H.[1], Osmundsen, V.[1], Fuller, Ch.A.[3], Chernyshov, D.[3],Zakutna, D.[4], Miranda, C.R.[2], Raaen, S.[1], Fossum, J.O.[1]

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The natural clay mineral vermiculite has been overlooked as a promising candidate for scalable production of large aspect ratio 2D wide band-gap semiconductors.

We combine here efficient methods for vermiculite delamination, which provides single nanosheets of ~1nm thickness. Addressing the challenges of vermiculite exfoliation, we have adapted and used an efficient method for producing single nanosheets from vermiculite. Our approach utilizes the cation exchange and swelling properties of vermiculite in organic solvents, in combination with ultrasonication mechanical treatment, to achieve effective delamination. This method significantly improves the feasibility and efficiency of exfoliating vermiculite, opening new possibilities for its use in advanced material synthesis and electronic applications.

In our pursuit of vermiculite-based electronics, we also measured the band gap of the exfoliated material, confirming that it can function as a wide band-gap semiconductor with antiferromagnetic ground state. This finding, supported by both experimental data and simulations, is crucial for the development of future technologies that require wide band gap semiconductors for electronic nanodevices operating at high frequencies or voltages. Delaminated vermiculite nanosheets act as semiconductors with a wide band-gap energy of 3.3-3.9 eV depending on the elemental composition, and with an antiferromagnetic ground state.

This study advances the understanding of vermiculite. With its natural abundance, affordability, non-toxicity, and ability to form high-quality nanosheets, vermiculite is a valuable and sustainable resource for future electronic, spintronic and photonics devices.

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Ultra-confined plasmons reveal moiré patterns in a twisted bilayer graphene-talc heterostructure

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Twisted bilayer graphene (TBG) shows remarkable electronic properties, including superconductivity and correlated insulating states [1]. On electrostatically gated TBG devices with high doping, scattering scanning near field optical microscopy (s-SNOM) reveals triangular domains due to the different optical conductivity of each of the stacking arrangements of the TBG superlattice [2]. In this work, we investigate the plasmonic properties of a twisted bilayer graphene (TBG) and talc heterostructure. Talc, a naturally occurring phyllosilicate, promotes p-type charging of graphene [3], supporting high charge mobility and strong interaction between graphene plasmons and talc's phonon polaritons. This interaction results in the formation of surface plasmon–phonon polariton (SP^3) modes, which are detected using infrared scattering-type scanning near-field optical microscopy (IR s-SNOM) at room temperature. Notably, without the need for electrostatic gating, our study reveals confinement of SP^3 modes in a TBG–talc heterostructure and a transition from surface plasmonic waves to the emergence of moiré superlattices, characterized by reflections at domain walls [4]. These findings provide fresh insights into the coupling mechanisms in hybrid materials and suggest promising applications in nanoscale optoelectronics.

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[2] B. Y. Jiang *et al.*, Nano Lett **17**, 7080 (2017).
[3] E. Mania *et al.*, 2d Mater **4**, 031008 (2017).
[4] T. C. Barbosa *et al.*, Nanoscale **17**, 9205 (2025)

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Ionic Transport in 2D Slits with Angstrom Precise Confinement Control

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Emerging technologies in energy storage, chemical sensing, and water purification increasingly rely on ionic and solvent transport under nano- and angstrom-scale confinement [1]. At these length scales (<100 nm), the transport is dominated by interfacial properties and confinement geometry, enabling mass fluxes that can exceed bulk transport by orders of magnitude. Two-dimensional (2D) materials have received increasing attention in recent years, primarily due to their ability to generate an abundance of highly ordered parallel slits through self-assembly into functional membranes. Understanding and experimentally validating the effects of the key parameters – slit height, layer charge, confined ion type, confined solvent, and electrolyte concentration – that govern confined transport has become a central focus. Commonly used 2D materials, including hexagonal boron nitride, transition metal hydroxides, graphene oxide and natural clays, have intrinsic material limitations that prevent the independent control and systematic variation of the key parameters. In addition, they often lack access to well-defined monolayer nanosheets with high aspect ratios. As a result, fundamental investigations are mostly limited to nanoscopic devices with individually defined channels, which suffer from low signal-to-noise ratios with most standard characterization techniques. A bulk-scale investigation of ionic and solvent transport in a 2D material with precisely defined slit geometry, tunable layer charge, and variable confined cation species has so far not been realized [2].

A suitable 2D material to independently control and vary these properties is the synthetic 2:1 sodium fluorohectorite $[Na_{0.5}]^{inter}[Mg_{2.5}Li_{0.5}]^{oct}[Si_4]^{tet}O_{10}F_2$ ($Na_{0.5}$Hec) [3]. Its rare property to undergo 1D dissolution and form a nematic gel allows angstrom-precise slit height control, simply by varying the volume ratio of clay to water [4]. The slit height can be adjusted in the range of the Debye length, which is considered the defining length scale of confined mass transport. Additionally, the material has exchangeable intrinsic interlayer cations, can be swollen with electrolytes of varying concentrations, and can also be synthesized with higher and homogeneous layer charge [5]. With the relevance of lithium-ion technologies in mind, the fluorohectorites were cation-exchanged from sodium to lithium ($Li_{0.5}$Hec/$Li_{0.7}$Hec) and then processed into monodomain films of ~50 µm thickness, offering 50,000 parallel slits. These were then probed for the slit height dependent ionic conductivity within a homemade in situ measurement cell that allows both the determination of slit height by small-angle X-ray diffraction (XRD) measurements in Bragg-Brentano geometry, and the measurement of the ionic conductivity by electrochemical impedance spectroscopy (EIS). Within this setup the key parameters that govern confined mass transport can be controlled and systematically studied, including a variation of the confined electrolytes concentration up to 100 mM. Confined conductivities of up to 0.25 S/m were observed in these thin films.

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[3] Stöter M et al. (2013) Langmuir 29, 1280-1285.
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[5] Dudko V et al. (2023) Adv Mater Technol 8, 2200553.

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Ultrathin natural biotite as a layered dielectric for van der Waals heterostructure and device applications

de Oliveira, R[1], Rodrigues, G. L.[2,3], de Oliveira, R. C.[4], Malachias, A.[5], Teixeira, V. C.[1], de Oliveira, A. J. A.[4], Gobato, Y. G.[4], Barcelos, I. D.[1] and Cadore, A. C.[2]

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Naturally occurring van der Waals crystals have garnered unprecedented interest among nanomaterials researchers in recent years. To date, more than 10,000 layered materials (LMs) have been computationally identified, however, only a few insulating and naturally occurring LMs have been thoroughly investigated [1-2]. Consequently, when a new LM is identified, its optical, magnetic, mechanical, and electrical properties are promptly examined. Moreover, with the advent of techniques capable of precisely stacking LMs on top of one another to create the so-called van der Waals heterostructures (vdWHs) [2], new applications and research directions continue to emerge. As a result, individual LMs and their vdWHs are often regarded as fundamental building blocks for future ultrathin devices [2]. In this context, biotite crystals, also known as black mica, stand out as an LM that is stable under ambient conditions and exhibits high-quality basal cleavage - an essential characteristic for vdWHs. In this study, we present a high-throughput characterization of biotite crystals, including their structural, optical, magnetic, and electrical properties, using various experimental tools, as well as state-of-the-art synchrotron-based techniques [3-5]. Finally, we demonstrate the use of biotite as a substrate and as an encapsulating layer in vdWHs and device applications. Thus, our study introduces biotite as a novel, low-cost LM with great potential for the development of future ultrathin nanotechnologies.

Acknowledgments: INCT Nanocarbono, FINEP, CAPES, CNPq and FAPESP (No. 2022/02901-4).

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[2] I.D. Barcelos, et. al., J. Apply. Phys., 134, 090902 (2023)
[3] A.R. Cadore, et. al., 2D Mater. 9, 035007 (2022)
[4] R. de Oliveira, et. al., Nanotechlonogy 35, 505703 (2024)
[5] R. de Oliveira, et. al., Submitted (2025

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Towards a delamination of iron(II)-rich synthetic mica

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Combining large surface areas and aspect ratios of silicate nanosheets with the advantages of functionalization through transition metals substitution could offer interesting systems for electrochemical devices. Compared to large band gap insulators natural micas, synthetic crystalline ferrous tainiolite, $Cs[Fe_2Li]^o[Si_4]^tO_{10}F_2$ has shown good electrical conductivity [1] due to the high content of transition metal. For muscovite-type mica nanosheets, a band gap narrowing (7 to 2.5 eV) has been observed after exfoliation [2]. Obtaining monolayers or double-stacks of this Fe-bearing material could allow novel applications, for example semiconductors for optoelectronics or incorporated in 2D heterostructures.

The aim of the present study is to delaminate a Fe(II)-rich synthetic tainiolite. Previous works have shown exchange properties of the highly charge (x=1) Fe-Tainiolite [1,3-4]. However, chemical delamination of this fluoro-mica's broad sheets has not been achieved so far. While for low charged smectites, such as Na-hectorite, delamination is spontaneous in water, for more highly charged Vermiculite, delamination requires first an ion-exchange for bulky yet hydrophilic organocations like megluminium before delamination via one-dimensional dissolution sets in [5].

For a mica, like synthetic Tainiolite, the delamination is at least expected to be a two-step process, since the pristine interlayer space is not hydrated. Several other barriers need to be overcome. Here, particle size (>100 µm) is a challenge. A certain activation energy for exchanges with hydrated interlayer cations is required. Also, the structural iron oxidation state must be monitored and controlled as it is related to the layer charge density and ion exchange capacity. Especially, to determine if the delamination is possible without oxidation i.e. layer charge decrease.

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Defects in Natural 2D Materials

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Two-dimensional (2D) materials have emerged as an outstanding platform for light emission, with unique opportunities for integration in nanoscale optoelectronic and photonic devices. In recent years, a range of 2D systems—including hexagonal boron nitride (h-BN) [add ref], transition metal dichalcogenides (TMDs) [add ref], and molybdenum trioxide (MoO_3)—have shown photoluminescent activity linked to intrinsic defects or excitonic effects. These findings are not only technologically relevant for the development of quantum light sources and novel sensors, but also scientifically intriguing, as they offer insights into defect dynamics and light-matter interactions at the atomic scale. The search for new two-dimensional materials is motivated not only by the desire to identify compounds with properties tailored to specific applications, but also by the potential to uncover novel physical phenomena during this discovery process. Within this class, phyllosilicates stand out as naturally abundant wide-bandgap semiconducting minerals, which can be exfoliated down to a few atomic layers [1]. This makes them cost-effective and environmentally sustainable alternatives to conventional 2D materials. Among phyllosilicates, talc ($Mg_3Si_4O_{10}(OH)_2$) is of particular interest. Known for its monoclinic structure and perfect cleavage along the {001} plane, talc exhibits a high density of intrinsic and impurity-associated defects [2]. These defects have a direct influence on its electronic and optical properties. In this work, we investigate the defect-related emission in naturally occurring talc from Minas Gerais, Brazil, through a combination of photoluminescence and cathodoluminescence spectroscopy. Our results contribute to the understanding of defect-induced optical activity in layered minerals and highlight the potential of talc as a platform for light emission at the nanoscale.

[1] R. Frisenda *et al.* Naturally occurring van der Waals materials. *npj 2D Mater. Appl.* **4**, 1–34 (2020).
[2] I. D. Barcelos *et al.* Infrared Fingerprints of Natural 2D Talc and Plasmon–Phonon Coupling in Graphene–Talc Heterostructures. *ACS Photonics*. **5**, 1912–1918 (2018).

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Manipulating heterogeneities of clay minerals at the nanoscale to tune their properties for nanodevice applications

De Oliveira, Raphaela[1], Gobato, Y. G.[2], Freitas, R. O.[1], Teixeira, V. C.[1], Malachias, A.[3], Krambrock, K.[3], Cadore, A. R. [1] and Barcelos, I. D. [1]

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Clays have been explored in several fields since ancient times, but only recently have non-swelling specimens been considered versatile two-dimensional (2D) materials [1]. The layered structure of phyllosilicates enables them to be exfoliated down to monolayers, producing flakes with atomically flat surfaces and large areas. Since they are large-bandgap insulators, they have initially been explored as naturally abundant and low-cost alternative insulators to hexagonal boron nitride, the most widely used 2D insulator. However, phyllosilicate clay minerals are complex systems with inherent heterogeneities. While heterogeneities can, on one hand, reduce the electrical insulating capacity of materials, on the other hand, they can enhance unique applications at the nanoscale, where proximity and confinement effects determine the overall system response. I will demonstrate in this presentation how we can use a synchrotron X-ray nanoprobe to perform fluorescence measurements for identifying and mapping impurities in ultrathin phyllosilicates with nanometric resolution, which may be impracticable using other techniques at the nanoscale limit [2].

In addition to the common presence of impurities, there is another type of heterogeneity that is rarely explored by the 2D nanodevice community: hydration. Clay minerals are well known to be hydrated, acting as nanocavities for water. However, the way hydration affects the fundamental properties of phyllosilicates at the nanoscale, particularly in their few-layer limit, has not been thoroughly discussed. In this presentation, I will demonstrate that the hydration of ultrathin phyllosilicates can alter the optical, mechanical, and dielectric responses of the system. To explore this, I will focus on the use of Kelvin probe force microscopy and scanning near-field optical microscopy as key tools for investigating hydration with spatial resolution at the nanoscale in ultrathin phyllosilicate minerals. In particular, clinochlore phyllosilicate mineral will be presented as a natural 2D platform for studying distinct water nanoconfinement phenomena with the natural formation of 2D aqueous nanochannels [3].

I will conclude this presentation by discussing emergent phenomena that can occur when phyllosilicates are combined with other materials to form van der Waals heterostructures, such as modifications to the emission of optically active monolayers on top of a clay mineral. This will exemplify how manipulating heterogeneities at the nanoscale can locally tune the properties of clay minerals, with potential applications in 2D-based nanodevices.

Acknowledgements to FAPESP (2022/08329-0 and 2019/14017-9) for the financial support, Prof. M. A. Fonseca for supplying the samples, as well as CNPEM, UFMG, and ALS for the scientific infrastructures.

[1] Frisenda R et al. (2020) npj 2D Mater Appl 4: 38
[2] de Oliveira R et al. (2024) Nanotechnology 35: 505703
[3] de Oliveira R et al. (2024) J Phys Chem C 128: 14388-14398

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LECTURE THEATRE 5, SWIFT – SESSION 10

Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges

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Geological value of the Si/Al ratio in natural zeolites: critical assessment of selected precursor reactions

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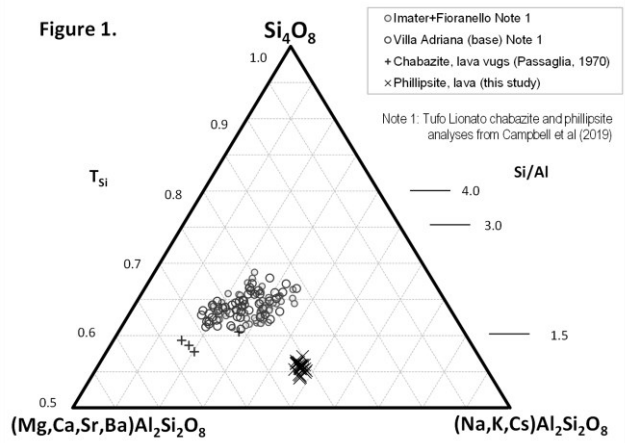
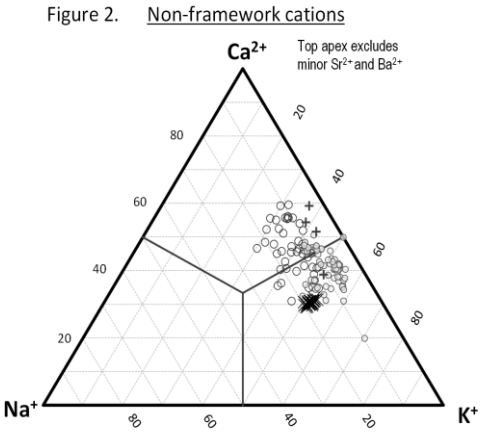
The Si-Al framework of natural zeolites is fundamental to their structure, composition and properties, and has been discussed extensively in relation to their initial formation from so-called 'zeolite precursor' phases, especially volcanic glass. This contribution examines the field, petrological and geochemical context of a very low SiO_2/Al_2O_3 phillipsite from 100-200-μm lava vugs of the Colli Albani volcano (Rome, Italy), with comparison compositions from other lavas [1] and associated zeolitized tuffs [2], Figs. 1 and 2. Zeolites were analysed by electron microprobe [3], and the 12 wt % proportion of phillipsite found in the Vallerano lava was determined by powder X-ray diffraction (Rietveld analysis) of a whole-rock sample.





As alkaline volcanic glass is highly reactive, a precursor phase of residual glass was first considered for the low Si/Al phillipsite. Campbell et al. [2] modelled the primary alkaline magmatic melt (Colli Albani) to determine the change in residual melt SiO_2/Al_2O_3 as higher-silica magmatic minerals such as olivine and clinopyroxene crystallized. The compositional trajectory of the modelled melt phase then served to represent precursor volcanic glass in closely associated zeolitized pyroclastic deposits, and, hence, to indicate the stage of fractional crystallization that the residual melt reached immediately prior to explosive eruption. For the phillipsite of the present study, its SiO_2/Al_2O_3 ratio of 1.42 is too low to be explained by a residual melt ratio of 1.82 at 789°C, 85% crystallized (the limit of the model). Furthermore, petrographic evidence of Sr and Ba enrichment in the late-stage magmatic assemblage of the lava (including hyalophane, apatite and residual melt), is not consistent with a glass precursor, because Sr and Ba were barely detected in the phillipsite. Therefore, the only feasible reactive precursor phases were (i) significant nepheline (SiO_2/Al_2O_3 = 1.2) and (ii) minor leucite (SiO_2/Al_2O_3 = 2.36). The possibility of an interim precursor of thomsonite cannot be ruled out.

Acknowledgement: D. Gatta, Univ. Milan (microprobe access).

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Hydronium exchange in ion exchange and dissolution of feldspathoids sodalite and cancrinite

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Sodalite and cancrinite are feldspathoid minerals that can be found in nature, bauxite residue or nuclear waste storage facilities [1]. Their formation is associated with the dissolution of aluminosilicate minerals such as kaolinite, smectites or mica under alkaline conditions. Feldspathoids can serve as nutrient carriers (K^+, NH_4^+) in bauxite residue and sequestering agents for radioactive nuclides (Cs^+, TcO_4^-) in nuclear wastes [1-3]. One concern, however, is their stability. Incorporated ions would likely be released once dissolved, while structural Al^{3+} and Si^{4+} reprecipitate as silica and aluminium hydroxide species. Acid leaching of hydroxysodalite has shown Na^+-H_3O^+ exchange with diluted acid (<0.1 M) and hydrolysis of framework under concentrated acid (>0.1 M) [4]. Additionally, hydronium exchange has been commonly found in zeolites, especially during the NH_4^+ exchange [5-6]. This study aimed to reveal the reaction mechanism between feldspathoids and H_3O^+ in acid dissolution and ion exchange reaction.

By mixing kaolinite, Na_2CO_3, and NaOH in a hydrothermal reactor, sodalite and cancrinite were synthesized at 100 and 230 °C, respectively. A batch experiment was conducted by manually mixing 0-4 mL of 0.1M HNO_3 with 10 mg of sodalite or cancrinite simultaneously. The pH was monitored intermittently until reaching a constant value. Ion exchange experiments were conducted by reacting solid with KCl, NH_4Cl, $CaCl_2$, and $MgCl_2$ and reversed exchange with NaCl. The solutions were analyzed with ICP-OES. The undissolved solids were washed, dried, and examined using XRD, FTIR, and SEM.

Both sodalite and cancrinite showed similar behavior under acidic conditions. The Na^+-H_3O^+ exchange was found by mixing feldspathoids with DI water, causing an increase of pH to 10. The occurrence of exchange even at this alkaline pH indicated that their high affinity toward H_3O^+. With the addition of < 600 cmol/kg H_3O^+, the pH gradually increased as H_3O^+ was incorporated, reaching equilibrium after 48 hr and creating a buffer zone between pH 6 and 8. The crystallinity of feldspathoids began to vanish with the addition of 500 cmol/kg H_3O^+, indicating they may tolerate up to approximately 400 cmol/kg H_3O^+ before the structure collapsed. The hydronium exchange and dissolution were believed to occur simultaneously within this region. With further acid addition, the H_3O^+ exchange continued to occur and eventually led to the complete dissolution of feldspathoids. The released Al^{3+} from the framework appeared to reprecipitate as an amorphous phase. The dissolution of this phase resulted in another buffer zone around pH 4, which ended at 2000 cmol/kg H_3O^+. This matched well with the reaction stoichiometry. Theoretically, 2400 cmol/kg H_3O^+ was required to completely dissolve feldspathoids. During the NH_4^+ exchange experiment, approximately 20% H_3O^+ was found and they were resistant to be reversed exchange by Na^+. Our results suggest that sodalite and cancrinite would remain stable under neutral to alkaline conditions, yet the hydronium exchange should still be considered and it may affect the performance of ion exchange.

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Characterization of natural zeolites of Argentina

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Natural zeolites have been extensively studied worldwide due to their distinctive properties. In Argentina, despite economically viable deposits identified at various locations across the country, there is only one commercial producer of natural zeolites from Paganzo region in La Rioja province, with the others remaining largely underexplored. This study addresses the gap in knowledge by focusing on the physicochemical characterization of natural zeolitic materials from volcanic tuffs in the province of Chubut, Argentina [1]. The evaluation includes mineralogical composition, porosity, and potential industrial applications. The characterization techniques used were as follows: X-ray Diffraction (XRD) to determine the present mineral phases, X-ray Fluorescence (XRF), N2 and CO2 Adsorption Isotherms for analysis of specific surface area, meso and microporosity, Cation Exchange Capacity (CEC), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared Spectroscopy (FTIR). The results confirm the predominance of clinoptilolite-heulandite series minerals, with minor phases of mordenite, quartz, and feldspars. The materials analyzed exhibit a micro-mesoporous structure and a high affinity for CO_2 adsorption, comparable to some activated carbons [2]. Their ion exchange capacity and thermal stability suggest promising applications in environmental remediation and gas separation technologies. These findings provide valuable insights for utilizing and optimizing natural zeolites from Chubut in various industrial processes.

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Natural Zeolite Modified with MnOx Coating: A detail investigation of an innovative material for treating soluble manganese (Mn^{2+}) and iron (Fe^{2+}) contamination

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Water contaminated with manganese (Mn^{2+}) poses risks to human health and the environment, with pollution originating from various industrial effluents and abandoned mine wastes. Mn^{2+} removal from drinking water is achieved through ion exchange, adsorption, biodegradation, and chemical oxidation, with active manganese oxides (MnOx) being promising candidates for this purpose.

This research presents a study on chemically modified zeolite (clinoptilolite) coated with manganese oxide for the removal of manganese (Mn^{2+}) from contaminated water. The objective is to evaluate the efficiency of this modified material in eliminating aqueous Mn^{2+}, primarily through chemical catalytic oxidation and the subsequent precipitation of an insoluble and non-toxic form of MnOx.

A detailed characterization of the material at different stages—including pre-manganese treatment zeolite, post-manganese treatment zeolite, and post-regeneration zeolite—reveals interesting data about the catalytic phenomena. The characterization techniques employed include X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

The contaminated and treated solutions were also characterized using ion-exchange chromatography, allowing verification of changes in the solution's chemistry. All data were applied to develop a geochemical model using PHREEQC software to gain a better understanding of the processes and mechanisms involved.

The crisscross of these evidences highlight the effectiveness of the chemically modified clinoptilolite and its potential for practical implementation in water treatment systems, as well as possible ideas for further investigation and adaptation to increase the potential of MnOx-coated zeolite.

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Challenges of Scaling Resilience: A Critical Review of Pettit et al. (2010) in the Natural Zeolites Sector

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This study aimed to identify the limitations and adaptation opportunities of the Supply Chain Resilience (SCRE) framework proposed by Pettit, Fiksel & Croxton (2010) [1], when applied to the natural zeolite sector — a supply chain marked by structural fragility, logistical complexity, and low operational maturity. The sector faces significant challenges to scaling operations and applying traditional resilience strategies, including informal business structures, lack of standardization, and weak inter-organizational collaboration. Through semi-structured interviews with supply chain experts, the study examined how the original framework's capabilities function in practice and whether they can adequately address the sector's real constraints. Findings revealed that key capabilities such as efficiency, flexibility, and anticipation often operate as vulnerabilities in this context. Conversely, new capabilities — such as human relationship strength and technical application expertise — emerged as essential to coping with uncertainty and sustaining continuity. The study proposes a revised interpretation of the SCRE framework tailored to fragile, underdeveloped industrial ecosystems like that of natural zeolites, where market and scalability challenges demand alternative approaches to resilience.

Keywords: Supply chain, resilience, natural zeolites, scalability, market challenges, capabilities, vulnerabilities.

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Actual and expected applications of Zeolite for remediation and waste management of radioactively contaminated nuclear sites

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Due to the excellent properties and natural abundance, zeolites have been utilised in the nuclear industry, especially for remediation of radioactively contaminated sites and waste management. Here, the authors would like to introduce our study with zeolite, which has been applied to the remediation of the Fukushima Daiichi Nuclear Power Plant site after the accident, as well as the study for future applications of zeolite in advanced nuclear power system.

Just after the severe accident on March 2011, huge amount of highly contaminated water was found in the basement of Fukushima Daiichi nuclear power plant and about to overflow. Hence, decontamination equipment with high-throughput (1200 ton/day) was emergently designed and constructed by international collaboration team. The authors measured ion-exchange properties of various zeolites for the contaminated water with radioactive elements and impurities such as sea water and oil, and a modified natural Zeolite (©KURION-Herschlite) was selected for use in parallel column system. The equipment was successfully started operation to keep high decontamination efficient [1]. As the treated water still contained radioactive nuclides such as Sr-90, it was stored in large tanks within the same site.

About 2 years later, certain amount of contaminated water was leaked from one of the tanks. The contaminated soil was excavated as much as possible, however additional measure was necessary to avoid diffusion of contamination into groundwater. The applied measure is so called, Permeable Reactive Barrier (Fig. 1), defined as an emplacement of reactive media in the subsurface trench designed to intercept a contaminant plume, to reduce the contamination of groundwater in down-gradient. It is a passive, in situ technology having a high potential to treat shallow aquifers at a lower cost. As the main contamination is Sr-90, natural clinoptilolite zeolite was selected according to our laboratory experiments and buried with gravel and natural apatite in the trench [2]. No significant increase of Sr-90 has been detected for the groundwater of down gradient for more than 14 years.

As the future nuclear energy system of ampoule safety, sustainability and waste burden reduction, metal fuelled fast reactor with pyrochemical reprocessing are currently studied in many countries. The authors have been studying the application of synthesized zeolite to remove Cs and Sr from used LiCl-KCl molten salt with high temperature (773 K) column as shown in Fig. 2[3]. The ion-exchanged zeolite is to be heated to transform into “sodalite” structure, a natural zeolite containing chloride in cages against leaching into water, suitable for radiological waste form of natural analogues.

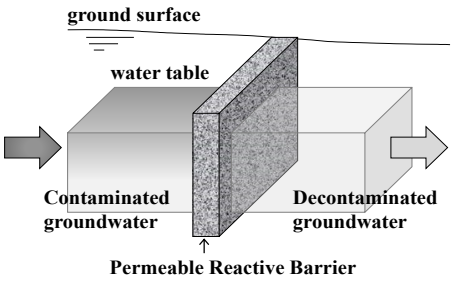

Fig. 1 Concept of *Permeable Reactive Barrier*

Fig. 2 High Temperature Zeolite Test Column

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Modified Zeolite for Groundwater Treatment: A Brazilian Plant Study

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In Brazil, around 18% of groundwater is used for public supply [1]. Alternative solutions such as wells, cisterns and reservoirs are a way of supplying water in rural areas or regions with low rainfall, such as the Northeast region of Brazil [1,2]. Currently, even wells can have their quality and quantity compromised, since water scarcity or irregular use contributes to reducing the quantity of water [2], while wells with a natural presence of metals can reduce their quality, requiring prior treatment. Therefore, the search for investment in alternative technologies that reuse existing systems becomes an option, with the aim of achieve the desired quality.

This study presents the use of chemically modified zeolite (Watercel ZF) in a public Water Treatment Plant (WTP) in the Northeast region, with the aim of meet the Brazilian drinking water regulations, of total iron content (Fe) (≤ 0.0003 kg/m³), turbidity (≤ 0.50 NTU) and apparent color (≤ 15 uH) [3]. The WTP serves a district in the northeastern semi-arid region (54,000 inhabitants [4] / 200 connections served by the WTP), and has the following stages: pumping water from artesian wells (average flow 0.00556 m³/s), dosing of aluminum polychloride (PAC), cationic polymer and chlorination, followed by direct upward filtration in sand. The sand bed was partially replaced with 0.53 m of Watercel ZF.

Data was evaluated after replacing the zeolite from June/2024 to December/2024 and it was compared with the operation of the sand filter during the same period in 2023. The raw water showed average total Fe values of 0.00237 kg/m³ (2023) and 0.00294 kg/m³ (2024), apparent color of 20.00 uH (2023) and 39.28 uH (2024), turbidity of 3.41 NTU (2023) and 7.76 NTU (2024). The data shows that the WTP had 0% compliance between June and November/2023 for the removal of average total Fe (0.00085 kg/m³), apparent color (40.35 ± 0.69 uH) and water turbidity (2.78 ± 0.49 NTU). The lowest values for turbidity (2.58 ± 0.33 NTU) and apparent color (40 ± 0.00 uH) were obtained in September.

After replacing zeolite, it was possible to achieve 80.92% of average total Fe removal (0.00031 ± 0.00016 kg/m³). Apparent color and turbidity, presented an average value of 11.27 ± 4.49 uH and 1.29 ± 0.93 NTU, respectively. The lowest values for turbidity (0.84 ± 0.64 NTU) and apparent color of (4.07 ± 2.68 uH) were obtained in December.

After adjusting the chemicals during operation, there was an 81.92% reduction in the average monthly consumption of PAC (79.5 kg) and 93.00% for polymer (27.37 kg). However, there was a 204% increase in the consumption of calcium hypochlorite (302.42 kg), which is used to regenerate the zeolite bed.

Therefore, the operational control of chemicals, combined with the use of alternative filter media, can promote the removal of metals such as iron, and generate savings such as the reduction of PAC and polymer. However, the system is still in the validation phase and is being monitored to this day to adjust turbidity and reduce chlorine dosage, with the aim of contributing to the sustainability of the system as a whole, without the need to alter it structurally.

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[4] Instituto Brasileiro de Geografia e Estatística - IBGE (2022) Censo Demográfico [N.I.]

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Synthesis of Zr^{4+}/Ag^{+} Modified Zeolite for Application in Fluoride and Pathogen Removal from Groundwater

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The use of clay minerals in the synthesis of zeolites has attracted wide attention from researchers. This is due to their SiO_2 and Al_2O_3 contents that allow the synthesis of zeolites with excellent adsorption and ion exchange capacities. This research used bentonite clay as a precursor material for synthesizing zeolite NaP modified with Zr^{4+} and Ag^{+} ions for use in fluoride and pathogen removal from groundwater. Bentonite clay was subjected to ultrasound-assisted alkali dissolution followed by hydrothermal treatment. Solutions containing 0.5 and 0.3 M for $ZrCl_4$ and $AgNO_3$ were mixed with a 2.5 M concentration of NaOH and 10 g of calcined bentonite. The mixture was sonicated for 2 hours and further treated hydrothermally at 105 °C for 90 minutes of hydrothermal time. The obtained material was characterized using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), Particle Distribution Analyzer, and Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS). The modified zeolite's fluoride removal efficiency and antimicrobial potency were evaluated through batch fluoride adsorption and well-assay diffusion experiments. A maximum fluoride removal percentage of 50% was achieved under optimal pH conditions of 6 ± 0.5, a contact time of 270 min, an initial fluoride concentration of 6.2 mg/L, and an adsorbent dosage of 0.5 g/100 mL. Regeneration studies showed that the material can be regenerated successfully for up to 5 regeneration-reuse cycles. Furthermore, the antimicrobial potency results showed a minimum zone of inhibition of 15 mm and 12 mm against the gram-negative *E. coli* and gram-positive *S. aureus* strains in the antimicrobial test. This study proved that the Zr^{4+}/Ag^{+} modified zeolite can potentially remove fluoride and pathogens from groundwater.

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Zeolitic Tuff for Ammonium Recovery from Anaerobic Digestates: Efficiency, Optimization, and Large-Scale Potential Application

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The increasing production of wastewater from livestock farming, industrial activities, and domestic sources poses significant environmental and economic challenges [1]. Excessive nutrient discharge into water bodies contributes to eutrophication, while the loss of valuable elements, such as nitrogen (N), represents a missed opportunity for agricultural reuse [2]. In this context, the development of sustainable and cost-effective strategies for nutrient recovery is crucial to promoting circular economy principles and reducing dependence on synthetic fertilizers. Implementing such approaches aligns with the European Green Deal and global sustainability goals, which advocate for resource efficiency and environmental protection [3,4].

This study explores the use of a zeolitic tuff for nitrogen recovery from various anaerobic digestates, including those from livestock (swine and cattle) and organic solid waste. The aim is to assess the feasibility of integrating this process into farm-scale treatment systems for nutrient recycling. The influence of digestate pre-treatment methods (e.g., microfiltration, clarification) on ammonium adsorption efficiency was also examined. A comprehensive set of experiments evaluated ammonium removal under varying conditions, considering (i) contact time, (ii) initial NH_4^+ concentration, (iii) ionic competition, and (iv) total solids. Adsorption isotherms and kinetic models were applied to understand the process mechanisms and optimize operational parameters.

Preliminary findings suggest that the ammonium removal efficiency is closely linked to digestate composition and physicochemical properties. Notably, livestock-derived digestates exhibited a higher nitrogen recovery potential compared to other sources. Moreover, pre-treatment methods, such as microfiltration and clarification, were found to enhance adsorption performance by reducing solid content and potential interferences. Considering the widespread availability of zeolite-rich tuffs and the substantial daily production of livestock digested, the proposed method is valuable for large-scale implementation. The method allows the recovery of several tons of nitrogen per year for agronomic applications without relying on chemical additives and offers both environmental and economic benefits. Following this approach two patents were presented producing NH_4-enriched zeolite as soil amendment, and struvite as fertilizer. This latter allowing also to recover P together with N.

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Assessment of the Potential Role of Zeolites in Biological Electro Molecular Mechanisms

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Clinoptilolite (CLN), a natural zeolite (NZ), is defined by its nano porous crystalline lattice, high surface area (>20-200 m²/g), and ion-exchange capacity [1], [2]. Structurally analogous to quasi-crystals, CLN can be conceptualized as a natural metamaterial capable of engaging in biological electro molecular interactions (EMIs). This theoretical model proposes that CLN modulates local biophysical conditions, enhancing cellular signalling, gene regulation, increased potential for electronic donation in living systems and possible biologic quantum coherence processes [3].

CLN provides bioavailable silicon (Si), an essential element with a recommended intake of ~20–30 mg/day [4], [5], crucial for regenerating piezoelectric connective tissues such as bone, fascia, dentin, collagen, and cytoskeleton. Si-mediated interactions affect cell signalling, membrane intra-extra voltage, and homeostasis, contributing to pleiotropic effects like epigenetic modulation and sanogenesis [6], [7], [8].

In hydrated and intracellular colloidal environments, CLN's reticulated lattice and negative surface potential of (−30 to −40 mV at pH 7) could support oscillatory resonance, electrostatic interactions, hydrogen bonding, and van der Waals forces [9], [10], [11]. These may enhance mitochondrial efficiency, reduce chromosomal aberrations, and modulate gut–brain axis signalling [12] [13], [14].

CLN's Structural cavities and unique physicochemical properties of Si could help stabilize transient molecular assemblies and could support quantum coherence in microtubule-like structures [15], [16], [17], [18], [19]. It is proposed that CLN's induces the formation of superconducting liquid crystalline water colloids, modulates local paramagnetic fields, and interacts with biophotons emitted during cellular metabolism, contributing to subquantum electro molecular phenomena such as bioelectric grounding. [20], [21], [22], [23].

Ultimately, this model proposes that CLN functions as a mineral interface capable of mediating electro-biological and quantum-level interactions. It may even encode holographic biogenic patterns and exhibit time-crystal-like behaviours, potentially influencing biological organization through quantum coherence [24], [25]. These insights could inform emerging fields like regenerative medicine, quantum biology, and targeted biophysical therapeutics.

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Evaluation of Philippine natural zeolite-based particle film for sustainable pest management in cacao

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Chemical residues from pesticides pose environmental and health concerns, necessitating sustainable pest control alternatives. Particle Film Technology (PFT), utilizing non-chemical mineral coatings such as kaolin [1} and zeolite, offers a promising eco-friendly approach to pest and disease management. Originally developed for disease control in fruit trees, PFT induces insect repellency and mortality through physical mechanisms such as abrasion and desiccation, as well as by acting as a barrier against pathogens. Despite its success in other crops, research on kaolin's efficacy against cacao pests remains limited. Preliminary studies indicate that local natural zeolite exhibits comparable repellency and barrier properties to commercial kaolin formulations, effectively deterring pests like the cacao mirid bug (CMB) and inhibiting black pod rot caused by Phytophthora spp. Zeolite also demonstrates high compatibility with entomopathogens (e.g., Metarhizium anisopliae) and microbial control agents such as Trichoderma spp., maintaining viability for at least one-week post-application. This facilitates integrated biocontrol strategies by combining physical barriers with biological agents, potentially reducing reliance on chemical pesticides. Additionally, the use of Philippine natural zeolite (PNZ) [2] as a carrier material, modified with a coconut-based surfactant, yielded a bio-coat (BioCoat-Z) that forms a durable, insect-repellent surface on cacao pods. Field trials showed complete coverage and significantly fewer CMB feeding lesions, indicating strong pest deterrence. The BioCoat-Z's capacity to inhibit pathogen growth and maintain efficacy over the pod's growth cycle underscores its potential as a sustainable pest management tool. This integrated mineral-based coating technology offers a cost-effective, environmentally safe alternative to traditional practices like plastic bagging, which can promote pathogen development. Further research is warranted to optimize formulation, application frequency, and long-term effects in cacao cultivation systems. The adoption of zeolite-based particle film, BioCoat-Z could significantly contribute to sustainable cacao production, aligning with global efforts to reduce chemical pesticide dependency and reduction of plastic sleeving use.

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Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes

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Designing Montmorillonite-Supported Metal Oxide Catalysts for Efficient Gas-Phase Glycerol Oxydehydration

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Clay minerals as catalysts has become one of the most active fields of research in biomass conversion technologies over the past years. In this context, glycerol can be utilized as a renewable C_3 feedstock for producing various value-added chemicals through gas-phase catalytic reactions. A key consideration to achieve efficient conversion of glycerol to desired product is to rationally design active and selective catalysts with proper functionalities and active sites. Montmorillonite (MMT), a naturally abundant 2:1 clay mineral with inherent acidity has shown great potential both as a catalyst and/or a catalyst support [1,2] and previous work in our group revealed that this low-cost acid-activated material (HMMT) could promote gas-phase glycerol conversion to acrolein at 320 °C and 1 atm with a yield as high as 45% at 83% selectivity [1].

In this study, we investigate HMMT-supported Mo–V oxide catalysts for gas-phase conversion of glycerol to allyl alcohol (C_3H_6O, an industrially important intermediate in organic synthesis) via consecutive dehydration and hydrogen transfer reactions [3]. The use of HMMT as a support allowed well dispersion of metal oxide particles with nominal loadings up to 5 wt % on the catalyst surface while the Brønsted acidic sites of HMMT facilitate dehydration of glycerol to acrolein at ~74% selectivity. The highest allyl alcohol yield (~22%) was obtained using this bifunctional catalyst with the nominal total Mo+V loading of 10 wt% at 320 °C. X-ray photoelectron spectroscopic characterization of the as-prepared and post-catalysis (spent) states revealed changes in the surface Mo(VI)═O species and V^{4+}/V^{5+} redox ratio; the latter was found to decrease due to the involvement of lower valence V^{4+} species in the hydrogen transfer reaction of acrolein. Meanwhile, the amount of surface Mo(VI)═O species with weak electronic metal–support interaction decreases after the catalytic reaction. Catalytic testing using an aqueous acrolein feed solution suggested the role of water as a hydride donor in transfer hydrogenation of this unsaturated aldehyde to allyl alcohol, whereas the addition of alcohol-containing compounds, such as 2-propanol and 1,2-propanediol leads to lower allyl alcohol selectivity with time-on-stream [3]. The result of this work could contribute to the design of clay mineral-based catalysts, specifically supported Mo−V oxide catalysts and reaction systems for efficient gas-phase glycerol conversion to allyl alcohol.

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Design of clay-based catalysts assisted by machine-learning

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Industrial processes such as biodiesel production, Volatile Organic Compounds (VOCs) removal, and chemical purification such as benzene, toluene, xylene (BTX) purification acid-activated clay-based catalysts are required as active material. Their performance is determined by pore morphology and surface activity, which are typically represented by properties such as specific surface area, pore volume, microporosity, and pH.[1]

Optimizing these catalytic properties is challenging due to the wide range of parameters involved in material processing and chemical treatment. To address this complexity, machine learning (ML) techniques have been successfully applied as a tool for optimal material design, significantly accelerating experimentation. [2] The developed algorithm allows the creation of a material design platform revealing nonlinear interactions of the clay with modifiers or active phase. The trained models were able to capture the chemistry behind the material performance and identify regions in the descriptor space where positive synergies optimized the catalytic properties. In particular, we have demonstrated the optimal catalysts design identifying process parameters of acid, acid concentration and its amount with respect to clay, temperature and time of the reaction.

As a first proof of concept, the optimized acid catalysts were synthesized and tested in oil refining revealing appreciable acid character improvement with the respect of pristine material. Specifically, it achieved 79% removal of chlorophyll-a in acid catalyzed degradation. [2]

The controlled clay acid treatment has opened new pathways for multifunctional environmental materials. In particular, it has identified the optimal condition for the synthesis of TiO_2-based nanoparticles using an acid-activated sepiolite as a growth template and carrier.

The resulting catalyst exhibited promising performance in water purification, NOx decomposition, and photocatalytic coatings.[3] We demonstrated the self-cleaning properties, as evidenced by Rhodamine B degradation rates exceeding 20% after 4 hours and surpassing 50% after 26 hours of light exposure when the catalyst was integrated into paints and mortars.[4] Furthermore, in specific mortar formulations we have observed over 50% degradation of volatile organic compounds (VOCs), highlighting their effectiveness as active decontaminating surfaces. These findings suggest the accelerated, scalable and sustainable approach to the design of versatile clay-based catalysts for environmental applications.

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Construction strategies of the organic-inorganic interface structures in phyllosilicates-based nanozymes and their environmental applications

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Recent advances in constructing organic-inorganic hybrid nanozymes using phyllosilicate minerals as functional supports have demonstrated significant potential for enhancing catalytic performance and environmental remediation. Our recent works summarizes a series of strategies for engineering enzyme-nanozyme interfaces on montmorillonite (Mt), nontronite (NAu-2), halloysite nanotubes (HNTs), and aminoclay-based substrates. By leveraging covalent immobilization, directional co-immobilization, and in situ synthesis, natural enzymes (e.g., lipase, glucose oxidase (GOx), horseradish peroxidase (HRP), α-amylase) were integrated with nanozymes (e.g., Fe-aminoclay (FeAC), Zn-aminoclay (ZnAC), Cu–Mn bimetallic aminoclay (CMAC)) to construct phyllosilicate-based nanostructured enzyme catalytic systems and spatially confined cascade catalytic platforms. Key achievements include: the development of amphiphilic APTES-functionalized Mt for lipase immobilization, demonstrating 4-fold enhanced activity (40.65 U/mg) and improved stability through interfacial activation [1]; the construction of a functionalized Mt-based α-amylase catalytic system regulated by the "allosteric effect," achieving effective modulation of the enzyme's microstructure and activity enhancement [2]; the exploration of enzyme-like catalytic effects in NAu-2, which served as supports to establish a natural enzyme-mineral nanozyme cascade catalytic bioplatform [3]; and the design of a GOx-FeAC@AHNTs nanoreactor that achieved a glucose detection limit of 0.47 μM via substrate channeling [4].

Structural optimization of organic-inorganic interfaces proved critical for improving mass transfer efficiency and catalytic synergy. For instance, the cofactor-directed immobilization of GOx and HRP on functionalized Mt yielded a dual-enzyme system with 79.3% residual activity after 30 days and 74% retention after 10 cycles, outperforming physically mixed systems [5]. Similarly, ZnAC nanozymes mimicking carbonic anhydrase activity exhibited superior CO_2 hydration kinetics (Km = 4.071 mM, kcat = 11.213/s) and stability under extreme conditions, enabling efficient CO_2 mineralization [6]. Environmental applications were further demonstrated by a CMAC-lipase microsystem (CMAC@Lipase), which degraded 72.8% of dimethyl phthalate within 48 h and maintained 53.5% efficiency after 10 cycles [7]. These strategies highlight the dual role of phyllosilicate supports in stabilizing enzymes and enhancing nanozyme activity, offering scalable solutions for pollutant degradation, biosensing, and carbon capture. Collectively, these work provides a foundational framework for designing high-performance enzyme-nanozyme hybrids with tailored organic-inorganic interfaces for sustainable environmental technologies.

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Silica/clay based Composites used in the Adsorption of FFA, Optimizing the Process by RSM

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A silica/smectite composite was synthesized by a sol-gel method using smectitic clay and rice husk ash (RHA). The obtained product was used in the adsorption of free fatty acids (FFA) from palm oil. The evaluation of the main effects and interactions effects of contact time, temperature and adsorbent dosage was carried on using Box-Behnken Design coupled to Response Surface Methodology (RSM). Analysis of variance showed that the mathematical model could explain more than 98% of response variation by its relationship with the factors. The Pareto charts of standardized effects (see Figure1) evidenced that all the explanatory factors were significant. Contact time was found to be more influential on the process. The factorial plots revealed that time-temperature interaction was synergetic and more influential. The theoretical optimization of the model using Response Optimizer Function showed an optimum for FFA removal of 94 % (28mg of KOH/g) at adsorbent dosage of 2%, contact time of 60 min and temperature of 90°C.

Keywords: Adsorption; Free Fatty acids; Factors' effects, Response Surface Methodology

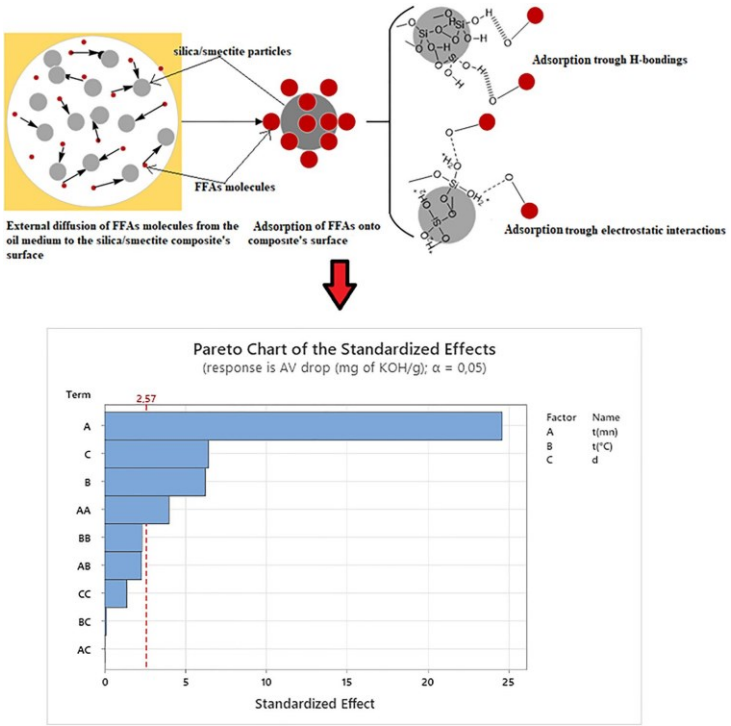

Figure1: Graphical abstract

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Amino-functionalized porous nanosilica modulates Pt nanoparticle morphology for low-temperature toluene catalytic combustion

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Pt nano-polyhedral catalysts exhibit exceptional activity in volatile organic compounds combustion due to their abundant low coordination sites, yet they face significant challenges in achieving both in situ growth and uniform dispersion on a support[1]. Herein, we synthesized a supported Pt polyhedral structured catalyst through the pre-amino functionalization of a montmorillonite-derived hierarchical porous silica support (Pt-APSiO_2). The surface-grafted amino silane on SiO_2 undergoes thermal decomposition during the calcination, forming NH_3 and H_2O as the gaseous byproducts. These gases served as dynamic modulators during the growth Pt nanoparticles, effectively resulting in the formatting of polyhedral nanoparticles through the chemisorption on surface of Pt crystal nucleus[2]. In the toluene catalytic combustion experiments, Pt-APSiO2 achieved a T_{90} of 148℃ while exhibiting excellent stability, maintaining over 95% catalytic activity after 72 h of continuous operation. The microscopic morphology and extended X-ray absorption fine structure results demonstrated that Pt nanoparticles possessed abundant surface steps and corners, where these Pt sites with low coordination numbers served as the primary catalytically active centers. Theoretical calculations revealed that the formed surface steps and corners caused an upward shift in the d-band center, thereby endowing Pt sites with stronger adsorption and activation of toluene and O_2 and a lower energy barrier for reactive oxygen species formation[3]. This study provides a novel strategy for the in situ synthesis of Pt nanoparticles with abundant low coordination sites, promising to enhance catalytic efficiency.

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Acidified Montmorillonite and Site-Specific V-Doping Keggin-Type NH_4PM Catalysts for Sequential Conversion of Glycerol to Acrylic Acid and Allyl Alcohol

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The gas-phase catalytic conversion of glycerol to acrylic acid and allyl alcohol in one-pot is considered as a potential green and sustainable process. To reduce the chance of over-oxidation of 3-hydroxypropanal (intermediate) in the process, in this work the gas phase catalytic reactions were carried out using a sequential-separated dual bed catalyst system; the upper bed contained the acid catalyst i.e. acidified montmorillonite (H-MMT) and the lower bed was unsubstituted/ V-substituted NH_4PM redox catalyst. The catalysts were characterized by PXRD, Raman, HRSEM-EDX, BET-BJH, XPS, NH_3TPD and O_2-TPD. The combination of H-MMT and primary V-doped NH_4PM (NH_4PMV) catalyst favoured the oxydehydration reaction and was susceptible to the selective conversion of glycerol to acrylic acid (Sel.- 63%). On the other hand, HMMT and secondary V-doped NH_4PM ($NH_4(VO)_xPM$) catalysts preferred the selective production of allyl alcohol via deoxydehydration reaction. Maximum allyl alcohol selectivity of 61% was achieved by 1:2 wt. ratio of HMMT and $NH_4(VO)_{0.2}PM$ (doping amount of VO species- 0.2)- dual bed catalytic system. O_2-TPD and XPS analyses unveiled that the V doping at the primary Keggin site of NH_4PM introduced more oxygen defects on the catalytic surface and facilitated charge transfer Mo^{+6} to Mo^{+5}. This combined effect promoted the partial oxidation of acrolein, leading to the selective production of acrylic acid. In contrast, secondary V-doped NH_4PM catalysts exhibited significantly fewer oxygen vacancies. As a result, they were less effective in facilitating the partial oxidation reaction of acrolein intermediate. However, these catalysts demonstrated high efficiency in catalyzing hydrogen transfer reactions, enabling the selective conversion of glycerol to allyl alcohol. Additionally, the following thermo-kinetic factors namely, activation energy (E_a), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), Gibb's free energy of activation ($\Delta G^{\#}$) were evaluated for the best catalytic systems (i.e. H-MMT+NH_4PMV and H-MMT+$NH_4(VO)_{0.2}PM$), providing insights into the factors contributing to improved performance. （Acknowledgements: The authors wish to acknowledge the financial support from the National Natural Science Foundation of China (W2433034; 22072136; 41672033), the Engineering Research Center of Non-metallic Minerals of Zhejiang Province (ZD2023K01), and Qing Yang Institute for Industrial Minerals (KYY-HX20220336; KYY-HX-20170557)).

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LECTURE THEATRE 6, UI CADHAIN – SESSION 34

Synthesis of geo-inspired clay minerals and associated hybrids

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Diameter and chirality of natural and synthetic imogolite

Picot Pierre[1], Gobeaux Frédéric[1], Charpentier Thibault[1], Belloni Luc[1], Takahara Atsushi[2], Wada Shin-Ichiro[3] and Thill Antoine[1]

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Imogolite is a natural tubular nanoclay first identified in 1962, whose structure was first described in 1972 [1,2]. As the aluminum atoms are positioned on a hexagonal lattice, it is possible to use the same formalism as for carbon nanotubes to describe imogolite. The chirality vector defined by C*(n,m)* links atoms on the network that will be joined upon rolling (see figure). In the 1972, a zigzag chirality (n,0) was proposed [2]. Later, molecular dynamics simulations confirmed that it is energetically more favorable compared to armchair configurations [3].

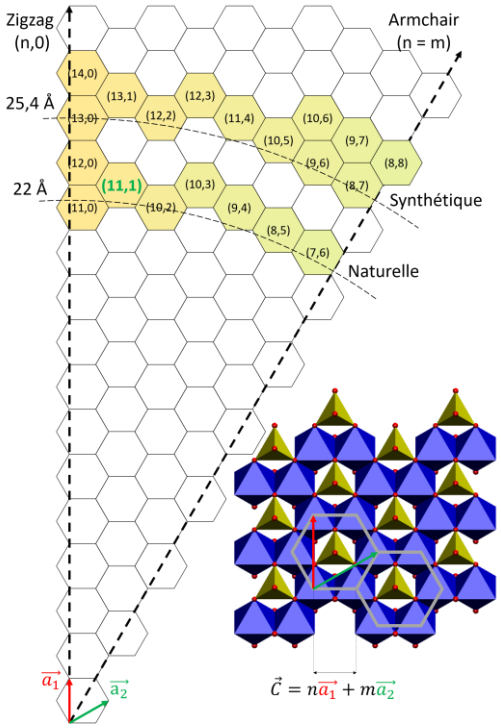

Figure: Possible chiralities for natural and synthetic imogolite.

There is however no consensus on the exact value of *n* (10, 11 or 12), which corresponds to the number of Si in the circumference. In 1977, Farmer et al. described a protocol for obtaining synthetic imogolite [4]. The synthetic nanotubes are larger than the natural ones and the diameter could be tuned [5]. Recently, D'Angelo et al. showed by molecular dynamics simulations and X-ray diffraction measurements on dispersions and powders that synthetic imogolite is not monodisperse and proposed a 50/50 mixture of (13,0) and (14,0) [6].

We have experimentally characterized natural and synthetic imogolite by several techniques (DRX, SAXS, IR, NMR and cryo-TEM) on powders and dispersions. We have also used molecular dynamic simulations on all possible chiralities. Our results show that a synthetic imogolite sample contains larger and more polydisperse nanotubes than a natural one. In the case of synthetic imogolite, the average diameter measured lies between the one of chiralities (13,0) and (14,0). We do not obtain the same proportion obtained by D'Angelo et al. nor rule out the possibility of the presence of other chiralities than zigzag and armchair. For the natural one, the average diameter lies between the chiralities (11,0) and (12,0). Analysis of the WAXS does not allow us to draw any definitive conclusions, nor does it rule out non-zigzag and armchair configurations. Surprisingly, the (11,1) chirality is the closest to experimental measurements. Theoretical discussions are performed to understand the implications of this slight polydispersity in the formation mechanism of imogolite nanotubes [7].

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From molecular precursors to allophane and imogolite: evidence and importance of intermediate nanostructures

Pierre PICOT[1], Fabienne TESTARD[1], Frederic GOBEAUX[1], Luc BELLONI[1] and Antoine THILL[1]

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Imogolite and allophane are naturally occurring clays formed through the alteration of volcanic glass under mildly acidic conditions [1]. They are typically found together in soils and share a common local structure (referred to as the imogolite-like structure, ImoLS) as well as an identical chemical composition: $(HO)_3Al_2O_3Si(OH)$. Both materials are hollow nanostructures, with imogolite adopting a tubular morphology and allophane a spherical one (Figure 2).

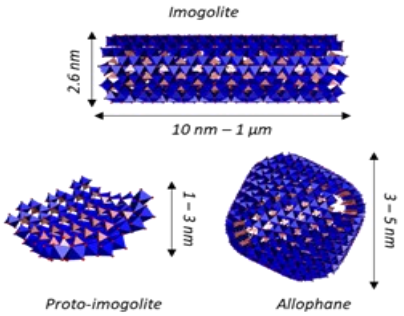

Figure 2: ImoLS family

These clays can be synthesized by mixing aluminium and silicon precursors under carefully controlled pH conditions, followed by heating for several days [2]. The resulting nanostructure depends on precursor concentration: millimolar conditions favour the formation of nanotubes, while higher concentrations yield nanospheres.

Although synthesis methods have been known for nearly 50 years, the mechanisms governing the transformation from precursors to imogolite remain relatively underexplored. One key intermediate, a nanostructured precipitate termed proto-imogolite, was recognized early and is depicted in Figure 2 [3]. However, the typically low concentrations used in standard synthesis protocols, along with the small size and high reactivity of these intermediates, have posed challenges for detailed characterization. To overcome these limitations, Levard et al. employed germanium-based imogolite, which allows for synthesis at higher concentrations [4]. Using a combination of analytical techniques, they proposed a tile-like morphology for proto-imogolite, sharing the same local structure as imogolite and measuring approximately 5 nm. This morphology was later confirmed by Thill et al. through cryo-transmission electron microscopy, marking the first direct imaging of proto-imogolite [5].

Thill et al. also investigated the mechanical behaviour of proto-imogolite using a structural model based on flexible octahedra and tetrahedra arranged in the ImoLS configuration [6]. Their study revealed a size-dependent transition in curvature: below a threshold, the nanostructure remains spherical, while above it, tubular forms emerge (Figure 3).

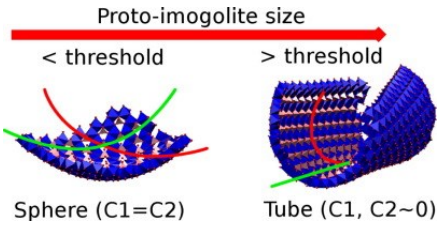

Figure 3: Sphere/tube

To further elucidate the role of intermediate structures in determining final morphology, we investigated the early stages of precursors precipitation that lead to proto-imogolite formation. In this presentation, we will demonstrate that the initial concentration affects the size of these intermediates, and that the final morphology corresponds to predictions made by the mechanical model [7].

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Experimental assessment of pH dependent allophane formation rates at low temperatures

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Clay minerals serve as scaffolding for the Critical Zone (CZ) architecture and buffers leeched solutes. Clays host important records of CZ evolution and environmental conditions in their chemical signatures, making them a powerful potential weathering proxy. Secondary clay formation further serves as a major fractionation pathway for a suite of weathering stable isotope tracers (Si, Li, Ca, Ba, among others). Yet characteristically slow kinetics at low temperatures relevant to the Earth's surface have made it challenging to study their formation and associated fractionation behavior of traditional weathering tracers in controlled, laboratory studies. Allophane, a highly reactive precursor to halloysite and kaolinite, is a commonly formed clay in basaltic andosols due to the high volcanic ash content. The fast reaction timescales of amorphous allophane formation provides an ideal system to begin evaluating kinetic behavior and construct a framework that can be used to address long-standing knowledge gaps in how clays form, under what timescales, and quantify their impact on weathering tracer signatures.

We first adapted methods from Wada and Wada 1980 at starting concentrations of dissolved Si and Al ~ 90 ppm to test the development of allophane across a temperature gradient (30 °C, 60 °C, and 90 °C) [1]. The low pH of starting solution limited precipitation and dissolved aluminum concentration increased as pH dropped over experimental duration. To promote precipitation, NaOH was titrated into the solutions. Solid phase precipitates characterized using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to confirm allophane as precipitated phase. Rapid removal of dissolved Si and Al from solution during buffered zone of the titration corresponds to a sudden change in the turbidity. δ30Si measurements of the fluid phase in the buffered zone rapidly become enriched with 30Si as 28Si is preferentially incorporated into allophane.

We hypothesize that high pH conditions resulting from primary mineral dissolution promote rapid allophane growth. This allophane can then transition into a thermodynamically favorable crystalline (halloysite, kaolinite) in response to changes in aluminum activity during the weathering process. Allophane, thus, can serve as the limiting step dictating reaction kinetics of halloysite/kaolinite. Through δ30Si measurements, we aim to test the extent to which the formation and aging of allophane into more crystalline form drives observed clay weathering stable isotope signatures [2].

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Strategy in host-guest assembly for organic light emitter interleaved into layered double hydroxide: to retain or release, that is the question

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Hybrids derived from synthetic Layered Double Hydroxides (LDH) have received a lot of attention due to their chemical tunability and their versatility in terms of compositions, particle size, making them interesting for a large number of applications [1] such as scavenger to clean up the environment, functionalized filler for polymer, as precursor for electrode material or as cargo for drug delivery etc... For the presentation, we will focus on their ability to accommodate anions, more specifically through two main aspects of such hybrid inorganic organic I/O LDH nanostructured assembly: their fine tuning from the side of the organic moieties, to optimize the emission of optically active guest, and their size matching with a co-inserted spacer when the functionalized guest needs to be not tightened but kept away from each other. It should also be mentioned that in their solid state, optically active molecules are either of the «Aggregation Caused Quenching» (ACQ) or «Aggregation Indued Emission» (AIE) type, thus strongly changing the strategy for their (co)-insertion between the LDH sheets.

The «fine tuning» aspect and the size matching of the interlayer space so called «SMIS» approach is illustrated by the well-known «textbook» fluorescent dye sulforhodamine (SRB) and its physicochemical and optical characterization when co-interleaved into LDH host [2]. Such strategy will be generalized to substituted perylene diimide (PDI)-based molecules having a very strong tendency to stack up, thus cancelling any optical emission. When co-interleaved into LDH host, the optical properties are fully recovered [3].

The presentation will end up giving some insights of the possible use of dual-properties molecules. Indeed, recalling the approach of theranostics in the field of health field, it is possible to use the optical properties of guest molecule but this time no longer immobilized because its migration must be prohibited but released to inhibit corrosion phenomena. LDH is known as a suitable cargo to deliver such molecule [4], the release is then triggered by the corrosion phenomenon itself. When I/O LDHs are used as filler for polymer coating, the optical activity of the delivered molecules is intended to alert that the coating is breaking down and corrosion is occurring.

So, to hold back or to let the guest spread, this is a question that depends on the intended application of the hybrid LDH. Of course, the presence of the host is not neutral and can synergistically bring properties (shifting the emission wavelength, participation in corrosion inhibition).

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The influence of reaction conditions on kaolinite synthesis

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The interest in the synthesis of alumosilicates, synthetic analogues of natural minerals, is associated with research aimed at gaining a better understanding of the processes and conditions of mineral formation. This also involves the synthesis of new structures and particles with various morphologies that may have potential industrial applications in industries such as pharmacology and synthesis of catalysts [1]. One of the most important factors determining the structure and properties of the final materials in the synthesis of inorganic particles and materials is the type of precursors used as initial components for the synthesis, as well as the conditions under which the maximum homogenization of the components occurs.

Three different types of silica precursors were used in this work: tetroethoxysilane (TEOS), Nanosil silicasol and methylamine silicate solution (Aminosilicate). The synthesis was carried out at different temperatures (200, 250, 300°C), duration (3 to 10 days) and pH (3.4 to 10.8).

The formation of synthetic analogues of kaolinite group minerals with different degrees of crystallinity can be observed with the use of different silica precursors. The highest degree of crystallinity was found in the samples synthesized using the silica precursor Nanosil. This is due to greater homogenization at the stage of alumosilicate gel formation. In the case of TEOS, the production of sufficiently homogeneous aluminosilicate gels for subsequent synthesis is complicated by a significant difference in the stability and chemical activity of aluminum and silica precursors in the aqueous medium at different pH values. Although a suboptimal homogenization technique was used in the case of aminosilicate as a silica precursor in the first synthesis step [2], its crystallinity index is higher than that of TEOS.

The increase in synthesis duration and temperature affected the increase in the degree of crystallinity of the synthesized analogues of the kaolinite group minerals and the size of their crystallites. The most significant changes in the synthetic samples were observed at different pH values. Well-ordered kaolinite is formed at low pH values (3.4), whereas at higher pH values—10.8—halloysite is formed with a small admixture of kaolinite, as determined by X-ray diffraction and infrared spectroscopy.

[1] Bergaya, F.; Lagaly, G. (2013). Elsevier: Amsterdam, The Netherlands, ISBN 9780080993645.
[2] Koroleva, T. et al. (2025). Materials, 18, 472

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Formation of iron-rich phyllosilicates in the $FeO–SiO_2–H_2O$ system during hydrothermal synthesis as a function of pH

Dzene, L.[1], Doggaz, A. [1], Dutournié, P. [1], Inoué, S. [2], Abdelmoula, M. [3], Jourdain, A. [1], Le Meins, J.-M. [1], Brendlé, J. [1], Martin, C. [4] and Michau, N.[4]

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The formation of iron-rich phyllosilicates can occur at different natural or engineered settings. However, the uncertainties of the thermodynamic properties of natural clay minerals are too great due to their lack of purity. Therefore, synthesis in laboratory can be foreseen to obtain samples with a sufficient purity, in a sufficient quantity and with controlled chemical composition. Our previous study found that the initial (OH/Fe) molar ratio significantly influenced the type of clay mineral obtained. The ratio between relative quantities of 2:1 and 1:1 type clay minerals increased significantly with $(OH/Fe)_{ini}$ [1].

In this study, the influence of pH in the hydrothermal synthesis of iron-rich phyllosilicates was investigated in the pH range 8.50–12.10 after the ageing of the precursor. The synthesized samples were characterized by powder X-ray diffraction, Raman and Mössbauer spectroscopies and transmission electron microscopy.

Three domains of pH were identified, and these correlated with element availability and their speciation in the solution. Below pH 9.67, mainly amorphous phases and iron oxides were observed. The formation of 1:1-type Fe^{III}/Fe^{II} phyllosilicate was observed between pH 9.67 and 10.75. Above pH 10.75, two types of phyllosilicate-like mineral phases were identified. In addition to 1:1-type Fe^{III}/Fe^{II} phyllosilicate, 2:1-type Fe^{III}/Fe^{II} phyllosilicate was found [2]. The findings show that pH governed the crystallinity and nature of the obtained Fe-rich phyllosilicate-like phases.

[1] Boumaiza H et al (2020) App Clay Sci 199:105876
[2] Dzene L et al (2024) Clay Min 59(2):73-84

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Synergistic chemical evolution of Fe-smectite and glycine during mineral crystallization

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Organo-mineral interactions involving swelling clay minerals play a key role in biogeochemical processes across both modern and ancient surface environments (e.g., soils, sediments), where these minerals are particularly abundant in fine-grained fractions. Due to their physicochemical properties and high specific surface area, these minerals can adsorb and concentrate organic molecules. Although often considered passive physical supports in adsorption experiments, laboratory studies on clay synthesis and dissolution have highlighted their high reactivity. When interacting with organic precursors, these molecules can influence clay mineral formation mechanisms, generating new forms of reactivity that, in turn, affect the dynamics of chemical species.

This study investigates the dual role of glycine in Fe-smectite crystallization under hydrothermal conditions (150 °C for 5 days in an inert atmosphere), exploring how this ubiquitous amino acid influences mineral formation processes. X-ray diffraction confirmed the crystallization of Fe-smectite over a range of glycine concentrations (0.08 to 0.6 M). Increasing glycine concentration led to a decrease in tetrahedral Fe(III) content and promoted the reduction of octahedral Fe(III) to Fe(II), as revealed by XRD, FTIR, and electrochemical analyses, consequently altering the measured cation exchange capacity. Glycine polymerization was significantly enhanced in experiments involving Fe-smectite crystallization compared to controls without minerals. The presence of Fe-smectite favored the formation of linear peptides over diketopiperazine (DKP), thereby facilitating the production of longer peptide chains. These findings reveal a mutual interaction between glycine and minerals, resulting in mineral phases with distinct structural properties and reactivities that enhance organic matter transformation. (Figure 1).

This study highlights how the co-evolution of smectite and organic molecules under hydrothermal conditions can generate specific reactivities and contribute to the complexity of organic matter. These findings offer new insights into the intricate mechanisms governing organo-mineral interactions in both past and present biogeochemical processes. [1].

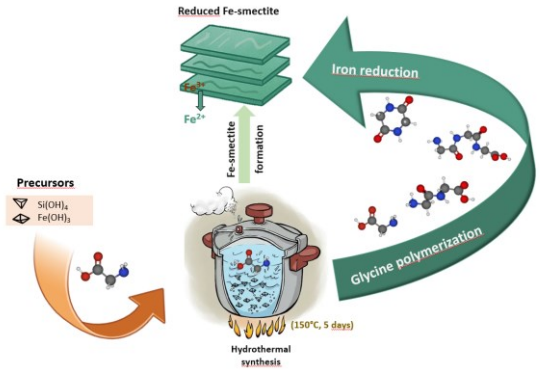

Figure 1: Mutual influence of glycine and Fe-Smectite during hydrothermal synthesis.

[1] Fkiri et al., 2025. Synergistic chemical evolution of Fe-smectite and glycine during mineral crystallization. Article submitted and currently under review.

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Experimental evidence for the evolution of crystal chemistry and morphology during saponite growth

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The impact of the initial materials' crystallinity on smectite growth processes remains poorly understood. In this study, the evolution of crystal chemistry and morphology of smectite growth were examined via experimental synthesis of tri-octahedral Mg–Ni-saponites. The Mg- and Ni-saponite precursors were separately prepared by hydrothermal syntheses at the same set of temperatures (i.e., 25, 150, and 220 °C) for one day[1-2]. The starting material was prepared by mixing an identical molar quantity of Mg- and Ni-saponite precursors in different combinations (pMg150 and pNi150, pMg220 and pNi220, pMg220 and pNi25, and pNi220 and pMg25). Suspensions of precursors were transferred to a polytetrafluoroethylene-lined autoclave and heated at 150 or 220 °C for a period of 14 to 90 days. Four series of samples were obtained, i.e. Series (pMg150+pNi150)150, Series (pMg220+pNi220)220, Series (pMg220+pNi25)220, and Series (pNi220+pMg25)220[3].

The crystal chemistry and morphology of samples were analysed using XRD, FTIR, and HAADF-STEM. The FTIR spectra of the precursors only exhibit the vMg_3OH and vNi_3OH bands, corresponding to Mg-saponite and Ni-saponite, respectively. The occurrence of vMg_2NiOH and vNi_2MgOH bands in the synthesized saponite indicates the dissolution of the corresponding Mg- and Ni-saponite precursors and recrystallization of Mg-Ni mixed saponite. The experimental results converge toward these main conclusions: (i) the formation of Mg–Ni-saponite solid solutions are promoted when the precursors are small particles, whereas large-particle precursors limit their own dissolution and do not yield Mg–Ni-saponite solid solutions under the experimental conditions; (ii) the Mg–Ni-saponite solid solutions yield in the system comprised of amorphous-like Ni-saponite germs and well-crystallized Mg-saponite precursors rather than the one composed of amorphous-like Mg-saponite germs and well-crystallized Ni-saponite precursors, because Ni exhibits a greater stability within saponite structure compared to Mg; (iii) the dissolution extent of precursor mixtures increases with longer synthesis time, higher synthesis temperature, and larger gap between synthesis temperature of precursors and of samples, and stabilizes once it reaches a certain value. Thus dissolution extent can be used for estimating the kinetic of Mg-Ni saponite crystallization from precursor mixtures. These results obtained from the experimental Mg-Ni saponite system are useful for predicting the evolution processes of smectite in nature systems.

[1] Zhang, C. Q., Petit, S., He, H.P., Villiéras, F., Razafitianamaharavo, A., Baron, F., Tao, Q., and Zhu, J.X. (2020) ACS Earth and Space Chemistry 4 (1), 14-23.
[2] Zhang, C.Q., He, H.P., Petit, S., Baron, F., Tao, Q., Gregoire, B., Zhu, J. X., Yang, Y.P., Ji, S.C., and Li, S.Y. (2021) American Mineralogist 106 (6): 909-921.
[3] Zhang, C.Q., Decarreau, A., Blanc, P., Baron, F., Yuan, Y.H., Tao, Q., Gregoire, B., Zhu, J.X., He, H.P., and Petit, S. (2024) Clays and Clay Minerals, 72.

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Electrophoretic Mobility Characteristics Resulted from Varing Layer Charge of Smectite

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Montmorillonite and saponite represent the typical smectite clay minerals with dioctahedral and trioctahedral structures, respectively. Their cation exchange capacity (CEC), colloidal behaviour, and surface activity are strongly associated with the layer charge. To unveil the electrophoretic mobility characteristics resulted from layer charge of smectite is of great scientific importance for tailoring their surface and interfacial functionalities toward advanced materials with a wide range of applications [1-3]. . In this study, synthetic saponite with different layer charges were synthesized via hydrothermal method by changing the Si/Al molar ratios in the precursor materials. Charge-reduced- montmorillonites were prepared by heat treatment of pristine montmorillonite in $LiNO_3$ molten salt. The composition and structure of the as-synthesized minerals with different layer charges were investigated by X-ray diffraction, X-ray fluorescence spectroscopy, scanning electron microscopy, and thermogravimetric analysis. The CEC value was determined by a hexaaminecobalt method and the layer charge was determined. The dispersibility and electrophoretic mobility of the treated smectite samples with different layer charges were investigated in colloidal systems by using a U-tube electrophoresis apparatus at different pH values and electrolyte backgrounds. As the layer charge of the treated smectite samples increased, the CEC values also increased. In the colloidal systems of the treated smectite samples with layer charges ranging from 0.35 to 0.50 e/phuc (per half-unit cell), the variation of their absolute electrophoretic mobility was measured. The absolute electrophoretic mobility of the tetrahedrally charged Mg-saponite and the octahedrally charged montmorillonite was compared. Under varying pH conditions, protonation and deprotonation of the amphoteric edge functional groups, and structural alterations of the smectite under acidic environments, were probed. Furthermore, the influence of cation concentrations and valence of the electrolyte solutions on the absolute electrophoretic mobility of the the treated smectite samples was investigated and discussed.

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[1] Li KJ, Zhou CH et al. (2024) Am Min 109: 633-655.
[2] Liu JH, Zhou CH et al. (2024) Langmuir 40: 5378-5390.
[3] Li CJ, Zhou CH et al. (2022) Langmuir 38: 14227-14237.

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On the all-inorganic protection of lead halide perovskite nanocrystals from the environment

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Lead halide perovskite nanocrystals are a fascinating class of materials with unique properties such as high absorption coefficient, high photoluminescence quantum yield, tuneable fluorescence, defect tolerance and anion mobility, which benefit applications such as optoelectronics, photovoltaics, and bio-sensing. Despite their great potential for said applications halide perovskite nanocrystals suffer from degradation upon exposure to air and moisture, losing their optoelectronic properties and leaching toxic ions. Although this challenge of stability has been tackled by researchers by formation of polymer shells around halide perovskite nanocrystals, however, few examples of all-inorganic encapsulation have been reported such as with mesoporous silica and alumina.

Due to their gas barrier properties and high heat resistance, clays and clay-like materials show great potential for encapsulation of halide perovskite nanocrystal, to improve their stability against water. Similar semiconductor–clay heterostructures have already been demonstrated to retain or even enhance semiconductor properties, while incorporating properties of the clays such as high adsorption capacity. [1-3] This work aims to overcome the challenge of halide perovskite nanocrystal lability towards water by encapsulating halide perovskite nanocrystals with layered silicates, δ-MnO_2 or layered titanates. Synthetic approaches including deep eutectic solvents, molten salts, and co-precipitation methods are being investigated towards the formation of halide perovskite–clay hybrid structures with improved water stability. Ultimately this work could pave the way for the fabrication of water stable halide perovskites, benefitting applications in bio-sensing and opto-electronics.

[1] Liu J et al. (2020) Chem Mater 32, 23:10015–10024
[2] Jatav S et al. (2020) ACS Appl Mater Interfaces, 12, 17:19813–19822
[3] Jatav S et al. (2021) ACS Appl. Mater. Interfaces, 13, 16:18713–18723

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A straightforward, one-step synthesis of a layered alkylammoniumsiloxane without additives

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Layered inorganic-organic composites have received considerable attention owing to their diverse properties, such as light absorption and emission. In some of them the inorganic layers and organic pendants covalently bond with each other. We call these materials “layered inorganic-organic covalently bonding hybrid (LIcO)” here. Syntheses of LIcOs have already been reported [1 - 4]. Environmentally friendly synthesis methods are needed for sustainable development and industrial application. Here we demonstrate a simple one-step synthesis procedure for the LIcO.

An LIcO, layered alkylammoniumsiloxane (PDOAS) was synthesized by a simple freeze-drying of methanol solution of dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DOA–TMS). The synthesized sample was characterized by high-resolution solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD) and so on.

Elemental analysis and the high-resolution solid-state NMR confirm that the synthesized material (PDOAS) consists of a siloxane framework and a dimethyl octadecyl(3-silylpropyl)ammonium group ($C_{18}H_{37}N^{+}(CH_3)_2C_3H_6Si\equiv$) with *all-trans* conformation of the long alkyl chain. XRD and transmission electron microscopy (TEM) further revealed a layered structure composed of stacked thin sheets with an interplanar distance of 3.6 nm. These analytical results have led to a proposed structural model for PDOAC: a layered arrangement of stacked organosiloxane sheets, where the organic dimethyloctadecyl(3-silylpropyl)ammonium group is covalently bonded to and positioned between the siloxane layers (Fig.). In this model, the long alkyl chains are arranged in an interdigitated monolayer structure with *trans* conformation. It is believed that the dealcoholization condensation reaction was promoted by the quaternary ammonium ion group of DOA–TMS itself. This straightforward synthesis method requires no additives and generates only MeOH as a byproduct, making it both environmentally friendly and cost-effective.

[1] Ruiz-Hitzky R and Rojo J M (1980) Nature 287: 28-30
[2] Fukushima Y and Tani M (1995) J Chem Soc Chem Commun 24: 241-242
[3] Shimojima A et al. (1997) Bull Chem Soc Jpn 70: 2847-2853
[4] Fujii K et al. (2016) Phys Chem Chem Phys 18: 19146-19157

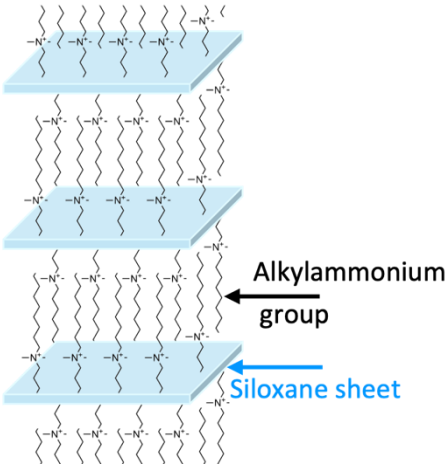

Fig. A proposed structure model for PDOAS

LECTURE THEATRE 6, UI CADHAIN – SESSION 5

Teaching, History, and Future of Clay Mineralogy (in honor of Dewey Moore and Bruce Velde)

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Dewey Moore: Teacher, Mentor, and Visionary

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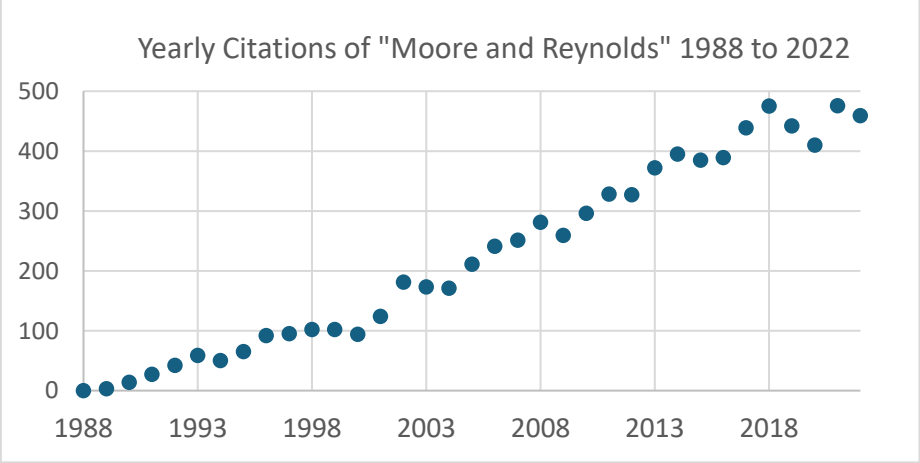
This presentation provides insight into the teacher, mentor and visionary behind the book *X-Ray Diffraction and the Identification and Analysis of Clay Minerals* by Moore and Reynolds (1989; 1997). This book has become a standard in practicing clay mineralogy, and most will have a copy in their office or lab. First published in 1989 and cited over 8500 times, averaging 237 citations annually and peaking at 476 in 2021, it remains remarkably relevant after 35 years (see figure below). Its enduring impact stems from a powerful synergy of its content, accessible language, and the compelling personalities of its authors, Duane M. (Dewey) Moore and Robert C (Bob) Reynolds.

Dewey taught Geology at Knox College, Galesburg, Illinois, from 1964 to 1987. He covered all but paleontology, including a range of mineralogy courses and clay mineralogy independent studies. He organized many fieldtrips and taught his students to be critical scientific thinkers, always giving them a new paper to read. Dewey was a mentor to many, especially to those students who were lucky to do an honors project with him, most of which later got PhDs in Geology. During his last sabbatical at Knox College, the first edition was written together with Bob Reynolds. Afterwards Dewey worked as a senior scientist at the Illinois State Geological Survey in Urbana, Illinois, until 2001. CMS and ICC meetings were always highlights for him. There he became known as the Renaissance man, a welcoming figure to students and was one of the founding members of the Friends of Illite, which all further solidified his influence in clay mineralogy and the Clay Minerals Society.

Dewey was visionary in writing the book. He recognized the need for a comprehensive yet approachable textbook and lab manual in clay mineralogy in a style that is accessible to students and researchers. Innovating was the cooperation with Bob Reynolds, the brain behind NEWMOD©, which calculates oriented XRD patterns of mixed layered clay minerals. Together, they created a resource that seamlessly integrated theoretical understanding with practical application, establishing "Moore and Reynolds" as the cornerstone text in the field, a testament to their foresight and enduring impact three and a half decades later.



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Teaching Clay Mineralogy: A survey of who, what, where, and how it is being taught

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[3]ISTerre, CNRS, Univ. Grenoble Alpes, France

The principles of clay science embrace multidisciplinary fields of study. To gauge the current state of teaching clay mineralogy a survey was conducted to find out who, what, where, and how it is being taught. The survey was open to any respondent, with invitations made by social media, listservs, and societal mailing lists. To encourage participation, the survey was kept brief. The key question or queries gathered were about: 1) Affiliation and location (replies were anonymous), 2) frequency of course offering and if clay mineralogy was not taught as a standalone, then in what other subject area was it covered with, 3) the level of offering (i.e., undergraduate and/or graduate), and 4) materials and resources used, such as books, software, and online resources. The survey had 50 respondents. Mapping the locations revealed that clay mineralogy is taught globally, with the higher concentrations of institutions located in Europe and the East/Central North America. Responses to how clay mineralogy is taught were: Clay mineralogy is taught every year (24%); Clay mineralogy is taught every other year 13%); Clay mineralogy is not taught as a course, but regularly included as part of another course such as, soils, sedimentology, material science (50%); and Clay mineralogy is taught but not emphasized beyond normal teaching of all systematic mineralogy (13%). Instruction spans across both undergraduate and graduate cohorts with the following distribution: undergraduate only (37%), graduate only (29%), and both (34%). A wide array of books used for teaching were listed[1-18], with Moore and Reynolds[1] being the most cited. Software used included: 1) NEWMOD, 2) Sybilla, 3) Profex, 4) Highscore, 5) EVA, 6)Topas, 7) CrystalMaker, 8) VESTA, 9) GSAS, and 10) MSA Crystal Structure Database. We recognize that there are many other useful texts, software, and resources available for teaching clay mineralogy not reported in this survey. However, this snapshot and cursory view of the state-of-the-art for teaching clay mineralogy suggests that the of teaching clay mineralogy is flourishing and its future is promising.

Book titles cited in survey and used to teach Clay Mineralogy:

[1] X-ray diffraction and the identification and analysis of clay minerals (1998) Moore & Reynolds	*[2] Origin and mineralogy of clays (1995) Velde*
[3] Handbook of clay sciences (2013) Bergaya, Theng & Lagaly	*[4] Environmental soil chemistry (2022) Sparks, Singh & Siebecker*
[5] Crystal structures of clay minerals and their X-ray identification (1980) Brindley & Brown	*[6] Clays in the minerals processing value chain (2017) Gräfe, Klauber, McFarlane, & Robinson*
[7] Clays (2005) Meunier	*[8] The science of clays (2013) Mukherjee*
[9] Environmental and low temperature geochemistry (2013) Ryan	*[10] X-ray-diffraction identification of clay-minerals-improvements induced by numerical data-processing (1995) Lanson & Bouchet*
[11] The chemistry of soils (2008) Sposito	*[12] Clays in the critical zone (2018) Schroeder*
[13] Clay minerals for petroleum geologists and engineers (1985) Eslinger & Pevear	*[14] Nanosized tubular clay minerals (2016) Yuan, Thill, & Bergaya*
[15] Chemistry of clays and clay minerals (1987) Newman	*[16] Clay mineralogy (1968) Grim*
[17] Applied clay mineralogy : occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clay (2007) Murray	*[18] Clay Mineralogy: Spectroscopic and chemical determinative methods (1994) Wilson*

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An update on the multidisciplinary science of applied clay research: A 2023–2025 bibliographic analysis

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Clay minerals are functional materials increasingly used to develop a diverse range of new applications. An overview of current applied clay research can be obtained by analysing available bibliographic databases to identify present-day research fields and current trends. Using the Web of Science® and software like EndNote™, Bibliometrix, and "R" (v4.3.1) to investigate i) the topics of published studies, ii) author collaborations, and iii) keyword networks, important information matrices can be identified for the core clay journals and more general multidisciplinary periodicals.

In 2024, we published the article "The multidisciplinary science of applied clay research: A 2021–2023 bibliographic analysis" in Applied Clay Science 258: 107471 [1]. A step-by-step method of dataset quality control and sorting revealed that clay terms related to adsorbents (34%) and composite material formation (over ~55%) were the most common in recent years. Composite materials were frequently researched for catalyst support, sensors, coatings, preservatives, foundry, drilling fluids, geotechnical barriers, fertilisers, animal feed and drug delivery. Environmental remediation had the highest presence among adsorption and catalysis of contaminants, in particular, from wastewater and other aqueous media. Smectite, kaolinite, and halloysite continue to be the most researched minerals in applied clay science. Among these, halloysite has gained significant popularity over the last ten years, particularly for catalytic support, drug delivery, and capture and storage of energy and CO_2. The number of applied clay research articles has doubled in the last decade due to increased contributions, especially from China, Brazil, and India.

Now nearly another two years have passed; so, let us apply the same search criteria and investigate further the trends of multidisciplinary research in applied clay science. This will also help understand the strength and position of the core clay journals (e.g., *Applied Clay Science*, *Clay and Clay Minerals* and *Clay Minerals*). This bibliographic analysis provides comprehensive search criteria that the clay community can reapply to future assessments.

[1] Biswas B et al. (2024) Appl Clay Sci 258:107471

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The future of clay mineralogy: Soil Forensic Examinations Using Advanced Laboratory Source and Synchrotron XRD Techniques

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Earth materials such as soils, rocks, minerals and human-made mineral particles like bricks provide excellent evidence to link criminals to crime scenes. This paper will demonstrate the power of particularly using synchrotron µ-X-ray diffraction (XRD) in combination with traditional laboratory XRD, Scanning Electron Microscopy (SEM) and pedological data, for forensic comparisons of trace amounts of earth materials to assist soil/geological-based criminal investigations. Through two investigations involving a cold murder in 1988 [1] and homicide in 2007 [2], this paper will demonstrate the value of synchrotron µ-XRD in crime investigations by developing critical forensic information from landscape to microscopic scales, which were used as evidence in two Australian Supreme Courts.

In the 1988 cold murder case [1], trace amounts of soil were identified on a 10-year-old victim's pyjama-top. Synchrotron µ-XRD provided greater sensitivity and resolution than the laboratory XRD source to better identify small amounts of pyrite and clay minerals on the pyjama-top. The very minute soil particles in the pyjama-top had a strong degree of comparability with hypersulfidic subaqueous soils containing pyrite in the Onkaparinga River estuary – providing evidence that the soils have similar origins. A 'predictive, soil–regolith model, from microscopic to landscape scale', was presented in the Supreme Court, which established that the tiny pyritic soil particles found on the victim's pyjama top are likely to have originated from a saline estuarine environment like the Onkaparinga estuary. SEM confirmed that the mineral particles are deeply impregnated in gaps between fibres of the fabric, which likely originated under water with force being applied on the pyjama-top – implying the victim was pushed into the mud. This was substantiated from transference shaking experiments where mineral particles are dominantly located on the surface of the fabric. The accused was found guilty by a Supreme Court judge of murder.

The 2007 murder investigation [2] involved comparing small (<0.5 mm diameter) red brick fragments and soil on the victim's clothing (mainly bra) and body (mainly hair) to a representative collection of brick fragments taken from old brick pavers in the front yard of the victim's home – even to one specific type of brick. While traditional XRD techniques were adequate for determining the mineralogy of the small red brick fragments, synchrotron µ-XRD with high X-ray intensity was found to provide greater sensitivity and resolution to quantify the mineralogy of polycrystalline minerals (cristobalite and mullite), especially on the victim's clothing. XRD data (particularly the synchrotron µ-XRD) show strong correlation between the XRD patterns from small, brick fragments on the victim's clothing and the XRD pattern from known brick fragments taken from the old brick pavers. More importantly, because of the diverse mineral composition of clay bricks, XRD analysis enabled the brick fragments to be exclusively classified and categorized within specific groups of clay bricks. The trial was before a judge only and he concluded that the mineralogy of the brick fragments on the victim's clothing and bricks from her front driveway indicated that she was initially attacked in her front yard and then transported to Kings Park where her body was buried.

[1] Fitzpatrick RW and Raven MD (2019). The forensic comparison of trace amounts of soil on a pyjama top with hypersulfidic subaqueous soil from a river as evidence in a homicide cold case. Geological Society, London, Special Publications, 492,197-218. https://doi.org/10.1144/SP492-2019-59R
[2] Raven MD, Fitzpatrick RW, and Self P (2019). Trace evidence examination using laboratory and synchrotron X-ray diffraction techniques. GSL Special Publications, 492, 165-179. https://doi.org/10.1144/SP492-2019-36R

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LECTURE THEATRE 7, DAVIS – SESSION 25

Fundamentals of Tubular Nanoclays

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Structure and Dynamics of Water Confined in Halloysite Nanotubes

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Understanding the behaviour of water confined within nanostructures is crucial for various applications such as drug delivery, general nanostructure loading/intercalation or ion immobilization. This study investigates the structure and dynamics of water molecules confined in halloysite nanotubes (HNTs) using molecular dynamics simulations with classical force field approach. Halloysite nanotubes provide a unique environment for water confinement due to their nanotubular morphology.

Through molecular dynamics simulations, we explore how confinement within HNTs affects the hydrogen bonding network, diffusion properties, and structural arrangement of water molecules. Classical force fields are employed to model the interactions between water molecules and the nanotube walls, allowing us to capture in detail the water behaviour at the nanoscale. Atomistic model of HNT itself was made according to [1]. We compare our findings with the water's structural and dynamic properties of imogolite published in [2] and with DFT based calculations of water structure above planar halloysite surface [3], highlighting the influence of nanoscale confinement.

We believe, these insights contribute to a deeper understanding of water behaviour in confined clay-based nanotubular structures, with implications for the design of new materials and technologies in fields such as drug delivery, catalysis, and environmental remediation.

[1] Gianni, E. et al. (2023) Journal of Molecular Structure, 1287.
[2] Scalfi, L. et al. (2018) Langmuir, 34(23), 6748–6756.
[3] Presti, D. et al. (2016) Physical Chemistry Chemical Physics, 18(3), 2164–2174.

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Integrated Computational and Experimental Approach for the Design of Halloysite Clay based Multifunctional Catalysts

Lisuzzo, L.[1], Lazzara, G.[1], Guercio, L.[1], Ferlito, F.[1], Ferrante, F.[1], Bertini, M.[1], Palella, A.[2], Aho, A.[3], Spadaro, L.[2], Murzin, D.Y.[3] and Duca, D.[1]

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Biomass valorization is one of the most challenging issues in the field of green chemistry and, despite significant progress in research, its chemo-catalytic conversion to value added products still requires major efforts. The design of multifunctional catalytic systems that can optimize the one-pot reactions from biomass-derived precursors to the required target molecules represents a critical goal. Within this framework, Halloysite Nanotubes (HNTs) display peculiar properties (i.e. hollow nanotubular morphology, different surface chemistry, high aspect ratio) which make them promising nanoparticles for the development of efficient catalysts. For this purpose, an integrated approach consisting of computational studies, based on a cluster approach within the density functional theory, and experimental analysis was exploited [1].

Hence, we studied the alkaline activation of the clay to accurately describe the formation and the configuration of silanols groups on the outer surface. These groups are of utmost importance, since they promoted the selective functionalization of the silicic surface and its covalent grafting with aminosilanes. Therefore, the hybrid nanocomposites possess different chemical groups that can act as anchoring sites for metals nanoparticles, such as the nitrogen centers in the organosilanes interacting with gold. The resulting amino functionalized halloysite decorated with gold on the external surface can be exploited for the catalyzed oxidation of organic molecules. Besides, the acidic activation of HNTs inner surface was also investigated and its protonation was enlightened at the atomistic level by considering both the reactions energy and the geometrical properties. It was also demonstrated that the energy required for the leaching of aluminum atoms can be supplied by the refilling of the structural vacancies. Experimental techniques showed that the nanotubular shape was maintained and the acidic treatment led to an increase in the total concentration of acid sites and to the formation of new Brønsted sites. Hence, the catalytic activity was tested in a model acid-catalyzed reaction, specifically the isomerization of o-xylene, and a clear correlation between the isomerization rate, turnover frequency (TOF), and the acidity of the sample was established.

The combination of computational modeling and experimental research can offer a thorough understanding of the materials, broadening their potential use in catalysis. In this context, harnessing the properties of halloysite could pave the way for the creation of a multifunctional catalytic system with two separate environments, thus facilitating the one-pot conversion of biomass precursors into high value molecules.

[1] Lisuzzo L et al. (2024) ACS Catalysis 14:18167–18203

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Toward Green Catalysis with Halloysite–Gold Nanocomposites Materials

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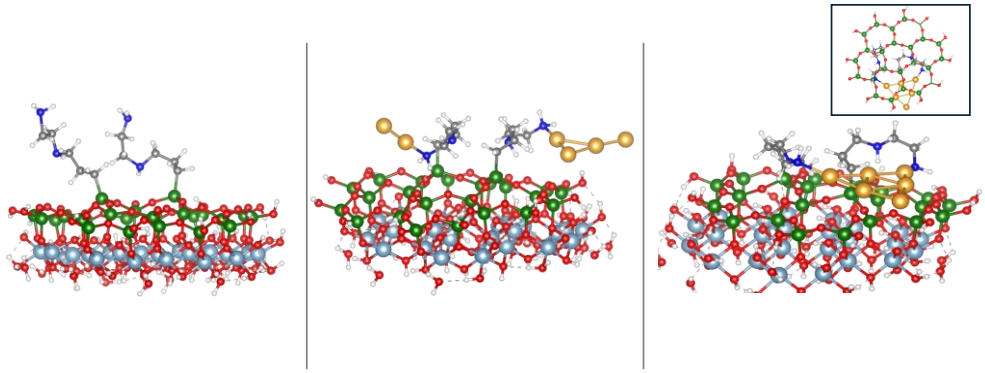
The development of sustainable catalytic systems for biomass valorization is a growing research priority, particularly in the context of replacing petroleum-derived plastics with bio-based alternatives. We investigated a hybrid catalytic approach for the synthesis of 2,5-furandicarboxylic acid (FDCA), a key monomer for green polymers, from lignocellulosic biomass (LCB). The conversion process involves two important steps: the acid-catalyzed dehydration of sugars to 5-hydroxymethylfurfural (HMF), followed by its oxidation to FDCA. To deal with the different reaction conditions and to stabilize the intermediates, we propose a use of functionalized halloysite nanotubes (HNTs), a naturally occurring, non-toxic nanoclay with chemically distinct inner and outer surfaces.[1]

In particular, the oxidation of HMF on the outer surface of modified HNTs decorated with gold nanoclusters was computationally investigated considering the halloysite/(3-Aminopropyl)triethoxysilane (APTES)/Gold composite. Using a variety of DFT functionals (M06, M06-2X, MN15, wB97X-D), a stability transition point from 2D to 3D geometries at 15 atoms was identified. Structural analyses confirmed that clusters with sizes below this threshold preferably adopt planar arrangements, while larger clusters stabilize in three-dimensional conformations.

Additional modelling explored gold cluster interactions with two 3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS) chains to simulate ex situ and in situ cluster growth.

The results obtained underline the potential of clays, particularly halloysite, as tunable supports in advanced catalytic systems for sustainable chemical transformations.

We acknowledge the PNNR SAMOTHRACE for providing the funds for this work.



Bertini M. et al. (2024) ChemCatChem 16(15):e202400179

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Filling halloysite nanotubes with functional materials

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Halloysite nanotubes (HNTs)—hollow silicate clay nanotubes—possess unique physical/chemical properties; meanwhile, their empty cylindrical cores also offer the storage of foreign functional materials, giving rise to a new set of hybrid nanostructures. Filling HNTs lumen not only reinforces nanotubes in the radial direction preventing from buckling but also endow them various new intresting properties. Encapsulation of a wide variety of inorganic and/or organic materials inside HNTs in different structural forms such as Au nanoparticles, Ag nanorods, and atomically thin nanowires has documented useful applications in devices such as antibacterial materials, self-healing materials, biosensors/chemosensors, drug delivery systems, lithium-ion batteries, microwave absorbers, etc. Up to now, several parameters have been identified to influence the filling process during both in situ and ex situ filling methods, but there is still a lack of complete understanding in the filling mechanism which governs the filling yield, size, and structure of HNTs, as well as those of filling materials. This talk will present an overview of recent progress made in the synthesis of filled HNTs and the study of their properties and functional applications. The existing challenges in the field and their possible resolutions will also be discussed.

Lisuzzo, L., Cavallaro, G., Pasbakhsh, P., Milioto, S., Lazzara, G. (2019). Journal of colloid and interface science, 547: 361-369.
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[3] Zhao, P., Hu, J., Feng, Y., Wu, F., Tan, C., Chen, X., Liu, M. (2024). Journal of Colloid and Interface Science, 655, 736-747.
[4] Feng, Y., Zhang, D., Chen, X., Zhou, C., Liu, M. (2024). Advanced Functional Materials, 34(7): 2307157.
[5] Zhang, J., Luo, X., Wu, Y. P., Wu, F., Li, Y. F., He, R. R., Liu, M. (2019). ACS Applied Materials & Interfaces, 11(4): 3690-3703.

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Patch Halloysite as Clay Precursor for Hydrogel and Multifunctional Inorganic Films

Calvino, M.M.[1], Lo Bianco, A. [1], Cavallaro, G. [1], Pasbakhsh, P. [2.3], Lisuzzo, L. [1], Milioto, S. [1], Lvov Y.[4], Lazzara, G. [1]

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Research on halloysite nanotubes has been mainly focused on samples from the primary sources like New Zealand, China and USA. However, it has been demonstrated by a few researchers that the geological deposit significantly influences the morphology and physicochemical properties of halloysite clay nanotubes. In this context, Patch Halloysite (PT_Hal), sourced from Western Australia (kind donation provided by Dr. Keith Norrish from his collection and research on Patch Halloysite (CSIRO Soils, Adelaide), stands out as one of the purest forms of halloysite (>98%). These nanotubes are also significantly longer and thinner than typical commercial ones, with lengths reaching up to 30 µm. This unique morphology gives rise to a tangled fibrous network, resulting in enhanced and unusual properties. In this study, we investigated the different rheological characteristics of Patch, highlighting the key role of the clay microstructure. We demonstrated that it facilitates the formation of gel-like systems that are not observed in halloysite from other natural sources [1]. Dynamic viscoelastic tests showed that PT_Hal is a non-Newtonian fluid and exhibits solid-like characteristics even at low concentrations, indicating a highly structured system. Interestingly, two distinct behaviors were observed depending on the clay concentration. Therefore, Patch can be classified as a pseudoplastic fluid at low concentrations and as a Bingham plastic fluid above 0.75 wt%, where a yield stress becomes detectable. Based on these results, we exploited the entangled nanotube network for the preparation of self-standing inorganic clay films [2]. Their thickness, easily tuned by changing the PT_Hal concentration, influences key properties such as transparency, mechanical strength, and water uptake.Remarkably, PT_Hal films display excellent fire resistance and thermal stability, effectively preventing flame propagation without showing macroscopic alterations or signs of degradation after direct exposure. In addition to their fire resistance, we propose PT_Hal films as precursors for advanced materials: through alkaline activation or thermal treatment, they can be converted into either porous geopolymers or ceramics with a compact morphology. Both treatments led to a marked increase in the hydrophobicity of the original PT_Hal film, likely due to enhanced surface roughness and changes in surface chemistry. The geopolymeric film demonstrates significantly enhanced CO_2 adsorption capacity, nearly doubling that of the original films, highlighting its potential as an efficient sorbent. These findings point out the exceptional versatility of Patch halloysite whose peculiar morphology enables the design of advanced inorganic systems, ranging from hydrogel to fire-resistant films and functional geopolymeric materials.

[1] Calvino M. M. et al. (2024) Journal of Molecular Liquids 394:123721
[2] Lo Bianco A. and Calvino M. M. et al. (2024) Small 20:2406812

Acknowledgements: This work was supported by “SiciliAn MicronanOTecH Research And innovation CEnter - SAMOTHRACE” (MUR, PNRR-M4C2, ECS0000002), spoke 3, Università degli Studi di Palermo.

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Halloysite Nanotubes Under the Microscope: Potential Occupational Risks and Toxicity Indicators

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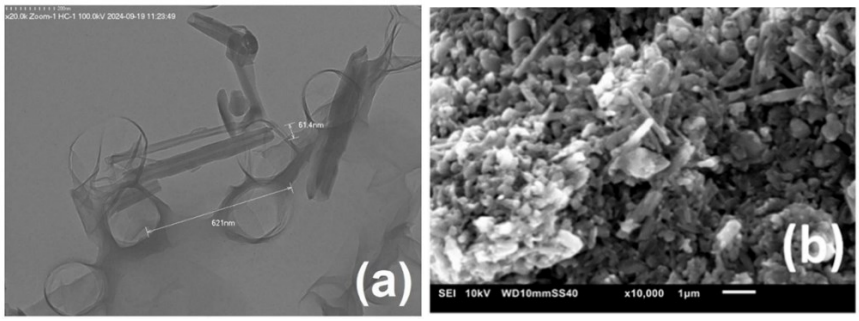
Halloysite is a mineral belonging to the kaolin group, with the ideal chemical composition $Al_2(OH)_4Si_2O_5 \cdot nH_2O$, and is used in a variety of industries, ranging from traditional ceramics to drug delivery. Halloysite commonly occurs as elongated mineral particles with nanometer-scale tubular, cylindrical, or fibrous morphologies. While previous research on halloysite has evaluated (with mixed findings) its toxicity upon ingestion for pharmaceutical applications, the International Agency for Research on Cancer (IARC) has never assessed its potential carcinogenicity via inhalation.

In this study, we investigate a commercial halloysite from Matauri Bay (North Island, New Zealand) in the context of occupational exposure to airborne nanoparticles in the ceramic industry. All data obtained from mineralogical, chemical, and morphological analyses (XRPD, TGA-DTA, XRF-WDS, BET, particle size distribution, SEM, TEM, Mössbauer and UV-Vis spectroscopies) were incorporated into the Fibre Potential Toxicity Index (FPTI) model [1–2], which has already proven to be a robust tool for assessing the toxicity potential of similar mineral fibres.

The mineralogical composition of the sample consists of approximately 90 wt% halloysite, with minor amounts of quartz and cristobalite. Morphometric analysis showed that halloysite nanotubes are respirable but do not qualify as "regulated fibres" due to their length being below 5 µm (average length: 1.5 ± 0.9 µm). The FPTI model yielded a value of 1.92(10), comparable to that of non-carcinogenic mineral fibres, suggesting—albeit cautiously—that halloysite is a safe, low-toxicity nanomaterial. However, XRPD and SEM analyses also revealed the presence of respirable quartz and cristobalite, both of which are classified as Group 1 human carcinogens. This project is part of PNRR–M4C2INV1.5, NextGenerationEU-Avviso 3277/2021 -ECS_00000033-ECOSISTER-spk5.



TEM (a) and SEM (b) of halloysite from Matauri Bay (North Island, New Zealand).

[1] Gualtieri AF (2018). Toxicol. Appl. Pharmacol.. 361:89-98
[2] Gualtieri AF (2021). Curr. Res. Toxicol. 2:42-52

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Halloysite – Fundamentals of powder XRD data in relation to hydration state, particle morphologies, and nomenclature: a short review of key features

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Powder x-ray diffraction (XRD) patterns of halloysite are influenced by two key factors; the state(s) of hydration of the interlayers and the size of the particles in the bulk specimen. The state(s) of hydration determine the distribution of layer spacings, whereas particle size correlates with the proportions of curved versus planar packets of layers in the particles.

Differences in the state of hydration are most obviously manifested in the positions and widths of the basal (00l) reflections. A fully hydrated interlayer gives a layer spacing of 10.0 Å. However, interlayer H_2O in halloysite is easily lost and the loss is not reversible. Nonethless, complete removal of all interlayer H_2O, to obtain a peak position similar to kaolinite, at around 7.1 Å, typically requires heating in an oven for a few hours at temperatures of around 300°C. Consequently, the positions of the basal reflections in the XRD patterns of 'as received' halloysite are typically observed at spacings that are intermediate between 10 and 7 Å. Analysis of the positions and widths of these peaks and of higher orders during progressive dehydration is interpreted in terms of interstratification of layers of three discrete hydration states [1]. These correspond to fully hydrated 10 Å layers, fully dehydrated 7.1 Å layers and partially hydrated layers with a spacing of around 8.4 Å. Depending upon the progress or stage of dehydration, interstratifications may show random (R0) or some combination of random and segregated arrangements. Additionally, 10 Å specimens, which by consensus are the *de novo* form of halloysite, seem always to include some dehydrated 7 Å layers [1]. Thus, neither of the ideal end members i.e. fully hydrated and fully dehydrated are readily observed.

Examination of the morphology and internal arrangement of halloysite particles show them to adopt two main forms. One of these is known as 'cylindrical' because the component 1:1 layers are curved forming spirally arranged packets of layers around a central hollow lumen. The other is known as 'polygonal' or 'prismatic' because they consist of packets of planar layers, analogous to planar kaolinite. Hillier et al., [2] demonstrated that the preponderance of these arrangements is related to the particle size distribution of an halloysite specimen, such that the smallest particles adopt cylindrical forms whereas larger particles show the polygonal arrangement, manifested by flat external crystal faces arranged in sectors, so defining a prismatic form. Although polygonal forms of halloysite typically form the larger particles they commonly have cylindrical cores [3] supporting a size dependent particle growth constraint on layer curvature.

Both cylindrical and polygonal forms may occur in largely hydrated 10 Å form though polygonal may be more prone to dehydration. When largely dehydrated (i.e. in 7 Å form) the predominant type of particle morphology may be readily assessed from the character of the 20,13 diffraction band. Specimens which are dominated by well-developed polygonal forms and hence planar layers show much greater modulation of the 20,13 band resembling the character of this band in kaolinites. Analysis of other diffraction bands in the random powder specimens reveals additional information on the structure of this extraordinary form of kaolin. If time allows the interrelation between some of the above characteristics and the evolving nomenclature of halloysite will be reviewed.

[1] Siranidi et al. (2024) Clays and Clay Minerals, 72, e33, 1–14 doi:10.1017/cmn.2024.37
[2] Hillier S et al. (2016) Clay Minerals, (2016) 51, 325–350
[3] Gray-Wannell et al. (2024) Clay Minerals, 1–13 doi:10.1180/clm.2023.37

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N-methyl formamide (NMF) intercalation in Halloysites

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Halloysite, a type of naturally hydrated and subsequently dehydrated clay mineral with nanotubular structure and chemical composition similar to kaolinite, is of increasing interest for industrial or environmental applications. Recent work [1] showed that the (-10Å) to (-7Å) dehydration transition of halloysite leads to structures, containing both ordered kaolinite-like and highly disordered domains. Despite chemical similarities, kaolinite and halloysite-(7Å) differ in reactivity, e.g. towards intercalation. In fact, a convenient test for distinguishing halloysite from kaolinite in soils has been developed based on such differences in intercalating formamide [2]. The present work extends a previous vibrational spectroscopic study on the intercalation of N-methylformamide (NMF) in kaolinite [3,4] to halloysite in an attempt to study their similarities and differences.

Cylindrical and polygonal halloysites, as well as low-order kaolinite KGa-2 were intercalated by NMF and measured by Attenuated Total Reflectance (ATR) in the mid infrared (4000–550 cm^{-1}) as well as Near Infrared (NIR) spectroscopy using homemade environmental cells. Supporting, X-ray Diffraction (XRD) and high-resolution Thermogravimetric analysis (HiRes-TGA) data are presented.

Opposite to kaolinite, which displays little or no changes in the position and width of the NH band of intercalated NMF and the inner OH stretching mode, halloysites display broader and shifting bands during the course of intercalation. In the case of halloysite, intercalation induces the re-ordering of interlayer stacking as seen by the narrowing of the inner OH band and the in-plane Si-O bands at ~3620 and 1120 cm^{-1}, respectively. NIR data on halloysite/NMF slurries confirmed the above results.

HiRes-TGA data on cylindrical and polygonal halloysites from the Dragon mine (Utah, USA) indicated that these have different intercalation capacities for NMF: At long times (more than 3 weeks), intercalation was 100% for cylindrical but only 65% for polygonal halloysite. Samples of mixed cylindrical-polygonal form exhibit intermediate values. A 1:1 mixture of halloysite and low-order kaolinite displays well-separated NMF intercalation events when monitored by NIR, as suggested in [2], but the estimation of the relative quantities of the two minerals is subject to errors if their intercalation capacity is not known a priori.

[1] Siranidi E et al. (2024) Clays Clay Miner 72: e33 1–14
[2] Churchman GJ et al. (1984) Clays Clay Miner 32: 241-248
[3] Andreou FT et al. (2022) Clays Clay Miner 70: 796–807
[4] Andreou FT et al. (2021) Appl Clay Sci 212: 106209

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LECTURE THEATRE 7, DAVIS – SESSION 7

Soil and Clay Chemical Analysis – Symposium Honoring M.L. Jackson

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How M.L. Jackson paved the way for our understanding of the mineralogy of soil clays: the case of the complex nature of interstratified clay minerals

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There are two sentences in M.L. Jackson's papers from the 1950s that are particularly striking: "The procedures have been further developed in this laboratory over a period of 14 years since the previous report" in the introduction to the article 'Segregation Procedure for the Mineralogical Analysis of Soils' [1] and "[...] also in accordance with the expectation of not uncommon occurrence of ternary, quaternary (mica-montmorin-vermiculite-chlorite), and greater randomness (binary-binary systems, etc.) through interstratification along the Z-axis" in the conclusion of the article 'Some analyses of soil montmorin, vermiculite, mica, chlorite, and interstratified layer silicates' [2]. These two sentences reflect the extraordinary methodological and conceptual developments required to demonstrate the complex nature of interstratified clay minerals in soils 70 years ago. These results form the basis of current concepts of weathering sequences of clay minerals in soils [3] to understand soil evolution.

Interest in revisiting M.L. Jackson's pioneering work on interstratified clay minerals in soils re-emerged in the 2010s, thanks to the opportunities offered by X-ray diffraction profile modeling. This approach makes it possible to describe in detail the crystal structures of interstratified clay minerals by providing the number, nature, proportion, and layer stacking sequences of the different layer types, and their relative proportions.

The analysis by X-ray diffraction profile modeling coupled with a sequential particle size fractionation previously developed by M.L. Jackson has been applied to various temperate soils [4,5,6]. The results show that interstratified clay minerals consisting of more than two types of layer are indeed common, often in the majority, and their proportion increases with decreasing particle size. All of M.L. Jackson's observations and interpretations of interstratified clay minerals in soils are therefore more relevant than ever!

[1] Jackson M.L. et al. (1964) Segregation Procedure for the Mineralogical Analysis of Soils. Soil Science Society of America Journal, 14: 77-81.
[2] Jackson M.L. et al. (1953) Some Analyses of Soil Montmorin, Vermiculite, Mica, Chlorite, and Interstratified Layer Silicates. Clays and Clay Minerals 2(1), 218–240.
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[5] Viennet J.C. et al. (2015) Investigation of clay mineralogy in a temperate acidic soil of a forest using X-ray diffraction profile modeling: Beyond the HIS and HIV description. Geoderma 241–242, 75–86.
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Oxidation-reduction Mechanism of Structural Fe in Clay Minerals

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The presence of iron (Fe) in soils and clay minerals was a topic of much interest to Professor M. L. Jackson and his students. His citrate-bicarbonate-dithionite (CBD) method for removing Fe (oxyhydr)oxides from soils is very famous and used extensively. The underlying principles governing this method are that Fe(III) is readily dissolved by chemical reduction (by dithionite) to Fe(II), without dissolving the clay minerals if the pH is buffered to about 7-9 (hence, the function of bicarbonate). The method then provides for chelation by citrate so the Fe can be carried out of the sample through centrifuge washing. In the process of using this method, they discovered that Fe in the structure of the constituent clay minerals was also reduced and remained in the clay mineral structure [1]. One of the purposes of their studies was to determine the effects of these processes on the cation exchange capacity (CEC) of the clay minerals. Roth and Tullock [2] observed no change in CEC even though an electron was added during the Fe(III) to Fe(II) reduction. They then proposed a reduction mechanism by which Fe reduction was accompanied by deprotonation. Later, however, Stucki [3] observed that the CEC measurement of CBD-reduced samples was unreliable unless the reduced sample was protected from reoxidation during the preparation and CEC measurement stages. By applying such protections, Stucki and Roth [4] observed that the CEC increased with increasing Fe(II) content in nontronite, but the increase failed to follow a 1:1 relationship, contrary to what would be expected from electron addition. This led to a revision in the proposed reduction mechanism, which evolved over several decades and involved adjustments in the stoichiometric relationship between structural Fe(II) and OH [5], characterization of defects in the clay mineral structure [6], and numerous studies of surface reactions [7, 8, 9]. The effects of Fe reduction in the environment and many other applications have also been studied .Stucki, Roth, and co-workers further discovered that structural Fe could be reduced by microorganisms [10-12]. A variety of microorganism strains have since been found to reduce structural Fe, and this has led to much further work toward understanding the phenomenon of Fe reduction in clay minerals [13-16].

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Interlayers and Interconnections: The Influence of M.L. Jackson on a Scientific Career

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Although I grew up in California and pursued my education at the University of California, Riverside—far from the University of Wisconsin—my academic journey was profoundly shaped by Professor Marion L. Jackson. I had the privilege of meeting Prof. Jackson on several occasions at meetings of the Clay Minerals Society and the Soil Science Society of America.

As a graduate student, I relied heavily on the detailed protocols presented in his seminal work, Soil Chemical Analysis – Advanced Course, which guided the methodology for my first publication [1]. Recognizing the central role that rigorous methodology plays in soil science and clay mineralogy, I later contributed as both editor and author to Methods of Soil Analysis, Part 3: Chemical Methods in the SSSA Book Series.

One of Prof. Jackson's former students, Professor Joe L. White of Purdue University, had a particularly significant influence on my career. During my graduate studies at UC Riverside, Prof. White visited our campus for several weeks, meeting informally with students and giving lectures. His visit had a lasting impact—it shifted the focus of my PhD research toward vibrational spectroscopy and the study of clay-organic and clay-water interactions, a field in which I remain active more than four decades later. Years later, I would unexpectedly join the faculty at Purdue University, where I continued to draw inspiration from other Jackson protégés like Charles Roth.

Much of my research career has centered on understanding the surface chemistry of clay minerals. Prof. Jackson's early insight into the strong and often irreversible binding of caesium to expandable clay minerals [2] deeply influenced my thinking about interlayer regions—those critical sites where water, organic solutes, and even atmospheric carbon dioxide [3] interact with nature's most abundant nanomaterial.

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Updating life at the edge: Clay mineralogy and the Kamchatka microbial observatory

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A presentation1 on clay mineralogy and microbiology of the Uzon Caldera, Kamchatka, Russia was given in 2007 for the Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award. Key points from this presentation were: 1) Learning jargon, cultures, and bureaucracies among interdisciplinary scientists takes time, 2) Disciplines operate across wide scales of time and space, 3) Sampling protocols and instruments are not always transferable, 4) Outreach for workshops, lectures, and documentaries require resources beyond the science itself. Museums and educators play a crucial role, and 5) Success comes from the willingness to say, "I don't understand. Please explain it again (and again)." The team2 discovered carboxydotrophs, ferric iron reducers, sulfate reducers, and arsenate reducers; identified through the isolation of novel species, most probable number field incubations, 16S rDNA clone libraries, metagenomic libraries, and radiotracer experiments. New species and genera identified were related to Carboxydocella, Carboxydothermus, Dictyoglomus, Thermoanaerobacter, Thermobaculum, Geobacillus, Bacillus, and Anoxybacillus. Phospholipid-derived fatty acid profiles and lipid stable isotope measurements provided an independent assessment of major microbial clades and dominant carbon fixation pathways. Archaeal lipid biomarkers, specifically glycerol dialkyl glycerol tetraethers (GDGTs), found in Uzon were distinct from those in other hot springs3. High-resolution electron microscopy revealed potentially functional interactions between nano-crystalline mineral surfaces (smectite, opal, pyrite, and ferrihydrite) and thermophilic microbes4. Hot spring chemistry indicated dissolved NH_4^+ levels averaging ~30 ppm, with some springs reaching 530 ppm. Fe-bearing, smectite-rich clay fractions exhibited NH_4^+ and organic-N exchangeability, confirmed by X-ray diffraction (XRD) d001 response, labeled ^{15}N measurements, and C/N ratios. The close association of NH_4^+-bearing Fe-smectites, anammox genes, and archaeal biomarkers suggests that clay mineral octahedral Fe-redox processes and interlayer nitrogen storage may play a role in high-temperature anoxic ammonium oxidation. Return expeditions to Uzon placed greater emphasis on clay minerals and evidence for widely dispersed ammonium oxidizing archaea (AOA)5, now identified as members of the phylum Thaumarchaeota. Correlations were made between increasing GDGT abundance and a redox gradient in mesophilic hot springs, transitioning from assemblages dominated by goethite/hematite to Fe-smectite/pyrite. The reduced muds are rich in NH_4^+ and Cu, key nutrients for AOA. Recent discovery6 of Candidatus Nitrosotenuis uzonnesis revealed the presence of an encoding gene for tubulin, a protein essential for microtubule structures. We continue to propose that redox-coupled nitrogen-iron interactions in smectite may serve as a mechanism for chemolithoautotrophic AOA activity. Recent studies of the Uzon Caldera have expanded into rare earth element geochemistry of the hot springs7 and the application of support vector machine (SVM) classification tools8. The SVM approach will utilize XRD and Vis/NIR (350–2500 nm) spectral data to train remote sensing models, enabling the mapping of mineral assemblages in Uzon's thermal fields and tracking potential hydrothermal facies changes over time.

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Coupled redox cycling of iron in clay minerals and organic matter transformation across redox interfaces

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A large fraction of organic matter (OM) in soils and sediments is associated with minerals to form mineral-OM associations, which are known to decelerate OM decomposition because of protection against microbial use. However, redox cycling of Fe in minerals at redox interfaces can transform OM, yet specific pathways of coupled Fe redox cycling and OM transformation are well understood. In this talk, we focus on processes and mechanisms of coupled iron-carbon (Fe-C) cycles across natural redox interfaces [1]. Specifically, oxygenation of structural Fe(II) in minerals generates reactive oxygen species (ROS), which directly transform OM including decomposition and polymerization [2-4]. ROS also affect extracellular enzyme activity and decomposing microbial activity, thus indirectly transforming OM through these pathways [5-6]. Fe(III) reduction contributes to OM oxidation through microbial anaerobic respiration. In return, OM plays an important role in Fe redox cycling by serving as electron donor, acceptor, shuttle, buffer, and conductor, as well as via adsorption to and coprecipitation with Fe minerals and complexation with Fe, all of which significantly alter Fe mineralogy and their reactivity [1]. Coupled Fe-C redox cycles occur in various environments and have major implications for greenhouse gas emission, biogeochemical cycles of elements, soil fertility and food security, biodiversity and ecosystem functions, and environmental behaviour of contaminants.

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Lithium extraction methods influence Li-isotope measurements of clays

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The mineral industry extracts Li from clays by complete destruction of the mineral using sulfuric and oxalic acids and heating. However, the total extraction of Li negates the possibility of interpreting the Li-isotopic composition (δ^7Li) because it mixes Li populations from surface and structural sites of the minerals. Only Li from octahedral sites record equilibrium conditions between the mineral and fluid, allowing evaluation of Li-sources. Therefore, it is critical to separate surface and interlayer Li from octahedral Li. To study the effect of adsorbed Li on δ^7Li of clays, non-destructive Li-extraction methods were tested using mannitol ($C_6H_{14}O_6$) and NH_4Cl to remove surface bound and interlayer Li, respectively, and to evaluate their effect on mineral δ^7Li values.

The Li-content and δ^7Li of clay mineral standards KGa-1 kaolinite and SWy-1 smectite (<2µm) were measured by spot analyses using secondary ion mass spectrometry (Table 1). Li was first measured on untreated minerals (labelled 'none') to test for homogeneity of the total Li in each sample. Next the surface adsorbed Li was removed by cation exchange using 1M NH_4Cl (shaken 24h), then rinsed in triplicate in deionized water (DIW). Assuming the cation exchange (xc) treatment effectively removed adsorbed-Li from external and interlayer sites of the clays, the remaining Li is fixed (bound) in the mineral structures (NH_4xc initial). Next, the Li adsorption capacity of the minerals was evaluated by saturation with 1M LiCl (δ^7Li –26 ±1.2‰). The mineral suspension (1g/40mls) was equilibrated 24h at room temperature, then rinsed in triplicate in DIW. Li that adsorbed to the mineral surfaces (Li xc) was measured along with δ^7Li of the mineral. Various concentrations of mannitol (0.1, 0.5 and 1.0M) were tested for adsorbed-Li removal. Finally, the Li saturated samples were exchanged again using 1M NH_4Cl to test for complete removal of Li from exterior and interlayer sites of the expandable clay (Li-sat + NH_4xc 2).

Kaolinite (KGa-1) adsorbed 15 ppm Li from the 'NH_4-xc initial' solution, indicating Li contaminant in the lab grade (Sigma-Aldrich) NH_4Cl. Li-exchange added 606 ppm Li with an isotopic composition of –10‰. The mannitol only partially removed Li from the kaolinite with 73% Li removed by 1.0M mannitol. Alternativ ly, NH_4xc 2 removed 100% of the adsorbed-Li, and the δ^7Li of the mineral returned to the original +2‰ compo tion. Smectite (SWy-1) did not change isotopic composition after the initial NH_4-exchange to remove surface Li. T ıe structural Li remaining was ~12 ppm. However, the smectite interlayer adsorbed a high amount of Li f ɔm the 1M LiCl solution. The average for adsorbed Li was 14,217 ppm (±10%), with a δ^7Li of –24‰, withii error of the solution composition. The mannitol treatment removed 97% of the adsorbed Li at the 0.5M conce tration. The 1.0M mannitol was unable to successfully remove the Li as indicated by the heterogeneity of δ^7 i values measured on different spots. Nonetheless, nearly 100% of the adsorbed Li was removed by NH_4xc 2 an the isotope ratio returned to the initial value reflecting the structurally bound Li composition.

In conclusion, these data show that mannitol can remove a substantial amount of adsorbed Li from mineral surfaces, however the amount removed depends on the concentration of the adsorbed-Li and the mannitol concentration. Partial removal of adsorbed-Li alters Li-isotope measurements of structurally bound Li, therefore interpretations of Li-isotope data on bulk clay samples can be misleading. Cation exchange with 1M NH_4Cl removes >99% of exterior adsorbed-Li and interlayer-Li, leaving only the Li held in octahedral sites of the clay. Only structurally bound Li in these sites reflect equilibrium conditions (temperature, fluid composition) that can be used to interpret Li sources.

Table 1. Results of Li-extraction on bulk clay Li-isotope compositions.

Treatment	δ^7Li ‰	SE ‰	Li ppm	SE ppm	n	% Δ Li
KGa-1 <2µm						
none	2.1	0.8	109	6	3	–
NH4 xc initial	-1.1	0.6	124	1	3	+14
Li xc	-10.0	0.6	730	48	4	+83
0.1M mannitol	-14.0	1.5	364	16	4	-40
0.5M mannitol	-0.6	0.8	193	4	3	-68
1.0M mannitol	-8.0	1.7	166	6	3	-73
Li sat + NH4xc 2	1.8	0.9	98	3	3	-100
SWy-1 <2µm						
none	8.4	0.5	11	0.1	3	–
NH4 xc initial	6.6	0.6	13	0.6	3	–
Li xc	-23.9	1.6	14,231	1678	3	+100
0.1M mannitol	-3.2	2.0	2,320	111	3	-84
0.5M mannitol	4.4	0.4	438	18	3	-97
1.0M mannitol	-18 to +8	0.7	1,852	126	3	-87
Li sat + NH4xc 2	6.5	1.4	15	0.8	3	-99.8

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The pink book: A useful resource for mineralogical research

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The pink book "*Soil Chemical Analysis – Advanced Course*" has been close to my desk for about 35 years now. I purchased my copy by check and return snail mail from M.L himself (probably Christie herself did the transactions) soon after meeting him for the first time at the 1990 Soils meeting in San Antonio, Texas. It is dog-eared from use but still holding up well despite torn-and-taped pages and stained with coffee and probably even soiled with clay. It must be noted that this pink book is more than a chemical analysis procedural book, but a treatise on physical-chemical processes for examining soil materials. It is equally well suited for the study of sediments, tailings and engineered barrier systems.

I've found myself turning to the pink book quite a bit in the past twenty years or so as my clay minerals research has shifted back toward environmental and economic sustainability outcomes. The pink book imparted valuable information about the preferential dissolution of opaline silicates from bentonites, which was used successfully to show improved performance of some bentonites to high pH leachates, such as those from red mud tailings dams [1, 2], research which partly contributed to me receiving the "Jackson Award" (the Christie M and Marion L Jackson Mid-career Clay Scientist Award) from The Clay Minerals Society at the Annual Conference, College Station, Tx, in 2014. More recently, the pink book has been highly important as a reference for my lab's work on using spoil and waste soils as supplementary cementitious materials in cements and concretes [3, 4]. Processes necessary to isolate the reactive fine fractions (mostly clay minerals) from non-reactive fine fractions (mostly non clay minerals) were already worked out by Professor Jackson more than 60 years ago, enabling us to ensure cement replacement levels are correctly based on the actual pozzolan content. This outcome is set to have a large impact on Victoria's Big Build here in Melbourne, enabling tunnelling spoil materials to be used directly on-site in concrete during the construction of a new subway rail system. Finally, identification of the mineral forms and chemical states in which critical minerals, high-tech metals and value metals reside in tailings from legacy gold and copper mines in southeastern Australia can be extracted, concentrated and processed largely from the principals laid down in the pink book. M.L Jackson was a highly knowledgeable and critically thinking scientist.

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Association of organic carbon with different forms of metal oxides in Australian soils

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A strong association of organic carbon (OC) with metal oxides, especially iron (Fe) and aluminium (Al) oxides has been observed in several recent studies. However, the role of various species of Fe, Al, Mn and Si in the preservation of OC in Australian soils remains poorly understood. To address this, we collected surface (0-20 cm) and sub-surface (20-40 cm) soil samples from 37 sites across New South Wales, Australia. We hypothesised that short range order (SRO) minerals of Fe, Al, Mn and Si contribute to OC stabilisation in both surface and sub-surface soils. Soil samples were subjected to three separate extractions, i.e., sodium pyrophosphate (PP) to extract organo-metal complexes, ammonium oxalate (OXL) to extract poorly crystalline and short-range order (SRO) minerals and dithionite citrate bicarbonate (DCB) to extract total metal oxides. The extracted solutions were analysed for Fe, Al, Mn and Si concentrations using inductively coupled plasma mass spectrometry (ICP-MS). Total carbon (TC) concentration in the original soil and the residue after each extraction were determined using a CHN analyser (vario MAX cube Elementar).

Soil organic carbon (SOC) extracted was in the sequence: $C_{PP} > C_{DCB} > C_{OX}$, with mean of 62 %, 41 % and 28 % C of the TC extracted. Paired t-test revealed that C_{PP} and C_{DCB} were significantly greater in surface soils than subsurface soils. The extraction sequence for Fe was: $Fe_{DCB} > Fe_{OXL} > Fe_{PP}$, with mean of 49 %, 9 % and 3 % of the total Fe extracted. Paired t-test showed significantly greater Fe_{PP} in surface soils than sub-surface soils. The sequence for Al was: $Al_{DCB} > Al_{OXL} > Al_{PP}$, with mean of 4 %, 3.9 % and 2 % of the total Al extracted. Concentrations of Al_{DCB} and Al_{OXL}. were significantly greater in surface soils than subsurface soils. Manganese was extracted in the sequence - $Mn_{OXL} > Mn_{DCB} > Mn_{PP}$, with an average of 78 %, 65 % and 43 % of the total Mn extracted. All forms of extractable Mn were significantly greater in surface soils than subsurface soils. All extractants extracted < 1% of the total Si. All forms of extractable Fe and Al showed significant positive correlations with extractable C, which suggest combined role of Fe and Al oxides in the preservation of SOC. The large portion of OC extracted by PP suggests that most of the C was present in organic-Fe/Al complexes in the studied soils. The significant amount of OC extracted by OXL suggests that C was substantially present in SRO and poorly crystalline Fe oxide while a relatively small proportion of OC extracted by DCB indicates that OC was associated in relatively small amount in crystalline Fe oxides.

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Career Research: Inorganic Contaminant Interactions at the Mineral-Water Interface and in Soils

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Soil contamination is important because of its risks to human and ecosystems health, and food security by degrading soil fertility and water quality. Dr. Arai, who is a recipient of 2016 Marion L. and Chrystie M. Jackson Soil Chemistry and Mineralogy Award from the Soil Science Society of America, has been employing a broad range of traditional soil chemistry and molecular-scale approaches at various temporal scales to better understand the mechanisms responsible for macroscopic reactions (e.g., adsorption, precipitation, redox reactions) of nutrients and inorganic contaminants, in soils.

His research focus is to understand the molecular level chemical reactions at the soil mineral-water interface that is responsible for the field-scale processes (e.g., nutrient cycling). This presentation gives an over view of his past to recent research in abiotic and biotic partitioning (i.e., adsorption, desorption, precipitation, and dissolution) reactions of inorganic contaminants at the soil mineral-water interface in soils with emphasis on the applications of molecular approaches and tools (e.g., synchrotron-based X-ray and vibrational spectroscopic techniques). Finally, his contribution to the soil science education and the future perspective will be discussed.

Clays on Mars: Their Identification from Orbit and Implications for the Martian Environment

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I am grateful to the Jackson family for recognition of my work investigating clays on the planet Mars. Clay minerals are widespread on Mars and play an integral role in characterizing and constraining geochemical environments on early Mars. However, clays were only confirmed on Mars about two decades ago. Prior to that time planetary scientists frequently argued in favor of dry conditions on Mars that did not support formation of clays, despite the chemistry of surface rocks and dust measured by the Viking landers in the 1970's consistent with phyllosilicates [1]. The challenge was that telescopic spectra of Mars did not include the expected vibrational bands for smectites or other phyllosilicates [2]. The spatial footprint of these early measurements was simply too vast. Finally, once the OMEGA and CRISM imaging spectrometers were able to collect data from orbit at Mars, we received the data needed to document phyllosilicates in thousands of locations on Mars [e.g., 3]. Light-toned outcrops of phyllosilicate assemblages are now known to be present across much of the martian surface where the ancient materials are exposed (see figure). I think Professor M. L. Jackson would have appreciated seeing the discoveries of abundant Fe-rich smectites on Mars.

Recent studies using CRISM images at 18 meter/pixel have revealed phyllosilicate horizons varying over time [4] and phyllosilicate assemblages varying regionally [e.g., 5]. Analysing regions on Mars where smectites are most abundant versus chlorite/prehnite or phyllosilicate-sulfate assemblages or poorly crystalline materials including allophane or imogolite has enabled placing constraints on environmental conditions on ancient Mars when these outcrops formed [6,7]. Phyllosilicates on Mars are also indicators of water and have implications for habitable conditions as well as preservation of prebiotic chemistry or biosignatures if life ever evolved on Mars [8].

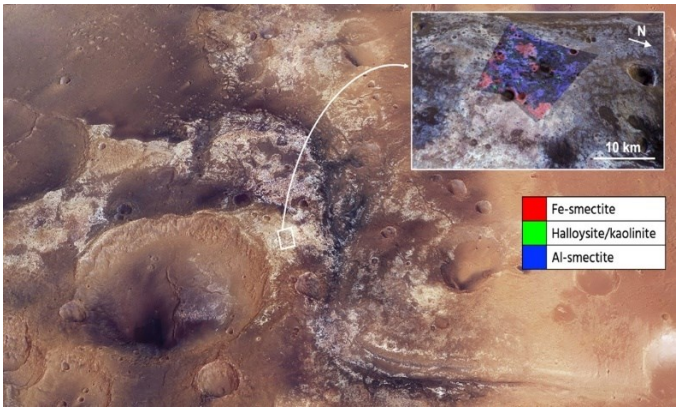

Figure 1. Mars Express High Resolution Stereo Camera (HRSC) view illustrating light-toned phyllosilicate outcrops at the Mawrth Vallis region of Mars. Inset shows oblique view of CRISM mineral map overlain on HRSC with 5x vertical stretch

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Modulation of Sorption and Transformation of Organic Contaminants in Clay Minerals

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Clay surfaces provide an excellent confined environment to modulate sorption/desorption and chemical reactions of many organic contaminants, which could serve as a control point to facilitate the beneficial use of clay minerals and intervene environmental contamination. In this presentation, we will elucidate the mechanism of sorption and transformation processes of organic contaminants on clay surfaces in three claimed patents.

Patent 1: Smectite clays with K^+ compensating the negatively charged sites frequently demonstrate the stronger affinity for many organic contaminants and pesticides than that by Ca^{2+}-clays. Compared to Ca-clay, K-smectite clays have less hydrated interlayer environment, optimal basal spacing, and larger available interlayer surface areas, which all favor the intercalation of the organic compounds. This leads to the use of Ca-K exchange reactions to control the magnitude of sorption and desorption, hence bioavailability and toxicity of organic contaminants in smectite clays [2, 3].

Patent 2: Smectite clays commonly occur as assemblages of stacked layers, with the interlayer spacing ranging $\sim$0.2 to 0.8 nm, depending on the type and hydration properties of the interlayer cations. The average distance between adjacent exchangeable cations depends on the layer charge density and surface area of the clay, as well as the formal charge of the cation, and ranges from $\sim$0.6 to 1.0 nm. The distinct structure and properties of smectite clay could be used as templates for synthesizing nano- or subnano-sized zero-valent iron (ZVI) clusters in the interlayer domains. We achieved the goal by reducing the exchange Fe(III) to single-atom ZVI within smectite interlayers. The resultant smectite clay-templated subnano-sized ZVI demonstrated superior reactivity and extreme efficiency to reduce many organic contaminants within the confined clay interlayer environment [1, 4].

Patent 3: Layered double hydroxides (LDH) are a class of environmental-friendly inorganic sorbents for sorption of per-and polyfluoroalkyl substances (PFAS) particularly anionic PFAS from water, owing to their relatively large surface areas and high abundance of structural positive charges within the minerals. Perfluorooctanesulfonic acid (PFOS) was strongly sorbed to LDH from water, then indole-3-acetic acid (IAA) was added, and the system was radiated under 24 W UV lamp. The results showed that approximately 90% of PFOS was decomposed within 8 hours of reaction, and up to 50% of PFOS was fully defluorinated as estimated from the measured fluoride concentration. Minimal reaction occurred in the system without LDH. The extensive reaction occurred in the LDH, most likely in their interlayers, owing plausibly to the facts that strong retention of PFOS and IAA in the confined clay interlayers, and the life span of the formed electrons in the less hydrated clay interlayers could be substantially extended. These factors combine to lead to the significantly enhanced reaction efficiency. Such reaction system has a high potential to be applied to treat trace levels of PFAS in water.

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Digital Soil Mineralogy – Some recent advances and future horizons

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In 2018 I used my Jackson lecture at The Clay Minerals Society annual meeting as an opportunity to present a case for a new concept and vision for soil mineralogy [1] which I called 'Digital Soil Mineralogy'. The concept came to me after many years of trying to improve the capabilities to do quantitative mineralogical analysis of soils at the then Macaulay, now James Hutton Institute in Scotland. Jackson was a pioneer of soil mineralogy recognising that "The determination of the composition and mineral content of soils and sediments is an important means of understanding soil properties, formation and (land) use capabilities." His classic self-published book is a compendium of methods and recipes that described the use of all manner of direct and indirect physical and chemical methods for making such determinations.

My own experience with quantitative mineralogical analysis of soils has been focused on the use of X-ray powder diffraction methods, widely acknowledged as the richest method of quantitative mineralogical analysis, in terms of the wealth of information about the nature and abundance of minerals in soils that it can provide; information that is not readily accessible by any other means. The concept and vision, if you will, of 'Digital Soil Mineralogy' was founded in my realisation that if one has a precise way of measuring XRPD data, one does not necessarily have to decipher the quantitative mineralogical information encoded in the diffraction patterns to determine the links between mineralogy and the properties and functions of soils. Instead, one can just treat the patterns as data, digital x-y 'signatures' of a soils mineralogical (and organic) make up. Indeed, we can also do this with many other forms of data output from a wide variety of determinative analytical methods commonly applied to soils. The key is the analytical method must have precision, which is very often founded on attention to sample preparation.

Treating XRPD data like this allows us to explore it with methods currently popularised in so called 'Data Science'. One example would be the use of cluster analysis. Another development that falls into the general area of 'Digital Soil Mineralogy' is the use of High-Performance Computers (Clusters) to perform the job of more traditional quantitative mineralogical analysis of XRPD data, but on hundreds or even thousands of samples simultaneously. Such methods rely on libraries but are extremely powerful as they enable the direct determination of both crystalline and amorphous phases, a key requirement to understand the properties of many soils. The 'quantum leap' for Digital Soil Mineralogy will be cross-calibration or data transformation, i.e. finding ways to transform the data from one instrument or lab to look like it was recorded on another. This will allow us to compare the mineralogical compositions of soils from anywhere in the world, which in combination with sets of georeferenced soil samples could greatly advance our understanding of soil mineralogy – property relationships.

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Mineralogical Controls over Environmental Fate and Behavior of Contaminants and Nutrients

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Understanding the role of mineralogical components in regulating the environmental fate and transport of both contaminants and nutrients is essential for predicting biogeochemical dynamics in surface and subsurface geo-systems. In addition, the remediation of complex contaminated surface and subsurface environments remains a pressing global challenge due to the persistence, mobility, and interactions of diverse contaminants' plumes within heterogeneous geologic media. This presentation focuses on the critical functions of clay minerals and Fe and Mn oxides—which are the most reactive and abundant soil mineral phases—in mediating the mobility, species transformation, and attenuation of key environmental constituents, such as contaminants and crucial nutrients. Specifically, we explore how these minerals influence the behavior of radionuclides (e.g., uranium and iodine), representing redox-sensitive and potentially mobile contaminants of concern, as well as nutrients (e.g., carbon and nitrogen), that are central to soil fertility and ecosystem health.

Clay minerals, with their high surface area, layered structure, and ion-exchange capacity, act as powerful sorbents and reactive interfaces for a variety of dissolved species. Iron and Mn oxides, particularly in nanoparticulate or poorly crystalline forms, contribute additional reactive surfaces and redox-active sites that can immobilize or transform both nutrients and contaminants. The interactions between these minerals and environmental solutes are governed by a range of physicochemical processes including adsorption, surface complexation, redox reactions, and co-precipitation, all of which are highly dependent on mineralogy, crystallinity, surface chemistry, and surrounding geochemical conditions.

This presentation synthesizes findings from laboratory experiments and microscopic and synchrotron-based spectroscopic analyses to elucidate how specific mineral phases control the speciation and environmental behavior of uranium and iodine. In parallel, we investigate how these same mineral phases influence the stabilization and transformation of organic carbon and nitrogen compounds, particularly in systems undergoing chemical changes, redox fluctuations or nutrient enrichment. Through this mineral-centric lens, the presentation highlights the dual role of soil minerals in both contaminant attenuation and nutrient cycling, emphasizing the importance of mineralogical context in environmental risk assessment and sustainable land management. By integrating mineralogy with geochemistry and biogeochemistry, this work contributes to a more mechanistic understanding of coupled contaminant-nutrient dynamics in soils and sediments.

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Tracking Mineral and Chemical Changes in Fertilized Soils: Combining Synchrotron X-Ray Techniques and Wet Chemical Methods Reveal Key Insights

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Differential behavior (plant response in terms of yield and/or concentration in grain) of the fluid and granular or different sources of macro and macro micronutrient forms have been repeatedly observed in field trials conducted in various soils. We employed wet chemical and electron microscopy, X-ray diffraction and several synchrotron-based X-ray techniques, namely, µ-X-ray fluorescence, µ-X-ray absorption near edge structure spectroscopy (µ-XANES), µ-X-ray diffraction and "bulk" XANES/extended X-ray absorption spectroscopy, to study the behavior and reaction products of different fertilizer derived-P, -Cu, -Mn, and -Zn in calcareous and/or acid soils. Combined use of various techniques suggested that when fluid, granular, or other formulations of fertilizers were applied to soil, not only did these nutrients diffuse further away from the point of application but also remained in solid forms with varying solubilities depending on the nutrient element and soil characteristics. In contrast, certain liquid or granular nutrient sources diffused comparatively little or stayed within the granule or zone of application and tended to transform into relatively less or more soluble solid forms depending on the nutrient and soil characteristics. Combining synchrotron techniques with conventional X-ray and wet chemical techniques helps examine complex soil fertilizer reaction zones. It aids our understanding of the reaction products of nutrients applied to soil. These approaches provide valuable insights for fertilizer source selection and efficient fertilizer management.

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Photochemically-induced abiotic Mn oxide nanoparticle formation

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Manganese (Mn) oxides are ubiquitous in aquatic environments, and their rich redox feedback among manganese ions and multiple oxidation states of solids enable various capabilities in engineered systems. These include the environmental degradation of contaminants and applications in batteries and water oxidation catalysts. Mn (III/IV) oxides also possess large surface areas and are highly active in adsorption, catalytic, and redox reactions.

We recently reported on photochemically-assisted, fast abiotic inorganic oxidation of Mn^{2+} (aq) to MnO_2 nanosheets and nanotunnels in the presence of various environmental chemistries. This new finding offers a new perspective on Mn(IV) oxide formation, previously primarily considered as biologically catalyzed pathways. Structural and oxidation state analyses have shown that superoxide radicals, generated from the photolysis of abiotic environmental constituents, can induce rapid oxidation and the formation of Mn(IV) oxide nanostructures (both in layered and tunnel structures) within several hours. These findings clearly indicate that abiotic Mn oxidation processes play a significant role in the formation of Mn(IV) oxide nanostructures, complementing the contribution of microbial processes.

In this talk, I will share our new insights into this intriguing Mn oxide redox chemistry and the resulting nanoscale structure formation in soils and aqueous environments. I will introduce how the abiotic photochemically-induced oxidation of Mn^{2+}(aq) and the nucleation of Mn oxides can be influenced by various environmental constituents such as nitrate[1], halides [2], natural organic matter[3], substrates (quartz [4-5] and plastics [6]), and other cations such as sodium, calcium, magnesium, cobalt, copper, and zinc. Then, I will discuss how these environmental constituents affect the structure and layer stacking of Mn(IV) oxide nanostructures. Our findings highlight the significant yet often underestimated impact of abiotic processes, occurring with sunlight exposure, on the fate of Mn in natural and engineered environmental systems. These insights also have profound implications for the sustainable synthesis of Mn oxide nanomaterials with desired structures, sizes, and electrochemical functionalities.

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An isotope approach to identify biologically mediated reactions and fingerprinting of sources of phosphorus

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Many (bio)geochemical processes that bring about changes in sediment chemistry, including diagenesis, normally begin at the sediment-water interface, continue at depth within the sediment column, and may persist throughout the lifetime of sediments. Because of the differential reactivity of sedimentary phosphate phases in response to diagenesis, dissolution/precipitation, and biological cycling, the oxygen isotopes of phosphate ($\delta^{18}O_P$) have been used for both contemporary and deep earth history. Therefore, this isotope could be useful for understanding the pathway of some of the major mineral transformations, such as smectite to illite, whether biologically catalysed or long-term thermal conversion.

In one case study, sequential sediment extraction of phosphate pools was combined with $\delta^{18}O_P$ to better understand authigenic and detrital phosphate phases in continental margin sediments in the Peru Margin [1]. The isotopes in authigenic phosphate pointed to two major processes of formation in the sediment: authigenic phosphate precipitated at/near the sediment-water interface in equilibrium with paleo-water and phosphate derived from hydrolysis of organic phosphorus, with subsequent incomplete to complete re-equilibration with porewater and precipitated deeper in the sediment column. The isotopes of detrital phosphate, on the other hand, suggested two possible terrigenous sources and their mixtures in different proportions: phosphate from igneous/metamorphic rocks and phosphate precipitated in source regions in equilibrium with meteoric water. The original isotopic compositions of at least one phase of authigenic phosphates and all detrital phosphates were found not to be altered by diagenesis and other biogeochemical changes within the sediment column.

Most recently, a series of recent advances have been made in analytical techniques aimed at developing isotope tracers to circumvent the limitations of conventional isotope ratio mass spectrometry (IRMS). One of such advances is the development of tandem mass spectrometry-based isotope methods using Orbitrap. This method has enabled the detection of isotope exchange at bridging and non-bridging oxygen sites in molecules, which allows identifying primary and secondary isotope effects during formation and hydrolysis. Further, it has enabled measuring structural and position-specific intact isotope fingerprints in organophosphorus compounds [2]- thus directly connecting parent and dephosphorylated products. Collectively, these results highlight the potential of an isotope-centric approach for connecting sources and biogeochemical processes in different systems, including sediment and clay-rich environments.

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On the interaction between clays and fungi: an alternative interpretation of the role of medicinal clays

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Clays have been used for their medicinal applications since the ancient times, with Lemnian Earth (LE), a local clay from Lemnos Island, Greece, being an acclaimed medicinal 'earth' of antiquity with a 2500-year history of use. Medicinal applications of clays include several domains including, geophagy, pelotherapy, antibacterial uses, hemostatic wound dressings and use as drug carriers such as antibiotics. These applications usually, but not always, involve interactions of various clay minerals with microorganisms, mainly bacteria, and have as a main target the restriction/elimination of bacterial activity.

Recently we examined the interaction of clays with a fungus and attempted to interpret the reactivity of the mixture [1]. We co-cultured a common fungus, Penicillium purpurogenum (Pp), with two separate clay slurries prepared from SWy-2 smectite and KGa-2 kaolinite. The leachate of the Pp+smectite co-culture was antibacterial *in vitro* due to the presence of secondary metabolites, inhibiting the growth of Gram-positive and Gram-negative bacteria. *In vivo* supplementation of regular mouse diet with leachates of Pp+smectite increased amongst others intestinal microbial diversity. Pp+kaolinite did not produce similar results. Untargeted metabolomics and analysis of bacterial functional pathways indicated that the Pp+smectite-induced microbiome increased production of short-chain fatty acids (SCFAs) and amino acid biosynthesis, known to modulate intestinal and systemic inflammation. The combination of increased microbial diversity and SCFA production indicated beneficial effects on the host microbiome. The therapeutic properties of the LE (terra sigillata, stamped earth), may have been based on their potential to modulate the gut microbiome.

The different behavior of the two clay minerals is attributed to their different structures. Smectite bears a negative layer charge that is balanced by the interlayer cations, and swells upon hydration or in contact with organic molecules. In contrast, kaolinite does not have permanent layer charge and thus it bears very low CEC due to unsatisfied bonds at crystalline edges and it does not swell. The negative charge of SWy-2 crystallite surfaces may repel negative membrane charge of *Pp*. Simultaneously, smectite readily adsorbs molecules from the agar nutrient (potato dextrose) in the interlayer, thereby increasing the interlayer space. Such a process will increase swelling and will facilitate delamination of the SWy-2 lamellae, thereby increasing the area of contact between smectite and *Pp*, and intensifying the interaction between the smectite and the *Pp*. Hence, smectite surfaces could act as stressors on the *Pp,* triggering increased production of secondary metabolites. Such an interaction between clay mineral and *Pp* was not observed in kaolinite because of the lack of permanent charge and lack of swelling of the crystals. The results of our experiments have shown that the co-leachates of fungus + SWy-2 smectite have the potential to modulate the gut biome in a way beneficial to the host.

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TUESDAY

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LECTURE THEATRE 1 – SESSION 20

Science and Engineering of Clays for Nuclear Waste Disposal (continued….)

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Granular buffer material after 12 years heating under early repository conditions

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A common design of a high-level radioactive waste (HLW) disposal system involves placing the waste canisters in tunnels or shafts filled with a bentonite-based buffer. In the Swiss concept [1], the canisters rest on a base of highly compacted bentonite blocks, while the space around the canisters is filled with granular buffer material (GBM, i.e. high-density, irregular pellets). During the early post closure period, the buffer is expected to experience maximum temperatures and remain largely unsaturated. To replicate these conditions, a 1:2 scale in situ test was designed and constructed at the Mont Terri Underground Research Laboratory in Switzerland, known as the HE-E experiment [2]. The experiment is being carried out in a 10-m long section of a 1.3-m diameter tunnel excavated in the Opalinus Clay. The test is divided in two sections: in one of them, a heater is placed inside a steel liner supported by MX-80 bentonite blocks and the upper part of the gallery is filled with MX-80 bentonite pellets (GBM). The heater system was switched on in June 2011 and has held a constant temperature on the heater surface of 140°C. The barrier is naturally hydrated with the water coming from the host rock, which is quite saline (19 g/L), containing significant amounts of chloride and sodium.

In order to obtain information about the state of the GBM after 12 years of service, a novel telescoped drilling procedure allowing the recovery of material from the bentonite buffer without interrupting the ongoing heating and data monitoring was developed. The procedure was applied to the HE-E test in 2023 by drilling two boreholes across the Opalinus clay and the buffer from a nearby gallery [3]. Samples from the two cores were characterised with the aim of analysing the physical, physico-chemical, mineralogical, chemical and textural changes in the GBM by effect of heat and hydration.

The determinations performed on site showed that the water content of the bentonite was higher than the initial one (6%) only in the 20 cm closest to the host rock, whereas it was lower than this value in the 20 cm closest to the heater. This is evidence of the slowness of hydration, given the limited water availability in the Opalinus Clay, and the intense drying close to the heater. The chemistry of the aqueous extracts was affected by the groundwater supply and the solubilisation processes close to the host rock. The chloride concentration increased from the host rock inwards (to a distance of 30 cm) well above the initial values, which proves the ingress of groundwater to this distance. Sulphate and sodium increased at the host rock interface, indicating the solubilisation of species by water content increase. Sulphate and sodium concentrations were also affected by high temperature, and they increased in the 10 cm closest to the heater. No changes in the montmorillonite content of the samples were identified, although it remained dehydrated for RH=55% in samples that had been submitted to temperatures higher than 100°C. Anhydrite (in trace amounts in the initial bentonite) concentrated in samples submitted to temperatures higher than 60°C. In contrast, no gypsum (originally contained in MX-80) is present in these samples. Cristobalite content increased towards the heater. As observed in other similar tests, the cation exchange capacity gradually decreased towards the heater. The current observations confirm the expectations for the GBM under early repository conditions.

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Experimental Characterisation of Water Affinity in a Colloidal Silica-Bentonite System

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Compacted bentonite is envisaged as an ideal backfill material during decommissioning of boreholes used for site investigations at proposed locations of the Geological Disposal Facility (GDF) in England. To backfill the borehole, the steel casing must be reamed out, prior to bentonite emplacement. Tests have shown that in heavily fractured mudstones, the borehole walls can collapse prior to emplacement of the compacted bentonite backfill. In this research, we investigate the potential for colloidal silica (CS) grout to stabilise the borehole walls during backfill operations.

Colloidal silica grout is an aqueous suspension of nanometric silica particles, that upon addition of an electrolyte, forms a stable hydrogel [1] [2]. This study aims to investigate the capability of the grout to stabilise the borehole walls during decommissioning. Here, we present results on the physical interaction between the CS grout and the compacted bentonite. First, we characterised the water affinity and redistribution to determine the effect of the CS grout on the wetting of the bentonite. Second, we investigated whether surrounding compacted bentonite with CS grout can mitigate against the well-recognised problem of differential swelling during bentonite saturation [3].

The bentonite used in our experiments was a sodium-type MX80 provided by Nuclear Waste Services (NWS). Two sets of laboratory experiments were carried out. The first to separately characterise and compare the water retention characteristics of bentonite and CS grout under free volume conditions using the static relative humidity wetting method. The second, to investigate the wetting characteristics of compacted bentonite, with and without the CS grout present. To investigate swelling, a constant volume cell was designed suitable for imaging within a Micro X-Ray CT, in which compacted bentonite could be progressively saturated and the resultant axial swelling pressure monitored. Two experiments were performed, one in which bentonite wetting occurred directly through a fracture, and one where the bentonite was placed in contact with saturated CS grout. X-Ray CT scans of each experiment were periodically taken to delineate the migration rate and shape of the saturation front within the bentonite.

The results indicate that the hydrogel nature of the CS grout allows for wetting of bentonite to saturation under constant volume. In addition, migration of the saturation front obtained from the X-CT data shows uniform wetting from the CS gel into the bentonite, which could alleviate the problem of differential swelling of compacted bentonite not only in borehole decommissioning scenarios, but also in engineered barrier systems within a GDF.

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Time-dependent rheology of charge and shape anisotropic clay gels: Role of electric double layer repulsive force in structural rejuvenation process, layer and face charge effects

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The time-dependent structural rejuvenation behavior was displayed by a range of clay gels such as Laponite, hectorite, sodium montmorillonite (NaMnt), kaolin and sepiolite [1-4]. In a case, the surface charge of a face was changed so as to meet the required condition. These clays possessed both shape and charge morphology. Its shape ranges from disk and plate to fibre [2,3]. The condition required for the display of such time-dependent behavior is that the EDL repulsive interaction in the face-face configuration must be strong to slow down the (+)edge-(-)face bonding process forming the gel network. Microstructure showing this type of bond being predominant will be presented including nuclear waste storage clay. Both the ageing and stepdown shear rate tests were used to study the structural rejuvenation process. Ideally the initial structural state of gel must be well-defined. In the ageing test, the gel structure was first broken down to an equilibrium state then the spontaneous strengthening with rest time was characterised by the yield stress measurement. In stepdown shear rate test, the shearing at 1000 s^{-1} will breakdown the structure and aligned in the anisotropic particles in the direction of flow and this defined the initial state before the stepdown. Direct evidence of the EDL repulsive force being responsible for this time-dependent behavior will be presented using the results of the stepdown shear rate test. When this EDL force is strong, the bonding process is slowed down and this gives rise to the time-dependent behavior. This causes the stepdown shear stress to increase with time. Even a small amount of added salt (0.002M) can increase markedly the (+)edge-(-)face bonding speed and the strength and density of these bonds. More low energy paths to bonding were created hastening the structural rejuvenation process [4].

A layer charge hypothesis was proposed to explain the different in the structural rejuvenation time-dependent behaviour between NaMnt and hectorite gels for pH and other effects. Kaolin suspensions were made time-dependent in the structural rejuvenation mode based on our proposed face charge hypothesis. Lastly if time permit, the time-dependent behavior of fibrous clay suspensions such as sepiolite and palygorskite will also be considered.

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Microstructure observation of cemented bentonite under the swelling state using electron microscopy

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In the geological disposal of high-level radioactive waste, swelling property of bentonite is essential to maintain low permeability and regulate the migration of radionuclides. Over the long term, bentonite may undergo cementation, where secondary minerals precipitate in pores and adhere to montmorillonite, degrading its swelling performance [1]. To ensure the long-term performance, it is crucial to understand how swelling capacity decreases by focusing on the interaction between montmorillonite and secondary minerals at nano- to micro scale. In this study, we employed electron microscopy to reveal the microstructure at the interface between montmorillonite and secondary minerals under the swelling state in cemented and uncemented bentonite, respectively.

Samples were collected from the Tsukinuno bentonite mine in Yamagata, Japan, which is known for producing Kunigel-V1. We compared two types of samples: bentonite ores that were cemented during diagenesis, and reconstituted samples in which the effects of cementation were eliminated by grinding and compressing. Previous studies on Tsukinuno bentonite have reported that cemented ores exhibit lower swelling pressure than reconstituted samples [1] [2]. To prepare samples for observation, millimeter-sized cut specimens were embedded in agar, immersed in ultrapure water for swelling, and then subjected to a stepwise replacement of water with ethanol and resin to preserve the swelling state [3]. SEM observations revealed areas where resin permeated into montmorillonite, as well as areas where it did not. In particular, montmorillonite was less permeable to resin and showed higher density within several hundred nanometers of the interface with silica, feldspar and carbonate, suggesting these minerals acted as potential cementitious minerals. A comparison between cemented ores and reconstituted samples indicated higher proportion cementitious minerals with densely distributed montmorillonite in cemented ores. Subsequently, TEM observation was conducted on ultrathin sliced samples prepared using an ultra-microtome. Results showed that basal spacings of montmorillonite within several hundred nanometers of the interface with cementitious minerals were smaller ($1.2 – 1.5\ \mathrm{nm}$) than those in other area ($1.3 – 1.7\ \mathrm{nm}$). Moreover, a comparison between cemented ores and reconstituted samples revealed that basal spacings near cementitious minerals were smaller in cemented ores ($1.2 – 1.4\ \mathrm{nm}$) than in the reconstituted samples ($1.3 – 1.5\ \mathrm{nm}$). SEM and TEM observations consistently suggest that swelling of montmorillonite is heterogeneous, with cementation particularly inhibiting swelling near cementitious minerals. This inhibition is likely due to the adhesion of these minerals to montmorillonite during bentonite formation that restricts water access and prevents full swelling in certain areas. Consequently, this incomplete swelling, observed at microscopic scale, may result in a decrease in the swelling pressure of cemented bentonite at macroscopic scale.

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Full pore size distribution of shale by combination of innovative gas adsorption isotherms, mercury intrusion porosimetry and laboratory nano-X ray tomography

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The pore size distribution of clay rocks and soils is crucial for understanding and modelling cation exchange, gas migration, solute diffusion, and hydro-mechanical behavior. This is resulting of the proportion of bulk water and the water within the double layer at the surface of minerals, as well as capillary and osmotic pressures, which are controlled by the pore sizes. Conventional methods, such as mercury intrusion porosimetry and gas adsorption isotherms, are commonly used to characterize the pore network across a wide range of scales. However, isotherms are applied to crushed powder samples which is inappropriate for assessing the preserved microstructure. Then, the two types of pore size distribution provided never successfully match to our knowledge. For this reason, nitrogen adsorption experiments were conducted on preserved rock blocks using an innovative approach with a kinetic control of adsorption equilibrium [1]. Pore size analysis was performed by simulating isotherms with Grand Canonical Monte Carlo kernels. This approach was applied to the Callovo-Oxfordian shale, which is planned to host the French nuclear waste repository. For the first time, this study provides a complete set of comparable data between mercury intrusion porosimetry and gas adsorption isotherms, accurately measuring pore throat and pore body size distributions. However, it is important to note that this coupling only probes pores ranging from the smallest micropores to macropores up to a size of 600nm. Therefore, a full description of the pore network is not yet achieved. The largest pores missing were imaged using laboratory nano X-ray tomography on a 1.5 mm wide core with a voxel size of 295 nm. Advanced in-house algorithms were applied to denoise and restore the numerical volume, and to accurately detect the pores. The segmentation of the pores allowed for the estimation of their size distribution, which was used to build a complete balance of the pore network.

To illustrate the impact of the enhanced pore size distributions achieved, a multiscale model implemented in the Code_Aster Finite Element software [2] was used to simulate an experimental swelling pressure curve that was recorded on the Callovo-Oxfordian shale. The results showed a significant improvement in consistency with the experimental data.

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Geochemical characterisation of porewater from poorly indurated Neogene and Paleogene clays in the Netherlands

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Argillaceous formations of low permeability have been selected in several countries as geological host rock formation for the disposal of radioactive waste. The general barrier function of the host rock is to retard and attenuate the migration of radionuclides to the biosphere. In this context, understanding porewater chemistry and water-rock interactions in clayey formations is important for the safety assessment of repository systems in clay-rich formations. Porewater chemical conditions and buffering abilities of the rock will control radionuclides concentration in the geological barrier over time.

In the Netherlands, poorly indurated clays are viewed as potential host formations in COVRA's research programme for the disposal of radioactive waste. The properties of these clay layers are poorly characterised, and currently largely inferred from material at shallower depths in Belgium (e.g. 220 m at HADES URL). In Spring 2022, high-quality cores and sediment samples were obtained from the multi-purpose research borehole DAPGEO-02 [1]. The Smet Coring System (SCS), previously applied in Belgium, was employed to extract cores of adequate mechanical quality. 64 cores were extracted at depths between 362 and 415 m beneath Delft, in either PVC or Shelby tube core barrels. The cores were air/light-tight sealed in aluminium bags, and then stored at 4°C. The cored succession belongs to the Miocene age (interval 364.10-390.5 m) and late Paleogene, Thanetian-early Eocene, Ypresian age range (interval 390.5-414.0 m). The lithological stratigraphy fits with four formations: the Diessen formation (364.1-382.95 m), the Groote Heide formation (382.95-390.5 m), the Ieper Member from the Dongen formation (390.5-393.9 m), as well as the Oosteind Member (393.9-402.0 m); and the Liessel Member of the Landen formation (402.0-414.0 m).

The mineralogy, geochemistry, and porewater chemistry were analysed from core samples of each formation: DAPGEO-02-C27, DAPGEO-02-C49, DAPGEO-02-C55, DAPGEO-02-C62 and DAPGEO-02-C71. The dry density and water content ranged from 1.54 to 1.62 g/cm3 and 21.5 to 28.1 %, respectively. The porewater was extracted using the squeezing technique at a pressure of 5 MPa, with the water collected inside septum vials to avoid exposure to air. In addition, the porewater was analysed as a function of squeezing pressure up to 50 MPa. The obtained porewater samples were very highly saline waters, with concentrations higher than seawater (SW), and salinity increasing with depth from 0.65 to 0.88 M, except in a transition zone with a sandy layer where the porewater is similar to SW. Br/Cl ratio is similar to SW, but a depletion of sulfate with respect to SW is observed, probably due to sulfate reduction and formation of pyrite, as observed in the rock samples, and according to the reducing conditions of the environment. Mg is also depleted probably due to its involvement in water-rock reactions and formation of smectite clay-rich mineral layers. Anion accessible porosity value is 0.8 for all samples, except in the sandy layer, where the value is 1.

Acknowledgement. This work is part of the Safe Environment for Clay Underground Repository (SECUUR) project (no. 19986), which is financed by the Dutch Research Council (NWO). The project used samples provided by COVRA and EPOS-NL (European Plate Observing System – Netherlands), which is partly financed by NWO.

[1] Vardon et al. (2022) https://doi.org/10.4233/uuid:fde70c00-cf65-4174-9cd3-89585a5e61bd

Acknowledgement: This work is part of the Safe Environment for Clay Underground Repository (SECUUR) project (no. 19986), which is financed by the Dutch Research Council (NWO). The financial contribution of COVRA as part of SECUUR is gratefully acknowledged. The project used samples provided by COVRA and EPOS-NL (European Plate Observing System – Netherlands), which is partly financed by NWO.

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The rationale for choosing bentonite in the engineered barrier system of the Russian deep geological nuclear waste disposal concept

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Disposal of high-level waste in a deep geological repository (DGR) is considered to be the safest option in the long term [1]. Safety of disposal is ensured by the multi-barrier principle, which includes a buffer layer of clay material. Geological exploration has revealed that the “Yeniseisky” site might be considered as potentially suitable for the construction of the DGR [2]. In order to justify the choice of buffer layer material for an engineered barrier system (EBS) in Russia, comprehensive work was carried out to study the composition, structure and properties of various clay materials [3]. Taking into account the Russian experience in the creation of EBS, bentonites from different deposits (10th Khutor, Taganskoe, Zyryanskoe, Dash-Salakhly, Kamalinskoe), kaolins (Kantatskoe, Kyshtymskoe, Kompanovskoe) and mixtures based on them were considered.

The composition, structure and properties of both initial powder samples [4] and those compacted to different dry densities were examined to assess the suitability of using clay materials as a buffer layer of the EBS. For each material, physical, physical-mechanical and water-physical properties (in particular water permeability and swelling) [5], sorption properties, including in relation to radionuclides, diffusion properties, as well as indicators of gas permeability and thermophysical properties were determined. All the conducted researches allowed to assign bentonites of the Minusinsk Depression deposits, in particular of the 10th Khutor deposit, as the most promising for development as a part of the buffer layer. The deposit is of volcanogenic-sedimentary genesis. It is located in a large bentonite-bearing province with reserves of about 14 million tonnes. In comparison with the other considered bentonites, the clays of the 10th Khutor deposit have a high resistance to thermochemical treatment [6]. The main basic properties of the material are: smectite content - 65-75%, cation exchange capacity 70-75 mg*eq/100 g, filtration coefficient - $6{,}42*10^{-13}$ and swelling pressure - 3,70MPa at dry density of 1,7 g/cm^3.

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Ion migration under gravitational fields for nuclear waste disposal

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Understanding ion transport under gravitational fields is essential for assessing the long-term behavior of radionuclides in deep geological repositories. While gravitational drift is typically neglected due to its minimal influence at laboratory scales, its cumulative effect over geological timescales and repository depths has not been thoroughly explored. In this study, we investigate the gravity-induced migration of Sr^{2+} ions through saturated bentonite under high gravitational acceleration using controlled centrifuge experiments. A measurable vertical shift of 0.23 - 0.27 mm was observed after six days at 1,670 g, corresponding to a drift velocity of 2.32×10^{-9} m/s and an ion mobility of 9.69×10^{11} m/N·s. These results reveal a steady-state equilibrium height, beyond which no further ion migration occurs. This study suggests a paradigm shift in nuclear waste disposal strategy—from a time-dependent model to a depth- dependent one—offering a potentially simpler and more definitive criterion for repository design.

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LECTURE THEATRE 1 – SESSION 12

Advances in structural characterization of layered compounds

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Thermogravimetric Characterization of *Trans*- and *Cis*-Vacant Dioctahedral Smectite Structures Reveals Acid Leaching and Interior Acid Storage

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Trans- and *Cis*-vacant (T_v and C_v) octahedral sheet configurations of dioctahedral smectites can be effectively characterized by X-ray powder diffraction (XRPD), but this requires saturating the clays with K^+ or Cs^+ and subjecting them to many wetting-drying cycles to improve the three-dimensional alignment of the layers, followed by X-ray powder diffraction (XRPD) and modeling of the diffractogram. This analysis can be accomplished much more easily, however, via thermogravimetric analysis (TGA). That is, layers with T_v configurations dehydroxylate at ~500 °C, whereas those with C_v configurations do so at ~700 °C, because the –OH groups in T_v configurations are closer together (across a shared octahedral edge) than in C_v configurations, and solid-state diffusion of octahedral cations must occur to transform C_v to T_v configurations before dehydroxylation occurs [1].

In nature some dioctahedral smectite minerals tend to form with one type of octahedral configuration, and some with the other. However, there are many smectites that exhibit dehydroxylation behavior consistent with a mixture of C_v and T_v layers. No clear explanation for this has emerged, although Földvári [2] suggests it might be linked to weathering.

We subjected a montmorillonite sample (Volclay) to acid treatments at various HCl concentrations and used XRPD, TGA, infrared spectroscopy, and chemical analysis of reacted solutions to characterize structural changes. Subsequent treatments were applied in some cases, including back-titration with NaOH solution to pH 7 and the introduction of salts (75 mM $MgCl_2$ + 200 mM NaCl) used in the Banin procedure for preparing acid-treated clays to catalyze RNA polymerization, a possible avenue for pre-biotic production of molecules necessary for the origin of life [3].

The results are consistent with the hypothesis that, as acid attack progresses, octahedral cations (primarily Mg^{2+}) are leached and replaced by H^+, but the leaching can be "healed" to some extent by reintroduction of Mg^{2+}. For instance, Volclay begins with a C_v configuration, but as acid attack progresses the dehydroxylation at ~700 °C decreases, while dehydroxylation at ~500 °C increases much more than can be explained by transition to a T_v configuration. This can be partially reversed when Mg^{2+} is supplied to the system.

This opens the door for reinterpretation of many TGA analyses of smectites, and may even call into question results obtained by XRPD. It also suggests a possible method for structural acid storage needed for RNA polymerization in acid-treated smectites.

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Confirmation of dehydroxylation of dioctahedral 2:1 layers in TEM by oxygen imaging using OBF-STEM

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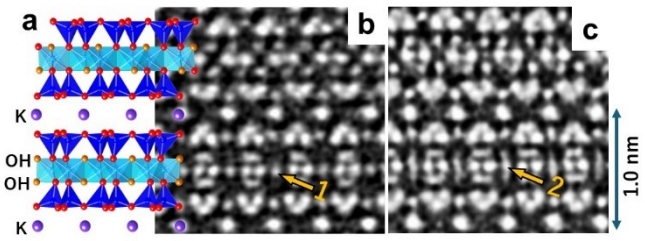
Bulk analyses, such as X-ray diffraction (XRD) and thermal analysis indicated the existence of two types of dioctahedral 2:1 layers, trans-vacant (*tv*) and cis-vacant (*cv*), depending on the location of vacant octahedral sites. However, many questions remain that cannot be solved by the bulk analyses, such as whether these different structures are related to local chemical compositions, whether their interstratification is possible, and more. In order to answer these questions, identification of the *tv*/*cv* layers by atomic imaging using high-resolution transmission electron microscopy (HRTEM) is expected. Kogure and Drits applied HRTEM to an illite sample in which the *tv* and *cv* layers were considered to coexist based on XRD, but all HRTEM contrasts showed only the *tv* structure [1]. Kogure thought that the reason for this is that electron irradiation in the TEM causes dehydroxylation of the dioctahedral 2:1 layer, similarly to sample heating, which leads to octahedral cation migration and formation of a *tv*-like structure, making it impossible to observe the original *cv* layer [2]. Recently optimum bright-field scanning transmission electron microscopy (OBF-STEM) has been developed as a low-dose atomic-resolution imaging method by using an aberration corrected STEM with a segmental detector [3]. To verify Kogure's hypothesis, we attempted to identify the oxygen positions in muscovite subjected to electron irradiation in a TEM by atomic imaging with the OBF-STEM.

A TEM sample was prepared from a single crystal of muscovite ($2M_1$) by focused ion beam (FIB) method. For comparison, another TEM sample was prepared from the same muscovite but heated to 900°C in air to dehydroxylate it. OBF-STEM images in this study were obtained by using an aberration corrected 300 kV microscope (JEM-ARM300F2) with an eight-segmental STEM detector. Most observations were conducted using a probe current of less than 1 pA at 300 kV. First, when comparing the OBF-STEM image of muscovite heated in air with the crystal structure of normal muscovite (Fig. a), no contrast is present at the hydroxyl (OH) positions, and a contrast considered to be oxygen was observed at the same height as the octahedral Aluminum (Arrow 1 in Fig. b). This is consistent with the structure of dehydroxylated muscovite reported by Udagawa et al. [4] using X-ray structural analysis. In contrast, an OBF-STEM image of unheated normal muscovite is shown in Fig. c. Oxygen contrast at the hydroxyl position was also not observed, and a contrast expanding perpendicular to the layers was observed, as indicated by Arrow 2. This is thought to indicate dehydroxylation progressed due to electron irradiation, and that the remaining oxygen is statistically distributed. These results confirm that electron irradiation in TEM induces dehydroxylation of the dioctahedral 2:1 layer, which makes it difficult to observe the *cv* 2:1 layer. In the presentation, we will also report the results of crystal structure analysis based on electron diffraction.



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Atomic-resolution OBF-STEM imaging for beam-sensitive clay minerals

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Clay minerals with phyllosilicate structures generally contain stacking faults to varying degrees. These stacking faults modify X-ray or electron diffraction patterns, however, it is generally difficult to determine the atomic arrangement at the stacking faults from the diffraction patterns. Therefore, efforts have been conducted to directly record the atomic structures of clay minerals containing stacking faults using transmission electron microscopy (TEM) with sufficient resolution. In the course of this research history, TEM observation techniques have evolved from conventional phase contrast imaging to annular dark- or bright-field imaging using Scanning TEM (STEM), and eventually to the use of aberration-corrected lenses, enabling an ultra-high resolution approaching 0.1 nm [1]. However, achieving such high-resolution imaging requires a certain amount of electron irradiation to the sample, and clay minerals easily change to be amorphous when exposed to such high-dose electrons, often making it difficult to obtain the expected high-resolution images. To address this challenge, the Optimum Bright Field (OBF)-STEM method has been developed, which allows the acquisition of ultra high-resolution images even with a small electron dose. In this method, atomic resolution images with a maximized signal-to-noise ratio can be obtained by applying a frequency filter according to the position and shape of the detector to the phase contrast image in each segment obtained from a segmented detector [2].

In this study, we applied the OBF-STEM method to kaolin group minerals which are typical clay minerals difficult to image at the atomic level due to radiation damage [3]. OBF-STEM images were obtained using an aberration-corrected 300 kV transmission electron microscope (JEM-ARM300F2) and an eight-segment detector (SAAF-Octa). Fig. 1 shows an OBF-STEM image of nacrite from Lodéve, France, recorded from the [100] direction, where contrast corresponding to all oxygen atoms, as well as Si and Al, can be visualized. This is likely the first time that atomic resolution images of kaolin group minerals have been recorded along the y_i axes. Furthermore, other images revealed the presence of novel stacking faults in nacrite. In this report, we also plan to present other previously unattainable atomic images of clay minerals using the OBF-STEM method.

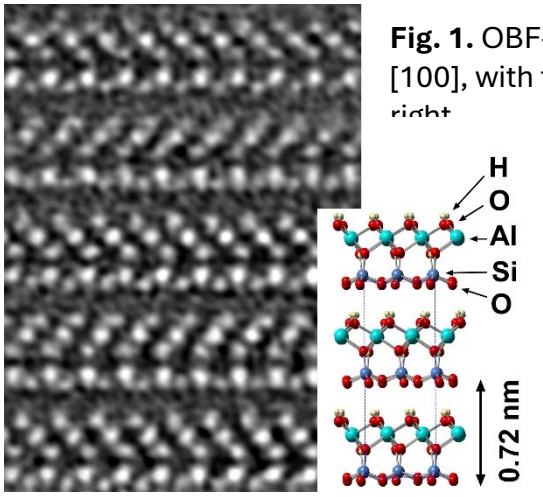

Fig. 1. OBF-STEM image of nacrite recorded along [100], with the corresponding structure model at the right.

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Local Surface Charge, Ion Adsorption, and Water Structuring at Layered Mineral–Electrolyte Interfaces: Insights from Atomic Force Microscopy

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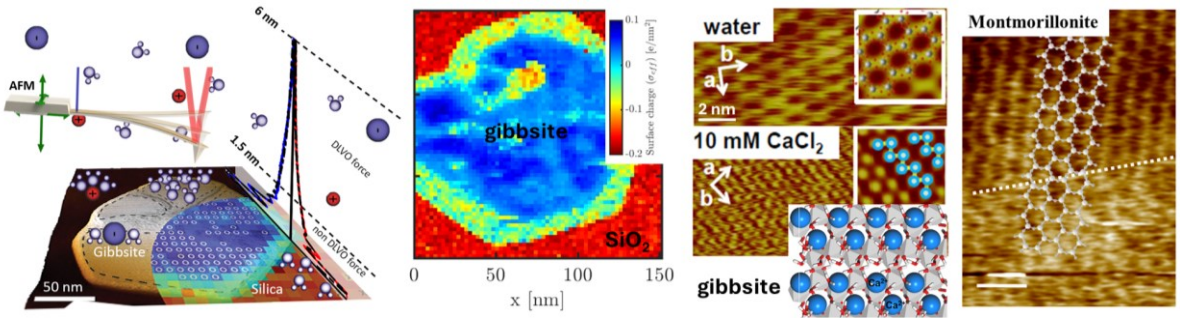
The The microscopic details of clay nanoparticles and layered mineral–electrolyte interface properties—such as surface charge distribution, ion adsorption, electrostatic interactions, hydration forces, and surface defects—play a crucial role in controlling macroscopic properties like colloidal interactions, rheology, CO_2 capture, contaminant transport, the mechanical stability of mineral particles, and various geochemical and industrial processes. Despite early studies of solid/mineral–electrolyte interfaces, a detailed understanding of the electric double layer structure has remained elusive, mainly because traditional methods like volumetric titration and electrokinetic measurements lack the resolution needed to quantify surface charge or observe ion behavior at (sub)nanometer scales. Here, we present a recently developed approach that combines colloidal-scale atomic force spectroscopy with atomic-resolution AFM imaging, providing both continuum- and atomic-scale information to reveal the structure of the electric double layer at heterogeneous mineral–electrolyte interfaces [1-4]. By applying dual-scale AFM, we uncover detailed charge distribution and surface structure, including hydration, on the basal planes of different clay and mineral surfaces (gibbsite, mica, kaolinite, illite, and montmorillonite) in contact with aqueous electrolytes [1-4]. Atomic-resolution images of these clay minerals show both perfect crystallinity and defects, such as vacancies, atomic steps, and disordered regions, which, along with adsorbed ions, significantly influence surface charge and the hydration structure [2, 4]. Dynamic force spectroscopy, analyzed using Derjaguin–Landau–Verwey–Overbeek theory with a charge regulation boundary, enables us to determine local surface charge with 10 nm lateral resolution and identify specific ion effects [1,3]. Atomic-resolution imaging captures the structure of the interfacial liquid and the arrangement of ions in the Stern layer, revealing that, unlike monovalent Na^+ and K^+, Mg^{2+} and Ca^{2+} ions exhibit strong preferential adsorption at specific sites on atomically flat mineral surfaces, thereby defining the interface probed by the AFM tip. Complemented by density functional theory, these experiments provide a detailed picture of mineral–electrolyte interfaces, charge formation, and the templated adsorption of cations, anions, and water, stabilized by hydrogen bonding [1].



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Specific Cr(VI) Removal through Colloidal Nanoparticles: Unraveling the Complex Interactions in Mg/Al LDH Anionic Exchange

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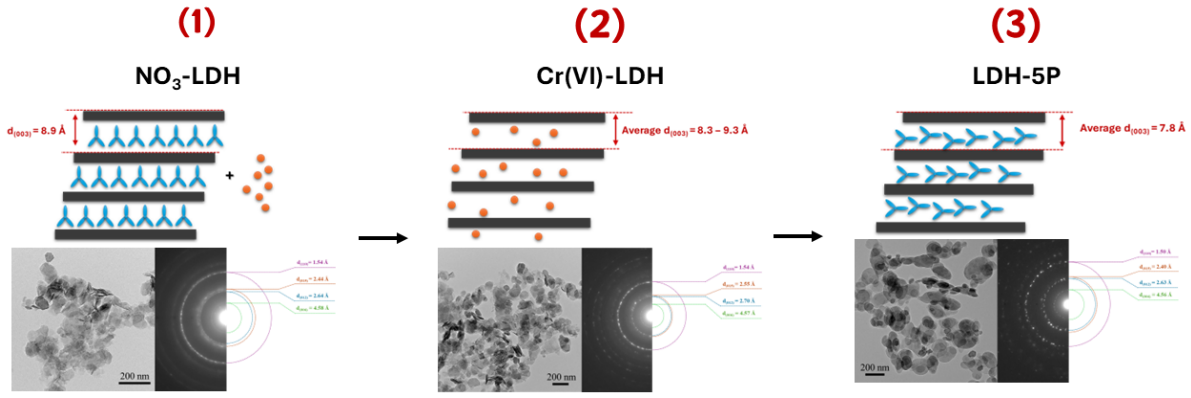
Preferred mode of presentation for the work: Oral

Hexavalent chromium (Cr(VI)) is a toxic pollutant requiring efficient removal/recovery methods from industrial effluents. Layered double hydroxides (LDHs) have emerged as promising materials for this purpose due to their anion exchange properties. However, the fundamental mechanisms governing the selective exchange and recovery of Cr(VI) from LDHs remain insufficiently understood [1].

This study investigates these mechanisms by synthesizing Mg/Al-NO_3 LDH nanoparticles via fast coprecipitation followed by hydrothermal treatment and subsequently saturating them with Cr(VI). Comprehensive structural characterization using PXRD, TEM, Raman spectroscopy, FTIR, and XPS revealed that both CrO_4^{2-} and $Cr_2O_7^{2-}$ coexist within the interlayer space in the dry state. Notably, upon hydration in the colloidal state, with CrO_4^{2-} becomes the predominant species [2].

Ultrafiltration experiments quantitatively evaluated the Cr(VI) recovery efficiency of various competing anions, establishing a clear selectivity hierarchy: $HPO_4^{2-} > SO_4^{2-} > CO_3^{2-} >> Cl^- > NO_2^- \geq NO_3^-$. The findings confirm that outer-sphere complex formation constitutes the primary mechanism at the LDH interface, facilitating potential regeneration through anionic exchange rather than permanent stabilization within the LDH matrix, which enables repeated Cr(VI) adsorption compared to other anions [3]. Thermodynamic exchange constants were calculated, demonstrating significant differences between intercalated divalent anions (K_{ex} values of 5.35, 1.73, and 0.13 for HPO_4^{2-}, SO_4^{2-}, and CO_3^{2-}, respectively) and monovalent anions (K_{ex} values of 2.78 10^{-6}, 1.32 10^{-6}, and 0.98 10^{-6} for Cl^-, NO_2^-, and NO_3^-, respectively). The observed structural changes accompanying the consecutive $2NO_3^- \rightarrow CrO_4^{2-} \rightarrow 2NO_3^-$ ion exchange are discussed in terms of thermodynamic constants differences. This work provides essential quantitative insights into the selective Cr(VI) recovery from LDHs.



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Exchange of interlayer K in mica and implications for mineral identification

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Mica minerals play an important role in controlling the cation exchange capacity of soils and sediments. Mica interlayer K^+ is usually considered non-exchangeable because of strong electrostatic binding. However, earlier studies showed that under low solid-to-liquid ratio and prolonged reaction times, up to 90% of interlayer K^+ can be exchanged from trioctahedral micas [1]. Once this exchange occurs, mica can swell and accommodate interlayer water and organic compounds. This makes it difficult to distinguish mica from vermiculite without determining the layer charge.

Here, we evaluated the extent of K^+ exchange in trioctahedral micas - biotite and phlogopite (Huayan, China), and dioctahedral muscovite (Rössing mine, Namibia) using a standard protocol for homoionic smectite preparation [2]. We separated initial minerals in fractions <2 µm, 2 – 20 µm and >20 µm and subjected them to three successive 24 h exchanges (1 g : 50 ml) using 0.1 M and 1 M NaCl and $CaCl_2$ solutions to assess the effect of solution concentration and cation valence on K^+ exchange. After ultracentrifugation and washing of excess salts with ultrapure water (resistivity 18.2 MΩcm), we prepared oriented clay slides and estimated the extent of exchange from the ratio of ~10 Å basal mica peak to the newly formed 14 Å "swelling" peak.

We observed that biotite exhibits substantial K^+ exchange, especially in $CaCl_2$ solutions and at higher concentrations. Smaller particles exchanged more K^+ than larger ones, even in the absence of complexing agents like Na-tetraphenylboron [3]. Phlogopite followed a similar trend but exhibited significantly lower K^+ exchange. Notably, particles >20 µm showed negligible exchange. Both biotite and phlogopite readily intercalated ethylene glycol vapor after exchange, highlighting their potential misidentification as vermiculite without applying any additional tests. Lastly, there was no K^+ leaching from muscovite, regardless of cation nature, solution concentration and particle size. These results are strongly reminiscent of the plant ability to feed on interlayer K^+ from trioctahedral micas but not from dioctahedral ones [4].

We show that K^+ can readily be exchanged from trioctahedral micas using widely applied protocols for preparation of homoionic smectites. This might lead to swelling and structural changes that complicate accurate mineral identification. K^+ exchange is particularly critical for the <2 µm fraction, where misclassification as vermiculite is most likely. These results underscore the need for careful interpretation of XRD data and consideration of mica reactivity in mineralogic studies.

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LECTURE THEATRE 2 – SESSION 47

Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling

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Ferrihydrite transformation in soils: The impact of organic carbon

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Ferrihydrite, a poorly crystalline iron mineral, constitutes one of the most abundant and reactive mineral components in soils and sediments. With a high surface area and point of zero charge (PZC) near pH 8, ferrihydrite is often linked to the sorption of high amounts of nutrients, contaminants and trace elements. However, in the absence of oxygen, Fe(III) can serve as an electron acceptor during microbial respiration. The reductive dissolution of Fe(III)-bearing minerals releases Fe(II) to aqueous solution. Interactions between aqueous Fe(II) and Fe(III) minerals can catalyze the transformation of the latter through electron transfer and atom exchange. This leads to the formation of crystalline products like lepidocrocite, goethite, or magnetite and impacts the release and re-distribution of ferrihydrite-associated trace elements and nutrients.

In nature, however, pure iron minerals rarely form. Rather, the ubiquitous presence of natural organic matter (OM) in soils and sediments promotes the formation mineral-organic associations. Coprecipitation of ferrihydrite with OM decreases particle size, changes the PZC, and alters mineral susceptibility towards microbial and abiotic reduction. For example, lab-based model studies consistently show that in the presence of aqueous Fe(II), OM-associated ferrihydrite undergoes less transformation than OM-free ferrihydrite [1]. Yet, these results contrast microbial reductive dissolution studies in which the presence of mineral-associated OM promotes the reductive dissolution of Fe(III) in ferrihydrite and leads to the release of associated OM [2,3]. Because of the important role that ferrihydrite plays for nutrient and trace element cycling in soils, it is critical to clarify the role of mineral-associated OM in these processes. This presentation will highlight recent studies focusing on the role of OM for ferrihydrite stabilization, recrystallization, or transformation in anoxic soils. Our findings contribute to a better understanding of the complex and dynamic interactions between minerals and organic matter occurring in soils and sediments.

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Schwertmannite formation and properties as an indicator of biogeochemical processes at low pH in acid sulfate weathering environments

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Schwertmannite is a metastable ferric oxyhydroxysulfate [$Fe_{16}O_{16}(OH)_y(SO_4)_z$ nH_2O where 16-y = 2z; 2.0<z<3.5] that is a ubiquitous mineral formed in acid sulfate soils (ASS) with sulfuric materials (pH<4) and in acid drainage environments [1,2]. Schwertmannite commonly forms in surface acid drainage waters with pH values between 3 and 4.5 and high dissolved iron and sulfate concentrations between 1000 and 3000 mg L. It controls the chemistry of many ASS and waters by buffering the pH and controlling the activity of metals and major ions [1,2]. There is a wide spectrum of occurrences and origins of schwertmannite in ASS and water environments as well as in anthropogenic sites including mines, spoils and tailings. Schwertmannite may also be a component of sediments in equatorial regions of Mars where seepages of acidic, saline meltwaters are thought to have occurred because of permafrost melting [1]. The presence and behaviour of schwertmannite is variable in terms of: (i) its specific occurrences, (ii) the environmental factors working during its formation, and (iii) post-formational alteration, for example:

(a) Schwertmannite is typically formed from oxidation and hydrolysis of dissolved Fe(II), which is accelerated in acid sulfate systems by acidophilic bacteria that have a metabolic requirement for sulfate, which is also a structural or stabilizing component of schwertmannite [1}. These reactions are favoured when Fe(II) and sulfate-rich groundwater discharging from acid sulfate soils enters more-oxygenated surface waters or drains [2}. These processes can cause impermeable Fe-rich layers to form in discharge areas and explains mechanisms leading to degraded soils, erosion and poor water quality.

(b) Schwertmannite has been found to form rapidly in ASS environments by dissolution of metastable sideronatrite [$Na_2Fe(SO_4)_2.OH.3H_2O$] in rainwater after rain events [3}. Sideronatrite formed via oxidation of pyrite (formed in subaqueous soils), after exposure to air for the first time in more than 100 years during Australia's Millennium drought. This alternative pathway for the formation of schwertmannite was verified by dissolving synthetic sideronatrite made in the laboratory under similar conditions found in nature (i.e. temperature, chemistry and pH) in distilled water.

(c) Schwertmannite is a metastable phase and transforms to goethite and/or jarosite over timescales of weeks to months, which was confirmed from laboratory incubation experiments using synthetic schwertmannite [1]. In coastal ASS schwertmannite persists on a much longer timescale than predicted by laboratory experiments, likely due to surface-site coverage by silicate, natural organic matter and phosphate. In anoxic acid-sulfate systems, the Fe(II)-catalyzed pathway has been found to exert a major influence on the transformation of schwertmannite to goethite and sulfide formation [4].

(d) Schwertmannite can be used: (i) to remove or scavenge arsenic or likely aluminium from waters in acid streams and in mine tailings as it has a high sorption capacity for metal and anionic contaminants such as As or Al [1], (ii) as a geochemical sampling medium for the detection of mineral deposits [1] and (iii) as an indicator of acid sulfate soil-water processes operating in landscapes [2].

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Coprecipitation and phase transformation OF Fe(III)/metal hydroxides with organics

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Iron hydroxides are important carriers for metals and organics via coprecipitation and adsorption processes in many natural aquatic and soil systems. Here, we studied Fe(III)–metal-OM coprecipitation under environmentally relevant conditions in solution and on soils with different mineral/organic compositions. SiO2 and Al2O3 were selected as model soil surfaces with Si-O and Al-O bonds, and model OM compounds containing –COOH/NH2 functional group which can complex with Fe/metal ions and Fe/metal hydroxide particles were selected. Our results showed that minerals and OMs significantly affected Fe/metal hydroxide coprecipitation and their later phase transformation. For homogeneous coprecipitation of Fe/metal hydroxide with organics, the strong complexation between -COOH and NH2 with Fe/metal ions and hydroxide particles led to OM and metal's coprecipitation with iron hydroxide. The incorporation of organics and metals in general inhibited the phase transformation of poorly crystalline iron hydroxide (i.e., ferrihydrite) to crystalline phases (i.e., lepidocrocite, geothite, etc.), while unexpectedly, proteins were observed to promote the oriented aggregation of ferrihydrite to form lepidocrocite. During phase transformation, the coprecipitated metal and organics could be released back into solution. For heterogeneous coprecipitation of Fe/metal hydroxide on soil surfaces, more precipitates formed on positively charged Al2O3 than on negatively charged SiO2, due to electrostatic forces between positively charged Fe hydroxide polymers and substrates. Adsorption of metal ions and OM containing -NH2 onto SiO2 surfaces altered the surface charge of SiO2 to be positive, and thus heterogeneous precipitation of Fe/metal hydroxide particles on SiO2 was greatly inhibited; meanwhile adsorption of OM containing -COOH onto Al2O3 altered its surface charge to be negative, and thus promoted heterogeneous precipitation of Fe/metal hydroxide particles on Al2O3. Furthermore, the (de)protonation of minerals (Si-O and Al-O) and organic coatings (-COOH and NH2) on soil surfaces could alter local solution pH, controlling the amounts and composition (i.e., Cr/Fe ratio) of the coprecipitates. Bonding formation between the substrates and heterogeneous precipitates were also found to affect the crystallinity and phase transformation of the newly formed Fe(III) hydroxide on substrates. This study advanced the fundamental understanding of Fe(III)-metal-OM/soil systems, which was essential to predict the fate and transport of iron, metal and organics in the environment.

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Microbially-mediated ferrihydrite transformation for controlling the mobility of Mo

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Molybdenum (Mo) is an essential nutrient in biological systems, catalysing the global biogeochemical C, N, and S cycles and other important redox processes. However, at high concentrations, it can be toxic to microorganisms, animals and plants. Iron oxides are ubiquitous in nature and represent a potential control on Mo mobility through adsorption and phase transformation in the presence of bacteria (e.g. Geobacter sulfurreducens). This study focuses on the ternary system of Mo(VI)-bacteria-iron oxyhydroxides, to understand the mechanisms of adsorption, redox, and mineral transformation among Mo(VI), Geobacter sulfurreducens, and iron oxyhydroxides, enabling predictions and controls of long-term Mo mobility and Fe mineral transformation under a variety of biogeochemical scenarios. The result will help to develop guidelines for soil health and provide strategies for soil contamination treatment.

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Photochemical Alterations of Fe-Organic Matter Coprecipitates Promoted the Organic Matter Preservation or Degradation: Role of Organic Matter Functional Groups

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Soil organic carbon (SOC) plays an important role in the Earth's carbon cycle, and reactive Fe minerals are significant determinants of carbon accumulation. Fe-organic matter (OM) coprecipitates transformation in deep soil under anoxic conditions has been intensively studied, while such mechanisms are insufficient to be applied in surface soil under oxic and sunlight conditions. Here, various characterization techniques were combined to explore the stabilization mechanisms and extended pathways of sunlight-driven Fe-OM coprecipitates transformation. In addition, to investigate the effect of different OM functional groups, sodium alginate (SA), bovine serum albumin (BSA), fulvic acid (FA), and dextran (DET) were selected as model OM compounds containing carboxyl, amine, aromatic, and hydroxyl functional groups which can complex with Fe ions and Fe hydroxide particles. Our results showed that each Fe-OM was not completely dissolved and released in sunlight condition, but reached stabilization after a certain degree of reaction. All Fe-OM coprecipitates released Fe mostly in the colloidal state (>100 kDa, <0.45 μm) and OM in the dissolved state (<100 kDa). Interestingly, total organic carbon and ICP-OES analyses showed two trends in the stability of Fe-OM coprecipitates with different functional groups, (1) both Fe and OM were released in Fe-SA, Fe-DET, and Fe-FA systems, and (2) Fe-BSA was very stable under light conditions, with no release of either Fe or OM. Solid-phase XPS and liquid-phase FT-ICR-MS analyses showed that these two trends were due to different photochemical alterations of Fe-OMs coprecipitates. The reactive functional groups (C–O–C/–COOH) of Fe-SA, Fe-DET, and Fe-FA solid phases were degraded, and these OMs with reactive functional groups were released into solution; on the contrary, the reactive functional groups of Fe-BSA solid phases were increased, which led to a tighter Fe-OM complexation and promoted the preservation of OMs. In summary, the properties of organic matter (e.g., functional groups) largely determine the stability of iron minerals to SOC. This study advanced the fundamental understanding of Fe-OM systems, which was essential to predict the fate and transport of OM in the environment.

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Clay Minerals Regulating the Fe(II)-Catalyzed Ferrihydrite Transformation under Anoxic Conditions

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Metastable ferrihydrite nanoparticles and clay minerals always coexist as heteroaggregates in nature due to their abundance, opposite charge, and large interface energy [1, 2]. However, the impact of clay minerals on the transformation of ferrihydrite under anoxic conditions remains elusive. This study systematically investigated the effect of distinct clay minerals on the Fe(II)-catalyzed transformation of ferrihydrite for the first time, clarifying the underlying nano-scale mechanisms. Our results demonstrated that clay minerals could affect the production and recrystallization of labile Fe(III) (an active Fe(III) intermediate species formed by oxidation of Fe(II) at the ferrihydrite surface) by dispersing ferrihydrite aggregates. This modulation led to different transformation rates, higher crystallinity of formed lepidocrocite, and enhanced goethite formation in the heteroaggregates. Importantly, montmorillonite can accommodate Fe(II) and labile Fe(III) within its interlayer spaces, which further led to the inhibited crystallization of Fe(II) to magnetite and long-term preservation of labile Fe(III). Additionally, clay minerals served as templates for forming dendritic goethite and hexagonal magnetite nanoplates. Our findings provide new insights into the complicated roles of clay minerals in controlling the ferrihydrite transformation and other iron (oxyhydr)oxides formation, which is significant for predicting the bioavailability of iron and the fate of other coexisting contaminants [3].

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Fe(II)-Catalysed Transformation of Ferrihydrite: Effects of Organic-Functionalised Solid-Liquid Interfaces

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Ferrihydrite is a metastable, nanocrystalline iron (Fe) oxyhydroxide present as a terrestrial weathering product ubiquitous in soils [1]. The spontaneous, heat-catalysed or aqueous Fe(II)-catalysed transformation of ferrihydrite into more crystalline Fe (oxyhydr)oxides is associated with substantial changes in specific surface area and sorption properties, where the pathways of transformation are directed by the presence of aqueous organic species and mineral surfaces (*e.g.*, clay minerals) [2]. Whilst previous works have largely focussed on the homogeneous precipitation of ferrihydrite with organic matter [3], the transformation pathways of heterogeneously precipitated ferrihydrite at solid-liquid interfaces, including those functionalised with organic matter, have yet to be investigated.

Here, the Fe(II)-catalysed transformation of ferrihydrite heterogeneously precipitated at idealised organic interfaces was studied as a function of surface organic ligand. Ferrihydrite heterogeneous precipitation and Fe(II)-catalysed transformation took place at low concentration to inhibit homogeneous precipitation, using fused silica (SiO_2) surfaces functionalised with -COOH, -SH, mixtures of -COOH and -SH (-COOH + -SH) and -NH_2 ligands to represent model organic functionalised mineral surfaces. Resulting heterogeneous phase assemblages were characterised using a combination of transmission electron microscopy (TEM) and synchrotron scattering techniques, with Fe isotope (^{57}Fe) tracing techniques employed to quantitatively study transformation kinetics and further elucidate the mechanisms of heterogeneous phase transformation.

Ferrihydrite precipitation was substantially affected by the organic surface ligands, with -COOH-bearing surfaces promoting precipitation through surface complexation effects and -NH_2 groups inhibiting precipitation through electrostatic interactions Following Fe(II)-catalysed transformation, transformation of ferrihydrite into more crystalline lepidocrocite and goethite with complete isotopic exchange with aqueous Fe(II) was observed for the homogeneous control samples, in agreement with previous works [3]. However, a substantial fraction of the heterogeneously precipitated ferrihydrite was retained at all surfaces without undergoing isotopic exchange with the solution phase regardless of organic functionalisation. This was shown to be attributable to the surface disrupting electron transfer processes, as opposed to spatial constraints on the access of Fe(II) to ferrihydrite imposed by the solid surface. Further, the resulting products of transformation were shown to be a function of organic surface ligands: complexation with -COOH groups resulted in slowed transformation to form predominantly lepidocrocite phase assemblages whilst transformation at the untreated SiO_2 and -NH_2-bearing surfaces resulted in more crystalline magnetite forming alongside goethite and lepidocrocite, with all transformed phase assemblages containing a substantial fraction of ferrihydrite. Transformation experiments over longer timescales were consistent with heterogeneous ferrihydrite comprising two fractions: (1) a fraction that rapidly underwent transformation, and (2) a fraction more strongly associated with the surface with a slowed transformation rate.

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LECTURE THEATRE 2 – SESSION 1b

Universal

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Ni- and Cr- bearing clays in green siliceous gemstones: a LA-ICP-MS study

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Green microcrystalline silica rocks are known in the gem trade as chrysoprase and chrome or chromium chalcedony if colored by nickel or chromium, respectively. More rarely, opaline varieties of both exist. These green gemstones generally occur in silicified laterites developed on ultramafic rocks. While the presence of Ni-bearing 2:1 clay minerals as pigments have been established for chrysoprase[1], the colorant phases of chromium-bearing chalcedonies are yet unknown. Here, we present a geochemical-mineralogical study using laser ablation inductively coupled plasma mass spectrometry in combination with X-ray diffraction analysis (XRD) and scanning electron microscopy to determine the colorant phases of the green silica-rich gem materials from ten deposits and to gain insights into their origin. Due to the inhomogeneous distribution of the colorant phase, the correlation of Ni or Cr with other elements from multiple analyses and crystal chemical constraints allow an attribution of analyzed elements to the green chromophore, to the silica phase, to fluid inclusions or evaporated pore fluids, or to ancillary inclusion minerals, such as iron oxides. XRD data help to identify the structure of the silica and clay minerals. Our new data show that chrysoprase and prase opal are colored by nano-sized willemseite (Haneti, Gumigil, Sarykulboldy) or Ni-bearing talc (Szklary, Golesh), rarely with additional Ni-bearing sepiolite (Golesh). The green rocks formed by co-precipitation of Ni-rich clay minerals with silica phases in open fractures probably during dry climatic phases in a lateritic environment. In contrast, chromium-bearing chalcedonies mostly originate by replacement of ultramafic rocks as evidenced by residual Cr-rich spinel inclusions, high immobile trace element contents, and field evidence. Three distinct types of green clay mineral inclusions are encountered: 1) Cr-bearing illite (Dikmen), 2) Mg-rich, Fe-Al-poor volkonskoite (Mtoroshanga, Ricón del Tigre), and 3) various Cr-Fe-rich smectites (Eskişehir). A hydrothermal origin is suspected for chalcedony with Cr-rich mica inclusions, while a supergene lateritic environment is envisaged for the two types of chrome chalcedony with Cr-rich smectites. The results of this study can be applied in origin determination of gem materials in archeological objects.

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GALOPER 2: Simulating and Analyzing Crystal Growth Processes in MATLAB

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Growth According to the Law of Proportionate Effect and by Ripening (GALOPER 2) is a MATLAB-based interactive application designed to simulate and analyze various crystal nucleation and growth processes. It is based on a defunct program written by D.D. Eberl of the US Geological Survey using Microsoft Excel macros.

Users can simulate a wide array of processes and combinations thereof, both naturally observed and theoretical, including surface- and supply-controlled growth, Ostwald ripening, and coalescence, facilitating the exploration of multi-step process combinations via a customizable "stack." The app provides a dynamic visualization of crystal size distribution (CSD) transformations over time, alongside tools for statistical analysis. Users can fit experimental or simulated CSD data to theoretical probability distributions (Figure 1), evaluate the plausibility of hypotheses for empirical CSD origins through Kolmogorov-Smirnov tests, measure and optimize fitting parameters and error/variance, and animate the progression of crystal datasets over time. Users can also fit simulated processes to empirical CSDs.

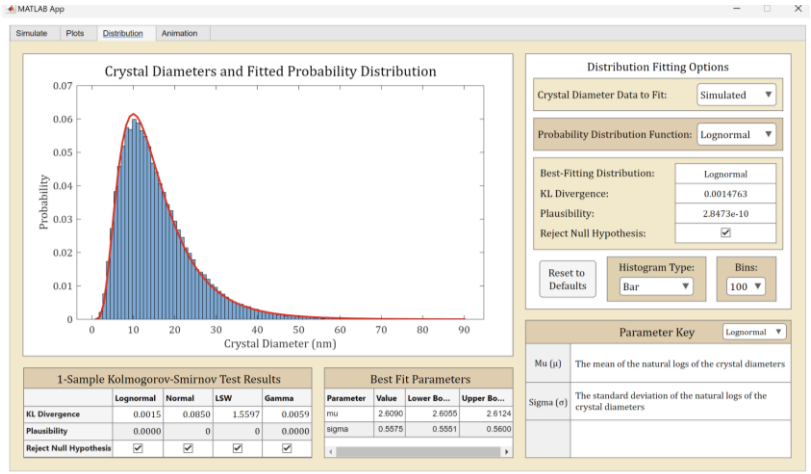

Figure 1. Digital screenshot of the GALOPER 2 MATLAB application created by Jansen Nye et al, Brigham Young

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Stimuli-induced excimer formation in confined space

Matejdes, M.[1], Škorňa, P.[1], Slaný, M.[1], Klement, R.[2], Kawamata, J.[3], Breu, J.[4]

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Two-dimensional layered materials offer a versatile platform for engineering tunable optical systems by leveraging confinement effects. We report the design of synthetic saponite heterostructures intercalated with naphthalene dipyridine dications[1], where controlled π-π stacking within the interlayer space enables dynamic modulation of emission.

Depending on the presence of specific solvents, like dimethyl sulfoxide (DMSO), in the interlayer space and molecular packing of intercalated organic cations, the organic cations can be found in monomeric, dimeric or highly aggregated species. Because the mentioned species have distinct optical properties, their presence can be easily revealed by conventional spectroscopic techniques. By DMSO-mediated interlayer expansion, the relative distribution of species changes, which in turn results in a change of photophysical properties. Once the DMSO is removed from the interlayer space the initial relative distribution of species is restored simultaneously with their initial photophysical properties mimicking e.g., the adaptive optical behaviours observed in bioluminescent marine ecosystems.

This stimuli-responsive material demonstrating solvent-triggered transitions between different species, can be potentially utilized in adaptive optical materials for sensors, light-emitting devices, and stimuli-responsive imaging platforms.

[1] Matejdes M et al. (2024) Mater Today Chem 42: 102436

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Mineralogical Properties of Two Hydrothermal Illite from Yeongdong County, South Korea

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Two types of illite from Yeongdong county, central region of South Korea, were investigated to supply as potential illite reference of the Source Clay Repository of The Clay Mineral Society. A greenish-white clay at MEDEXX (IYd-1) was distributed in alteration zones within micaceous schist, and a white clay at Yongkoong (IYd-2) was found as fracture-fillings and intergranular deposits in plagioclase-rich granitic gneiss. Both illites are associated with hydrothermal alteration of mica schist and granitic gneiss, respectively. To assess mineralogical and chemical properties of the illites, size fractionation and electron microscopic analyses was performed on both illite deposits.

IYd-1 contains impurities of quartz and kaolinite that can be removed by size fraction less than 0.5 μm, and IYd-2 contains more impurities including quartz, kaolinite, albite, and microcline that can be removed by size fraction less than 0.5 μm, except micro-sized albite and microcline. SYBILLA modeling was performed for the glycolated XRD profiles of each clay resulting in no expandable layer in the illite structure. The polytypes of IYd-1 and IYd-2 were both $2M_1$, inherited from hydrothermal alteration of muscovite and plagioclase, respectively. Average chemical composition of IYd-1 and IYd-2 were calculated by electron probe micro analysis (EPMA), showing that both illites contain high contents of interlayer potassium (0.84-0.88), typical composition of “end-member illite” [1, 2].

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Characterization of Illite Clay Mineral in Norwegian Quick Clay

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Quick clay is an extremely sensitive soil type capable of rapid liquefaction upon disturbance, often resulting in catastrophic and deadly landslides, as observed in Norway, Sweden, Finland, Russia, Canada, and the USA. This geohazard is a remnant of the last glacial period, caused by post-glacial isostatic rebound and the subsequent leaching of stabilizing cations. The resulting loss of ionic bonding weakens the characteristic “house-of-cards” structure of the clay minerals [1]. Current stabilization techniques, such as deep mixing with lime-cement, are widely used due to their cost-effectiveness and simplicity. However, they contribute significantly to CO_2 emissions.

The consortium *Sustainable Stable Ground* aims to explore alternative, more sustainable stabilization strategies by investigating quick clay from the atomic to the geological scale. In this study, we focus on illite—the dominant clay mineral in quick clay [2]. Samples from the Tiller-Flotten deposit in the Trondheim area (Norway) were analysed and compared to a 94.2% pure illite reference sample from the USA.

A comprehensive suite of analytical techniques was employed to identify and characterize illite, including X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Thermogravimetric Analysis (TGA)[2]. Surface area was evaluated using the Brunauer–Emmett–Teller (BET) method and the methylene blue spot test, both of which indicated relatively low values compared to those commonly reported in the literature. Additionally, we examined the influence of various salt and polymer suspensions on sedimentation behaviour and zeta potential. These findings enhance our understanding of illite’s role in the mechanical and chemical behaviour of quick clay and support the ongoing search for innovative, low-carbon stabilizers for sensitive clay soils.

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High oxygen barrier coating using non-toxic nanosheet dispersions for flexible food packaging film

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One of the major challenges in the circular economy relating to food packaging is the elimination of metallised film which is currently the industry standard approach to achieve the necessary oxygen barrier performance. There is an urgent unmet need for scalable solutions that can replace this aluminium coating with a solution-deposited or coextruded layer that can be recycled without separation from the rest of the packaging materials. Two-dimensional (2D) inorganic nanosheets are impermeable to gas molecules so exploiting their potential for high aspect ratio platelet structures is an effective approach to construct tortuous pathways to lower molecular diffusion rate through polymeric materials. The key challenges for high gas barrier food packaging materials are (i) the preparation of stable, high aspect ratio non-toxic 2D nanosheet dispersions and (ii) the use of an existing commercial coating technique. Here, we report the synthesis of high aspect ratio 2D non-toxic layered double hydroxide (LDH) nanosheet dispersions using a non-toxic exfoliation method in aqueous amino acid solution. High gas barrier coating films can be prepared using this food safe liquid dispersions through a bar coating process. The oxygen transmission rate (OTR) of 12 µm PET coated film can be reduced from 133.5 cc/m2/day to below the instrument detection limit (<0.005 cc/m2/day). The O2 permeability of this film is estimated to be below 0.0007 x 10–16cm3(STP)·cm/cm2·s·Pa, giving a barrier improvement factor (BIF) of 24640. In comparison, a commercially available 12 µm metallised PET has an O2 permeability of 0.0349 x 10–16cm3(STP)·cm/cm2·s·Pa. Most importantly, these coated films are also transparent and mechanically robust, making them suitable for flexible food packing while also offering new recycling opportunities.

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Effect of Al powder and CTAB addition on the properties of porous metakaolin based geopolymers

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Porous geopolymers has emerged as one of the most promising inorganic porous materials over the last decade, due to their inexpensive and easy fabrication process, suitable properties, thermal and chemical stabilities, and extensive application fields [1]. Geopolymers can be used for coatings and adhesives [2], new binders for composites, new cement for concrete and waste encapsulation, new precursors for zeolites and ceramics, new template for carbon and others [1]. Geopolymers have a variety of characteristics that offer alternatives for ceramic matrix composites reinforced with fibers [3], [4]: low-cost constituents and processes, rapid processes, reduced environmental impact. This work aims to study the effect of the proportion of aluminum powder (Al) and hexadecyltrimethylammonium bromide (CTAB) on microstructural, thermal and mechanical properties of metakaolin based geopolymers. Al and CTAB are respectively used as porogen and surfactant agents, and their proportions varied from 0 to 0.3 wt% of metakaolin. The quantity of metakaolin and alkali activators (NaOH and Na2SiO3) are the same for all samples. After dissolution of NaOH pellets into Na2SiO3, powder mixture of metakaolin with Al and/or CTAB is gradually added to the activated solution and mixed at 700 tr/min for 2 minutes with a paddle stirrer then poured into cylindrical molds, geopolymerized at 50°C for 24h and oven-dried at 50°C for 24 hours after being removed from the molds. Different properties of the as-obtained porous geopolymer were characterized by X-ray tomography, SEM analysis, porosity measurements, mechanical resistance determination through compressive tests, open density, thermal analysis (TGA/DTA and thermal conductivity) and identification of phases with XRD analyses. The obtained results show that porosity ratio increases with the proportion of CTAB and varies from 11 % (0 wt%Al and 0.1 wt%CTAB) to 64 % (0.3 wt% of Al and CTAB). Compressive strength rises from 0.5 MPa (0.3 wt% of Al and CTAB) to 20.5 MPa (0 wt% of Al and CTAB). Open density also varied with proportions of CTAB and Al. The most dense sample is the one obtained without Al and CTAB, whereas the less dense one is obtained with 0.3 wt% of those two additives. These results show that the introduction of the mixture of Al and CTAB into the metakaolin based geopolymer formulation contributes to the development of high porous media and consequently decreases the mechanical resistance.

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LECTURE THEATRE 3 – SESSION 44

Synthesis and Applications of Modified Clays in Environmental Remediation

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Exploring Polycaprolactone, Halloysite Nanotubes, Diatomaceous Earth, and their composites for Acetic Acid Mitigation in Museum Display Cases

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Airborne pollutants, particularly volatile organic compounds like acetic and formic acids, pose a significant threat to the preservation of cultural heritage artifacts stored in enclosed environments, including museum display cases. Effective mitigation strategies are crucial for the long-term conservation of these collections. However, most adsorbent materials currently used in museum contexts have drawbacks in terms of specificity, adsorption efficiency, and reliability.

Halloysite nanotubes (HNTs) and diatomaceous earth (Diat) have emerged as promising sustainable adsorbent materials due to their high surface area, chemical stability, and tunable adsorption properties. Their incorporation into biodegradable polymer matrices, such as polycaprolactone (PCL), further enhances their potential for sustainable pollutant control.

This contribution presents preliminary findings on the performance of PCL-based composite materials incorporating varying amounts (5% to 50% by weight) of HNTs and Diat for acetic acid adsorption.

After extracting natural acids from the samples, they were exposed to acetic acid from a controlled pollutant generator. Emission studies in micro-chambers evaluated the adherence of the adsorbed acid to the material. Ion chromatography was used to assess the acid retention and off-gassing behaviour of the materials. Additionally, Oddy tests were conducted to evaluate their potential adverse effects on both organic and inorganic materials.

Preliminary results indicated that, compared to charcoal, pristine HNT and Diat exhibited good adsorption capacities, with HNT achieving the highest uptake. In PCL/HNT composites, maximum adsorption was observed at a 35 wt% HNT concentration, while the 50 wt% formulation resulted in reduced efficiency, likely due to particle agglomeration limiting the accessible surface area. In contrast, adsorption in PCL/Diat composites steadily increased with higher Diat content. Emission studies revealed that the acid desorbed from HNT and Diat samples after 7 days at 30 °C, while composites containing 50 wt% of these materials effectively retained the adsorbed acid. Furthermore, Oddy tests indicated that while pristine HNT, PCL, and their composites may pose concerns when in proximity to metal and paper-based artifacts, those incorporating Diat exhibited no significant acid emissions, suggesting their suitability for museum applications.

Ongoing investigations aim to evaluate further the long-term performance of these materials in preventive conservation strategies. However, the promising preliminary results highlight the potential of modified clay-based composites as a passive and sustainable alternative for mitigating airborne pollutants in museum settings.

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Nonionic Organoclay: a versatile material for the sorption of organic contaminants

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In this contribution, the preparation of nonionic organoclays based on nonionic alkylpolyether surfactants [1-2] will be discussed with a particular attention of the importance of surfactant state: monomer or self-arrangements beyond the critical micelle concentration determining the arrangement of the confined amphiphilic molecules within the internal structure of the layered materials. The environmental properties of the nonionic organclays, used as adsorbents for the removal of organic contaminants (pharmaceutical products as well as other contaminants) that will be also particularly discussed and compared to those of conventional cationic organoclay systems (i.e. prepared with alkylammonium cationic surfactants) and raw clay minerals. Due to their dual hydrophilic/hydrophobic features, nonionic organoclays, unlike cationic ones showing a hydrophobic surface, and untreated clay minerals displaying a hydrophilic behavior, represent the most polyvalent material for the adsorption of a wide range of micropollutants showing different chemical nature [3].

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Elaboration of glyphosate pesticide electrochemical sensor based on synthesized organophilic saponite

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Glyphosate is one of the most used herbicides in the world despite its well-documented harmful effects on living organisms including humans [1,2]. Trace amounts of this compound were effectively detected in water, soils and crops. Electrochemical sensors that can be easily miniaturized are highly solicited for this type of on-site environmental analysis. This allows precise monitoring of contaminant concentrations while taking into account their biodegradation into more or less toxic secondary metabolites. In this work, a sensor applied for the detection of glyphosate in environmental samples was developed by modifying a carbon paste electrode with a synthetic saponite functionalized with a cationic organophilic organosilane (Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DOTPAC)). The effective synthesis of the synthetic clay mineral and its functionalization was confirmed by several characterization methods (XRD, FTIR, ^{29}Si NMR, TGA, SEM and electrochemistry). The carbon paste electrode modified by this hybrid material showed an intense and exceptionally stable glyphosate oxidation signal, certainly due to the combined effect of the organophilic and cationic character of the organoclay. These interesting performances led to the application of the sensor for the electrochemical quantification of this pesticide. After optimization of some experimental parameters (including composition of the paste, pH of the detection medium and effects of some interferences), a calibration curve was plotted in the glyphosate concentration range 10 µM and 85 µM. The designed sensor displayed a sensitivity of 0.24 µA μM^{-1} and a detection limit of 0.2 µM. Application in some natural samples such as tap water and well water showed recoveries close to 100% and confirmed the effectivity of the elaborated sensor in real water samples.

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Enhanced VOC removal from natural rubber emissions using combined water scrubbing and surface-modified Philippine natural zeolites

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Volatile organic compounds (VOCs) emitted during natural rubber (NR) processing pose significant environmental [1] and health risks [2, 3] due to their contribution to air pollution and potential carcinogenicity. This study explores a hybrid approach integrating water scrubbing with adsorption techniques to effectively mitigate VOC emissions from heated NR at 210°C. To optimize adsorption efficiency, Philippine natural zeolite (PNZ) [4] was surface-modified via two distinct methods aimed at enhancing hydrophobicity: a wet chemical treatment with cetyltrimethylammonium bromide (CTAB) and a dry plasma treatment incorporating hexamethyldisiloxane (HMDSO). The modified adsorbents—CTAB-modified zeolite (CTABZ) and plasma-treated zeolite (PMZ)—were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) to assess structural and surface modifications.

A custom scrubber-adsorbent setup was constructed, wherein VOC-laden gases generated from heated NR were introduced at the bottom of a plate tower scrubber with perforated plates, with water supplied from the top and recirculated to ensure maximum contact. The gas effluent was subsequently passed through beds of the different zeolite adsorbents, and VOC concentrations were monitored using a photoionization detector (PID). Results demonstrated that plasma-modified zeolite (PMZ) exhibited superior adsorption capacity, achieving near-complete VOC removal. When combined with water scrubbing, the system attained a 100% removal efficiency, highlighting its potential for industrial application.

This dual-stage process capitalizes on the high sorption capacity and thermal stability of natural zeolites, further enhanced by surface modifications that increase hydrophobic interactions with organic vapours. The integration of water scrubbing effectively pre-conditions the gas stream by removing water-soluble components and particulate matter, thereby improving adsorption performance. The findings underscore the efficacy of surface-functionalized zeolites coupled with wet scrubbing as a sustainable and cost-effective solution for VOC control in NR processing plants. This approach not only mitigates air pollution but also aligns with environmental regulations, offering a promising pathway toward cleaner natural rubber manufacturing operations.

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Organo-modification of clay minerals for remediation, and a focus on bentonite-chitosan adsorbents for heavy metals

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Many different materials can be used for the remediation of many different pollutants and from within many different environments, be it for example, air, land or water. An important and vital class of materials used as adsorbents for remediation are clay minerals and to enhance their performance they can be modified, again by using many different chemicals or materials.

The organo-modification of clay minerals can bring several advantages including suspension stability, ease of use and recovery, cost, maintain non-toxicity and most importantly to enhance and maximise adsorption capacity, efficiency or specificity. Understanding the clay minerals behaviour, their surface interactions during and after modification, and their physicochemical properties are critical to designing and optimising performance. Their large surface areas, cation exchange capacity, and edge sites together with the properties of the modifier enable a large arena of numerous factors to consider, control and optimise.

This presentation will in general discuss the above and then as an example focus on recent research [1-2] involving bentonites and the modifier chitosan, a sustainable material with strong and utilisable adsorption properties. Chitosan has the added advantage of having a controllable aqueous solubility in low pH, which can be neutralised to allow precipitation and effective agglomeration of suspended clay minerals. This research specifically concerns the remediation of heavy metals, a worldwide concern due to the severe consequences (sometimes fatal) of high toxic levels on human, animal, marine and plant health.

The results show there needs to be a balance between retaining cation exchangeable sites, since organo-modification at exchangeable sites can render them ineffective, whilst still propping open the interlayer space for ease of access to exchangeable sites. Access to the adsorption sites on the organo-modifier are also important and thus the location of whether within the interlayer space or at external surfaces can become important. These aspects plus others will be considered.

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Development and evaluation of non-expansible pillared Quick Clay for pollutant removal in water

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Wastewater treatment is a major environmental challenge. Natural and modified clays can be effective in removing various contaminants form water. Among clay modification techniques, pillaring enhances specific surface area, acidity, and interlayer spacing, thereby improving adsorption interactions. By selecting appropriate metals to insert in the clay, these techniques also grant catalytic properties to the materials, enabling them to degrade certain persistent contaminants. While well-studied with swelling clays, this approach remains largely unexplored for non-expandable clays such as sensitive clays (SC), a glaciomarine clay made mostly of illite and chlorite.

This study aims to develop and evaluate pillared SC for pollutants removal. The research objectives are: (1) to develop a method for pillaring SC using aluminium and iron polycations; (2) to study the adsorption and trapping of heavy metals (Cu, Cd, La), an endocrine disruptor (estradiol), and a PFAS (PFBS); and (3) to evaluate the catalytic degradation potential of iron-pillared clays.

Pillaring is carried out by adapting a classical method: SCs are pretreated with acid, complexing agent and cation solution to facilitate the intercalation of the metal polycation. The pillared clays are characterized (XRD, ZRF, BET, CEC, zeta potential) and sorption processes are studied. The pillaring, the characterisation and the sorption experiments were also done on montmorillonite for comparison.

Results show that Al-pillared SCs exhibited an 80% increase in interlayer spacing and a 500% increase in specific surface area, reaching values comparable to those of pillared montmorillonite. The Al-pillared SCs maintained strong affinity for metals and showed a threefold increase in estradiol adsorption capacity. Their CEC increased markedly from 11.8 to 71.6 meq·100g^{-1}, whereas pillared montmorillonite exhibited a decrease from 67.5 to 51.9 meq·100g^{-1}. These contrasts highlight the significant influence of the base clay's swelling behavior on the final properties of the pillared material.

Iron-pillared SCs and montmorillonite showed high uptake of iron polycations (95 % and 91 %, respectively). The Fe-pillared SCs removed up to 68 % of Cu and 87 % of Cd, outperforming their montmorillonite counterparts (10 % removal for both metals). These preliminary findings suggest that pillared SCs, particularly with Al and Fe, offer promising potential for removing cationic pollutants such as heavy metals and dyes.

Future work will focus on evaluating the adsorption of organic pollutants, the catalytic degradation potential of iron-pillared SCs, and the stability of the incorporated iron.

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Preparation of calcium-aluminum layered bimetallic hydroxide and study on their adsorption properties for U (VI)

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Layered bimetallic hydroxides (LDHs) consist of positively charged lamellar bodies with interlayer anions [1], and their unique lamellar plate topology endows them with excellent adsorption properties in the field of environmental remediation . For U(VI) adsorption removal, Jingwei Tu et al [3] prepared MgAl-LDHs by co-precipitation-oven-drying method, which demonstrated significant selectivity in low-enriched uranium systems (0.2-5 mg L^{-1}). Further studies showed that the layered bimetallic oxides (LDOs) obtained by high-temperature calcination inherited the nanostructural properties of the precursors and possessed better U(VI) adsorption properties.

Phosphogypsum (PG), as an industrial by-product rich in calcium resources, shows potential application value in the field of uranium-containing wastewater remediation. The oriented synthesis of layered bimetallic hydroxides (LDHs) has attracted much attention, and such materials can not only inherit the advantages of calcium source of PG, but also significantly enhance the selective capture ability of uranium and environmental friendliness. Based on this, this study proposes to use PG as a single calcium source to prepare Calcium-aluminum layered bimetallic hydroxide (CaAl-CO_3-LDHs)for the purification of uranium-containing wastewater. The regulation laws of pH, contact time, initial U(VI) concentration temperature, dosage and competing ions on the adsorption behavior of layered bimetallic hydroxides were systematically investigated. The data were fitted with isothermal adsorption, kinetic and thermodynamic model systems to elucidate the adsorption performance characteristics and mechanism of action, and to evaluate the potential for practical applications.

The adsorption capacity of CaAl-CO_3-LDHs was stabilized above 187.0 mg g^{-1} at pH 3-9 and t=45 min. The maximum adsorption capacity was 1054.73 mg g^{-1} at 45 ° C. Moreover, the adsorption process of CaAl-CO_3-LDHs was dominated by the chemical adsorption in monomolecular layer, and adsorption of U(VI) was a heat absorption and spontaneous process. is a heat-absorbing and spontaneous process.In real uranium-contaminated wastewater, the CaAl-CO_3-LDHs adsorbent could achieve 85.2% U(VI) removal with good recyclability. The adsorption mechanism was explained by spectroscopic characterization, which showed that uranyl ions form C-O-U or M-O-U structures by interacting with C-O and M-O bonds in layered bimetallic hydroxides. This study provides an environmentally friendly synthesis strategy for the development of highly efficient calcium-based adsorbent materials, which is expected to be applied in the field of uranium-containing wastewater treatment, realizing “treating waste with waste” .

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Computational Insights into Styrene Adsorption by Pristine and Modified Smectites

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Clay minerals, known for their high surface area, ion-exchange capacity, and ability to adsorb a wide range of contaminants, are increasingly recognized as effective adsorbents for environmental remediation. Their natural abundance, low cost, and eco-friendly properties make them ideal candidates for addressing widespread chemical pollutants [1]. The focus on developing efficient, sustainable adsorbents for chemical pollutant removal is a critical area of current research. Organoclays, have emerged as robust materials capable of adsorbing both organic and inorganic pollutants, with the potential to trap pollutants in water and soil for environmental remediation [2].

This study investigates the potential of pristine smectites, such as montmorillonite (Mnt) and saponite (Sap), both modified with poly (2-methyl-2-oxazoline) (PMOx), as suitable adsorbents for styrene, a hazardous environmental pollutant [3]. Using the Density Functional Theory (DFT) method with the D3 scheme for correction of dispersion interactions [4], the stability and adsorption behavior of pristine smectite clays (Mnt and Sap) in comparison to modified hybrid clays (Mnt+PMOx and Sap+PMOx) for styrene were examined.

These findings demonstrated the potential of Mnt+PMOx and Sap+PMOx hybrid structures as efficient and eco-friendly materials for styrene removal, contributing to developing sustainable adsorbents and offering promising solutions for the remediation of hazardous contaminants from polluted environments.

Acknowledgments

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Targeting zearalenone and deoxynivalenol: Two distinct mycotoxin elimination strategies using kaolin group-based mineral materials

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While rainfall and warm temperatures support healthy crop yields, high humidity combined with temperatures between 5-25°C create ideal conditions for fungal growth. Some fungi benefit medicine by producing antibiotics and other drugs, but others generate harmful secondary metabolites – mycotoxins. Zearalenone (ZEN) and deoxynivalenol (DON) are among the most frequently detected and often co-occur. Their presence has been reported not only in animal feed but also in various foods and aquatic environments. Their persistence is concerning: ZEN's estrogen-like activity is linked to reproductive disorders, while DON has been associated with brain damage and suppression of anti-apoptotic genes – making their removal a major scientific challenge.

To address this challenge, our primary objective was to develop an efficient strategy for removing ZEN and DON. Photodegradation kinetics was studied under 10 mW/cm^2 UV light, using toxin concentration of 10 ppm and a photocatalyst dosage of 0.75 g/L. To reduce the cost of the process and enhance material performance, 3 mineral supports were selected: a platy kaolinite-rich sample (M), Sigma-Aldrich halloysite (HS), and synthetic calcined kaolinite nanotubes (MNC). Each support was impregnated with 20 wt% of a semiconductor: (i) TiO_2, (ii) g-C_3N_4, or (iii) a 1:1 mixture of both. After 25 min of light exposure, ZEN removal efficiencies reached 98.8% and 97.7% with the MNC-based materials loaded with the g-C_3N_4 and the TiO_2/g-C_3N_4 mixture, respectively. The results indicated the superior performance of the nanotubular-based photocatalysts, as materials containing platy kaolinite exhibited significantly slower degradation kinetics. This finding was supported by the photochemical and photoelectrochemical measurements, which revealed the extended charge carrier lifetimes and the presence of trap states - emphasizing the beneficial role of the nanotubular mineral supports. The UHPLC-ESI-MS/MS analysis enabled the identification of intermediate products, supported by mechanistic studies that indicated $O_2^{\bullet-}$ and •OH radicals as the key species driving ZEN degradation. ECOSAR software confirmed that the resulting lower-mass, simpler compounds generated through photodegradation are less toxic than the parent molecule, as the process led to the cleavage of ZEN's aromatic ring [1].

However, DON was not susceptible to the mentioned approach. Modifying the samples through Ag-doping, reduced graphene oxide impregnation, and testing alternative semiconductors demonstrated that this methodology is not effective for the mineralization of non-polar DON. A change in strategy – introducing potassium peroxymonosulfate (PMS) to generate alternative reactive species, along with the synthesis of supported TiO_2/magnetite composites – yielded satisfactory results, with the MNC-based sample removing 98.7% of 5 ppm DON after 45 min using a material dosage of only 0.25 g/L.

This project was supported by the National Science Centre Poland, under a research project awarded by Decision No. 2021/43/B/ST10/00868.

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Effective removal of lead (II) ions from aqueous solutions using modified waste mica

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Mica deposits are rich in India, with nearly two thirds discarded as waste during the cleaning and processing stages. In this study, modified waste mica was used to remove toxic lead from the liquid environment. Waste mica was nanoconverted and activated using sulphuric acid and intercalated with humic acid and subsequently utilized for lead removal from water. Acid activated waste mica were characterized by elemental analysis, XRD, FTIR, BET, and SEM to evaluate the physicochemical changes due to the acid treatment and humic acid intercalation. Adsorption conditions of pH, contact time and initial metal concentration were optimized for the maximum lead removal by batch incubation experiments with an adsorbent dose 0.1/10 mL solution and initial metal concentration 245 ppm. The results indicated that the prepared nano mica and acid modified waste mica along with humic acid could remove 99.85% and 99.03% of Pb (II) respectively, at pH 8 with a contact time of 4 hours at 25°C. According to the findings, the nanoconverted waste mica and acid modified waste mica along with humic acid intercalation are suitable and recyclable sorbents for lead adsorption from aqueous solutions. It is interesting to note that the regeneration capacity of the waste mica improved through a combination of acid treatment and subsequent humic acid (HA) modification.

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Use of layered double hydroxides (LDHs) for short chain PFAS removal in water treatment: impact of structure and surface properties

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Perfluoro alkyl substances (PFAS) are present in a wide range of products: manufacture of Teflon, aqueous firefighting foams, paint or adhesives [1]. They form a class of compounds of increasing concern due to their persistence and are even labelled as “forever chemicals”. Moreover, the toxicity of short chain PFAS is demonstrated and well documented and they are bioaccumulable in drinking water[2,3]. Conventional solutions for their removal like activated carbon or ionic resins show limited efficiency versus short chain PFAS, i.e. substances presenting a carbon chain length of 7 atoms or less [4].

This article deals with the use of layered double hydroxides (LDHs) as mineral adsorbents for PFAS removal in drinkable water. These layered structures are seen as promising materials regarding short chain molecules adsorption as they are more hydrophilic than their long chain counterparts which shows good affinity with activated carbon. The PFAS adsorption was tested in potable water and the specificity of this study was that competitive adsorption between 20 PFAS molecules with short and long chains was considered. The adsorption capacity was measured vs. activated carbon by Liquid chromatography – Mass Spectrometry (LC-MS).

The tested PFAS molecules comprise sulfonic and carboxylic acids groups. Therefore, they exhibit a hydrophilic head and a hydrophobic tail. In order to address the adsorption of such compounds, two key parameters of the LDHs were tested, namely their charge density and a hydrophobic functionalisation. ZnAl-CO_3 LDHs with different ratios Zn:Al ratios of 2, 3 and 4 were synthesized to achieve different surface charges and then calcined to maximise the adsorption properties [5]. The resulting products were characterized by XRD, FTIR and SEM, which shows that a high purity LDH was obtained, with carbonate anions intercalated in the interlayer. It was shown that the lower the surface charge, the higher the PFAS adsorption, as a total PFAS adsorption of 6.2 µg/g was achieved for a Zn:Al ratio of 2:1, while no adsorption was measured for a Zn:Al ratio of 4:1. On the other hand, the hydrophobicity of the ZnAl-CO_3 LDH was enhanced by surface treatment with 1H,1H,2H,2H perfluorooctyltriethoxysilane called “SiCF”[4]. The adsorption capacity was increased up to 8.0 µg/g using a hydrophobizing agent. In both cases, PFSA were better removed than PFCA. Comparing these results, it seems that hydrophobic interactions are predominant even on short chains PFAS.

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Rapid removal of chromium (VI) and diuron from aqueous solution by novel Sepiolite-based nanocomposite: Material characterizations, enhanced performance and mechanism

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The novel magnetic Sepiolite/Fe_3O_4/nZVI nanocomposite (nZVI@SepH-Mag) and sepiolite-supported Fe_3O_4 magnetite (SepMag) composite were prepared and used to achieve the removal of contaminant (Cr (VI) and diuron). For nZVI@SepH-Mag, this composites were characterized by XRD, FTIR, BET, SEM and TEM. The characterization results indicated that the structure of the composite consisted of small nanoscale zero-valent iron (nZVI) and magnetite (Mag) particles uniformly anchoring on the surface of acid-activated sepiolite (SepH). Batch experiments were used to analyze the effects of main factors on Cr (VI) removal. A 100 % removal efficiency in 60 min and enhanced reaction ratio was reached by the composite comparing other existing materials. The kinetic of the adsorption and possible Cr (VI) removal mechanism of the hybrids were also evaluated and proposed. Based on the removal products identified by Raman, XRD and XPS, a reduction mechanism was proposed. The results indicated that the SepH and Mag can inhibit the agglomeration and enhance the dispersibility of nZVI, and Mag and nZVI displayed good synergetic effects[1]. For SepMag, this composite was prepared for diuron degradation. The samples were characterized by XRD, XRF, FTIR, BET, SEM and TEM. The chemical state of Fe in SepMag composite before and after degradation experiments was characterized by XPS. The enhanced degradation efficiency for diuron was attributed to the effective generation of hydroxyl radical in ultrasound/SepMag/H_2O_2 system. The degradation rate of diuron depended upon the composite amount, hydrogen peroxide dosage, initial pH of solution and temperature. The degradation reaction was also optimized by changing the ultrasound intensity and Fe_3O_4 content in the composites. Moreover, mineralization and degradation pathway were evaluated on the basis of total organic carbon and liquid chromatography mass spectrometry. It was confirmed that with the assistance of ultrasound treatment SepMag composite has potential advantages for the removal of diuron from aqueous solution[2].

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LECTURE THEATRE 4 – SESSION 35

The Role of Clays in Human Health and Biomedical Sciences

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Modification of clay minerals for biomedical applications

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Nanotechnology, and thus nanomedicine, are important tools for the development of innovative treatments for biomedical applications. Up to now, different nanomaterials have been successful used as carrier systems for a series of biologically active species for applications ranging from cancer treatment, bioimaging or personalized medicine.

Among them, clay minerals are emerging nanomaterials for application in this field. Being natural and biocompatible, with an innate capacity to be internalized by cells via endocytosis [1], clay minerals have been used as carrier systems for several hydrophobic species which benefit in terms of enhanced availability in physiological conditions, sustained release and promising biological activity [2,3].

Modification of clay minerals surfaces, both supramolecular and covalent, represents an important synthetic tool to enhance clay minerals properties, expanding their application fields [4].

Herein, last examples of modification of halloysite nanotubes, a clay mineral belonging to the kaolin group, and hectorite, belonging to smectite group, are reported and discussed.

The advantage of covalent modification over the supramolecular one will be presented and discussed in terms of physico-chemical, morphological and kinetic release features. Application in cancer treatment, theranostic, food packaging and as antibacterial agents will be also shown, highlighting the potentiality of the proposed chemical approaches.

Acknowledgments: This work was supported by National Recovery and Resilience Plan (NRRP), funded by the European Union– Next Generation EU-DD 1409 Progetti di Rilevante Interesse Nazionale (PRIN) 2022 PNRR published on 14-09-2022 by the italian MUR, Missione 4 (Istruzione e Ricerca) Component 2, Investment 1.1. Project Title: Small Molecule Anticancer Ligands Library from mediterranean plants (SMALL)– CUPB53D23025910001.–Code P2022YJZ5F. Authors are thankful for the support offered by the Spanish Project PID2022-137603013-100 (Ministerio de Ciencia, Innovación y Universidades).

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Halloysite nanotube-based shuttle for intracellular transport of Peptide Nucleic Acids (PNAs) in Gene Therapy

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Peptide nucleic acids (PNAs) have gained significant attention in recent years as promising molecules for gene therapy [1]. As synthetic DNA analogs, PNAs offer distinct advantages over traditional oligonucleotides (ONs). Due to their remarkable binding affinity for complementary DNA or RNA, combined with high thermal and chemical stability, PNAs represent one of the most promising and versatile classes of therapeutic agents both in antigene and antisense strategy. In antigene approach PNAs block gene expression or alter gene splicing. They act as G-quadruplex binders and triplex-forming agents [2], effectively targeting the duplex DNA. In antisense strategy PNAs are involved in steric blocking of RNA, inhibiting miRNA and mRNA. When hybridized to complementary mRNA, they can induce translation arrest by obstructing the ribosome, block peptide elongation upon binding the transcript, or interact at splicing sites to alter splice variant production.

Despite these promising applications, the use of PNAs is hindered by two major challenges: low solubility and limited ability to cross cell membranes. To address these limitations, we have modified PNAs and conjugated them to various carriers that enhance the delivery and efficacy of the molecules. Numerous platforms we exploited and investigated for PNA delivery, such as polymeric nanoparticles [3], inorganic diatomites [4], oncolytic adenoviral vectors [5,6], Ferritin protein and Halloysite nanotubes (HNTs) [7], whose surfaces can be modified to accomplish targeted delivery and improve the therapeutic effectiveness of potential PNA-based drugs. Among the wide plethora of PNA carriers, HNTs have proven to be an ideal candidate for delivering genetic materials into cells due to their peculiar properties [8]. HNTs are natural, low-cost aluminosilicate clay with a unique ability to cross cellular membranes.

Biocompatible and eco-friendly delivery techniques provide stability, protection, and controlled release allowing for effective absorption and prolonged circulation and have promising medicinal applications that ensure patient safety and environmental friendliness. By leveraging HNTs as delivery vehicles, we aimed to overcome the barriers to PNA effectiveness and enhance their therapeutic potential. This research field seeks to explore and harness the unique properties of PNAs to develop innovative tools that have the potential to revolutionize the field of biomedical engineering.

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The Influence of Clay Pores Volume and Surface Charge on Isoniazid Adsorption and Release

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Due to their unique physical and chemical properties, clays have applications across various fields, including the pharmaceutical industry, which has increasingly explored their potential. The use of clay to enhance animal and human health dates back to ancient times. However, it was only in the mid-20th century that the interactions between clay and drugs began to be systematically studied [1]. Key characteristics such as swelling capacity, cation exchange capacity (CEC), physical structure, chemical composition, porosity, and surface charge significantly influence the interaction between clay particles and organic molecules [2]. Considering these factors, an essential question arises: What is the most suitable clay for applications in drug delivery systems? To address this question, seven smectite clays were studied to evaluate how their characteristics affect the adsorption and release of isoniazid (INH). Isoniazid, a crucial drug for treating all forms of tuberculosis, exhibits chemical properties that allow it to remain neutral (at $4 < pH < 9$) or positively charged (at $pH < 4$). Drug adsorption experiments were conducted under neutral and cationic conditions, while drug release was simulated to mimic oral drug delivery. Clay characteristics, including pore volume, surface charge, mineralogy, and chemical composition were analyzed. Additionally, clay-drug hybrids were characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and cytotoxicity assays. In its neutral state, the adsorption of isoniazid was primarily influenced by the mesoporous structure and clay pore volume [3]. Under cationic conditions, clays with lower surface charge demonstrated stronger interactions with the drug, resulting in higher adsorption capacities and reduced drug release in the stomach acidic environment. Furthermore, the quantity of drug adsorbed in the neutral state impacted the release profile, offering enhanced protection in the stomach environment when the drug was adsorbed at the clay's monolayer capacity. Notably, the adsorption of isoniazid under acidic conditions aligned with the dosage of INH tablets (100 mg). The cytotoxicity assays showed that clays and clay-INH hybrids can be considered safe for drug intake applications. This study concludes that while various clays exhibit potential for isoniazid adsorption, future research should identify clays with lower surface charges at pH 2 to further enhance drug adsorption. Additionally, reducing drug release in the acidic stomach environment could improve its bioavailability in the intestine, where absorption occurs. This would increase drug efficacy against tuberculosis, minimize side effects, and ultimately enhance patients' quality of life.

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Exploring Halloysite Nanomaterials for potential theranostic applications

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Theranostics combines diagnosis and therapy in a single platform, improving treatment and disease management. Fluorescence bioimaging is widely used for its non-invasive nature and sensitivity as a diagnostic technique [1], but many organic chromophores have low water solubility, limiting their use. [2] To overcome this problem, carriers have been developed to enhance solubility and fluorescence at target sites. [3] Particularly, the use of nanomaterials in theranostic has garnered significant interest, and among the emerging materials, halloysite nanotubes (HNTs) are gaining attention as a promising candidate for potential theranostic applications. HNTs hold great potential as carriers for biomedical applications. [4] Over the years, different chemical modifications of HNTs surfaces have been adopted obtaining promising nanomaterials for the delivery of active species for different types of therapeutic effects. [5] Herein we explore the potential use of halloysite as a nanomaterial for potential theranostic application such as chemodynamic therapy, and sensing. Specifically, we present the synthesis and characterization of various halloysite-based systems incorporating different fluorescent probes, highlighting their photophysical properties, morphology features, and results from chemical experiments designed to evaluate their potential as theranostic nanomaterials.

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A Perspective of Halloysite and Carbon Dots-Based Nanomaterials

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Halloysite is a natural clay mineral characterized by a mainly hollow, tubular structure (HNTs). Due to their high mechanical strength and excellent biocompatibility, HNTs are considered a versatile core material for creating functional nanosystems with potential applications in both technology and nanomedicine. Recent studies have shown that modifying halloysite with fluorescent molecules can enhance the physicochemical properties of both the HNTs and the attached chromophores.[1]

In particular, the direct synthesis of Carbon Dots (CDs) on the outer surface of HNTs, utilizing the formation of covalent bonds, leads to the formation of photoluminescent nanomaterials (HNTs-CDs) with unique chemical and photo-physical properties that can be exploited in various fields of application. [2-4]

In this work reports the synthesis and characterization of HNTs-CDs nanomaterials, obtained through the use of different sources of carbon and nitrogen, and their various applications based on their distinct properties. Specifically, these have been used as biological sensors for the detection of Fe(III), and finally, as fillers for the reinforcement of natural polymer materials, in order to obtain protective films useful for food packaging.

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Development of a nanoemulgel system based on Opuntia ficus-indica seed oil and nanoclays: a promising approach for skin biocompatibility and antimicrobial performance

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Developing biofunctional topical systems for wound treatment is a growing field, especially in chronic lesions where inflammation, bacterial colonization, and oxidative imbalance hinder tissue repair. This study developed and characterized a clay-based nanoemulgel (NE) system incorporating Opuntia ficus-indica (OFI) seed oil, focusing on its biological performance. OFI seed oil is known to be rich in linoleic and oleic acids, sterols, and phenolics with antioxidant and antimicrobial properties [1]. Specifically, linoleic acid can modulate inflammation and promote angiogenesis at the wound site [2]. The nanoemulgel was composed of a stable oil-in-water nanoemulsion using Tween® 80 as an emulsifier and various clays (Laponite® XLG, Pangel S9®, Cimsil G30®, Veegum® HS) to enhance viscosity and release. Nanoemulsification improved the bioavailability and dermal penetration of the highly lipophilic OFI oil, allowing for more efficient application and reduced irritancy [3]. The optimized formulation containing 3% w/w Laponite® (NE_Lap 3%) exhibited superior biocompatibility and biological efficacy. Biological evaluation using the Dermal Irritection® assay confirmed its classification as non-irritant, while antimicrobial assays demonstrated selective activity against Gram-positive bacteria such as *Staphylococcus aureus*, *Streptococcus pyogenes*, and *Propionibacterium acnes*, which are common in wound infections and skin disorders [4]. The raw OFI oil alone showed no inhibitory activity, emphasizing the role of the formulation in facilitating diffusion through the aqueous environment and bacterial membranes [5]. These findings highlight the synergy between OFI oil and clays in a nanostructured carrier and reinforce pharmaceutical technology's importance in unlocking the therapeutic potential of natural lipophilic compounds. This system is a strong candidate for chronic wound healing and other dermatological applications.

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Surface Characteristics of Geologically Ancient Occluded Quartz from Bentonite and Their Toxicological Implications: A Case of Guilt by Association?

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Crystalline silica in the form of quartz is one of the most common minerals on the surface of the earth. It has long been known that exposure to respirable size particles of quartz, especially those generated by industrial activity, cause human respiratory disease. In 1997, IARC declared respirable crystalline silica to be a Group 1 carcinogen, the highest level IARC assigns [1]. This decision was based primarily upon animal research, published between 1987 and 1997, that used freshly crushed quartz, especially Min-U-Sil or DQ12. IARC did state that "… Carcinogenicity in humans was not found in all industrial circumstances…" and that "Carcinogenicity may be dependent on … external factors affecting its biological activity …" Previous researchers have shown that the presence of other minerals, including aluminum containing clays, reduces quartz toxicity [2][3]. Our research has shown that the chemical, mineralogical and morphological characteristics of geologically ancient (95-100 Ma) quartz isolated from four geographically separated and stratigraphically distinct Wyoming bentonites (Quartz Isolates) fundamentally differ from that of other types of quartz. Quartz Isolate particles ubiquitously consist of a core of one or more domains of crystalline silicon dioxide that are completely occluded by a layer of aluminosilicate. In all cases, the transition from the aluminosilicate particle surface to the silicon dioxide core domains occurs abruptly at an atomic level. Research has shown that the aluminosilicate surface is not removed by 90-day exposure to rat lung fluids, dispersant chemicals, acids or industrial mechanical milling [4][5]. This, coupled with the authigenic origin of these particles, strongly suggests that the aluminosilicate surface is an intrinsic part of quartz particles from Wyoming bentonites. This differentiates this type of quartz from other types of naturally occurring quartz and, particularly, from the type of crushed quartz used in animal testing as a surrogate for industrially generated respirable quartz that is a human health hazard. Research over the past 50 years to define the causative agent for the hazard posed by industrially generated, respirable quartz has focused on the surface characteristics of the quartz particles and their ability to cause long lasting, progressive inflammation in the lung. It has been widely recognized that a variety of materials, when applied to freshly fractured quartz particles, can act to significantly reduce their inflammatory potential. Recently Pavan, et al [6] have documented the presence of a new class of moieties on the surfaces of fractured quartz particles they call nearly free silanols (NFS). They have determined that NFS are responsible for the inflammatory effect that leads to lung disease. Creutzenberg et al [7] have shown that Quartz Isolate has a very different, and significantly reduced, inflammatory time progression profile compared to DQ12. Nevertheless, all quartz is currently regulated in the U.S. as single material for health purposes. The nature of Quartz Isolate from Wyoming bentonites, coupled with its distinctly different inflammatory potential, calls into question whether this unique type of quartz should be regulated in the same fashion as industrially generated freshly fractured quartz or, if it should be evaluated and regulated as a distinctly different material.

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Clays in Epoxy composites: a new tool against healthcare associated infections

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Healthcare associated infections (HAIs) represent the most frequent and serious complication of healthcare occurring in different types of care settings. In the last decades, much scientific evidence has been collected regarding the role played by inanimate surfaces in the transmission of nosocomial pathogens with particular attention to High Touch Surfaces, HTSs. To prevent and control the microbiological contamination on HTSs different technologies (UV devices, cold plasma technology, etc.) have been developed as alternatives to conventional cleaning. More recently, self-disinfecting surfaces with incorporated antimicrobial substances have been proposed. Epoxy resins have long been recognized as versatile materials with widespread applications due to their exceptional mechanical properties, ease of processing and tunable chemical properties that make them particularly suitable for preparing composites exhibiting improved characteristics, such as antimicrobial activity by integration with antimicrobial functionalities [1]. Modified clays, which in principle could address the problem of antibiotic resistance, too, have been considered [2]. First, two commercial epoxy resins 1(EC157/W152LR) and 2(MGS/RIMH235) which are the starting materials for realization of multifunctional nanocomposites, have been investigated in vitro to ascertain their antimicrobial activity [3]. Then, nanocomposites based on resins 1 and 2 have been prepared by addition of different amounts of Cloisite 15A(C15A), an organo-modified clay with an ammonium salt bearing different aliphatic chains (65%C18, 30%C16 e 5%C14) to promote compatibilization between the polymer and the clay [4]. Preliminary results showed that composites based on resin 2 and different percentage (5%, 8% and 10%) of C15A demonstrated a high antibacterial activity (R value >4 Log) against S.aureus ATCC 6538 within a contact time of 24 h. Antiviral activity was also observed for the composites either when the virus suspensions were put in contact with the resins and when they were exposed to buffer solutions in which the resins had been incubated. Against Human coronavirus-OC43, a virus infectivity reduction (>4 Log) was observed with composites containing 5% of C15A at 24h with both protocols; a modest antiviral effect (about 1 Log) was however also observed for the nanocomposites with 1 and 3% of C15A. All the nanocomposites proved to be more active than resin 2 as it is. Under the same experimental conditions Herpes Simplex Virus-1 showed a lower sensitivity (approximately 2 log reduction) and only for nanocomposite with 5% of C15A. It is to note that resin 2 shows a more marked antiviral activity compared to the nanocomposite. No significant reduction of Adenovirus-5 infectivity was observed in any condition tested.

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Photoactive Clay/Polymer Nanocomposite Surfaces: A Promising Strategy for Combatting Pathogenic Biofilms

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Clay-polymer nanocomposites represent a promising class of materials with various potential applications, including biomedicine. A key challenge in the development of bioactive polymer composites is to ensure that the bioactive components remain accessible at the polymer surface.

In this study, an innovative strategy for the preparation of antimicrobial polymer surfaces is presented in which thin layers of organically modified saponite (Sap) containing a bioactive photosensitizer are fused with liquid polymer precursors [1] or melts [2], resulting in nanocomposite films that are only a few micrometers thick [2]. These surfaces contain photosensitizers (PS) such as phloxin B [1,2] and erythrosin B [3] in high concentrations, which enable photodynamic inactivation (PDI) of bacterial biofilms. The structural characterization confirmed that the intercalation of the polymer into the organoclay films ensures strong bonding between the polymer and the films without significantly altering the properties of the polymer bulk [2]. When irradiated with a green LED lamp or laser, the materials effectively killed *Staphylococcus aureus* biofilms and achieved up to a 10,000-fold reduction in bacterial growth [3].

The antimicrobial efficacy was primarily determined by the presence of PS molecules and reactive oxygen species induced by irradiation and also bioactive surfactants in the organoclays. Efficacy was not influenced by the expression of efflux transporters nor the ability to form a robust biofilm by bacteria. This is an important result indicating that the material is effective against *S. aureus* strains regardless of their resistance or virulence factors [4].

The results underline the potential of photoactive nanocomposite surfaces for biomedical applications, especially for the modification of medical devices to prevent biofilm formation.

This work was supported by the Slovak Research and Development Agency under contract No. APVV-22-0150 and APVV-21-0302. Support from the VEGA grant agency 1/0484/24 is also gratefully acknowledged.

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Study of anti pathogens activity of zeolite, activated by silver ions (Ag^+)

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In modern sciences and technology it has started a new era of technology, in which the nano-dimensional particles are interconnected, arranged, and nano-structured products are created. Based on this technology, the activation of natural zeolites with silver ions has been shown to be important in removing a heavy metals and toxic gases from animals body, increasing the activity of gastrointestinal enzymes, destroying intestinal pathogens, and reducing the properties of antibiotic-resistant microorganisms [1,5]. Therefore, based on the results of obtained by the international scientists and researchers, as well as on our previous studies, we have identified its antimicrobial activity by activating silver ions based on the natural zeolite ion exchange capacity of the Tsagaantsav deposit in Mongolia.

Purified zeolite from the Tsagaantsav deposit was used in the experimental. Separation of minerals and clays from zeolite was carried out in accordance with ER2001-0148 (updated by David Vaniman). Activation of purified zeolite with silver ions was carried out in three scenario using the methodology of Yi Zhang and Sheingland Zhong (2008). Intestinal pathogens *E.Coli* 29 and *Salmonella*-0068, certified in the Veterinary drug testing and certification laboratory, and pure chemical reagents manufactured by *Sigma*-Aldrich and *SCIENCE* were used.

Results of the installation of silver ions in zeolite show that, 325.02 mg/kg of silver ions were determined in the third scenario, while 249.3 mg/kg in the second. The displacements of Na^+, K^+, Ca^{2+}, and Mg^{2+} cations are shown in table 2, where the Na^+ displacement is the highest in the scenario 2. In other words, Ag^+ is replaced by Na^+ and placed in a hollow channel, so its volume is reduced. In the Scenario 3, the Ag^+ content is highest, but the Na^+ migration is low, possibly due to the presence of Ag^+ on the surface of the zeolite molecule.

Experimental test results show that zeolite activated with silver ion inhibits the growth of *E.coli*-29 and *Salmonella*-0068 strains by 98-100%. However, in the group of negative control or pathogenic strains grown alone, it was not possible to count the colonies at 10^1 - 10^3 dilutions, *E.Coli*-29 2*10^8 - 11*10^6 CFU/mL at 10^4-10^6 dilutions, and *Salmonella*-0068 at 6*10^8 - 23*10^6 CFU/mL. In groups using positive controls or purified zeolites and silver ions, no pathogens grew at 10^1 dilutions, and colonies could not be counted at subsequent dilutions.

Thus, silver-activated zeolite has the potential possibility to replace antibiotics against pathogenic bacteria. It is also more likely to be effective when it used in combination with antibiotic-resistant antibiotics.

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Geophagy and cultural practices among the Businenge of western Guyana: a physico-chemical and mineralogical characterization of ingested *pemba* clays

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The consumption of white clay, locally known as *njang pemba*, among the Businenge communities of western Guyana is a well-documented practice within both the medical field and local society. However, it remains poorly understood in its full cultural complexity and is currently subject to controversy. Pemba are theoretically handmade balls composed of white clay. Their use is predominantly associated with women and is often linked to pregnancy, thereby being categorized medically under *pica*, a pathological eating behavior.

Nonetheless, oral consumption of *pemba* cannot be entirely reduced to a clinical framework. It appears to be intricately connected with (i) adaptive behaviors such as geophagy, interpreted as an appetite suppressant or as a protective response to plant toxins, parasites, and other pathogens, often in contexts of food insecurity; and (ii) symbolic practices, deeply rooted in ancestral spiritual traditions and the cultural territories shaped by marronage. From a strictly health-related perspective, ingestion of *pemba* poses potential risks, particularly those associated with the intake of metals and metalloids.

This study aims to enhance understanding of geophagic practices through a detailed physicochemical and mineralogical characterization of 15 clay samples of *pemba*, each representing distinct local uses. The goal is to explore potential links between the mineralogical forms of these materials and the bioaccessibility of elements such as Al, Fe, As, Pb, Ni, V, Zn, and Cr.

The samples underwent comprehensive mineralogical analysis (X-ray diffraction - XRD; Fourier-transform infrared spectroscopy - FTIR), chemical analysis for major and trace elements (X-ray fluorescence - XRF), and solid speciation via X-ray absorption spectroscopy (XAS) at the SOLEIL synchrotron facility (France). Al speciation was assessed at the K-edge (E_o = 1.559 keV) using the LUCIA beamline, while V K-edge (E_o = 5.465 keV) and As K-edge (E_o = 11.875 keV) were examined on the DIFFABS beamline. Granulometric analyses confirmed a predominantly clay-sized fraction in all samples. The chemical and mineralogical (qXRD) data consistently reveal that *pemba* clays are primarily composed of kaolinite, with minor occurrences of halloysite in certain samples. This finding is particularly notable given that local populations rely solely on empirical knowledge to identify and use these materials. Variations in kaolinite crystallinity corroborated by Al K-edge XANES spectra.

Regarding trace element content, the average concentrations were relatively low such as 150 mg/kg for Cr, 151 mg/kg for V, 50 mg/kg for Zn, 43 mg/kg for Pb. Nevertheless, XAS investigations revealed distinct speciation patterns, particularly for Pb, V and As. Bioaccessibility assessments, conducted according to BARGE (in vitro gastric and gastrointestinal) protocols, demonstrated low bioaccessibility for all measured elements. Among them, Al showed the highest bioaccessible fraction, followed by Fe and Zn.

A final discussion will explore the relationships between mineralogical speciation and bioaccessibility, contributing to a better understanding of both the potential health impacts and the cultural dimensions of *pemba* consumption.

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Covalent functionalisation of natural clays for environment remediation

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Water scarcity is causing growing concern worldwide posing serious risks for human health and environment quality. Remediation of polluted water represents a valuable strategy to reduce water consumption [1]. To this aim, a number of remediation strategies have been explored [2]. The most commonly used water purification systems involve expensive, energy-demanding plants. For this reason, alternative wastewater remediation methods are highly required. A barely explored, versatile alternative, which is gaining growing interest, is the use of natural-derived clay minerals as low-cost, eco-compatible functional platforms for the development of hybrid efficient remediation systems [3,4].

In this context we present the synthesis and application of new covalently functionalised Sepiolite derivatives, decorated with different 1,8-naphthalimide moieties, able to perform adsorption and degradation of model pollutants in water by using visible light irradiation. The synthetic approach of the new hybrid photocatalysts is reported comparing traditional and microwave assisted syntheses. The complete chemical and morphological characterization of the new obtained nano-systems were performed by means of thermogravimetric analysis, dynamic light scattering and Z-potential measurements, transmission and scanning electron microscopies (TEM and SEM) coupled with EDX. While the optical properties were evaluated by using UV-Vis and Fluorescence spectroscopies. Photocatalytic activity of each new photocatalyst towards several organic pollutants was evaluated in water using visible light source. Moreover, the photodegradation by-products were studied by means of ESI-MS spectrometry. Remarkable abatement performance towards organic pollutants in water were observed for the new remediation nano-platforms, demonstrating also 8-cycle reusability without performance loss.

Acknowledgement: This work was supported by European Union (NextGeneration EU)-MUR-PNRR project SAMOTHRACE (ECS00000022)

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LECTURE THEATRE 5 – SESSION 6

Origin and Age of Clay Minerals in Soil and Sediment

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Reconstructing kaolinite formation conditions and ages in lateritic profiles from central Amazonia: Insights from EPR Spectroscopy

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Lateritic profiles were formed during ancient periods and thus serve as key archives of landscape evolution and past environmental and climatic conditions. Kaolinite, a dominant clay mineral in these weathering systems, provides valuable insights into the timing and mechanisms of weathering processes through its crystal chemistry parameters such as the degree of crystalline disorder, the content of structural trivalent iron, and the concentration of radiation-induced defects used as geochronometers [1][2].

In this study, we examined a lateritic profile developed on Proterozoic sandstones in the Presidente Figueiredo region (Central Amazonia, Brazil), using electron paramagnetic resonance (EPR) spectroscopy and geochemical analysis to identify and date multiple generations of kaolinite. This approach allowed us to distinguish two distinct kaolinite populations within the profile. The first group consists of kaolinites from the saprolite zone, which are well-crystallized and iron-poor (~400 ppm Fe^{3+}), with EPR ages decreasing from 25 ± 7.5 Ma to 1.6 ± 0.5 Ma downward. These values suggest sustained formation at a stable weathering front, likely supported by lateral water flow and a relatively long residence time above the impervious sandstone and under the duricrust. In contrast, kaolinites from the upper horizons and mottled zone exhibit higher Fe^{3+} content (*circa* 800 ppm) and much higher structural disorder, with upward rejuvenation from 41.7 ± 12.5 Ma to Quaternary ages at the topsoil, indicative of episodic reworking and rapid weathering events. Kaolinites encapsulated within two levels of the duricrust yield ages (~34 Ma and ~8 Ma), consistent with major paleoenvironmental transitions previously reported in the region [1,2].

Our study builds upon recent methodological advancements in EPR dating of kaolinite [2, 3, 4], applying these developments to reconstruct the multi-phase evolution of lateritic profiles in Amazonia over geological time. This work further demonstrates the reliability of EPR—kaolinite geochronology as a powerful tool for decoding long-term tropical weathering dynamics and relating them to paleoclimatic and geodynamic forcing.

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Dating the polytypes of illite to decipher the successive hydrothermal events leading to uranium mineralization in the Athabasca basin, Canada

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In the Athabasca Basin, uranium deposits are spatially associated with structural trends between the unconformity and alteration structures (faults) that are likely the main conductor of hydrothermal fluids [1]. The observation of the spatial distribution of those alteration structures indicates that multiple hydrothermal episodes were active since 1.7 billion years. The mineralogy of those alteration halos and their timing are not well defined, limiting our understanding of the geological processes leading to the formation of high-grade unconformity-related uranium deposit.

Because the clay fraction could contain multiple generations of minerals, the dating of illite (K-rich clay) is performed on separated size fraction using the K-Ar method [2]. As each fraction could contain multiple illite generations, individual ages have little geological meaning. Assuming that the clay assemblage contains a mixture of only two illite populations, the set of individual dates can be extrapolated to determine two end-member dates reflecting the oldest and youngest geological events [3]. This method requires the quantification of the proportion of the two populations of illite so to evaluate the dates at 0% and 100% of one population (100% and 0% of the other).

Assuming that the populations of illite differ in polytype, their quantification relies on XRD analyses performed on each clay fraction. Literature often describes $2M_1$ (detrital) co-existing with 1M (authigenic) polytype of illite but in the proterozoic basin of the Athabasca, mixtures of only cv-1M and tv-1M authigenic polytypes are identified. This unique feature marks the complexity of the clay mineral assemblage in proterozoic basin, challenging the treatment of XRD data towards innovating modeling of the diffractograms. Two quantification methods are evaluated, both relying on the extensive work of Drits *et al.* [4]. The first relies on Rietveld modelling and the second on the comparison of the XRD diffractograms with patterns modeled by the Wildfire© software.

The proportion of tv- and cv-1M being quantified, the set of individual dates can be extrapolated at 100% cv-1M and 100% tv-1M. Two distinct dates are determined (no overlap of the uncertainties), the oldest being attributed to the cv-1M, in agreement with Drits *et al.* [4] who assumes the cv-1M more stable than tv-1M. The two dates agree reasonably well with literature data on the timing of uranium mineralization and fluid circulation in the Athabasca basin, validating the quantification method on the polytype of illite.

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Soil clay minerals on Byers Peninsula (South Shetland Islands, Antarctica) "R.A. Howie Memorial Lecture"

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Byers Peninsula, on Livingston Island, is the most extensive ice-free area in the South Shetland Islands. The peninsula is a hotspot for fauna and flora where soils are slow to develop due to the harsh conditions. In this work, clay minerals of 11 soil profiles were studied by X-Ray Diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FTIR), with the aim to compare soil clay minerals formed on different geomorphological contexts and parent material for identifying processes involved in their formation. The samples were obtained from: a) zone I, in the southwestern sector, where soils are formed over detrital sedimentary rocks on Holocene raised beaches at 6 m a.s.l. (SP1, SP5 and SP11); debris slope at 12 m a.s.l. (SP9); middle platforms at 34 and 36 m a.s.l. (SP6 and SP8) and upper platforms at 69 and 76 m a.s.l. (SP2 and SP10); and b) zone II, in the eastern sector on the upper platform from 71 to 88 m a.s.l. (SP3, SP4 and SP7) developed over volcanoclastic rocks and close to the Rotch Dome Glacier.

XRD analyses show in zone I that clay minerals exhibit significant variations. The three soils on raised beaches contain mainly smectite and chlorite; the one on debris slope has smectite, kaolinite and mica; those on the middle platform are both mostly constituted of smectite; whereas both on the upper platform present smectite, chlorite and corrensite. FTIR analyses, however, indicate differences between both soil clays on the middle platform (Fig. 1a). SP6 has absorption bands typical of dioctahedral smectite (3626, 1030 and 915 cm^{-1}), but SP8 shows bands at 3420, 1006, 742 and 680 cm^{-1}, which could be attributed to vermiculite. Furthermore, SP2 and SP10, from the upper platform, show absorption bands attributed to Mg-rich chlorite (3560, 3420, 1090, 760 and 650 cm^{-1}). In zone II, the clay minerals in SP3, the soil nearest to the glacier, are chlorite and scarce vermiculite, whereas SP4 and SP7 contain chlorite and smectite. The latter soil, the furthest from the glacier, consists mainly of smectite. FTIR spectra show that the two soils closest to the glacier have absorption bands characteristic of Mg-rich chlorite, while SP7 shows dioctahedral smectite bands (Fig. 1b). The differences in clay mineralogical composition indicate that the soil furthest from the glacier is more developed and is most likely related to a different lithology of the bedrock and of the surface sediments like till material.

The XRD and FTIR analyses have provided useful information on the chemical and mineralogical composition of the clay minerals. The combination of these techniques has revealed a wide variety of clay minerals in the soils, which are related to the parent material as well as the geomorphological history, specially that related to the glacial retreat.

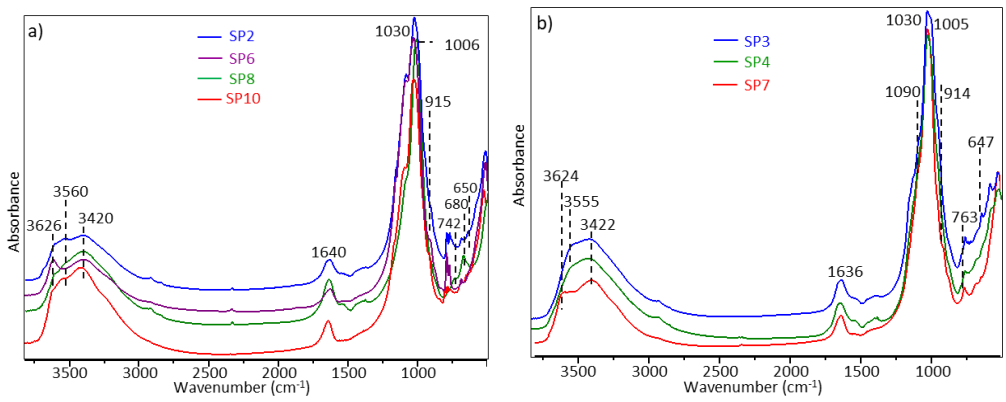

Fig.1. FTIR spectra of soils from: a) zone I and b) zone II.

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Evidence of massive authigenic kaolinite proportions in Early Cretaceous silico-clastic deposits: the impact of marine weathering on paleoclimate interpretation

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The Early Cretaceous is characterized by major climatic and geodynamic variations [1, 2]. This period records intense volcanic activity associated with the formation of oceanic crust, such as the opening of the Atlantic Ocean. The destabilization of oceanic margins, coupled with sea-surface temperatures rise, led to considerable weathering of continental borders and the accumulation of thick silico-clastic sediments in marine sedimentary basins. Numerous mineralogical analyses, conducted on these sediments in the 1980s, concluded that clay mineral assemblages were rich (i) in primary clays (chlorites and illites) resulting from the dismantling of oceanic margins, and (ii) in kaolinites formed by the development of well-drained soils on slopes.

These observations are intriguing because the strong correlation between the proportions of primary clay minerals and kaolinites indicates contrasting weathering conditions. These two different stages of weathering appear difficult to observe within the same assemblages, especially because primary clays, particularly chlorites, are poorly resistant to the strong hydrolysis conditions required for kaolinite formation [3]. New investigations on oceanic boreholes 361 (Cape Basin, South Africa), 364 (Angola Continental Margin), and 959 (Ivory Coast Margin) of International Ocean Discovery Program (IODP) reveal high proportions of authigenic kaolinites in the coarsest deposits. These vermicular clay minerals often fill porosity in sandstones during early diagenesis [4]. Although authigenic kaolinites may derive from the recrystallization of smaller detrital kaolinites, they mainly result from the degradation of K-feldspars [4, 5]. These authigenic clays form by the interaction between primary minerals and acidic fluids arising from the compaction of organic matter in the surrounding layers [5, 6]. Thus, kaolinite minerals in Early Cretaceous silico-clastic deposits of Atlantic domain would not reflect hydrolysis conditions during this period. They would primarily serve as the cement binding the coarse particles resulting from the dismantling of the margins. These observations raise questions about some palaeoclimatic interpretations, including the coupling of physical alteration and hydrolysis in a warm/humid and active tectonic context.

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[3] Chamley H (1989) Clay Sedimentology. Springer Verlag, 623p.
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Origin of smectite and influence of volcaniclastic material on a Paleocene-Eocene Thermal Maximum clay assemblage record from the Norwegian-Greenland Sea (IODP Expedition 396)

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Clay mineralogy records provide important climate archives of weathering and hydrology through time, but these paleoclimate signals may be obscured by authigenic or diagenetic overprinting. The International Ocean Discovery Program Expedition 396 drilled an expanded Paleocene-Eocene Thermal Maximum (PETM) succession from the Modgunn Hydrothermal Vent Complex in the Northeast Atlantic Norwegian Continental Margin. The PETM succession here contains a significant input of volcanic ash from the North Atlantic Igneous Province volcanism and is marked by the frequent occurrence of discrete ash beds (centimetre scale) and by thicker ash-rich deposits. Three major lithological units were identified from the Late Paleocene to the Early Eocene in holes U1568A and U1567B: Late Paleocene bioturbated mudstone (Unit VI), laminated mudstone from the PETM onset and earliest PETM body (Unit V), and ash-rich mudstone in the later PETM body (Unit IV). Smectite is the dominant clay mineral throughout the record, with minor components of illite, kaolinite, and chlorite. However, the potential transformation of volcanic ash into authigenic smectite after deposition complicates the use of clay mineralogy as a proxy for paleoclimate and continental weathering at this site.

We apply X-ray diffraction (XRD) analysis to quantify the mineralogical composition and electron microscopy (SEM and TEM) to characterise the chemical and morphological make up of the clay-sized fraction to discriminate between continental weathering processes indicated by detrital clay minerals and early diagenetic processes by the input of volcaniclastic material. Our results reveal two major compositional phases of the clay-sized fraction roughly aligning with lithological units. In upper Units VI and V, smectite is predominately Al-rich montmorillonite-beidellite and is highly correlated with other detrital clay types, indicating a pedogenic source. In Unit IV, a relative increase in volcanic material to background sedimentation – through enhanced bioturbation and/or a change in volcanic production – led to enhanced *in situ* alteration of volcanic ash and the pervasive formation of Mg-rich (cheto type) authigenic smectite. This record confirms authigenic smectite is a minor component of the clay fraction in the latest Paleocene and early PETM and therefore paleoclimate signals are preserved. By contrast, in the later PETM, the authigenic smectite is formed directly from the dissolution of volcanic material and hinders paleoclimate signals.

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Clay Mineralogy coupled to Hf-Nd Isotopes: deciphering chemical weathering and mechanical erosion in the Late Cretaceous climate evolution

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The carbon cycle, which plays a major role in the evolution of atmospheric CO_2, is controlled over the long term (> 1Ma) by the degassing of mantle CO_2 and by continental weathering, which consumes CO_2 through silicate weathering reactions. We present here a synthesis of the links between tectonic, long-term evolution of silicate chemical weathering intensity and climatic changes during the late Cretaceous, using clay mineralogy, isotopic composition of Nd ($\varepsilon_{Nd(t)}$) in the clay fraction to assess local sources and a new geochemical proxy $\Delta\varepsilon_{Hf(t)}$ to track the local silicate chemical weathering [1, 2].

Several sites have been selected to track chemical weathering in relation to uplift phases on the west African margin (Site DSDP 959, Site DSDP 356), the south Africa margin (site DSDP 361) and along the South American margins (sites DSDP 356 and ODP 1259). The response of chemical weathering and mechanical erosion from these sites is greatly dependent of regional features [2, 3, 4, 5]. Overall, the clay mineral assemblages display a large dominance of smectites pointing to a relatively hydrolysing climate with contrasted seasons associated to a low relief. By contrast, illite and chlorite (sometimes coupled with reworked kaolinite and fibrous clays), when not formed during burial conditions, reflect enhanced mechanical erosion. Some kaolinite-rich intervals recognized have been associated with enhanced chemical weathering notably during the Maastrichtian in the western African margin (site DSDP 959). Palygorskite, on the other hand, commonly formed in evaporitic conditions, is used to highlight periods of enhanced aridity such as during the Turonian-Santonian interval in the Brazilian margin or during the Maastrichtian and early Cenozoic in the South African Margin.

A marked increase in chemical weathering is identified during the end of the Cretaceous (ca. 85-70 Ma) in the eastern South American margin from the Santonian to the Maastrichtian, consequent to an uplift of the nearby Brazilian margin. Such an uplift would have led to the establishment of a locally more hydrolyzing climate on the eastern side of the formed relief (rain shadow effect), supported by decreasing palygorskite and increasing smectite proportions in sediments, thus enhancing chemical weathering of the margin.

In the South African margin, proximal boreholes with the higher thickness indicate a clear burial diagenetic effect with illitization process in depth. However, the more distal site DSDP 361, not affected by burial diagenesis, show a concomitant enhancement of both physical erosion and silicate chemical weathering during the Campanian-Danian interval (ca. 77–62 Ma). In this area tectonics played also a major role, favouring a regional climate through the evolution of a rain-shadow effect.

Finally, mineralogical and geochemical data, which are located on margins affected by different climatic, geological and tectonic conditions, suggest a major role of tectonic uplifts affecting the southern Atlantic margins of Africa and South America in silicate weathering and the CO_2 budget, potentially increasing the global cooling of the late Cretaceous.

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[5] Corentin et al. (2024) Marine Geology 476, 107374

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Clay mineral response to hyperthermal events in coastal settings: new insights from Eocene deposits in the Paris Basin

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Clay mineral assemblages can provide valuable insights into weathering conditions in marine or lacustrine environments, but littoral and fluvial environments corresponding to transit zones can be questioned about their ability to record a climate signal [1]. These environments, influenced by climate and sea-level fluctuations, as well as rapid palaeogeographical changes, present optimal conditions for the neoformation, transport, and sedimentation of clays. Understanding the mechanisms affecting clay minerals in coastal and fluvial environments is therefore crucial for interpreting the mineralogical signal in the sediments of distal basins in terms of climate in a source-to-sink approach.

In this study, we combine more than 1 400 clay mineralogy (X-Ray Diffraction and electron microscopy) and organic carbon isotope analyses to investigate the impacts of the Eocene hyperthermal events in the coastal settings of the Paris Basin. We propose the first high-resolution synthesis of the climatic and weathering evolution of the Paris Basin during the early-to-middle Eocene, providing valuable insights on the impacts of hyperthermal events on clay mineralogy in coastal settings.

Our results first provide evidence of the local transformation of smectite to kaolinite within soils during the Paleocene-Eocene Thermal Maximum (PETM). This process, evidenced by interstratified kaolinite-smectite, reflects tropical conditions in the Paris Basin during the PETM favouring strong chemical weathering. During the Early Eocene Climatic Optimum (EECO), enhanced hydrological conditions evidenced by clay minerals are however hindered by differential settling mechanisms highlighted in estuarine environments. Kaolinite formed in soils during pronounced hydrolysing conditions and transported during high runoff events are only observed in the proximal part of the estuary while smectite and glauconite predominates in the more distal part. During the Middle Eocene Climatic Optimum (MECO), rapidly changing hydrolysing conditions successively favour either runoff as evidenced by detrital kaolinite, or chemical weathering, when smectites predominate. More arid conditions however promote complex interactions between microbial activity, dolomite formation, and the neoformation of fibrous clays in evaporative settings, especially during the Late Lutetian Thermal Maximum (LLTM).

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Early diagenetic overprint on Eocene-Miocene lacustrine clay minerals: Influence of phreatomagmatism and microbial activity in the Limagne Basin, France

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The Limagne Basin (Massif Central, France) comprises thick lacustrine deposits, including marls, evaporites, microbial carbonates, and interbedded clay horizons. This basin is a key area for recording major climate events during the Eocene to Miocene interval. The clay mineralogy of these deposits may serve as a proxy for evaluating hydrolysis and precipitation processes within lacustrine sediments and soils [1,2]. However, it is essential to consider the primary conditions that influenced these processes. The predominant clay mineralogy is composed of smectites, with minor illite. Pure illite horizons in lacustrine deposits recognized in the basin are questioned, as this mineralogy is commonly associated with burial diagenesis and/or hydrothermal activity. We suggest here that microbial activity in the lake, evidenced by microbialites [3,4] could have enhanced illitization by trapping potassium and iron in biofilms, as seen in some cases during early diagenesis [5,6]. Scanning electron microscope (SEM) and transmission electron microscope (TEM) observations reveal two populations of illite with different crystallite sizes, confirming the presence of both inherited illite and neoformed illite. Ongoing dating using in situ Rb/Sr and K/Ar methods are being conducted to validate the ages of both populations and the early diagenetic overprint. Additionally, the impact of successive volcanic events on the clay mineralogical composition of the lacustrine system is discussed. Indeed, detailed field investigations and petrographic, mineralogical, and geochemical analyses of volcaniclastic deposits, indicate phreatomagmatic events contemporaneous with lacustrine sedimentation. New U/Pb (LA-ICP-MS) analyses of zircons from volcanic and volcano-sedimentary deposits confirm that volcanic activity is concurrent with the lacustrine sedimentation. The presence of volcanic grains weathered into analcime, anatase, natrolite, authigenic smectites, and occasionally kaolinite vermicles suggests that volcanic activity could influence clay mineral composition, indicating an alternative mechanism beyond purely climatic effects. Consequently, we propose a model in which clay sedimentation in the Limagne Basin may resulted of three mechanisms: 1) primarily detrital sedimentation linked to runoff and climate change as evidenced in other regions of the basin; 2) microbial activity although this hypothesis requires further confirmation; and 3) volcanic activity that introduces authigenic clay minerals (smectite and kaolinite) into the system through the weathering of volcanic ash and grains.

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[2] Warr et al. (2024) App Clay Sc 256: 107419
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[4] Vennin E et al. (2021) BSGF 192 41
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[6] Li et al. (2019) App Clay Sc 177: 91–113

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Varve-like sediments in caves from the northern rim of the Dachstein Massif (Austria)

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Fine-grained clastic sediments with bright and dark laminae, informally called “Bright Cave Loam” (BCL) are present in caves of the Dachstein Massif below an altitude of about 1700 m a.s.l. The Dachstein Massif, with an area extent of 580 km^2, is one of the largest karst massifs in Austria. The BCL represents the topmost layer in a number of caves of the area and has a maximum thickness of 6 m.

In the past, the mm- to cm-thick laminations of the BCL were assumed to be glacio-lacustrine varves caused by seasonal or longer climatic rhythms. To investigate this theory, samples were taken from two different caves, Hirlatzhöhle (from 1000 m a.s.l.) and Dachstein-Mammuthöhle (1400 m a.s.l.).

Sedimentological methods used were grain size analysis and X-ray diffraction (XRD) for the bulk- and clay mineralogy. Wherever possible, individual laminae of the BCL were analysed separately.

The results of the bulk mineralogy show that darker laminae mainly consist of calcite (32–75%) with secondary amounts of quartz (2–5%), dolomite, ankerite, and traces of K-feldspar and goethite. In the dark laminae clay minerals are more abundant (11–60%) than in the bright laminae. Overall, the bright laminae have the same mineralogical constituents, but show slightly higher amounts of calcite and quartz. Clay mineralogy shows a laminae dependent pattern for all clay minerals except smectite. Illite is the most abundant clay mineral and is, together with kaolinite and chlorite, slightly enriched in the darker laminae.

The bright and dark laminae can also be distinguished by grain size analysis. The dark laminae have a higher percentage of clay-sized particles. The maximum grain size of both lamina types is coarse silt. Components up to medium silt are very well sorted.

In conclusion, the BCL was likely formed under conditions of slack-water facies and can be interpreted as a result of glacial backflooding in the Pleistocene. This also explains the altitude control of the BCL. The bright, carbonate-rich, and coarser-grained laminae originate from more energetic meltwater during spring and summer; in winter there is lower discharge, the remaining clay minerals are sedimented resulting in the thin, darker laminae. The studied sediments can thus be interpreted as varves.

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Clay Minerals Markers of Paleo-conditions

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The dramatic rise in the Earth's oxygen about ~2.3 billion years ago, evolution of life, and tectonic instability resulted in several changes in geological and geochemical conditions of the early Earth's atmosphere-ocean system. The oxygen dropped around ~1.8 Ga and was relatively stable for the next ~1 billion years during the so-called "boring period", characterized by steadied climatic conditions, delay in complex life evolution, and relative tectonic stability. Therefore, understanding the prevailing depositional and post-deposition events recorded in sediments deposited during this geologic age are vital in paleo-condition reconstructions of early Earth history. This crucial period is well represented in the non-metamorphosed sedimentary rocks from two exceptional well preserved basins: the Francevillian (2.1 Gyrs) and Taoudeni (1.1 Gyrs). Here, we used mineralogical, petrological, and geochemical approaches on different materials from outcrops, drill cores and biological remains [1] (fossils): **(i)** to understand the taphonomy of early soft-bodied organisms in Palaeoproterozoic sediments. After the deposition of dead organisms on the clayey sediment, an illitization process, which depends on the availability of dissolved K driven by bacterial activity, started from the first stages of preservation by moulding the lenticular-shaped forms and proceeded in the pores of the other macrofossils after their pyritization. At the fossil level, the intensity of illitization is controlled by the mode of preservation and the evolution of the associated permeability. In the nonpyritized lenticular-shaped specimens, illitization was not achieved, preserving I-S mixed-layer minerals, while in the pyritized forms, the illitization degree was more extensive. In comparison, I-S mixed-layer minerals are almost absent in pyritized abiotic concretions. A second process, which occurred later, consists of general chloritization from fluid circulation. Our detailed results show that each specimen behaved like a microsystem with its own physico-chemical and mineralogical evolution during preservation/diagenesis. This finding allows us to propose a conceptual model of the taphonomic history, describing the fossilization stages for each type of specimen. **(ii)** to determine the effects of post-depositional processes, including diagenesis and impact of magmatic intrusions observed in only one of the studied drill cores [2]. The clay minerals are mainly chlorite, kaolinite, illite, and illite/smectite mixed-layer minerals. However, the drill core with sill intrusion experienced a series of textural, mineralogical, and chemical transformations induced by brittle deformation, thermal overheating, and fluid circulation.

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[2] Ghnahalla et al. (2023) Precamb Research 388, 107003

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Climatic significance of clay minerals in Cenozoic sediments

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Over the last decades, clay minerals have been widely used as proxies for paleoclimate reconstructions in both marine and lacustrine settings. In those studies, the climate interpretation is derived from the evolution of potential clay proxies over core depth or time. The most common proxy corresponds to the clay mineral abundance in bulk or fine < 2 µm fraction, the height or surface peak ratio between two clay minerals (e.g. kaolinite/chlorite, smectite/illite) or the abundance ratio between at least two clay minerals. Among those approaches, the measurement on X-ray diffraction diagram of peak height or surface ratio between two minerals is the most objective as it is not sensitive to the method of quantification of the clay minerals.

The clay mineral proxy presents, however, two main limitations. First, only the detrital clay minerals may record climate variability. Detrital clay minerals are formed by continental weathering, they are carried by surface transport to the adjacent sedimentary basins and are redistributed by surface and/or deep currents. In a sedimentary core, the variability in the clay mineral assemblages reflects either variable physical and chemical weathering conditions in the watershed, typically with a significant link to climatic conditions, or changes in the mineral source, the latter being associated with various transport agents. Second, the use of clay minerals as climate proxy is mainly valid for Cenozoic sediments less affected by burial diagenesis than older sediments.

In this presentation, examples of various clay-derived proxies retrieved from the literature and ongoing research [1] on clay mineral variability in marine or lacustrine sedimentary records will be presented and interpreted in terms of climate control and transport paths. The interpretation of sedimentary clay minerals is easier if the source areas and transport agents are known. In proximal deposition environments (e.g. deltas) clay minerals are significantly controlled by the watershed climate conditions. In distal sedimentary basins, these controls are easiest to decipher when two source areas are characterized by distinct clay assemblages and different transport agents. When different sources are involved, a combination of mineralogical and geochemical (element and isotope ratios) proxies allows to trace the detrital provenance, but they also indirectly provide information on transport pathways and paleocurrents.

The numerous marine and lacustrine drilling projects conducted worldwide represent an interesting database from which to conduct further clay mineralogical studies on Cenozoic sediments.

[1] Fagel N (2024) Clay Minerals. https://doi.org/10.1180/clm.2024.17

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LECTURE THEATRE 4 – SESSION 40

Clays in Mining

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A new exploration in surrounding of Michaľany-Lastovce bentonite deposit, East Slovakia – mineralogical, geochemical and petrological characterization

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Slovakia, with annual production around 300 kt, ranks among the Top 10 bentonite producers in the world. There are two areas in Slovakia where bentonite deposits are concentrated, namely, the Central Slovak Volcanic Field (8 active deposits) and the Eastern Slovak Neogene Basin (2 active deposits). The Michaľany-Lastovce bentonite deposit is the largest in the East Slovakia, with 8.8 Mt of reserves. The deposit is mined by LB MINERALS SK, s.r.o with production about 20 kt per year

The Michaľany - Lastovce deposit is composed of Sarmatian volcano-sedimentary rock formations, with the thickness up to 30 m. The rock filling of volcano-sedimentary formations represents various intensively argilitized rhyolite tuffs and tuffites, tuffitic clays and bentonites, as well as scattered limnosilicite and diatomite. Bentonite forms a fine-grain, white, light grey to greenish grey plastic rock. (Harcek J., 1963; Horský S., 1994; Slavik et al., 1971).

The objective of presented study is to determine the mineralogical composition of borehole samples obtained by REGOS, s.r.o during their exploration in the vicinity of the Michaľany - Lastovce deposit in 2022.

21 samples have been collected from six boreholes, dried, sieved, separated and studied by: CT, XRD, IR spectrometry, DTG, optical and electron microscopy. The cation exchange capacity has been determined by methylene blue and Cu-trien techniques.

X-ray microtomography confirmed the pyroclastic parent material, mostly inhomogeneous with various fragments of rocks and minerals. Grains below 0.5 mm, embedded in a fine-grained matrix, predominate, but exceptionally it is possible to find lithoclast grains over 1 cm. The montmorillonite content mostly varied between 35 and 45 wt.%. Bentonite contains also opal-CT(C), approximately in 1:1 ratio to montmorillonite. Presence of both cis- and trans-vacant positions in the dioctahedral sheets were determined by thermal analyses.

Acknowledgement: The work was supported by the project APVV-20-0175.

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[2] Horský S (1994) Výpočet zásob bentonitu na výhradnom ložisku Michaľany -Lastovce, GP, SNV, Košice, 17s.
[3] Slávik J et al. (1971) Mineralia Slovaca 12–13: 561-573.

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Clay Characterization Challenges: Insights from Methylene Blue Index and X-Ray Diffraction Analyses of Coal Mine Wastes from Alberta

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Clay minerals in mine waste present ongoing challenges for processing, dewatering and reclamation in mining operations around the world. This study explores the characterization of clays from coal mine wastes using methylene blue index (MBI) and X-ray diffraction (XRD), with a comparison to previously analyzed clay-rich oil sands wastes. The coal mine waste samples analyzed here were collected from five coal mines in Alberta as part of a project to investigate the critical element potential of coal mine wastes in the province. This work was completed under the Alberta Geological Survey's (AGS) Mineral Mapping Program, funded through the Minerals Grant provided by the Government of Alberta. The final results of this project will be made publicly available on the AGS website once complete.

While both coal and oil sands wastes are dominated by fine-grained aluminosilicates, the preparation and quantification of clays differ considerably due to their variations in mineralogical complexity and sample composition. The coal waste samples presented unique challenges in the preparation of oriented clay slides for XRD, where the clays exhibited frequent cracking and peeling during drying and treatment steps. These difficulties were less pronounced in oil sands tailings. Interestingly, some coarse rejects from coal mines and fly ash samples showed low MBI values, yet XRD clay analysis revealed moderate to high proportions of mixed-layer clays with smectitic interlayers. The contrasting behavior between coal and oil sands waste samples highlights the need for multi-method approaches to clay characterization in mining. One potential explanation of the difference is that MBI is a water active surface probe. Some coal tailings may be hydrophobic due to upstream interactions with collectors and/or other process additives, whereas oil sands processing is water-based and does not change the hydrophilic nature of the clays. While MBI remains a rapid screening tool and useful proxy for water active surface area/clay content, our findings emphasize that insights from other techniques such as particle size analysis and XRD, are important when dealing with the complex nature of real mining samples.

These insights have implications for tailings management and reclamation in both coal and oil sands mining operations, where clay characterization is critical for understanding dewatering and geotechnical behaviors. These observations support the need for integrated clay analysis workflows that combine proxies such as MBI with physical properties (particle size) and mineralogical analysis (XRD). Understanding the limitations of each method is essential for proper understanding of clay behavior in mining.

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Characterising and predicting the flotability of gangue minerals from X-ray diffraction patterns: A case study of talc

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After years of continuous mining, high-grade copper ores are running out as copper demand increases, provoking the need to mine low-grade copper ores. However, low-grade copper ore deposits are often closely associated with hydrophobic gangue minerals like talc ($Mg_3Si_4O_{10}(OH)_2$), making selective recovery of the valuable minerals more difficult [1]. The experience of miners demonstrates that some talcs are more flotable than others, which causes issues for processing and requires methods that can easily and accurately be used to understand this difference in flotability across different mine sites.

This study used XRD to determine the morphologies of various talcs, which is a quick and easy way to understand how talcs float on mining sites. The orientation of the crystal plane obtained from XRD data of the talc peak intensity between positions 19 and 21° was used to quantify the morphological index (MI) [2] of the talcs, a measure of their aspect ratio. This was defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid using the monoclinic Miller indexing (hkl). There was a strong correlation found between the platy morphology quantification obtained from XRD and that from X-ray CT 3D analysis of talcs. For precise and accurate analyses, wet sample preparation methods were developed prior to the use of both X-ray and XRD techniques. The XRD results revealed that the particle morphology of talc ranged from platy to blocky, depending on its geological location. The flotability of the talcs varied based on their morphology index in a flotation test conducted on talc ground to a particle size of 106 to 53 µm. The talcs with the highest MI, regarded as highly platy, were more flotable than the other talcs, and the reverse was true for those with the lowest MI. This suggests that the flotability of various talcs is affected by their varying degrees of platiness. Hence, the XRD-determined morphological index of talc could be a straightforward tool for predicting their flotation in a real ore and determining the best course of action to maximise mineral recovery in a flotation system. Also, XRD gives the mineralogy of the sample directly, which simplifies the process of quantifying the platy morphology of the target mineral from a complex ore.

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[2] Holland HJ, Murtagh MJ. An XRD morphology index for talcs: The effect of particle size and morphology on the specific surface area. JCPDS-International Centre for Diffraction Data 2000, Advances in X-Ray Analysis 2000;42.

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The Role of Water Chemistry on Clay Behavior in Mine Process and Tailings Circuits

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To size and design dewatering flowsheets and containment structures for storing mine tailings, metallurgical and geotechnical engineers rely on measuring certain engineering properties of the tailings. These engineering properties, themselves are derived from certain intrinsic properties of the solids and water components within the specific mineral tailings.

This paper describes the current lack of a universal mine tailings classification scheme which can be used to categories and predict the dispersive behaviour of tailings. The dispersive behaviour of tailings appears to be dependant on both the intrinsic clay types within the solids and the chemistry of the water component within the tailings slurry.

A conceptual model for describing the intrinsic dispersive behaviour of clays within the tailings is provided which correlates to engineering properties such as the dewatering, consolidation and rheological properties of the tailings on a macro scale.

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Impact of Clay Activity and Surface Chemistry on Polymer-Assisted Dewatering of Oil Sands Fluid Fine Tailings

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Effective management and reclamation of fluid fine tailings (FFT) produced by Canadian oil sands operations remain a major challenge due to the complex behaviour of clay-rich suspensions. As of recent estimates, the total volume of FFT in the Athabasca oil sands region has reached 1,486 Mm^3, consisting of a mixture of sands, silt, clay, water, residual bitumen and various organic compounds [1]. In this study, we investigated how clay activity and surface chemistry influence the performance of polymeric flocculants in dewatering FFT. Three FFT substrates (~ 31 wt.% solids), each characterized with distinct clay activity level as determined by methylene blue index, were treated with three different polymer chemistries provided by SNF Inc., alongside aluminum sulfate as a coagulant.

One FFT substrate, containing a higher residual bitumen content (5.7 wt.%) compared to the other two (~1.4 wt.%), showed coagulation behaviour despite having dispersive porewater chemistry, suggesting that bitumen coating on clay surfaces may have altered their surface properties. The polymers' dewatering performance was evaluated through multiple techniques, including 24-hour net water release, settling tests for over 30 days, filter press, centrifugation, and capillary suction time (CST). Two mixing conditions were tested: optimized mixing (terminated at peak torque of flocculation) and extended shearing for 5 minutes post-peak to assess the resistance of polymer-solids aggregates to shearing and how that may influence the dewaterability, an important consideration for field-scale.

Our findings demonstrate that both clays' activities and their surface properties control the flocculation behaviour and dewatering performance. Additionally, polymers performing well in one test might underperform in others, highlighting the limitations of relying on a single evaluation method for performance assessment, which could lead to misleading conclusions. This work provides insights into clay-polymer interactions in FFT systems and supports the design of more robust and targeted polymers for tailings treatment, contributing to sustainable mine closure and reclamation goals.

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Lime Treatment Impact of In-Line Flocculation Polymer Performance and Strength Development of Deposited Tailings

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Fluid fine tailings (FFT) are the primary by-product generated during oil sands processing. FFT consist of solids, water, trace amount of residual bitumen, and organics compounds. In this context the clay minerals (primarily very fine grained illite-smectite, illite and kaolinite) present in tailings solids exhibit properties that hinder dewatering and consolidation, posing a significant challenge to effective tailings management and reclamation efforts. In oil sands tailings treatment, most operators use a technology called in-line flocculation, which involves adding a flocculant, and often a coagulant, to tailings during their transfer to settling ponds. This process facilitates water release and yields soft clay-rich deposits that are difficult to reclaim as landforms. Since reclaimed landforms are crucial for site restoration, these soft deposits require further treatment, such as capping, blending with sand, or retreating in order to become suitable materials for constructing final landforms. Lime has long been used in traditional construction applications to stabilize clay-rich soils and the fundamentals of this technology can be applied to clay-rich tailings treatment. Unlike in lime soil treatment, directly mixing lime into in-situ tailings deposits is logistically challenging and costly. This study explores integrating lime treatment into the in-line flocculation process to cost effectively enhance the stability and strength of soft tailings deposits. Two fluid fine tailings samples, from oil sands operations, were treated with lime before and after polymer addition. The ability to release water, their Atterberg limits and their response to a vane shear test were measured to determine the optimal dosing for both lime and the polymer. Lime treatment was compared to incumbent methods, including polymer-only and alum (ALS) + polymer treatments.

The study measured dewatering characteristics including net water release, release water quality, and filtration rate, alongside solids content and undrained shear strength at 1 and 35 days. The results demonstrated that a small amount of lime prior to the polymer addition can reduce the polymer dosage by 30-60%. A large quantity of lime after polymer addition significantly improved tailings texture, strength and dewaterability. A split dosing strategy (low dose lime + polymer + a high dose of lime) offered both initial water release and enhanced filtration. The undrained shear strength of the lime treated tailings increased by 4 to 7 times compared to incumbent methods. Further research is required to expand the understanding of both long-term strength development and geotechnical performance to assess how the use of lime augmented in-line flocculation can support the development of landforms required during mine reclamation.

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LECTURE THEATRE 6 – SESSION 1a

Universal

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A Deep Learning Approach for Mineral Identification With X-Ray Powder Diffraction Patterns

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Quantitative X-ray Powder Diffraction (QXRPD) is a powerful analytical technique for determining the composition and crystallographic structure of mineral mixtures. The accuracy of QXRPD analysis heavily relies on the expertise and interpretation of the professional, introducing the risk of human error. To address this challenge, our research focuses on developing a deep-learning model designed to identify mineral phases directly from X-ray powder diffraction (XRPD) patterns. By leveraging the power of deep learning, our model aims to enhance the precision and reproducibility of mineral identification while reducing dependency on expert judgment.

Our methodology involves designing a deep learning architectures to develop a multi-label classifier for mineral phase identification. We utilize a Convolutional Neural Networks (CNN) architectures due to their proven effectiveness. We employ data augmentation techniques to combat the lack of real-world XRPD patterns and create a synthetic dataset to train and test our models.

Our research demonstrates the potential of leveraging innovative deep learning algorithms to improve the accuracy and reliability of QXRPD analysis. By mitigating the risks of human error, this work represents a step forward in modernizing mineral phase identification. Furthermore, our approach underscores the value of incorporating advanced deep learning techniques into geoscientific workflows, highlighting methodologies that may not yet be widely adopted by the audience. Our research serves as a foundation for future advancements in integrating artificial intelligence into geology, ultimately empowering geologists with more consistent analytical tools.

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Data quality of low angle X-ray powder diffraction

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Powder X-ray diffraction is an essential analytical technique for the identification and quantification of clay minerals. Over the past decades, advancements in detector technology [1] have enabled both scientific research and industrial applications to collect data at increasingly faster speeds using the favourable Bragg-Brentano geometry. These improvements have also enhanced data quality, facilitating in-depth analysis of clay-bearing materials.

Given the structural characteristics of common clay minerals, the low-angle region is particularly crucial for identifying and quantifying specific mineral species. However, this region of powder diffraction data is susceptible to additional artifact signals, such as air scattering and potential contributions from the sample holder. These factors can complicate the identification and even confirmation of disordered phases within a reasonable collection time.

Various techniques exist to optimize the low-angle region, including classical shielding of the diffracted beam, fixed and motorized anti-scatter screens, and variable divergence slits. Each method impacts data quality to varying degrees.

As the industrial use of clay-bearing materials, such as supplemental cementitious materials (SCMs) in the form of calcined or activated clays in cement, continues to grow in efforts to reduce carbon dioxide emissions [2], the fundamental understanding of different (calcined or activated) clay mineral reactivity [3] as well as reactivity in cementitious systems [4] and interaction with concrete and mortar additives [5] will become increasingly important. Additionally, identifying suitable source clays will drive the demand for reliable diffraction data and efficient data collection equipment.

This contribution aims to demonstrate the benefits and limitations of each approach using real-life samples, highlighting best practices for optimizing low-angle data quality without compromising data integrity.

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Identifying clay minerals based on oxide compositions using MinMatch

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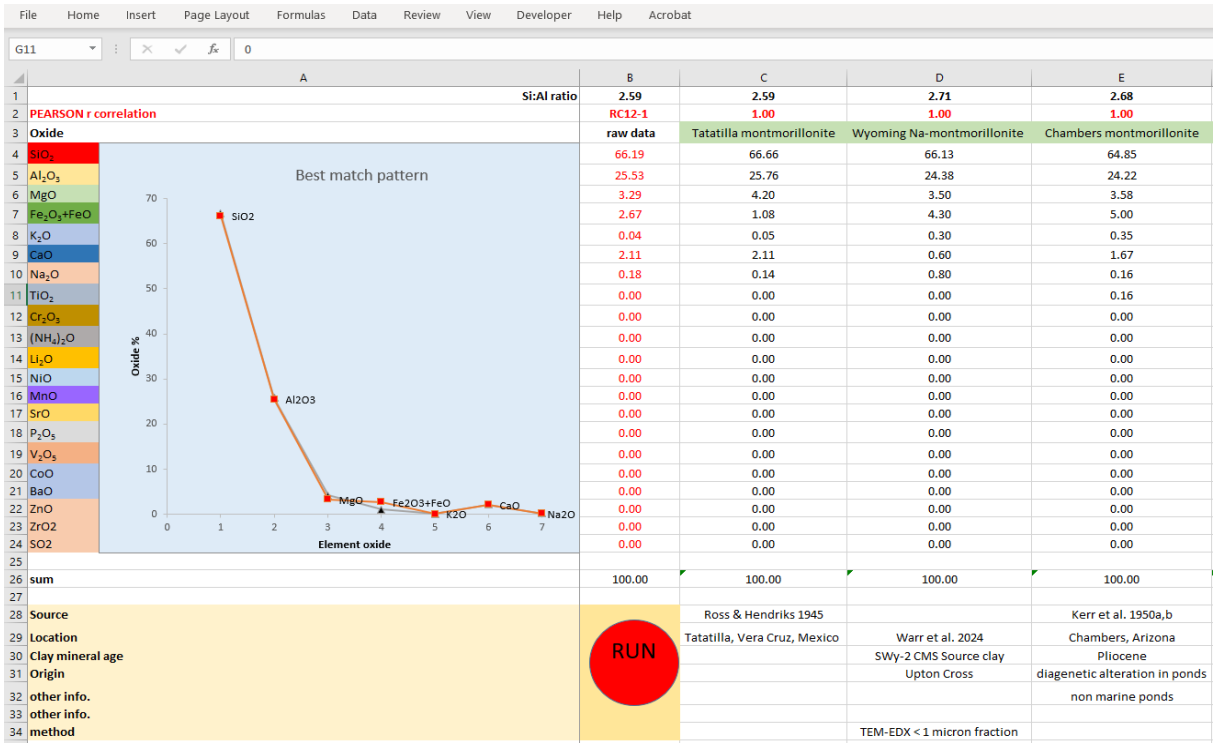
Determining the chemical composition of clay minerals forms a basis of recognition that is complementary to X-ray diffraction (XRD) analysis and is used to establish structural formulas and layer charge characteristics. Such elemental oxide data is commonly attained by electron microscopy using energy dispersive X-rays (EDX) or by conventional microprobe analysis. Alternatively, analytical results may be obtained by standard spectroscopy methods applied to purified minerals fractions, such as X-ray fluorescence, atomic adsorption, or induced coupled plasma techniques. In this contribution, we present a MinMatch spread sheet that contains over 500 compositions of clay minerals and associated accessory minerals common to clay deposits. A demonstration of its use is given based on the 12th Reynolds Cup competition where oxide compositions were determined using EDX with scanning and transmission electron microscopy [1]. An automatised search and match macro has been integrated into the spreadsheet. This selects the best match files in the database based on the highest Pearson "r" correlation function of the matching datasets. Using the Si/Al ratio along with visual pattern matching are two supplementary methods for selecting best matching patterns. We demonstrate how the MinMatch.xls database can be used to help with mineral identifications and to optimise quantifications made by XRD methods. Some of the pitfalls of the approach in dealing with mixed mineral analyses and amorphous phases are also highlighted. The appearance of the interface of MinMatch is show in the figure below.



	A	B	C	D	E
1	Si:Al ratio	2.59	2.59	2.71	2.68
2	PEARSON r correlation	RC12-1	1.00	1.00	1.00
3	Oxide	raw data	Tatatilla montmorillonite	Wyoming Na-montmorillonite	Chambers montmorillonite
4	SiO_2	66.19	66.66	66.13	64.85
5	Al_2O_3	25.53	25.76	24.38	24.22
6	MgO	3.29	4.20	3.50	3.58
7	Fe_2O_3+FeO	2.67	1.08	4.30	5.00
8	K_2O	0.04	0.05	0.30	0.35
9	CaO	2.11	2.11	0.60	1.67
10	Na_2O	0.18	0.14	0.80	0.16
11	TiO_2	0.00	0.00	0.00	0.16
12	Cr_2O_3	0.00	0.00	0.00	0.00
13	$(NH_4)_2O$	0.00	0.00	0.00	0.00
14	Li_2O	0.00	0.00	0.00	0.00
15	NiO	0.00	0.00	0.00	0.00
16	MnO	0.00	0.00	0.00	0.00
17	SrO	0.00	0.00	0.00	0.00
18	P_2O_5	0.00	0.00	0.00	0.00
19	V_2O_5	0.00	0.00	0.00	0.00
20	CoO	0.00	0.00	0.00	0.00
21	BaO	0.00	0.00	0.00	0.00
22	ZnO	0.00	0.00	0.00	0.00
23	ZrO2	0.00	0.00	0.00	0.00
24	SO2	0.00	0.00	0.00	0.00
25					
26	sum	100.00	100.00	100.00	100.00
27					
28	Source		Ross & Hendriks 1945		Kerr et al. 1950a,b
29	Location		Tatatilla, Vera Cruz, Mexico	Warr et al. 2024	Chambers, Arizona
30	Clay mineral age			SWy-2 CMS Source clay	Pliocene
31	Origin			Upton Cross	diagenetic alteration in ponds
32	other info.				non marine ponds
33	other info.				
34	method			TEM-EDX < 1 micron fraction	

[1] Warr LN et al. (2024) Clays Clay Minerals 47:303-322

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RockJockML: An updated version of RockJock for the modern geologist

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Quantitative phase analysis (QPA) of whole rocks and sediments using X-ray powder diffraction (XRPD) is a standard, workhorse technique for many types of geologists and soil scientists, and there are many techniques for performing the analysis. Although XRPD patterns of single phases are usually very diagnostic, patterns of complex mixtures can be quite difficult to deconvolute. That is, the combination of diffraction peaks present might conceivably be modelled by more than one combination of minerals. The algorithms employed by standard XRPD analysis software to help the user choose phases to include typically involve simple peak-matching routines, which cannot mimic the sorts of background knowledge expert analysts use to make such decisions (e.g., the relative prevalence of different minerals, which minerals are likely to occur together, and the results of other analytical techniques).

RockJockML is a full-pattern summation QPA program for analyzing XRPD patterns of geological materials. It is based on the original RockJock program created by D.D. Eberl of the U.S. Geological Survey in Microsoft Excel, but updated to provide dramatically increased processing speed, an intuitive workflow, and several features designed to help the user more accurately pick phases for inclusion in the analysis. The program was created in the MATLAB language, but is deployable in a standalone version for Windows, Macintosh, and Linux operating systems without the need for a MATLAB license. It can be downloaded at http://geol.byu.edu/bickmorewiki/, where documentation and training materials can also be found.

Some of the methods available for phase selection in RockJockML are user driven, while others are automated using models generated by machine learning algorithms. The requirement of domain expertise, and the inability to apply a simple, straightforward algorithm to address the problem, is exactly the scenario where machine learning techniques are best applied. In this talk we detail several of the tools and algorithms included in RockJockML that help a user determine the best mixture with varying degrees of intervention. We will detail how the use of association rules in conjunction with a forward method for selecting methods from most to least prevalent can determine mixtures with no intervention. We will also discuss how a new technique called *lift boosting* can help a user fine tune a mixture to more accurately match a sample. Finally, we will preview some future algorithms that will be included in RockJockML that utilize deep learning to determine mixtures quickly and accurately.

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A comparison of ATR and transmission FTIR spectroscopic methods as tools for qualitative and quantitative analysis of clay mineral identities and properties

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Fourier-transform infrared (FTIR) spectroscopy is a common spectroscopic method used for the analysis of organic, inorganic, and mineralogical species, and can provide both qualitative and quantitative data. In clay mineralogy, FTIR analysis is especially useful because it can differentiate between similarly structured clay minerals based on cation occupancy of di/trioctahedral sites, and the behavior of hydroxyl groups [1]. Given that traditional X-ray powder diffraction analyses require strenuous effort to distinguish various clay minerals, easy-to-use FTIR methods could provide complementary data while saving effort and time.

In this project, we have explored the usefulness of attenuated total reflectance FTIR spectroscopy (ATR-FTIR) for quantitative mineralogical analysis, because such analysis takes mere minutes to perform. However, the results of ATR-FTIR analyses of pure mineral powders and mixtures of minerals show that variations in interparticle effects and sample penetration depth cause the spectral peaks to shift location and change shape in a manner that would be difficult to account for in a quantitative manner.

Therefore, we are currently testing more traditional transmission FTIR methods in which samples are heavily diluted (<0.3%) in KBr pellets. Preliminary data indicates that transmission spectroscopy does not suffer from the same problems as ATR-FTIR, likely due to the extreme dilution of the samples.

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VNIR-SWIR spectroradiometric study of ground samples from the Tajo Basin

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Spectroradiometry has been used for mineral characterization and mineral prospection for decades, although in recent years there has been an increasing interest in its use due to the increasing availability of high-resolution portable equipment that can be used both in the laboratory and in the field (especially in the VNIR-SWIR range). Nowadays, one of the most important applications of these spectroscopic techniques is their use for remote sensing studies, where there does not have to be a physical availability of the samples. However, there is an important issue that must be addressed when studying natural polymineralic samples by infrared spectroscopy: the interaction of the different minerals and how they affect their respective detection limits [1,2]. The aim of this work is to determine the spectral signature of the Mg-rich bentonites of the Tajo Basin to be applied to remote-sensing studies for their prospection in the area, as continuation of previous works [3].

For such purpose, 60 ground samples (from the top 15 cm of the surface) and 28 samples from a Mg-rich bentonite quarry in the proximities of the locality of Esquivias from the Esquivias area (Tajo Basin, Spain) were collected and characterized by different techniques. X-Ray diffraction (XRD) allowed the identification and semiquantification of the minerals which compose the samples, using a Bruker D8 Advance diffractometer and a full routine for clay minerals identification. The VNIR-SWIR spectra of the samples were obtained using an ASD FieldSpec 4 Hi-Res spectroradiometer. The spectra were subject to different treatments of the data, such as performing their continuum removal (CR) and their first (1D) and second (2D) derivatives. Finally, the chemical composition of the samples was obtained using the Hitachi X-MET8000 handheld X-Ray fluorescence analyser. The statistical treatment was done with PAST V4.03 and SPSS V27 software suites.

The mineral associations established from the XRD results were used to obtain their respective spectral signatures by averaging the spectra of the samples that fell within them. When performing an unsupervised classification by clustering the spectra and the spectral signatures in the range from 1300 to 2500 nm, it was possible to observe the influence of even small quantities of gypsum, which caused mixings of spectra belonging to different groups, whether using the regular spectra, the CR, 1D and 2D. Gypsum does not only affect the groupings of the samples, but it also can also mask some of the absorption features originated by Mg-rich smectites. Other parameters obtained from the CR, 1D and 2D (such as the positions, depths, full widths at half maximums, asymmetries, intensities, etc. of the absorption features) were used for performing statistical analyses focusing on the detection of Mg-rich smectites within the samples. The best results for prospecting Mg-rich bentonites were obtained when considering data from the 2D, both positions and intensities.

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[2] Santamaría-López A and Suárez M (2024) Minerals 14(11): 1098
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LECTURE THEATRE 6 – SESSION 2+11

Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies

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Clay minerals survey along the Martian Crustal Dichotomy to Assess Aqueous Conditions on Early Mars

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Over nearly two decades numerous studies have revealed evidence for widespread aqueous activities on Mars' surface, likely occurring from Noachian to Hesperian epochs [1,2]. Clay-bearing deposits are valuable targets to constrain the water history on early Mars and consequently search for signs of life [3]. The possible co-occurrence of carbonates throughout these deposits may also suggest a high potential for biosignature preservation. Nevertheless, the definitive characterization of these deposits remains a challenging task. This study builds upon our previous works [4] by focusing on hyperspectral data gathered by the CRISM instrument onboard NASA's Mars Reconnaissance Orbiter mission [5] to analyze the spectral signatures of clay deposits in the 1–4 µm range, and their potential mixtures with carbonates. We collected data along the Martian crustal dichotomy – the boundary between the ancient, cratered highlands and the northern lowlands – where extensive clay deposits are exposed, selecting several regions of interest (ROIs). For all ROIs we conducted a spectral survey to determine the exact positions of the band centers for key clay absorptions around 1.4, 2.3, and 2.4 µm, and after applying a continuum removal to emphasize the absorptions. Band centers observed for the clay deposits show some variations from one region to another, as expected from ferromagnesian clays on Mars. Nontronites (Fe-rich) are extensively detected around Mawrth Vallis, whereas saponites (Mg-rich) are more locally distributed across Nili Fossae and Lybia Montes. Oxia Planum – ESA's ExoMars rover landing site – exhibits more "*intermediate*" clays such as vermiculites or even ferrosaponites. These variations may depend on the relative abundance of iron and magnesium in the clay structure, or even the oxidation state of iron [6]. Additionally, clay deposits often display a shallow absorption near 2.50–2.53 µm, suggesting the presence of carbonates intermixed with the clays. Overall, the carbonates possibly found in these deposits appear to have variable compositions, spanning within the siderite (Fe-rich) and magnesite (Mg-rich) series. This may indicate the presence of carbonates as siderite/magnesite solid solutions, likely reflecting multiple alteration events [7].

This work follows previous in-situ and orbital measurements and prepares for upcoming missions and campaigns on Mars (e.g., ExoMars rover mission, Mars Sample Return, etc.), by offering a more comprehensive understanding of clay mineralogies to inform the search for biomarkers.

Fundings: This work is supported by the Italian Space Agency (ASI) [ASI-INAF n.23-3-HH.0]

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[4] Brossier et al. (2022) *Icarus* 386: 115114
[5] Murchie et al. (2007) *JGR Planets* 112: E05S03
[6] Michalski et al. (2015) *EPSL* 427: 215–225
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Distinguishing detrital from authigenic phases in a subaqueously altered basaltic sandstone: A Mars analog remote sensing study

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On Mars, the detailed characterization of clay minerals, their associations with other phases, and deducing the environments in which they formed is essential for understanding that planet's aqueous history. Although clay minerals have been detected across Mars' surface from orbit [1-2], distinguishing their presence as components of sedimentary rocks versus alteration products in weathered basalt presents challenges, even from the Martian surface. This study evaluates the effectiveness of current and potential future rover-based remote sensing techniques in resolving mineralogy of sedimentary rocks of basaltic composition and distinguishing detrital from authigenic components (e.g., cementing agents). We compare a subaqueously deposited basaltic sandstone with weathered parent material (basalt), both of which contain clay minerals and zeolites. We seek to understand likely sources of uncertainty in identifying these two disparate rock types on Mars and to constrain what may be reasonably interpreted about water-rock interactions when restricted to bulk chemical/mineralogical properties and remotely-sensed datasets.

Samples were analyzed using powder X-ray diffraction (XRD), Electron Probe Microanalysis (EPMA), X-ray fluorescence (XRF) elemental mapping using a breadboard version of the Perseverance rover PIXL instrument, and Near-Mid IR reflectance spectroscopy. EPMA data were used to construct 4 µm/pixel mineral maps for comparison with high resolution (~3 µm/pixel) spectral maps and to identify textural features, detrital grains, and authigenic components (e.g., cement). We find that authigenic clays are Fe/Mg-rich and can be easily overlooked in lower spatial resolution elemental maps (e.g., Perseverance PIXL data), but this is partially mitigated when combined with high spatial resolution reflectance spectroscopy. We also find that near-IR wavelengths are biased towards detection of hydrous alteration products, which may lead to their overestimation in those data.

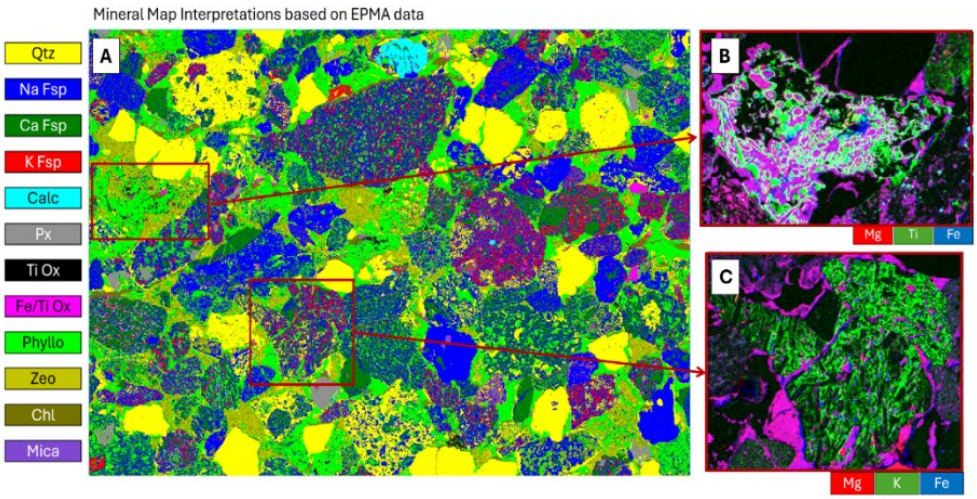

Figure 4. (A) Mineral map derived from EPMA data of a basaltic sandstone that provides sufficient detail to distinguish detrital grains from cement. **(B)** RGB composite of elemental maps of a highly degraded grain, revealing textures suggestive of vesicles lined with microcrystalline titanium oxide and filled with Mg/Fe-rich phyllosilicate. **(C)** RGB composite of acicular Na-Ca plagioclase within a fractured K-feldspar matrix, with fractures filled by Mg/Fe-rich clay minerals.

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Characterizing Phyllosilicate-Sulfate Assemblages at Mawrth Vallis as Indicators of Environmental Change on Mars

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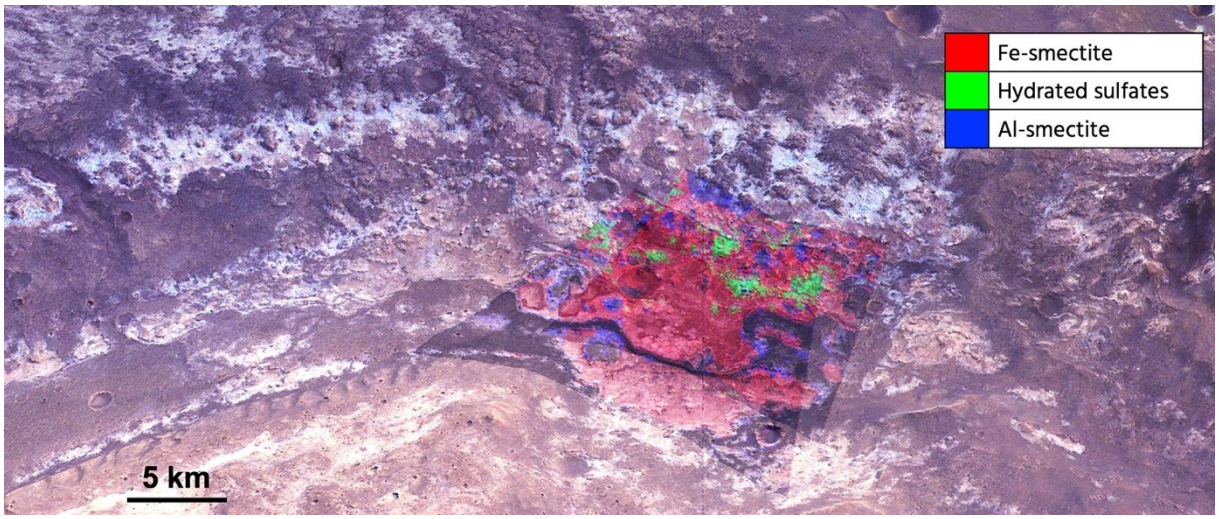
The Mawrth Vallis region of Mars contains some of the most abundant phyllosilicate outcrops on the planet. Coordinating the mineralogy, morphology, and geologic maps of these phyllosilicate assemblages along the large channel cutting through the Mawrth Vallis region provides evidence of the ancient martian environments these minerals formed in. Transitions from Fe-rich smectites to sulfates to Al-phyllosilicates and Si-rich phases indicate changing geochemical conditions over time. Specific phyllosilicate and sulfate minerals are mapped using vibrational bands in CRISM images at a spatial resolution of 18 m/pixel (see figure), outcrop morphologies are documenting using HiRISE views at <1 m/pixel, and regional geologic maps are constructed using CTX images at 6 m/pixel and stereo HRSC images at 12 m/pixel (see figure).

Spectral features in the region ~1.4-2.6 µm in CRISM images are most useful for identifying and characterizing phyllosilicates and associated minerals. The H_2O combination band is observed near 1.91-1.92 µm in most smectite outcrops and additional features are used to constrain the mineral assemblages. The Fe-rich smectite outcrops include Fe-OH bands near 1.42 and 2.29-2.30 µm. The Al-smectite units include Al-OH bands at 1.41-1.42 and 2.20-2.21 µm, while small locations containing halloysite/kaolinite and alunite have additional bands near 1.39-1.47, 1.75, 2.17, and 2.32 µm. Sites including hydrated Mg sulfates include a drop in reflectance near 2.4-2.5 µm but do not have OH bands in the 2.2-2.3 µm range. Sites containing bassanite have bands at 1.78 and 2.27 µm in addition to strong H_2O bands near 1.43, 1.92 and 2.5 µm. In some cases these bassanite-like regions also contain weak gypsum-like features. Analysis of the morphologies of the sulfate-bearing outcrops suggests these units arose separately from the phyllosilicate-rich units. This diversity at the tens of meters scale as seen from orbit is consistent with changing pH, salinity, and cation availability, representing change over time in the early geochemical environment at Mawrth Vallis.



Oblique view of CRISM mineralogy map over HRSC at bend in Mawrth Vallis channel.

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Formation of jarosite in a nontronite bearing deposit on Mawrth Vallis, Mars

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The Mawrth Vallis region contains one of largest clay bearing deposits in the Chryse Planitia basin, part of the northern low-lands on Mars [1]. The nontronite bearing layer at the base contains an ovoid shaped depression, possibly the remnant of a meteoritic impact, within which the hydrous sulphate mineral jarosite has been detected [2]. The formation of jarosite is hypothesized to be the product of interaction of acid-water with the phyllosilicate [2]. This study attempts to model the possible genesis of jarosite and its localized occurrence.

The age of the clay deposits in the Mawrth Vallis region is estimated to be early to mid-Noachian [3]. This period is characterized by a denser atmosphere with mean annual temperatures below zero degree Celsius, and is characterized by cycles of reduction and oxidation events [4]. A jarosite deposit associated with nontronite indicates that an oxidizing event was associated with the acidification of the water [2]. Modelling of the acid-clay interaction was carried out using the REACT module within the Geochemist's Workbench (GWB 12.0.6). Thermodynamic calculations were performed using the V8 R6+ database (https://www.gwb.com/data/thermo.com.V8.R6+.tdat). 1 kg of pure nontronite-K under oxidizing conditions [4] and at ambient Noachian CO_2 fugacity [5],was allowed to react with model acidic water of composition used by Tosca et al. [6] with some amount of Fe^{2+} (Table-1), at different water-to-rock (W:R) ratios, under both open (CO_2 buffered, W:R>1) and closed (CO_2 unbuffered, W:R<1) system conditions [7]. Interaction with restricted waterbody detached from the atmosphere is considered to approximate closed system conditions, while non-static near surface water represents open system conditions [7]. Phases considered to be improbable in occurrence were suppressed in the models; these include epidote, phlogopite, muscovite, K-feldspar, andradite, annite, minnesotaite, greenalite, phengite, tremolite, hematite and nontronite [8]. Goethite was not suppressed as there are traces of this mineral have been reported in the locality [2].

Under closed system conditions, at all W:R ratios, goethite is obtained as the major phase in the end product. It is therefore unlikely that jarosite formed by alteration under restricted environment. Under open system conditions, goethite is initially the major phase in the end product at low W:R ratios, but at moderate (3:1) W:R ratios and higher, jarosite becomes the dominant phase when the model acidic water is used for interaction. The model therefore suggests prevalence of an open system condition for jarosite precipitation at moderate water-to-rock ratios. Meteoritic impact in the region may have caused the pooling of acidic water within the crater, which interacted with the surface driven water as well as the atmosphere. The origin of acidic water is hypothesised to have been caused by the upwelling of groundwater and interaction with surface water resulting in the oxidation of Fe^{2+} and lowering of the pH [9]. Oxidation of the sulphide species may have contributed to formation of the sulphate component and further lowering of the pH [9].

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Ions	Conc
Cl	0.25 mol/l
So_4^{2-}	1.0 mol/l
Fe^{2+}	5 mg/l
pCO_2	10^{-5}
pO_2	0.05

Table-1: Atmospheric condition in the Noachian time. For the simulations, we had to put Al^{3+}, Ca^{2+}, K^+, Na^+, Mg^{2+}, HCO_3^- and SiO_2 (aq.), at very low concentration, as the module requires the ions to run the program.

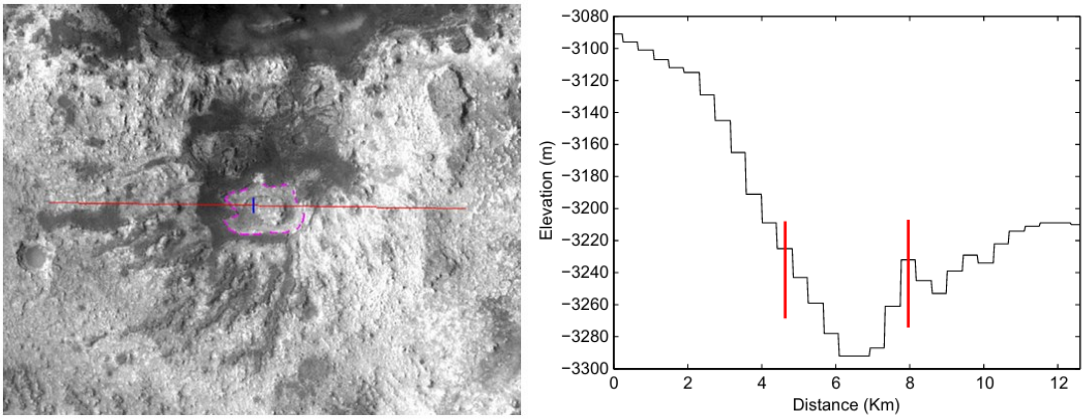
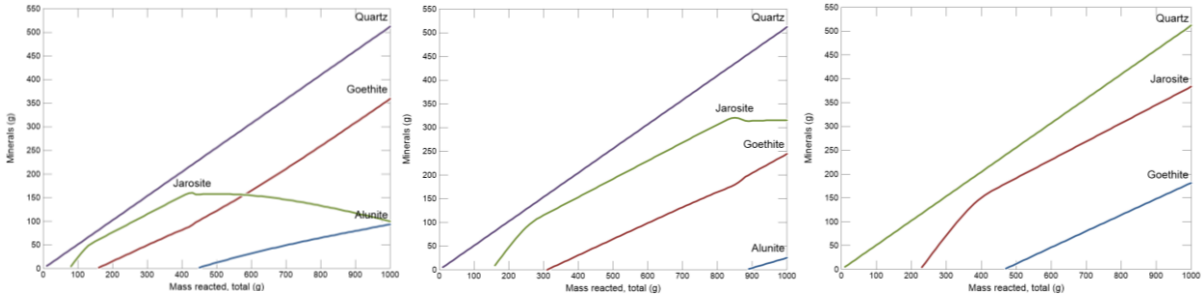
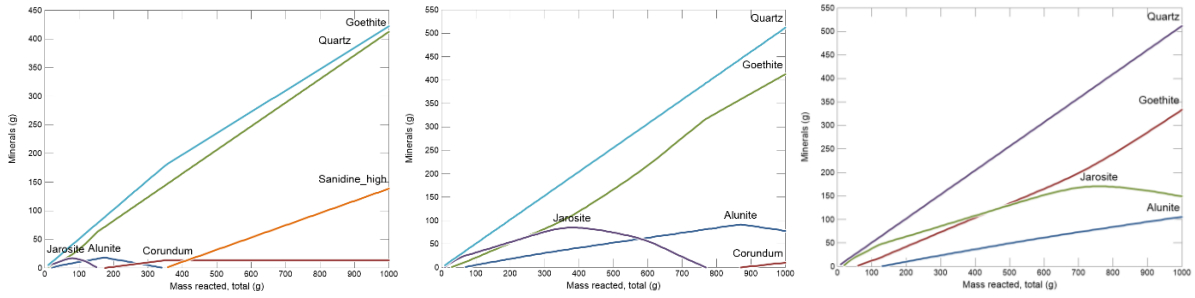


Fig 1: left: THEMIS image highlighting a jarosite-bearing ovoid outlined in magenta. The red line marks the MOLA transect displayed on the right, with the blue cross-hatch indicating the lowest point in the topographic profile. right: Topographic profile derived from gridded MOLA data along the transect shown to the left. Vertical red lines denote the western and eastern boundaries of the ovoid. (Farrand et al. 2009)



A. W:R = 1:1 B. W:R = 2:1 C. W:R = 3:1

Fig 3: The results of the simulations under the close system condition.



D. W:R = 0.1:1 E. W:R = 0.5:1 F. W:R = 1:1

Fig 2: The results of simulation under the open system condition.

Cation-Exchange Reactions in Nontronite – Indicator for Water Reservoir and Active Geochemical Processes on Mars

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Nontronite, a Fe-rich smectite clay, and various salts (e.g., sulphates, chlorides) are widespread on Mars [1-3] and are key to understanding the water dynamics and geochemistry of Mars, as their formations are closely related to the past interactions between rocks and liquid water [4]. Although liquid water is unstable on the current Mars (average surface conditions at -50 °C and 6 mbar CO_2), nontronite and salts serve as key indicators for potential liquid water and habitable environments on Mars due to their excellent water-loving properties.

However, we poorly understood nontronite and its interactions with salts, particularly regarding water sorption and retention. This is because previous studies have extensively focused on its smectite counterpart - montmorillonite clay, leaving a knowledge gap on nontronite. To fill this gap, we studied the water sorption and retention of nontronite (NAu-2, Ca-rich interlayer) and nontronite-salt systems in the presence of water vapour and ice under ambient and Mars-like conditions by using dynamic Vapor Sorption (DVS), Raman spectroscopy, X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM). Additionally, the water vapor sorption of nontronite clay was modelled using the composite isotherm model, derived specifically for smectites.

Our DVS and modelling results showed that nontronite formed an additional monolayer of water at 40 − 50 % relative humidity (RH) at 25 °C, with condensation began around 60 % RH. These results varied depending on the type of interlayer cations and coexisting salts. While monovalent salts only improved the water sorption of nontronite at RH > 80 %, this property was enhanced even at low humidities (5 – 30 % RH) in the presence of divalent salts. These interactions promoted ion mobility, cation-exchange reactions, and new hydrated mineral formation facilitated by thin adsorbed water films at interface. Based on Raman and XRD data, nontronite also retained brines of divalent chlorides at low temperatures. Especially, the mixtures of nontronite and divalent chlorides melted ice at temperatures below the eutectic temperatures to form liquid water.

In conclusion, divalent salts enhance water sorption of nontronite even under arid conditions, with nontronite selectively retaining salty water at low temperatures. Especially, new hydrated minerals can form via the interactions between nontronite and divalent salts with water vapor. It suggests that nontronite interacting with salts and water vapor/ice on Mars might form and retain liquid water following Martian diurnal cycles. Therefore, our findings provide essential insights not only into clay science but also into the aqueous geochemical processes on Mars and water preservation in Martian regolith. Furthermore, this research contributes to the broader search for water and habitability on Mars, which supports ongoing and future Mars missions.

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Formation mechanisms of hematite in Gale crater, Mars: insight from hematite crystallite sizes

Peretyazhko, T.[1], Szczerba, M.[2], Rampe, E.[3], Bristow, T.[4], Tutolo, B.[5], Ming, D.[3], Vaniman, D.[6], Morris, R.[3], Ralston, S.J.[2], Haney, N.[2], Blake, D.[4], Chipera, S.[6], Downs, R.[7], Hazen, R.[8], Morrison, S.[8], Treiman, A.[9], Yen, A.[10], Tu, V.[2], Thorpe, M.[11], Achilles, C.[12], Des Marais, D[4], Grotzinger, J.[13], Castle, N.[6], Craig, P.[6], Hausrath, E.[14] and Simpson, S.[2]

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Hematite is a widespread Fe(III) oxide on Mars and has been identified in Gale crater by the Mars Science Laboratory *Curiosity* rover. Hematite was detected by the Chemistry and Mineralogy (CheMin) X-ray diffraction (XRD) instrument in the samples drilled along *Curiosity* traverse exploring ~600 m of vertical stratigraphy. The variations in the width of hematite XRD peaks indicated that the crystallite size of hematite varies between the samples [1, 2]. We calculated crystallite size from whole powder pattern modelling of the collected XRD data. Our results revealed that the crystallite size ranged from 5 to 60 nm at lower elevations but remained unchanged and did not exceed 10 nm at the highest positions of the stratigraphic column. Crystallite size calculations for (110) and (104) XRD peaks also revealed that hematite crystallites were of equant shape. These findings suggested that hematite grew equally in all crystallographic directions, but the formation mechanism of equant shape hematite remained unknown.

To determine how equant shape hematite formed in Gale crater, we calculated crystallite sizes for synthetic hematite formed by Fe(III) hydrolysis, aqueous alteration of amorphous Fe(III) oxyhydroxide ferrihydrite, and thermal alteration of various Fe(III) oxyhydroxides. We also fitted lognormal distributions of crystallite sizes in Gale crater to constrain hematite growth mechanism.

A comparison of the data for synthetic hematite with the results from Gale crater showed that hematite of < 10 nm size and of equant shape could form by aqueous alteration of ferrihydrite at neutral to alkaline pH and by thermal alteration of ferrihydrite at low temperatures. Calculated lognormal distributions of crystallite sizes showed that samples with larger hematite crystallites did not have contributions of small crystallites, suggesting Ostwald ripening as the growth mechanism. Our analysis of XRD data suggests that hematite crystallites of small size could form in Gale crater by alteration of ferrihydrite in aquatic systems or by low temperature solid state alteration of ferrihydrite. The increase in crystallite sizes at lower elevations could be due to Ostwald ripening during late diagenesis.

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Mineral mapping in Uzon Caldera for classifying surficial alteration terrains over time and implications for similar studies of Mars

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The Uzon Caldera in the Kamchatka peninsula, Far East Russia, is a large area of post-eruptive volcanic hydrothermal activity. Igneous and lacustrine sedimentary rocks have been variably altered, including silicic, argillic, and zeolite-type alteration. While there are numerous works on the Uzon Caldera, there are few studies on the use of the Uzon hydrothermal field mineralogy as a Martian analog[1,2,3] and use of satellite remote sensing for time-series studies[4]. This study aims to evaluate extant surficial alteration in five hydrothermal fields in the caldera and determine the viability of mapping local-scale surficial alteration defined by fine grain mineral assemblages. A combination of Advanced Spaceborne Thermal Emission and Reflectance Radiometer (ASTER), ground truth laboratory study of Visible to near-infrared (Vis/NIR, 350-2500 nm), and X-ray Diffraction (XRD) data were used for this study. ASTER data were processed to remove atmospheric and vegetation effects. A support vector machine (SVM) classification algorithm was used on the ASTER data to create mineral maps to quantitatively classify the presence of clay, zeolite, sulfate, hydroxide, and iron oxide minerals. Maps of mineral groups are based on a unique combination of absorption features correlated with mineralogy. Laboratory Vis/NIR spectra of rock and soil samples collected from each hydrothermal field were used to provide ground truthing for these mineral maps. XRD data verified the presence of mineral and amorphous phases. These mineral maps were compared to the ground truthing data to determine the accuracy of mapping local surficial alteration and its applicability in both terrestrial and Martian environments.

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New model for NIR band assignment in 2:1 dioctahedral Fe-rich phyllosilicates

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Identification of clay minerals on Mars relies heavily on NIR spectroscopy, both remote and in situ. Difficulties arise for full characterization where Mg^{2+}, Fe^{2+} and/or Fe^{3+} are major octahedral cations, most especially in trioctahedral 2:1 phyllosilicates but also in dioctahedral clays [1]. In such cases, the $(Metal)_nO$-H combination band is displaced from the wavelengths specific to the $(Mg^{2+})_3O$-H, $(Fe^{2+})_3O$-H and $(Fe^{3+})_3O$-H vibrations and their assignments are obscured, together with the detailed chemistry and mineralogy of the clay.

Models have been developed in the past to systematize the effect of cation octahedral composition on the wavelength of O-H bands [2], but such models considered only cations directly linked to the OH groups. Previous investigations have also evaluated cation ordering in the octahedra and cis-trans position occupancy in 2:1 dioctahedral clays [3,4,5], providing a guide for further models.

We investigated three glauconite samples from the Filo Negro section in Seymour Island, Antarctica, one corresponding to the K-Pg boundary and two from levels ~1.5 and ~4 m above, both Palaeogene. They are interstratified glauconite-smectite with 83-85% glauconite layers, and their octahedral compositions (from SEM-EDS and Mössbauer spectroscopy) are:

	Fe(III)	Mg	Fe(II)	Al
K-Pg	1.32	0.31	0.18	0.19
1.5 m above	1.25	0.31	0.17	0.26
4 m above	1.12	0.33	0.18	0.36

NIR analysis of the samples showed four obvious bands, while the spectral deconvolution showed six bands, indicating that the bands correspond to complex combinations of cations around OH groups. We assigned band wavelengths based on: 1) trans-vacant structures, as established for Fe-rich 2:1 clays [5]; 2) first-order control is by the average charge/radius (q/r) of the two cations linked to OHs; and 3) second-order control is by the average q/r of the two next-neighbour cations closest to each OH. This model was used to generate cation distributions that matched the relative areas of the OH bands. Good matches were found for all samples where Mg, Fe^{2+} and Fe^{3+} never occupied adjacent sites, while other "rules" were different for each sample, as controlled by octahedral Al content.

Our model establishes for the first time how next-neighbouring cations modify OH wavelengths in phyllosilicates and provides an improved tool to infer clay chemistry on Mars from NIR data.

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Exploring serpentinization: Insights from Cabeço de Vide (Portugal) as an analog for Mars

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Historical milestones in space exploration, including Mars missions, have expanded our knowledge of the cosmos. The detection of serpentines on Mars provides evidence of past water activity, offers potentially habitable environments for microbial life, and preserves organic compounds and biosignatures [1]. The Perseverance rover mission aims to identify past environments capable of supporting life, search for biosignatures, collect samples, and prepare for future human exploration. Jezero Crater, the landing site of the Mars 2020 mission, exhibits diverse mineralogy, including serpentines, which are crucial for understanding the geological and astrobiological context of Mars [2].

Understanding the complex processes that led to the emergence and evolution of life on Earth is fundamental for exploring the possibility of life elsewhere in the universe. Serpentinization, a geochemical process where olivine is hydrated to form serpentine, magnetite, and brucite, involves the hydrothermal alteration of ultramafic rocks, leading to the production of hydrogen and abiotic methane through Fischer-Tropsch-type synthesis [2]. This study focuses on the ultramafic rocks of Cabeço de Vide (CdV), Portugal, as an analogue for similar processes on Mars. Due to its accessibility and active serpentinization, the hydrothermally altered mafic-ultramafic complex of CdV offers a unique opportunity to investigate continental serpentinized rocks on Earth. The CdV ultramafics are not ophiolites but are associated with the intrusion of mafic/ultramafic plutons [3].

The main objectives of this work are the mineralogical and chemical analysis, as well as the investigation of biosignatures preserved in the serpentinized rocks of Cabeço de Vide (CdV). Through biosignature studies, it is possible to distinguish biogenic and non-biogenic materials present in the samples using elemental and isotopic composition, as well as identifying specific lipid compounds produced by microorganisms.

Similar studies provide valuable data for interpreting Martian samples and advancing our understanding of the potential for life on Mars. These findings contribute to the broader field of astrobiology and clarify a crucial missing link in understanding the actual geological processes leading to the serpentinization of ultramafic rocks and their possible contribution to the origin of life.

Acknowledgments: This work was funded by the Fundação para a Ciência e Tecnologia (FCT), through GeoBioTec research unit (UIDB/04035) and a PhD grant (2024.03653.BD).

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Amorphous constituent of sialic/silicate rust in nakhlites

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Phyllosilicate-bearing and related products of aqueous alteration of Martian origin in nakhlites occur mainly in veins of "sialic or silicate rust" ("sialic rust" of terrestrial origin; [1] and references therein), dominated by generally amorphous material with phyllosilicate-like compositions. The silicate rust is relatively easy to study microanalytically, but the fine-scale heterogeneous mixture of diverse constituents requires nano-analysis. In those Mars meteorite groups that contain evidence of Martian aqueous alteration, the silicate-bearing alteration products are common parts of a phase association often called "silicate rust" or "sialic rust" [the history and use of these terms is reviewed in [1]) that commonly includes several or all of the following: a hydrous Fe-(±Mg)-silicate phase, excess silica (amorphous; recently well-characterized as opal-A [2]), ferrous oxides *sensu lato* (including oxides and oxyhydroxides), and carbonates with diverse cations.

The most common vein material in nakhlites, silicate rust, has homogeneous Z-contrast (atomic-number contrast) in Scanning Electron Microscope-Backscattered Electron (SEM-BSE) images [1 and references therein]. Most of this silicate rust is amorphous, exhibiting no diffractive volumes in Transmission Electron Microscope-Selected Area Electron Diffraction (TEM-SAED) [1 and references therein]. The volatile-rich nature of the vein material is evident near the fusion crust in the form of vesiculation and variegated Z-contrast [3,4]). The facts that the veins are crosscut by the fusion crust and that vesiculation and variegation of Z-contrast only occur near the fusion crust indicate that usually homogeneous meteorite-interior vein material lacking vesicles predates the meteorite's arrival at Earth and originated on Mars [5 and references therein].

Early work noted the compositional affinity with smectite and hypothesized origin from a gel (as in sol-gel synthesis of artificial smectite-like phases) [6,7], with small parts of the community subsequently referring to the silicate rust veins in nakhlites as "gels." However, as "gel" is rigorously defined as soft [8] and morphological characteristics from SEM analysis do not support such softness of silicate rust, it was concluded that the term gel is not appropriate and "nanocrystalline phyllosilicate" was proposed instead [9].

Published analyses of silicate rust veins in nakhlites by Electron Probe Microanalysis (EPMA), SEM-Energy Dispersive X-ray Spectroscopy (SEM-EDS) and TEM-EDS have been compiled, and compositional ranges for each oxide have been extracted from the compilation [1]. The ranges of major tetrahedral cations Si, Al, and Fe(III), octahedral cation Mg, and interlayer cations Ca and K (Na not considered due to unreliable results with vacuum-column electron-beam methods) are all very similar between hydrous veins that contain some nanocrystalline phyllosilicate material and hydrous veins that are entirely electron-amorphous [1]. Amorphous nakhlite vein material is quantitatively indistinguishable from nakhlite vein material containing nanocrystalline smectite-group clay minerals and other phyllosilicate minerals [1].

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Phengite textures in Precambrian impact spherules reveal extreme shock disintegration mechanisms

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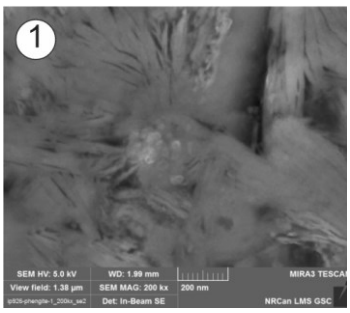
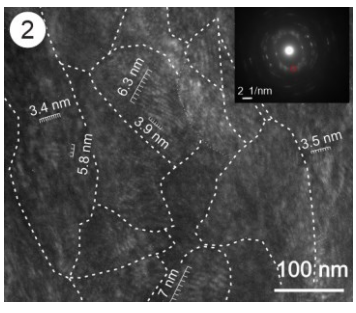
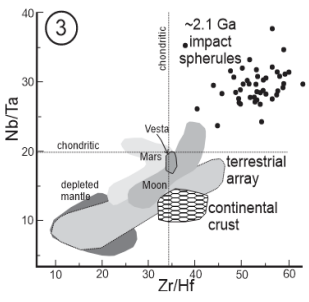
Spherules in a 2.1 Ga mudstone bed from northern Canada have preserved textural, mineralogical and geochemical features that provide insight into shock processes and source characteristics. The spherule-bearing bed, about 8 cm thick, has a 0.5 ppb Ir anomaly and variable proportions of spherules averaging about 700 µm in diameter. Spherules are cryptocrystalline (50 nm-50 µm grain size) and chemically zoned from K_2O-rich (up to 7 wt %) cores (0-500 µm) to CaO-rich (up to 24 wt %) mantles. Mantles comprise metamorphic assemblages of prehnite-quartz-K-feldspar-chlorite, whereas cores contain phengite* (Ph) in addition to the mantle assemblage. The mantle assemblage defines sub-greenschist facies (~310°C; <0.3 GPa) conditions imposed during ~1.85 Ga orogenesis. However, Ph contains up to 3.72 Si afu, suggestive of ultra-high (~8 GPa) crystallization pressures.

Phengite occurs as clusters of tiny (50 nm- 5 µm) particles (Fig. 1: *SEM BSE Ph image*). Examination by electron back-scatter diffraction (EBSD), TEM selected area electron diffraction (TEM-SAED), XRD and micro-Raman reveals a complex pattern of partial crystallinity. Both EBSD and SAED patterns indicate amorphous or nanocrystalline structure, whereas XRD and micro-XRD patterns indicate crystalline mica, and Raman spectra distinguish crystalline Ph from local muscovite neoblasts. Dark-field (DF) images based on SAED diffraction haloes show patterns of intersecting, amorphous, nm-scale lamellae separating nm-scale relics of crystalline Ph (Fig. 2: *particle domains annotated on TEM DF Ph image; corresponding diffraction haloes in inset image*). By analogy with planar deformation features in shocked quartz and other minerals, the amorphous bands in Ph particles are interpreted as shock-induced lamellae produced during a ~2.1 Ga impact-cratering event. Taken together, the fine particle size and network of intersecting lamellae appear to represent two stages in progressive mineral comminution: the first produced strongly damaged, airborne dust particles ejected from the crater; if carried to completion, the second stage would have further disintegrated these fragments into a dense, ultrafine aerosol of mixed crystalline and amorphous nanoparticles (<5 nm).

Geochemical analyses by LA-ICP-MS transects provide 48-element bulk compositional estimates for 41 spherules, and LA-ICP-MS elemental maps were produced for 5 spherules. Relative to average upper crust, the spherules have significantly higher high field-strength-element (Ti, Zr, Nb, Ta, Hf) contents. These elements are among the least mobile during alteration and metamorphism; their distribution and concentration are interpreted as intrinsic spherule characteristics. Most of the major- and trace-element compositional features can be explained by a dominant proportion of Precambrian continental crust (crater ejecta), however high Nb, high Nb/Ta, high Zr/Hf (Fig. 3: *trace element ratios relative to known solar system objects*) and abundant Ph are difficult to reconcile with known terrestrial source materials. Their origin could reflect an impactor derived from a source where geochemical fractionation occurred in a magma ocean, unlike known solar system materials.







*commonly used name for Si-rich (>3.1 atoms per formula unit (afu)) muscovite, discredited by the International Mineralogical Association

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LECTURE THEATRE 7 – SESSION 26

1D Nanoporous Clay Materials and Their Industrial Applications

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Designing functional nanoarchitectures through cross-assembly of 1D clay minerals

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Functional nanoarchitectures emerge at the intersection of Nanotechnology, Supramolecular Chemistry, and Materials Science, representing nanoarchitectonic strategies first introduced by Ariga and Aono [1]. These strategies enable the design of nanoscale structures by integrating diverse components into hierarchical materials with enhanced properties, using preparative tools like molecular self-assembly, layer-by-layer assembly, template-assisted synthesis, etc., that are employed to achieve tailored functionalities.

The application of nanoarchitectonics concepts to one-dimensional (1D) clay minerals - such as sepiolite, palygorskite, halloysite and imogolite - leads to innovative architectures that take advantage of their unique morphologies, nanoporous structures, large surface areas, and multifunctional characteristics. These materials demonstrate effectiveness in potential applications covering biomedicine, environmental remediation, industrial processes, and energy solutions, benefiting from their stability and versatility.

This communication examines cross-assembly strategies, focusing on the integration of 1D clay minerals with other low-dimensional materials, including carbon nanotubes (e.g., MWCNT) and filamentous biopolymers (e.g., nanocellulose, nucleic acids), as well as two-dimensional (2D) materials (e.g., smectites, vermiculites, layered double hydroxides—LDHs) and three-dimensional (3D) nanoparticles (e.g., carbon dots, silica, nanosized metal oxides). The resulting hybrid nanoarchitectures arise from interparticulate interactions primarily governed by van der Waals forces, hydrogen bonding, or electrostatic mechanisms.

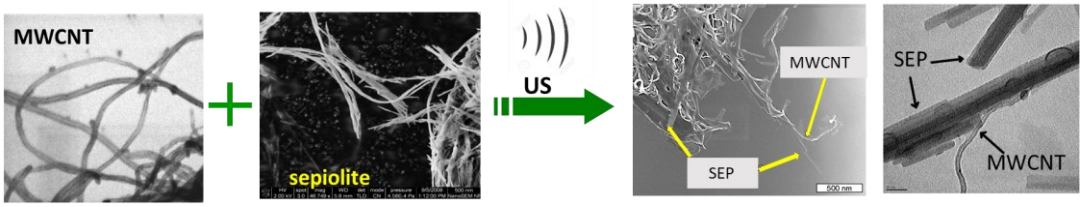

Fig. 1. Example of nanostructured material obtained by combining two 1D components: sepiolite and MWCNT [2.

Examples introduced here include advanced hierarchical materials with enhanced surface properties, such as adsorption, as well as improved magnetic, electrical, electrochemical, and bioactivity features, among others. Sepiolite exemplifies a fibrous 1D clay mineral capable of forming hybrid composites by assembly diverse nanoparticles (see for instance example illustrated in Fig. 1), offering promising applications [2-4]. Cross-assembly and nanoarchitectonic strategies extend to other nanoporous clays with 1D morphologies—such as palygorskite, halloysite, and imogolite—which present additional opportunities for tailored functionalities. These opportunities will be discussed in this communication, including considerations of fundamental principles, applications, and future perspectives.

Acknowledgements: AEI, Spain & ERDF A way of making Europe, EU (PID2022-137889OB-I00)

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Sustainable fibrous clay-based bionanocomposites as additive for the improvement of high strength art papers

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The demands of mechanical and manual printing such as intaglio printmaking and other multiple reproduction techniques on standardized paper supports pose a challenge in the field of engraving etching and stamping on paper. In this process, the paper, previously moistened, is subjected to high pressures of at least 2500 kg/cm², between an iron, zinc or copper plate or matrix to transfer the ink deposited on the matrix. Many standard papers present problems for using in these processes such as weaknesses that lead to premature degradation when subjected to wetting and subsequent application of intense mechanical pressures to force ink absorption. In general, the best papers for this application incorporate additives and processing that make them expensive. Hence, identifying strategies that improve paper strength while simultaneously advancing sustainability is of great importance. In this context, we have explored a new approach that combines the use of fibrous clays and polysaccharides to produce bionanocomposites that can be easily compatibilized with different types of pulps to develop a new type of high strength papers for mechanical printmaking.

Based on ISO 9706 [1], the preparation of various bionanocomposites based on the assembly of pectin and other polysaccharides, e.g., chitosan, with fibrous clays, sepiolite and palygorskite, to be used as additives to cellulosic pulps to develop papers with specific physical and mechanical properties suitable for printing and conservation applications, has been explored and patented [2]. Specifically, cellulosic pulps from eucalypt and flax were used, and requirements were established for paper sheets with a grammage between 200 and 300 gr/m^2, white or off-white color, visible grain and texture, high opacity and without coating. Additionally, papers have to meet a minimum resistance to press pressure of 2500 kg/cm², together with good wettability and elasticity, no acidity that could alter the ink, absorption in layers without subsequent transfer, and neutral pH with an alkaline reserve to resist external agents such as humidity and fungi. The presence of fibrous clay in the resulting papers is crucial as it ensures a high degree of interaction with the selected polysaccharide, resulting in the formation of an additive that is also capable of achieving a high degree of adhesion to the cellulosic pulp, resulting in excellent mechanical properties with Young's moduli from 0.73 to 2.38 GPa, which are similar to those measured for commercial art papers with different feature (from 0.76 GPa to 2.1 GPa). In addition, the adsorbent properties of the fibrous clay in the additive favor the stabilization of the inks used in printing. The possibility of using biopolymers from waste, such as pectin from citrus waste or chitosan from mollusc shells, as well as the incorporation of cellulosic pulp from agrowastes, such as olive tree pruning, affords to obtain papers not only with better mechanical properties but also more sustainable.

Acknowledgments: The authors gratefully acknowledge the funding by projects PID2022-137889OB-I00 (AEI, Spain & ERDF A way of making Europe, EU), ACIF-2021-0008 (Generalitat Valenciana & European Social Fund) and TEC2024-BIO-27 (Community of Madrid).

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Bioinspired superhydrophobic coatings based on attapulgite

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Bioinspired superhydrophobic surfaces are a highly interdisciplinary area of research, encompassing biomimetics, wettability theory, fabrication methods, and a wide range of potential applications. Over the past two decades, significant advancements have been made in these areas. However, the practical implementation of superhydrophobic surfaces have stagnated due to common bottlenecks, such as inadequate overall stability and the complexity and costliness of fabrication processes.

To address these challenges, we focus on polymer/attapulgite nanocomposites as a foundation for investigating the core scientific issues that underpin the technological bottlenecks associated with superhydrophobic surfaces. By leveraging natural clay minerals to construct bioinspired micro-/nanostructures, we have developed a series of superhydrophobic coatings that exhibit excellent overall performance. These coatings have been successfully applied in various fields, including rain erosion protection for 5G antenna covers and radar domes, as well as anti-icing applications for new energy facilities [1-3]. Additionally, we have explored their potential applications in lithium battery separators, solid-state electrolytes, and solar-driven interfacial evaporation [4,5]. Our research addresses the scientific challenges involved in industrialization, practical application, and future use, providing novel insights into the high-value utilization of attapulgite resources.

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Sepiolite modification with phosphatidylcholine to improve adsorption and controlled release of amphotericin B

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Sepiolite offers interesting properties for health care applications such as biocompatibility, large surface area and porosity, and strong adsorption capability [1]. Although less used than phyllosilicates for drug delivery purposes, several studies have reported the suitability of this fibrous silicate as a carrier of drug molecules such as the antibiotic neomycin [2] or the antiparasitic praziquantel [3] to facilitate their controlled release. In the case of hydrophobic drugs, the interaction with sepiolite can increase their solubility and improve their bioavailability. Modification of the external surface of sepiolite with phosphatidylcholine (PC) has also been proposed to increase its affinity for molecules with low water solubility [4]. Such strategy can be of great interest to develop a delivery system for amphotericin B (AmB), a broad-spectrum antifungal used for the treatment of various types of infections caused by fungi, which is poorly soluble in water and is typically combined with phospholipids in commercial formulations.

Thus, the present study addresses the immobilization of AmB on sepiolite following several synthetic routes: i) direct adsorption of AmB on sepiolite; ii) previous modification of sepiolite with a PC bilayer followed by AmB adsorption; iii) simultaneous adsorption of PC and AmB on sepiolite; and iv) formation of AmB-loaded PC liposomes, which are then immobilized on sepiolite. The physicochemical characterization of the resulting Sep-AmB and Sep-PC-AmB materials confirmed that the presence of PC contributes to increase the amount of immobilized AmB, reaching values close to 30% in contrast to that obtained for Sep-AmB (17%). The FTIR characterization of the Sep-PC-AmB materials confirmed the interaction of PC molecules with sepiolite through hydrogen bonds established with the silanol groups located at the external surface of the clay fibers. The AmB release studies were carried out in phosphate-buffered saline (PBS), showing that both Sep-AmB and Sep-PC-AmB materials provide a prolonged release of AmB for up to one month, but with faster release kinetics in the PC-based material. To evaluate their potential application in the treatment of eumycetoma, a skin infection disease with a high incidence in tropical and subtropical regions, in vitro antifungal assays were carried out against *Aspergillus flavus*, one of the main causative agents of such disease. The inhibition halos were higher for Sep-PC-AmB, confirming the benefit of sepiolite modification with PC as a delivery system of AmB.

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Molecular simulation study of the adsorption of Cu(Ⅱ) on palygorskite

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Palygorskite is a magnesium-rich fibrous clay mineral with a high specific surface area and high porosity. It is widely used in many fields such as agriculture, materials, and environment. As a mineral material that can be used for soil remediation and treatment of heavy metal pollution, the surface and interface properties of palygorskite have attracted much attention. Among typical heavy metals, it was found in the experiment that palygorskite can retain cooper ions in the soil well. However, the microscopic mechanism of palygorskite fixing copper ions is difficult to obtain from experimental means. Recently, as the ClayFF molecular simulation software was upgraded to ClayFF-MOH[1], the force field of copper ion is also improved[2]. Therefore, molecular simulation methods can better describe the interaction between palygorskite and copper ions. We employed ClayFF-MOH and new copper ion force field parameters to perform molecular simulation researches on the adsorption of cooper ions on palygorskite. We calculated the adsorption structure and free energy of copper ions inside and outside the tunnels of palygorskite, and analyze these microscopic information to explore the adsorption mechanism of copper ions on palygorskite , including comparing the fixation strength of copper ions inside and outside the tunnels, and find out the influencing factors of adsorption.

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Beneficiation and application of β-sepiolite in the field of environment and energy

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Originating from Xiangtan, Hunan province, the low-grade sedimentary sepiolite ore grades at 28.90 %, within which, quartz, talc, and calcite act as its principal gangue minerals. In order to improve the grade of sepiolite to the most and simplify the beneficiation process, the flowsheet of water leaching - sieving - dispersion - sedimentation was carried out, according to the nature of the raw ore. The grade at 92.77%of sepiolite was realized after efficient purification, and the enrichment ratio came to 3.21[1].

The novel magnetic sepiolite/Fe_3O_4/nZVI [nanoscale zerovalent iron] nanocomposite (nZVI@SepH-Mag) and sepiolite-supported Fe_3O_4 magnetite (SepMag) composite were proved to achieve the removal of contaminants (Cr (VI) and diuron) well. The Sep can inhibit the agglomeration and enhance the dispersibility of nZVI and Mag, Mag and nZVI displayed good synergetic effect[2, 3].

Sepiolite (Sep) nanofibers were coated with carbon and nanoscale SnO_2 to prepare an emerging nanocomposite (SnO_2–C@Sep), which exhibited to have enhanced the electrochemical performance. Sepiolite acts as a steady skeleton, carbon coating principally led sepiolite from an isolated to an electric state, and decoration of nanoscale SnO_2 was beneficial to the functionization of sepiolite. The nanocomposite SnO_2–C@Sep possessed enhanced lithium storage properties with stable capacity retention and low cost[4].

As a conclusion, sepiolite can be purified, and its applications in the fields of environment and energy is undoubtedly massive. 1D clay sepiolite has broad application prospects.

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Injectable halloysite-based nanocomposite hydrogel for antibacterial and hemostatic wound management

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Wound management remains a significant challenge in trauma care, particularly in controlling bleeding, preventing infection, and promoting tissue regeneration. Effective treatment is often hindered by the complexity of wound architecture, the inaccessibility of deep wounds, and the limitations of conventional wound dressings. In this study, an injectable halloysite-based nanocomposite hydrogel, comprising oxidized bacterial cellulose (oxBC), gelatin, and halloysite nanotubes (Hal), is developed to address these challenges. This nanocomposite hydrogel exhibits in situ gelation under physiological conditions, enabling it to conform to deep and irregular wound surfaces while providing mechanical reinforcement. The incorporation of Hal not only enhances the hydrogel's hemostatic properties by facilitating clot formation, but also ensures antimicrobial activity through targeted and sustained drug delivery, reducing the risk of antibiotic resistance and secondary infections. Additionally, the biocompatibility and hemocompatibility of this nanocomposite hydrogel further confirm its safety for wound management, making it a promising hemostatic and antimicrobial solution that can improve wound care outcomes, enhance patient recovery, and reduce complications.

Keywords

Antimicrobial drug delivery; Hemostatic agent, Halloysite nanotubes, Multifunctional polymer nanocomposite; Wound management.

Biohybrid xerogels with halloysite clay nanotubes and chitosan for sustainable applications

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Halloysite nanoclays (HNTs) and chitosan (Chit), environmentally friendly, abundantly available, and low-cost materials, were used to design a new xerogels in a systematic protocol without requiring sophisticated equipment or high energy input (Figure 1). Xerogels were derived from the hydrogels to assess the potential applications of the newly developed material in environmental field [1].

Initially, colloidal dispersions of Chit/HNTs were prepared and characterized. Rheological investigations of colloidal dispersions confirm the formation of hydrogels with a crosslinking agent exhibiting a dramatic increase in zero-shear viscosity alongside improved storage moduli. These hydrogels are subsequently transformed into self-supporting xerogels via a straightforward solvent casting technique. The final properties of the xerogels are influenced by the halloysite content, with the materials displaying enhanced thermal stability and exceptional mechanical.

These biohybrid structures show significant promise in environmental remediation applications, demonstrating high efficiency in the adsorption of organic compounds from water and exhibiting potential for atmospheric CO_2 capture. Crucially, the presence of an inorganic framework within the xerogels prevents structural collapse during drying, enabling precise control over morphology and form. Overall, the combination of sustainability, cost-effectiveness, and multifunctionality positions these xerogels as a compelling solution for pollution mitigation across a range of environmental settings.

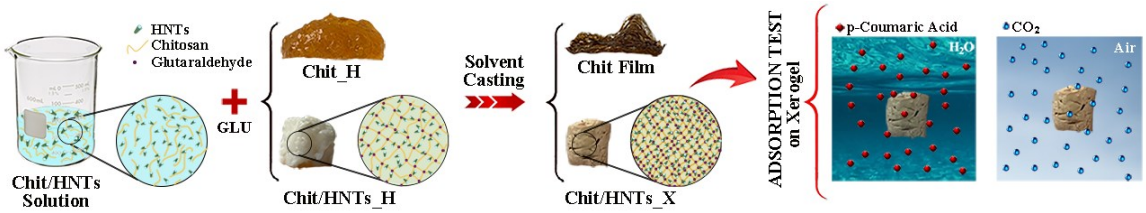

Figure 1. A scalable, systematic method was developed to create colloidal dispersions(C), hydrogels(H), and xerogels(X) using natural HNTs and Chit. These materials were tested in capturing pollutants from water and air as presented in the drawing.

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Hydrophobically modified halloysite nanotubes for the formulation of a water in oil pickering emulsion gel

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[3]Haute Ecole Arc Conservation-Restauration, HES-SO, Espace de l'Europe 11, 2000 Neuchatel, Switzerland.
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Among innovative gel formulations for metal conservation, a sustainable organogel based on bioderived polyhydroxybutyrate (PHB), ethyl lactate (EL) and chelating agents has been lately explored, bringing promising results [1]. However, since ligands are usually found in the form of aqueous solutions, both the hydrophobicity of PHB and the not ideal mixture of EL in water should be considered.

In this regard, we developed a PHB-EL organogel, containing the chelating water solution in the form of a water in oil (W/O) Pickering emulsion with Halloysite nanotubes (HNTs) as emulsion stabilizers. The inorganic reverse micelles were obtained by selective modification of HNTs shell using hexadecyltrimethylammonium bromide (C16Br) (Fig.1). This cationic surfactant provides the formation of nanotubes with a hydrophobic external surface and a hydrophilic core [2]. C16Br-HNTs were assessed based on their size, structure, contact angle, and ζ-potential measurements, with the attempt to better understand the way they act as Pickering stabilizers.

After the preliminary chemical and physical characterization of the gel properties, the removal of corrosion layers from a copper substrate was tested. Both the cleaning efficiency and the release of residues on the treated surfaces were analyzed. A controlled cleaning was obtained through the systematic regulation of the gel application time. Therefore, this work proposes an optimization of the previously studied organogel [1], obtaining a more homogeneous structure due to the presence of the W/O Pickering emulsion.

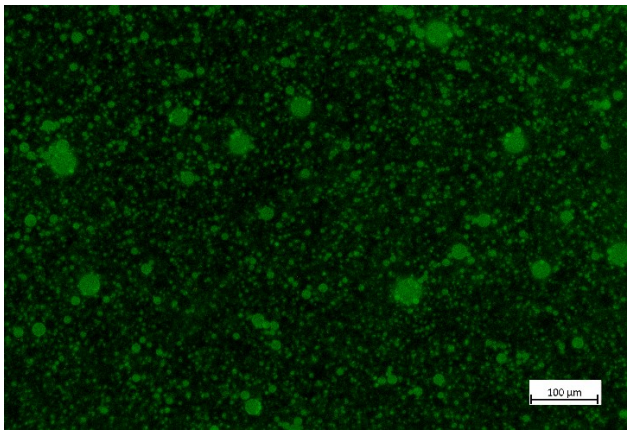

Figure 1. Chelating water solution in EL W/O Pickering emulsion using functionalized Halloysite nanotubes. Ligand was labelled with Rhodamine B.

[1] Passaretti A et al. (2021) Appl. Sci. 11:3405
[2] Cavallaro G et al. (2015) Langmuir 31:7472-7478

Preliminary investigation on the role of halloysite nanotubes in methane hydrate formation

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Hydrate-based gas storage has attracted growing interest due to its safety, high volumetric efficiency, and potential for large-scale gas storage under low-temperature and high-pressure conditions. Methane hydrate (MH), an is an ice-like crystalline compound formed by methane and water molecules, is considered a promising medium for such storage. Various porous materials, such as silica gel, metal-organic frameworks, and carbon nanotubes, have demonstrated effectiveness in promoting MH formation and storage.

Halloysite, a naturally abundant clay mineral with a distinctive nanotubular morphology and microstructure, holds potential as a sustainable alternative to layered clay minerals for MH storage. These unique structural features may significantly influence the thermodynamic and kinetic behaviors governing MH formation in halloysite-based systems.

In this study, differential scanning calorimetry was employed to investigate the effect of halloysite nanotubes on MH formation. The results reveal that, under constant initial pressure, MH nucleation time increases with the water content in the halloysite system but remains shorter than that observed in pure water (Fig. 1a). Heat flow analysis indicates that the enthalpy peak area of MH decreases with increasing water content, while it increases with pressure at a fixed water content. The highest MH conversion was achieved at a water content of 30 wt% (Fig. 1b). Moreover, the phase equilibrium conditions for MH in high water content systems (50 wt% and 60 wt%) closely resemble those in pure water. In contrast, lower water content systems (30 wt% and 40 wt%) exhibit significantly higher phase equilibrium pressures, with decreasing water content corresponding to increasing equilibrium pressure (Fig. 1c). These findings suggest that halloysite nanotubes play a crucial role in modulating MH phase equilibrium, likely through a “nano-confinement effect.” This mechanism warrants further investigation. Overall, this study provides new insights into the role of nanotubular minerals in MH formation and offers a valuable reference for understanding interfacial reactions between clay minerals and MH, as well as the development of nanotube-based materials for gas storage applications.

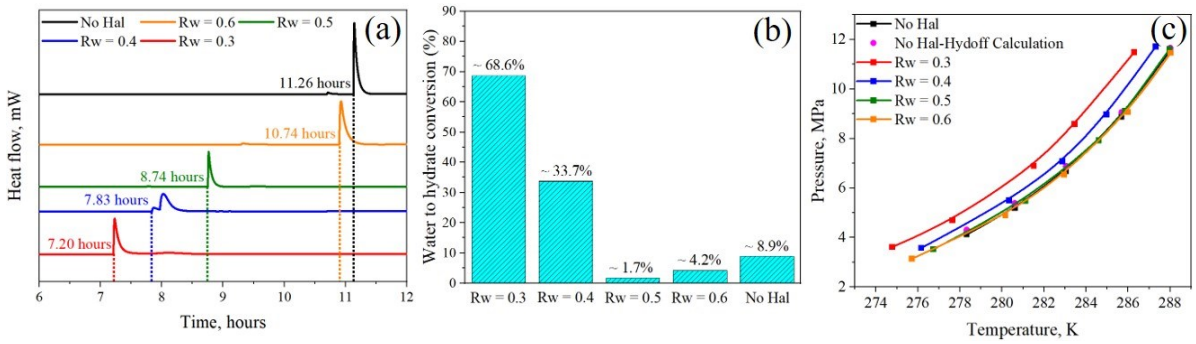

Fig. 1. MH nucleation time (a), conversion (b), and phase equilibrium conditions (c) in halloysite systems.

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From imogolite to Imogolite-Like-Structures family, 15 years of exciting discoveries

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Imogolite is a natural tubular nanoclay identified in 1962, whose structure was first described in 1972 [1,2]. It is also a metastable clay mineral that cannot be easily collected in large scale natural deposits. It can be retrieved from soils after long and tedious purification process. Fortunately, soon after its discovery, methods were discovered to produce synthetic imogolite [3]. Initially, these methods were mostly adapted to diluted conditions therefore limiting the yield for this material. The work of Levard et al. in two JACS papers revealed the possibility to go beyond this limit first for germanium based imogolite and one year later for silicon based imogolite [4,5].

The possibility to produce easily large quantity of concentrated imogolite suspension has enabled new perspectives and considerably accelerated the research in this area.

In this context, the last fifteen years have witnessed a succession of exciting discoveries and breakthroughs that have transformed the field and opened many potential applications.

In this presentation, we will review some of these breakthroughs:

- the discovery of double-walled imogolite and the discussion on the interplay between adhesion and curvature [6]
- the synthesis of hybrid imogolite and the improved accessibility of the internal cavity [7]
- the progress on the understanding of the surface properties of imogolite and its wall polarization [8]

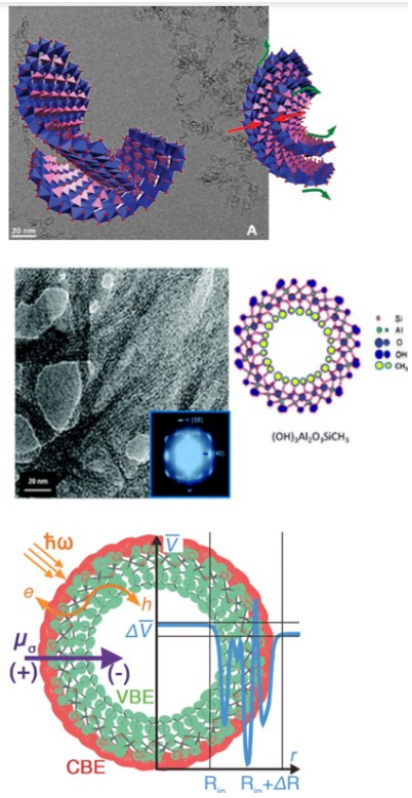

Figure 5: discovery of double-walled imogolite, hybrid imogolite and wall

All these seminal papers have triggered new perspectives with many follow-ups and potential applications. We will discuss some of them.

[1] Yoshinaga N and Aomine S (1962) Soil Science and Plant Nutrition, 8:22-29
[2] Cradwick P et al. (1972) Nature Physical Science, 240 :187-189
[3] Farmer et al (1977). J. Chem. Soc., Chem. Commun, 13:462-46
[4] Levard et al. (2008) JACS 130, 18, 5862-5863
[5] Levard et al. (2009) JACS 131, 47, 17080-17081
[6] Maillet et al. (2010) JACS, 132, 4, 1208-1209
[7] Bottero et al. (2011) PCCP, 13 , 2, 744-750
[8] Poli et al (2016) J. Phys.: Condens. Matter 28, 074003

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Tailoring functional properties in hybrid composites through geopolymerization: From fire resistance to pollutant capture

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Geopolymers[1], characterized by their three-dimensional Si-O-Al frameworks, are gaining increasing attention for their low environmental impact and notable functional properties, in respect of traditional Portland Cement. This work explores their applications beyond structural uses, focusing on the development of nanocomposite materials[2] with enhanced flame-retardant and adsorption performance. Two systems were designed and studied: Hydroxypropyl cellulose/halloysite nanotube (HPC/HNTs) composites for flame-retardant applications and alginate/HNTs gel beads for pollutant absorption were geopolymerized to enhance the functional potential of clay-based systems, resulting in significantly improved fire resistance and sorption capabilities. In both cases, successful geopolymer formation was confirmed through X-ray diffraction (XRD), Thermogravimetric (TGA), and Scanning electron microscopy (SEM) analyses. Thermogravimetric measurements were also employed to evaluate the CO_2 adsorption capacity of the samples, while dynamic mechanical analysis (DMA) provided insight into their mechanical properties. Geopolymerized gel beads exhibited markedly improved CO_2 uptake compared to their non-geopolymerized counterparts, attributed to increased porosity visible in SEM micrographs. Hydrocarbon absorption tests with dodecane further confirmed the enhanced sorption capacity of the geopolymerized beads. In parallel, HPC/HNTs composites treated with the same geopolymerization strategy displayed significantly improved flame-retardant behavior, with flames extinguishing in less than 0.5 seconds after ignition removal, far outperforming untreated films. These findings demonstrate the versatility of geopolymers in functional composite systems, offering a pathway toward materials that combine environmental sustainability with high performance in thermal and adsorption applications.

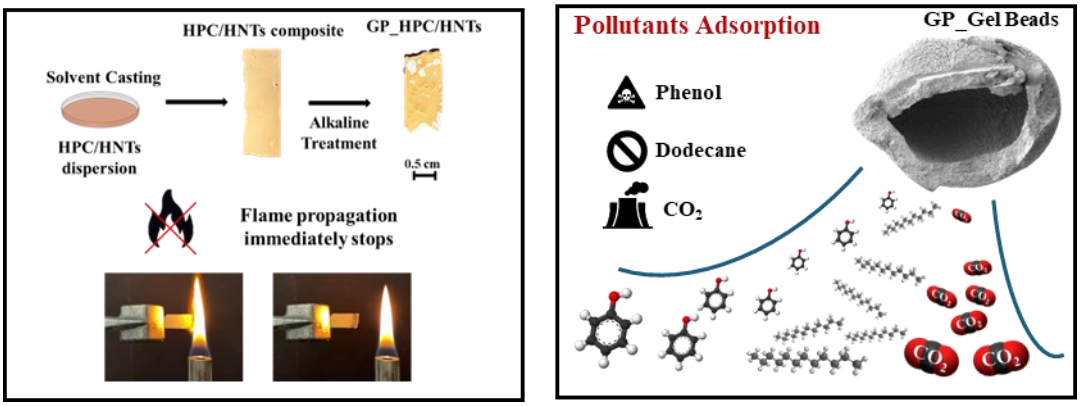

Figure 1. Geopolimerized HPC/HNTs Films for flame resistance properties (left) and Geopolimerized Gel Beads for pollutants adsorption (right).

[1] A. Lo Bianco, M. M. Calvino, G. Cavallaro, L. Lisuzzo, P. Pasbakhsh, S. Milioto, G. Lazzara, Y. Lvov, *Small* **2024**, *20*, 2406812.
[2] M. M. Calvino, G. Cavallaro, S. Milioto, G. Lazzara, *Environmental Science: Nano* **2024**, *11*, 1508.

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A comparative study on geopolymerization of nanotubular halloysite and platy kaolinite

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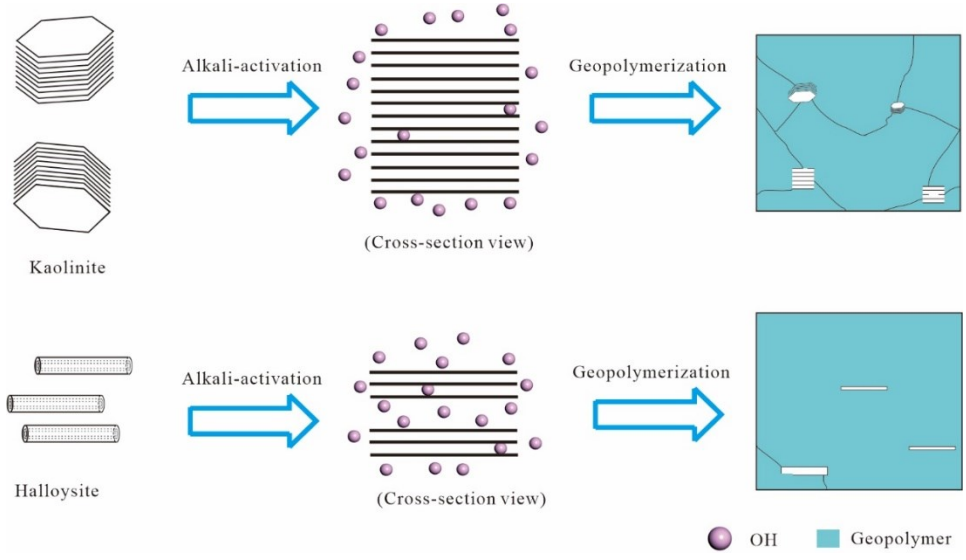
Geopolymer is an inorganic polymeric material with poly-aluminosilicate chains or networks, exhibiting great potential for cement substitution due to its excellent compressive strength, thermal stability, and durability. Geopolymer can be synthesized by mixing aluminosilicates (e.g., kaolinite, illite, etc.) and an alkaline solution, followed by curing at slightly elevated temperatures. Clay minerals are the most used precursors for geopolymer preparation.

As 1:1 dioctahedral clay minerals, kaolinite and halloysite have similar chemical compositions. Halloysite often possesses a nanotubular structure and differs in surface reactivity compared to platy kaolinite. The morphological contrast between the two clay minerals likely changes their geopolymerization behavior.

To get insights into the geopolymerization mechanism of alkali-activated nanotubular halloysite and platy kaolinite, a combination of techniques, comprising X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and scanning electron microscopy (SEM), and transmission electron microscopy (TEM), among others, was used to study the effects of SiO_2/Al_2O_3 ratio on the microstructure and properties of geopolymers derived from the two kaolin clay minerals. The results indicate that calcined halloysite showed higher geopolymerization reactivity than calcined kaolinite. In addition, the mechanical properties of clay-based geopolymer depended on not only the SiO_2/Al_2O_3 ratio but also the morphology of clay. Crystalline zeolite A and geopolymer were produced after alkali-activation of kaolin with a SiO_2/Al_2O_3 ratio of 2.5; and these products possessed porous and inhomogeneous microstructure, resulting in poor compressive strength. Geopolymer with a compact microstructure and high compressive strength were produced after the alkali-activation of kaolin with SiO_2/Al_2O_3 ratios exceeding 2.5. Regardless of the synthesis parameters, halloysite-based geopolymer exhibited higher early compressive strength and possessed a more compact and homogeneous microstructure than kaolinite-based geopolymer. This can be attributed to the nanotubular microstructure of halloysite, which can release more Si and Al during alkali activation than platy kaolinite. These results indicated that the different morphology and microstructure among clays have a significant impact on the microstructure and compressive strength of as-prepared geopolymers.



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How does the geological deposit affect the properties and applications of halloysite clay?

Cavallaro, G.[1], Lo Bianco, A.[1], Calvino, M.M.[1], Milioto, S.[1], Pasbakhsh, P.[2], and Lazzara G.[1]

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Halloysite clay is distributed worldwide in several geological deposits, which affect its composition, structure and morphological characteristics as well-documented in literature. On the other hand, the influence of the geological source on catalytic activity, biocompatibility and colloidal behaviour of halloysite is generally underestimated.

Herein, we compare the catalytic actions of halloysites from different deposits (Dragon Mine, Matauri Bay, Latah County and Djebbel Debbagh Guelma) towards degradation of ascorbic acid and photodegradation of ibuprofen. The variable catalytic efficiencies of clay nanotubes can be attributed to the presence of MnO and ZnO impurities in their composition. Within 80 minutes, the degradation of ascorbic acid is ca. 85-90% in the presence of clay nanotubes containing larger Mn and Zn amounts (halloysites from Matauri Bay and Djebbel Debbagh Guelma deposits). In contrast, halloysites with lower Mn and Zn contents (from Dragon Mine and Latah County) present smaller catalytic actions towards the degradation of ascorbic acid (ca. 65-70% within 80 minutes). Similar effects are observed for photodegradation of ibuprofen.

The peculiar composition of halloysite influences also its biocompatibility. In particular, the cytotoxic effect of halloysites is mostly dependent on the TiO_2 impurity content.

As concerns the colloidal behaviour, halloysites from different sources exhibit peculiar sedimentation kinetics and rheological characteristics. Among clay nanotubes, patchy halloysite (PT-Hal) from Kalgoorlie (Siberia) present promising properties because of the high aspect ratio, which favours the self-assembling between the nanotubes leading to the formation of gel-like system at very low concentration [2]. Based on both rheological investigations and geometrical considerations, the volume fraction required to generate the nanotubes entanglement is 100 times lower for PT-Hal with respect to halloysite from Latah Country. Interestingly, the addition of electrolytes does not prevent the formation of PT-Hal gel as evidenced by flow ramp tests at variable ionic strength.

The entanglement of patchy halloysite nanotubes dispersed in aqueous medium at variable concentrations (from 0.5 to 5 wt%) can be exploited to fabricate inorganic films using the casting method from water [3]. In contrast, the casting of aqueous suspensions of halloysite from Dragon Mine does not lead to the formation of films because of the nanotubes do not self-assemble in agreement with their smaller aspect ratio. Due to their inorganic composition, the films based on patchy halloysite nanotubes present tensile properties comparable to polymeric materials. As example, the elastic modulus of PT-Hal film is 1710 MPa. As a consequence of their inorganic composition, films based on patchy halloysite possess flame-resistance and heat barrier capacity that can be promising for the development of refractory materials.

[1] Calvino MM (2024) J Mol Liq 394:123721
[2] Lo Bianco A (2024) Small 20:2406812

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Fabrication of porous adsorbents from eco-friendly aqueous foam for high-efficient removal of organic pollutants and sustainable utilization

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[1]Key Laboratory of Clay Minerals of Gansu Province, Research Center of Resource Chemistry and Energy Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

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Porous materials have garnered significant attention in water pollution control due to their high specific surface area and efficient mass transfer properties. However, traditional adsorption materials, such as activated carbon, rely on energy-intensive processes like high-temperature activation, which limits their large-scale application. Although recently developed polymeric porous materials have enhanced adsorption performance, techniques such as phase separation and templating still suffer from high costs and insufficient environmental sustainability. Water-based foam formwork, as a green alternative, faces challenges due to poor foam stability. Pickering foam technology improves stability through amphiphilic particles, such as modified Fe_2O_3/SiO_2, but its surface modification process remains complex.

Based on the principles of green chemistry, our research group has proposed a novel strategy for cooperative foam stabilization utilizing natural plant-derived active ingredients and clay minerals. Research indicates that saponins extracted from Sapindus mukorossi, gallploid, and other plants form a composite interface with one-dimensional attapulgite (APT) through intermolecular interactions. The nanorod-like structure of APT enhances the suspension properties of the system, while its surface-active groups synergistically interact with saponins to stabilize foam and significantly extend its lifespan. The binding sites between saponins and APT were identified using gradient dissolution analysis. Building on these findings, a multistage porous composite adsorption material was developed via free radical polymerization, demonstrating effective removal capabilities for cationic dyes and antibiotic pollutants [1-3].

To address the challenge of adsorbent regeneration, the team developed a carbonization-based regeneration and resource recovery technology [4-6]. Through controlled pyrolysis, the spent adsorbent is converted into a porous carbon/clay composite, thereby restoring its performance. When utilized for soil improvement, the regenerated material can enhance water retention capacity, increase organic matter content, and improve soil aggregate structure. The "adsorption-regeneration-improvement" technology system has achieved a green life cycle. Relevant outcomes offered a novel pathway for the sustainable development of environmental functional materials.

[1] Yu H et al. (2021) J Environ Sci 102: 352.
[2] Duan, F et al. (2022) Colloid Surf A 648: 128695.
[3] Duan, F et al. (2023) J Clean Prod 416: 137757.
[4] Deng X et al. (2023) Bioresour Technol 388: 129754.
[5] Duan , F et al. (2023) Chem Eng J 474: 145942.
[6] Deng X et al. (2024) Bioresour Technol 35: 103679.

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THURSDAY

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LECTURE THEATRE 1 – SESSION 29

Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials

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Organic-inorganic hybrids having a talc-like structure for light-driven applications

Dullin, T.[1,2], Brendlé, J.[1], Schuller, A.-S[2], and Ley, C. [2]

[1]Institut de Science des Matériaux de Mulhouse CNRS UMR 7361, Université de Haute-Alsace, Université de Strasbourg, Mulhouse, France; jocelyne.brendle@uha.fr
[2]Laboratoire de Photochimie et d'Ingénierie Macromoléculaires - EA4567, Université de Haute Alsace, Université de Strasbourg, 3b rue Alfred Werner, 68093 Mulhouse, France

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Organic-inorganic hybrids having a talc like structure (TLH) can be prepared by a process based on sol-gel chemistry which enables the formation of the materials under mild conditions in a one-step method. In this case, thanks to the use of organoalcoxysilanes as silicon sources, functional groups are covalently linked to the silicon atoms of the tetrahedral sheets and are pending in the interlayer space and present at the surface [1].

The goal of this study is to create a new type of photopolymerizable organic-inorganic hybrids talc-like structure containing photopolymerizable groups and Thioxanthone, a chromophore which has often been used as triplet sensitizers and photoinitiators of polymerization and has interesting photophysical properties [2]. These hybrid materials would be able to react with light, thus opening the way to new applications in various technological fields.

A series of TLH and TX-TLH were prepared starting from organotrialcoxysilanes having different functionalities (*3-methacryloxypropyl, 3-aminopropyl,* 3-glycidyloxypropyl and mixtures of two or three of them), an ethanolic solution of magnesium salts and sodium hydroxide. The key parameters governing the synthesis were finely tuned for each system. It was shown that room temperature (20°C) and short aging times lead to the formation of lamellar structures as confirmed by X-Ray diffraction. The stability of the Si-C bond and the presence of TX was proven by Fourier transformed Infrared spectroscopy. ^{13}C and ^{29}Si solid state nuclear magnetic resonance shed respectively light into the structural investigations of the attachment of pendant organic chains to the inorganic framework as well as on the integrity of TX and the degree of polycondensation of silicon species.

The determination of quantum yields and lifetimes of luminescent species enable gathering information on the influence of TX confinement on the photophysical and photochemical properties. Finally, photopolymerization was performed by using Digital Light Processing (DLP).

This set of experiments showed that the combination of TX and TLH leads to very interesting hybrid materials showing original properties.

[1] Brendlé J (2018) Dalton Trans 47: 2925-2932
[2] Christmann J et al (2021) J. Phys. Chem. B 121: 1972-1981

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Photochemistry of 2D Molecular Assemblies on Clay Mineral Nanosheets

Yohei Ishida

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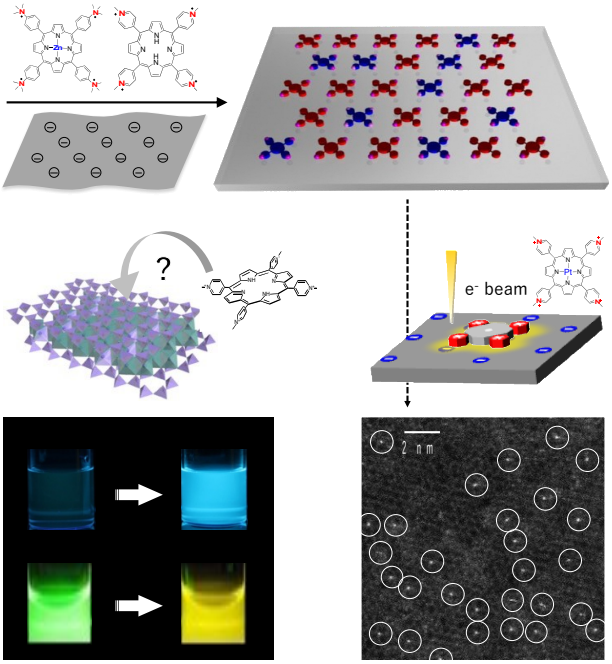
In living systems, the flexible and complex higher-order structure of proteins work as “ultimate” reaction fields that impart both flexibility and regulation, and enable various functions such as enzyme and photosynthetic reactions. The objective of this talk is to discuss the utilization of the surface or interlayer of anionically charged inorganic clay mineral nanosheets as chemical reaction fields for molecular guests via multiple electrostatic interactions [1].

1) Molecular structures are altered by the atomically flat surface, which restricts molecular motions and vibrations, thereby suppressing non-radiative deactivation pathways. This results in strong emission enhancement, applicable to a wide variety of molecules, and we termed this phenomenon “Surface-Fixation Induced Emission” [1].

2) Since host–guest electrostatic interactions play a key role, photochemical reactions involving two or more types of molecules can be easily designed. For the first time, photochemical reactions with near-unity quantum efficiency were achieved on inorganic surfaces. These findings enabled the design of multi-step light-harvesting systems that utilize the entire visible spectrum, combined with subsequent electron transfer reactions to mimic natural photosynthetic complexes [2]. This strategy was further extended to noble metal nanoparticles and clusters [3].

3) To achieve a molecular-scale understanding of these multiple electrostatic interactions, I recently employed scanning transmission electron microscopy (STEM) and successfully obtained the first atomic-scale images of free-standing monolayer clay nanosheets and their supramolecular complexes [4]. I am currently expanding this technique for the direct imaging of molecular and supramolecular structures, aiming to understand their unique functions governed by multiple electrostatic interactions.



[1] Ishida Y. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2886. (Account)
[2] Ishida Y. *Pure Appl. Chem.* **2015**, *1*, 3. (Account)
[3] Ishida Y. *et al. Acc. Chem. Res.* **2017**, *50*, 2986. (Account)
[4] Ishida Y. *Langmuir* **2024**, *40*, 6065. (Invited Feature Article)

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Insight on the photocatalytic properties of ZnAl-Cl LDH derived mixed oxide toward degradation of persistent herbicide in water

Hao Wang[1], Claude Forano[1], Monier Guillaume[2], Réveret François[1], Mohamed Sarakha[1], Vanessa Prévot[1]

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[2]Université Clermont Auvergne, CNRS, INP Clermont, Institut Pascal, F-63000 Clermont–Ferrand, France

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Layered Double Hydroxides (LDHs) containing transition metals are materials with tunable chemical compositions and unique lamellar structure. They have received extensive advertence in recent years due to their photoactivity, and particularly in the photocatalytic degradation of various pollutants, such as bisphenol A through advanced oxidation processes (AOPs). Upon thermal treatment, the layered structure of LDHs collapses, leading to the formation of non-stoichiometric, metastable mixed metal oxides with semiconducting properties. Such chemical transformation can enhance photocatalytic performance by increasing the surface area and improving redox properties [1].

In this study, a series of Zn_2Al_1-Cl-LDOs photocatalysts was synthesized via a coprecipitation method and subsequently calcined at different temperatures (300, 500, and 700°C). These materials were then employed as persulfate (PS) photoactivators to degrade chloridazone (CLZ), a selective herbicide belonging to the pyridazinone-derived pesticide class [2].

The Zn_2Al_1-Cl-LDOs were systematically characterized by XRD, SEM, BET and bandgap measurements. The results indicated the successful formation of $ZnO/ZnAl_2O_4$ mixed metal oxides with high specific surface area and narrow bandgap, providing abundant active sites for photocatalysis. Photocatalytic performance of the Zn_2Al_1-Cl-LDOs calcined at 300, 500, and 700°C was evaluated through the degradation of CLZ with/without PS under UVA irradiation. As shown in Fig.1 Zn_2Al_1-Cl-500°C/PS/light system exhibited the highest degradation efficiency achieving 94.3% CLZ removal within 4h. Compared to pure $ZnAl_2O_4$ and ZnO obtained by calcinated at 500°C, the heterojunction interface formed between $ZnO/ZnAl_2O_4$ in the Zn_2Al_1-Cl-500°C sample significantly promoted charge transfer resulting in enhanced photocatalytic activity. XPS, photoluminescence and radical quenching experiments further confirmed that oxygen vacancy (V_o) generated during calcination facilitated the separation and transfer of charge carriers, while also playing a key role in activation of PS to generate $HO^{\bullet}$ and $SO_4^{\bullet-}$ radicals, the main active species involved in CLZ degradation. Moreover, the effects of operational parameters such as catalyst and PS dosage, initial pH were systematically investigated within the Zn_2Al_1-Cl-500°C/PS/light system. In summary, this work provides insights into the relationship between the structural features of Zn_2Al_1–Cl LDOs and their photocatalytic performance, with potential implications for the design of efficient photoactivators for environmental remediation.

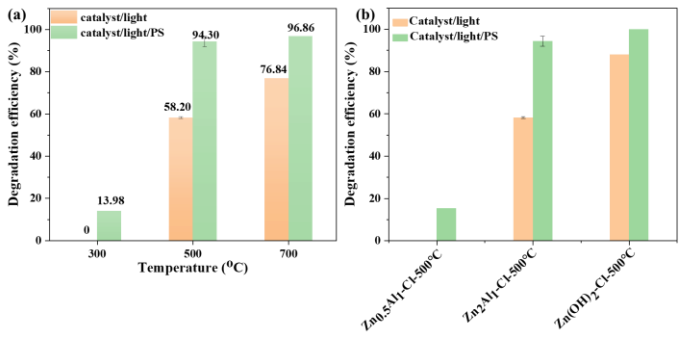

Fig.1. Effect of different calcination temperatures (a) and oxides compositions (b) on CLZ photodegradation with/without PS.

[1] Ali Khan, A., et al. (2023) Journal of Energy Chemistry. 84: p. 242-276.
[2] El-Said, W.A., et al. (2018) Journal of Environmental Chemical Engineering. 6(2): p. 2214-2221.

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Proton conductivity of montmorillonite nanosheet membranes and their application as electrolytes in fuel cells

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Solid oxide proton conductors that can operate at low temperatures are becoming increasingly important because of the demand for the development of solid oxide fuel cells (SOFCs) and protonic ceramic fuel cells (PCFCs). Herein, we report a proton-intercalated montmorillonite nanosheet ($H_{0.33}/(Al,Mg,Fe)_2Si_4O_{10}(OH)_2$,) membrane for use in fuel cells. The montmorillonite nanosheets were obtained by exfoliating low-cost and environmentally friendly clay minerals (montmorillonite), which are abundant on Earth and free from environmental pollutants such as fluorine. The montmorillonite nanosheets membrane exhibited high proton conductivity (0.02–0.005 S/cm2 at 90 °C) and superior hydrogen gas barrier properties compared with Nafion. A fuel cell fabricated using the montmorillonite nanosheet membrane operated from -10 to 140 °C, bridging the gap between conventional low- and high-temperature fuel cells. The montmorillonite fuel cell showed a power density greater than 250 mW cm^{-2} at 90 °C. The achieved power density is three times greater than the highest value reported for a fuel cell constructed with an inorganic solid electrolyte and operated at 90 °C. Silicate nanosheets, being an inorganic solid, exhibited a more than 100 times greater hydrogen barrier performance than polymer solid electrolytes such as Nafion while exhibiting high flexibility and good mechanical strength despite being an inorganic solid. This high fuel cell performance is speculatively attributed to the presence of stable intercalated protons, the high hydrogen barrier performance and the good flexibility of the membranes. This study, in which we found that environmentally and economically friendly nanosheets can be used as electrolytes for fuel cells that support the SDGs, is expected to significantly contribute to future society and open new research fields.

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Clay mineral-based separators and solid-state electrolytes for advanced lithium metal batteries

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High-energy lithium metal batteries play a crucial role in promoting the rapid development of fields such as pure electric vehicles and aerospace. However, their commercialization is severely constrained by technical bottlenecks, such as lower ion transfer and poor interface stability. By tuning the performance of separators or solid-state electrolytes, these bottlenecks can be effectively addressed, significantly enhancing the electrochemical performance of the battery without increasing its volume or mass. This strategy is key to developing high-energy, long-life, and high-safety lithium metal batteries.

Clay minerals, due to their high specific surface area, tunable microstructure, and excellent ion exchange capability, exhibit great potential in the development of new energy storage materials. However, current research has yet to fully reveal the intrinsic relationship between the "microstructure-surface chemistry-electrochemical performance" of clay minerals, particularly the ion transport dynamics, which remains unclear and constitutes a key scientific challenge for their application in energy storage. Therefore, by integrating specialized wettability surfaces and electrocatalysis, we have innovatively proposed a strategy that utilizes clay minerals and their surface/interface chemical control. This has led to the successful development of various clay mineral-based battery separators and the elucidation of the impact of their surface chemistry on polysulfide adsorption, electrocatalysis, and ion transport in lithium metal batteries[1-3]. Additionally, we have developed a range of montmorillonite-based composite solid-state electrolytes, uncovering how their microstructure and surface active sites influence the ion transport and electrochemical stability of composite solid-state electrolytes [4,5]. The in-depth exploration of these issues not only provides innovative solutions to improve the safety, energy density, and cycling life of lithium metal batteries but also opens new avenues for the high-value utilization of clay minerals.

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Aggregation behaviour of colloidal clay-organic hybrids observed by utilizing fluorescence correlation spectroscopy

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Fluorescence correlation spectroscopy (FCS) is a statistical analysis, via time correlation, of stationary fluctuations of the fluorescence intensity. Fluctuations in fluorescence intensity, depending on the intensity or quantity of molecular diffusion, physical and chemical reactions, and aggregation, from a small area of the sample are measured using confocal microscopy or two-photon excitation microscopy. An inverse Fourier transform of the intensity spectrum (power spectrum) yields temporal autocorrelation. FCS and dynamic light scattering (DLS) are both powerful techniques used to study particles in solution. Although FCS can be applied only for fluorescent samples, it can be applied for analyses of a wide concentration range of samples, compared to the case of DLS. This advantage of FCS should be suitable for analyzing interaction between organic fluorophores and colloidal clays. Therefore, in the present study, the aggregation behavior of colloidal clay particles upon adsorption of cationic organic fluorophores was investigated by FCS excited through two-photon process.

As for a clay, synthetic saponite (SSA, Kunimine Industries, Japan) was employed. Dispersion of SSA with a concentration of 0.05 g/L was mixed with a water solution of MPBBI or MPBBI-PEG (See Figure 1). Immediately after mixing MPBBI solution, the size of fluorescent particle in the sample measured by FCS was about 100 nm which is almost the same as that for colloidal pristine SSA measured by DLS. This indicates that SSA-MPBBI hybrid should be dispersed in the colloid without aggregation. The size was almost constant for 20 hours after mixing SSA and MPBBI water solution. However, the size was increased to be 200 nm after 26 hours. This fact indicates the aggregation of hybrid began from 20 hours after mixing SSA and MPBBI solution. When MPBBI-PEG was hybridized, the size of the fluorescent particle after mixing was also about 100 nm. However, the size was almost constant for 22 hours. This fact suggests introduction of hydrophilic PEG chain into the hybridized chromophore may prevent aggregation of hybridized particles. We also measured the change of the size of fluorescent particle by addition of organic solvent to aqueous dispersion of SSA-MPBBI hybrid prepared under the same condition described above. Immediately after addition of dimethyl sulfoxide (DMSO) or ethanol, size of the fluorescent particle was increased from about 100 nm to 200 nm. Thus, the aggregation of hybrids induced by addition of organic solvent was clearly observed.

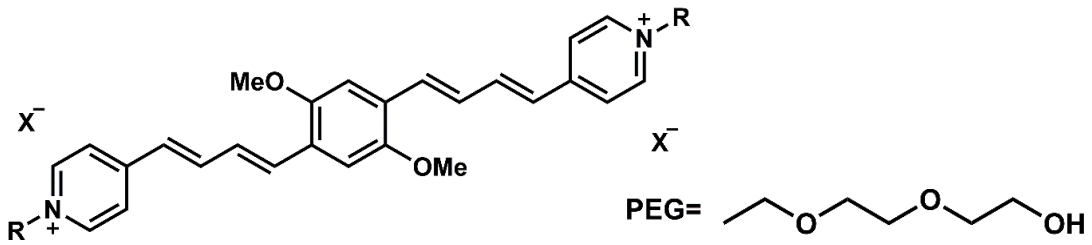

Figure 1. Molecular structures of 2,5-dimethoxy-1,4-bis[N-methyl-4-(1,3-butadien-1-yl)pyrinium]-benzene iodide (MPBBI (R = CH_3, X = I)) and 2,5-dimethoxy-1,4-bis{1-[2-[2-(2-hydroxyethoxy)-ethoxy]ethyl]-4-(1,3-butadien-1-yl)pyrinium}benzene Iodide (MPBBI-PEG (R = PEG, X = I)).

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Materials Design of Bentonite by Purification and Organic Modification

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The function of the layered materials has been designed by the composition of the each layer (nanosheet) [1], intercalation and the hybridization with other nanomaterials [2]. Among available layered materials, bentonites and their derivatives have been used in a wide range of industry, while new application and new materials are expected. In this presentation, our recent approaches of exploring bentonite and the modification for the on-going application as well as for the development of novel application will be introduced.

An iron-containing smectite is found to be the first example of naturally occurring photocatalyst for hydrogen evolution from water and aqueous methanol. The photocatalytic hydrogen evolution of the present clay mineral was accelerated through host-gest reaction which is an important advantage of the layered clay mineral. In addition, size-controlled Pt nanoparticles were immobilized homogeneously on the platy particles of the clay mineral to boost the photocatalytic hydrogen evolution. The present photocatalyst exhibited high stability in acidic environment and upon photocatalytic recycling test.[3]

On the other hand, there is a demand for clay minerals with low colored impurities (with high whiteness) for the study on photophysics and photochemistry of the adsorbed molecular species and for several industrial application.[4] Along this line, a purified bentonite with useful whiteness was developed [5] and used as a component of nanocomposite hydrogel of gelatin[6-8] and a microporous material (pillared clay).[9]

Raw materials, process for the purification, and organic modification with surfactants of varied molecular structures and composition of the organoclay were examined to design the functions.

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Self-Assembly of Monodisperse Nanosheets Into Columnar Nanofibers

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Inorganic nanosheets obtained by exfoliation of layered crystals are known to form intriguing colloidal liquid crystals (LCs). [1] They have been applied for fabrication of anisotropic polymer composite materials, structural color materials, etc.[2] However, large polydispersity in lateral size of the nanosheets limited precise design of self-assembled structures and materials design.

Here, we demonstrate that very unusual mesophases are reversibly formed by self-assembly of anionic *monodisperse* nanosheets (mNS) in combination with various cationic species (Fig. 1).[3] In an as-prepared tetramethylammonium (TMA)/mNS aqueous dispersion, mNSs with the thickness of 0.65 nm and the lateral size of 14 nm were isotropically and uniformly dispersed. As [mNS] and [TMA] increased, one-dimensional columnar nanofibers (ColNF) formed; the ColNF was composed of alternating stacking of TMA and mNS with the periodic distance of 1.7 nm as revealed by small angle X-ray scattering and transmission electron microscopy. The ColNFs formed fluid columnar nematic LC phase as observed by crossed polarizer observation. Crystalline fibrous bundles of ColNF were also formed. The formation and dissociation of these mesophases were reversible and controllable by many factors such as solvent composition, kind of interlayer cations, and temperature.

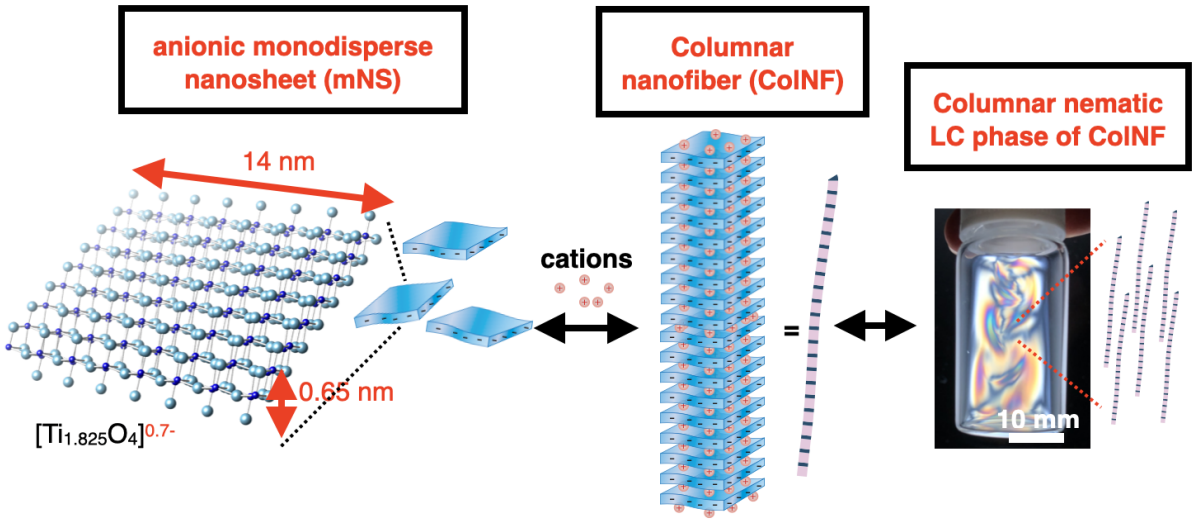

Fig. 1 Schematic drawing and the photograph under crossed polarizers of the ColNF dispersion.

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Columnar brucite-type layered metal hydroxides with tunable shape and surface properties associated with edges

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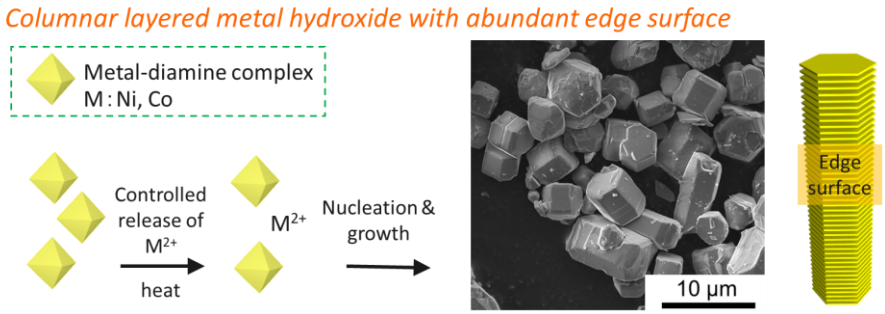
Lateral planes of layered crystals, commonly referred to as edges, have attracted increasing attention due to their chemical and physical properties, which differ significantly from those of the basal planes. Research advances in spatially resolved electrochemical analysis of layered materials have revealed the remarkable properties associated with edge surfaces, including enhanced charge transfer rate, high areal capacitance, and increased redox ability [1][2]. One of the promising strategies to exploit these surface characteristics associated with edges for practical applications involves tailoring the crystal morphology to increase the proportion of exposed edges, typically by preparing columnar crystals composed of vertically stacked layers. Recently, we discovered that columnar layered transition metal hydroxides (β-$Ni(OH)_2$ and β-$Co(OH)_2$), with an aspect ratio of thickness to lateral size greater than one, can be synthesized using metal-diamine complexes as precursors under specific conditions [3]. In this study, we further evaluated the controllability of both the size and aspect ratio of columnar crystals, as well as the edge-specific characteristics of columnar hydroxide crystals (Scheme 1). The stability and concentrations of the metal-diamine complexes were key parameters in determining the crystal shape. The average size along stacking direction of columnar β-$Co(OH)_2$ crystals was controlled between 1–10 µm, while maintaining an aspect ratio between 1 and 2 by varying diamine/Co ratio. Furthermore, anisotropic crystal growth was further promoted at more concentrated conditions, resulting in the formation of columnar β-$Co(OH)_2$ crystals with high aspect ratio exceeding 20. Infrared spectroscopy and electrochemical measurements revealed that the columnar crystals contained abundant OH groups and metal cations with characteristics distinct from those found on basal planes. These findings highlight the potential of edge properties as a new design parameter for the functionalization of layered materials.



Scheme 1. Shape-controlled preparation of columnar brucite-type layered metal hydroxides with abundant edge surface

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[2] Wei J et al. (2025) J Am Chem Soc doi.org/10.1021/jacs.5c00438 (ASAP article).
[3] Muramatsu K et al. (2022) Inorg Chem 61:8490-8497.

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Bridging the gap between osmotic and crystalline swelling in smectites clay minerals using levitated droplets

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The swelling behavior of smectite clay minerals has been extensively investigated due to their critical role in construction stability, environmental applications or in pharmaceutical and cosmetic industries. Two distinct swelling regimes have long been recognized. The crystalline swelling involves the incorporation of a few water sheets between clay layers, which is probed on clay powders placed in a humid environment [1]. At the opposite, the osmotic swelling corresponds to the complete delamination of individual clay layers in a solvent, involving the study of particles organization in suspension [2]. Although a linear transition between osmotic and crystalline swellings has been proposed [3], a complete description of smectite swelling has never been achieved.

Here, we propose to take advantage of acoustic levitation coupled with Small Angle X-ray Scattering (SAXS) to follow the evolution of the interlayer space of a smectite in a single levitated droplet. The advantage is to be able to observe rapid, non-equilibrium phenomena over a wide concentration range, while avoiding anchoring effects during drying [4]. The results reveal a gradual shift from osmotic swelling to crystalline swelling, marked by a transition from a pure nematic glass to a coexistence zone where the nematic phase contracts and a saturated crystalline phase emerges, ultimately progressing to an unsaturated crystalline state (Figure 1). This transition occurs through a continuous process in which the interlayer space decreases from four water layers to zero water layers, forming interstratified interlayers structures along the way [5].

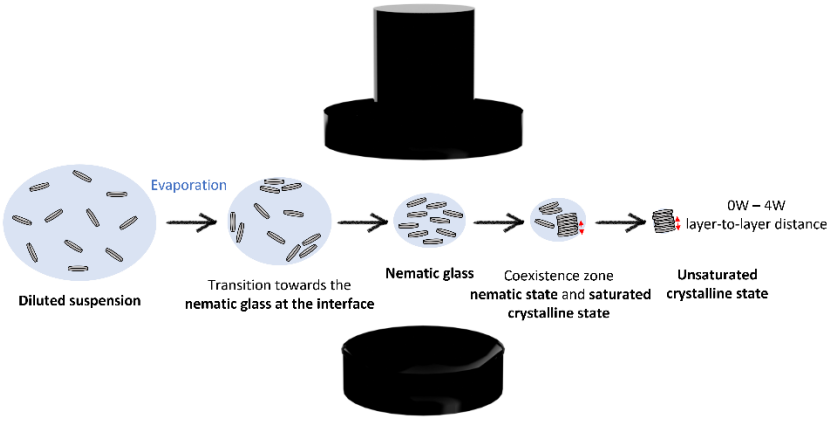

Figure 1. General mechanism of smectite dehydration. This scheme summarizes the evolution of the microstructure of smectites from dilute dispersions to the dry state probed by acoustic levitation.

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Sub-nanometer thickness engineering of amorphous silica nanosheets

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Amorphous silica is one of the most widely used silica-based materials, and there are various chemical protocols for creating diverse nanostructures with controlled morphology. In particular, the molecularly thin amorphous silica has potential as the platform for exploring the amorphous structure but also offer access to novel properties that emerge from their 2D structure.[1] Although various methods using lamellar surfactant assemblies as templates have been developed, the resulting nanosheets lacked precise thickness control, likely due to their disordered interfaces. Here, we established a method using solid-state surfactant as templates for synthesizing molecularly thin amorphous silica nanosheets and succeeded in accurately controlling the thickness of the nanosheets.[2] The silica-surfactant lamellar hybrids were prepared by adding tetraethoxysilane into the dispersion of the non-ionic surfactant. The critical factor to obtain the lamellar hybrids suitable for exfoliation was the synthetic temperature lower than the Krafft point of surfactant and the kind of head group (Fig.1a). Then, we synthesized lamellar hybrids below Krafft point using various kinds of non-ionic surfactants with different PEO group lengths (C18E2, C16E10, Tween40, and C18E20,). The obtained lamellar hybrids were exfoliated into the ethanol, and the thicknesses of nanosheets were investigated by the AFM measurement. The thicknesses of nanosheets synthesized using C18E2, C16E10, and Tween40 were 0.9, 1.5, 2.0, and 2.5 nm, respectively (Fig.2 b). The thickness of the nanosheets corresponds to the length of the hydrophilic head groups, which indicates that we can control the thickness of the nanosheets by the design of solid-state surfactant lamellae.

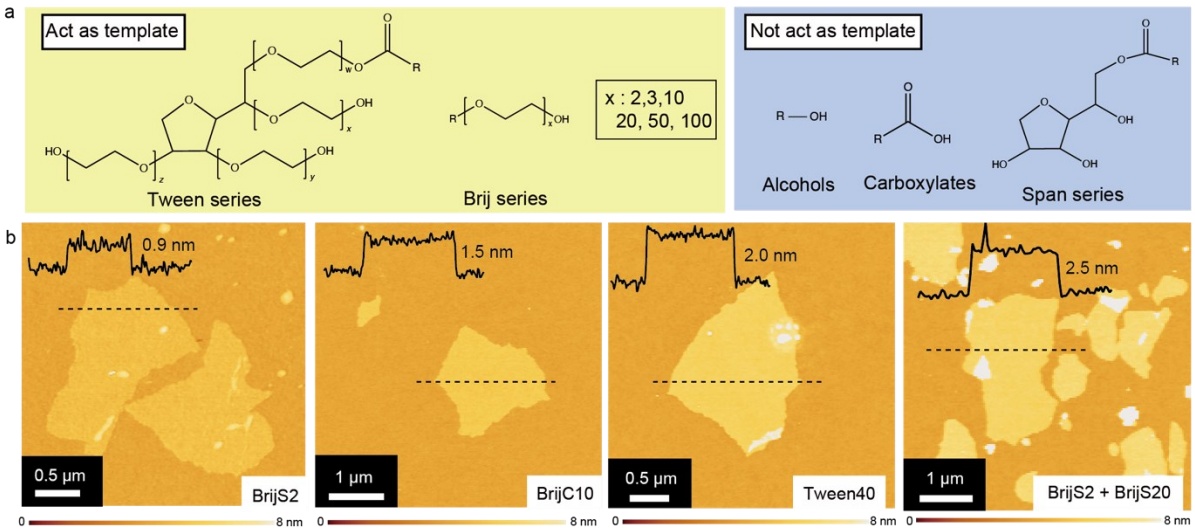

Fig.1 The control of the thickness using various kind of solid-state surfactant as templates. a, the chemical structure of surfactants, b, AFM images with height (solid line) and the corresponding evaluated place (dashed line).

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From Quenching to Fluorescence Enhancement: Central Metal Effects in Porphyrin–Smectite Hybrids

Boháč, P.[1] , Budzák, Š.[2] , Sasai, R.[3], Planetová, V. [1], and Bujdák, J.[1, 4]

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Metaloporphyrins are widely recognized for their excellent and tunable photophysical properties, making them promising candidates for applications in optoelectronics and photosensitization. However, the translation of these molecules into functional solid-state systems—essential for practical deployment—introduces complex challenges, particularly due to alterations in excited-state dynamics upon surface immobilization.

In this study, we explore the role of the central metal ion in modulating the photophysical behavior of three metallated derivatives of meso-tetra(N-methyl-4-pyridyl)porphyrin—Ni(II), Pd(II), and Pt(II)—after their adsorption onto synthetic smectite (Sumecton), a representative layered silicate. Despite their structural similarity, the central atom exerts a pronounced influence on the photophysical outcomes of the hybrid systems.

Ni(II) porphyrin exhibits strong fluorescence in aqueous solution, which is substantially quenched upon adsorption due to enhanced intersystem crossing and non-radiative deactivation, as supported by theoretical calculations. This behavior highlights its potential in singlet oxygen generation for photodynamic therapy. In contrast, Pd(II) porphyrin demonstrates a marked fluorescence enhancement upon fixation, attributed to molecular planarization and suppression of non-radiative pathways. Chemometric analysis an DFT calculations revealed the formation of a new emissive species, stabilized by surface interaction. A similar phenomenon was observed for Pt(II) porphyrin, which retained fluorescence in both solution and adsorbed states, with chemometric deconvolution indicating two distinct emissive forms, which was supported by DFT and TD DFT calculations. Notably, adsorption induced spectral shifts and additional radiative features, suggesting that complex structural reorganization at the solid interface took place.

These findings emphasize the critical role of the central metal in directing surface-induced photophysical modulation and demonstrate the potential of layered silicates as versatile platforms for the development of photoactive hybrid materials.

Acknowledgment: The work was supported by the Slovak Research and Development Agency under contract No. APVV-21-0302, and APVV-22-0150 . Support from the VEGA grant agency VEGA. VEGA 2/0161/25 is also gratefully acknowledged.

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Stabilisation of iron-oxo dimers in a natural layered clay for photocatalysts comparable to TiO_2

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Because solid photocatalysis is a (potentially) feasible means of tackling environmental and energy issues, research into a pioneering solid photocatalyst, TiO_2, is still growing. In addition, the development of solid photocatalysts alternative to TiO_2 has been burgeoning due to its cost-ineffectiveness, environmental and health concerns. An ultimate alternative to TiO_2 is naturally occurring photocatalysts; however, few reports have demonstrated natural materials showing photocatalytic activities higher than or comparable to that of TiO_2. Here, exploiting the little-known fact that Fe^{3+}-oxo oligomers show good photocatalytic activities while are extremely unstable and difficult to stabilise[1,2], we report a method for stabilising Fe^{3+}-oxo dimers by utilising a natural smectite clay matrix[3]. The material shows a good photocatalytic activity toward the oxidation of formic acid in water and formaldehyde in air comparable to a benchmark TiO_2 photocatalyst (P25). We perform extensive analyses, calculations and modelling to elucidate the structure of the stabilised dimers responsible for the photocatalytic performance of the proposed material.

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Characterization of Polymer Hybrids from Imogolite and Halloysite

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The surface functionalization of tubular nanoclays—specifically imogolite and halloysite—was investigated through the selective binding of organophosphonic acids and organosilane compounds, followed by their application in polymer hybrid materials. Imogolite surface modification was achieved via specific interactions between phosphonic acid groups and alumina sites on its outer surface. Surface-initiated atom transfer radical polymerization (SI-ATRP) was then conducted using a selectively adsorbed phosphonic acid-functionalized ATRP initiator to graft polymer brushes onto the imogolite surface. Additionally, a layer-by-layer (LBL) thin film composed of phosphorylated cellulose nanocrystals (P-CNC) and imogolite was fabricated by exploiting the specific binding between phosphonic acid groups and imogolite. This LBL P-CNC/imogolite hybrid film exhibited excellent mechanical properties.

Selective modification of both the exterior and interior surfaces of halloysite nanotubes was also demonstrated. Aqueous phosphonic acid was used to bind to alumina sites within the lumen, rendering the interior hydrophobic. Subsequent treatment with organosilanes yielded bifunctionalized halloysite nanotubes with distinct modifications on the inner and outer surfaces. The successful loading of hydrophobic organic compounds into the modified lumen was confirmed. SI-ATRP was also performed using a selectively adsorbed DOPA-functionalized ATRP initiator to grow polymer brushes from the nanotube lumen. Furthermore, a halloysite-based film adsorbed with a catechol-bearing fluoropolymer, P(FAC8-co-DOPAm), exhibited exceptional superamphiphobicity, attributed to the nanoscale surface structure formed by the halloysite.

Finally, our recent discovery of naturally occurring clay within biofilms on biodegradable plastics will also be introduced.

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LECTURE THEATRE 2 – SESSIONS 39+42

Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils

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Essential role of minerals in modulating the dynamics of soil organic carbon

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The association of organic matter (OM) with minerals can often extend the residence time of OM in soils. The resulting mineral associated organic matter (MAOM) structures can take several forms that range in their composition, reactivity toward dissolution, and relative protection of the OM against solubilization or decomposition. Organic matter in MAOM structures can be present as surface adsorbed species, as a co-precipitate or aggregate structure with highly disordered minerals, or fully encased within a mineral pore or aggregate of clays. Over the past 15 years, my group has examined the association of organic matter with minerals across a range of scales and collaborative arrangements from global meta-analyses to observational measurements across soil landscapes, to mineral specific experiments in the laboratory. This presentation will synthesize our findings across multiple collaborative publications as well as new work from my own group to provide a mineral-centric overview of the role of minerals in soil organic matter dynamics. Globally, we've found that although the abundance of clay-sized particles does explain soil OM abundance in drier ecosystems, SOM abundance is more often best explained in humid systems by the abundance of oxalate-extractable iron (Fe) and aluminium (Al) (a proxy for short-range-ordered (SRO) minerals) and mesic systems by exchangeable calcium (likely a proxy for divalent cation bridges and potentially SRO Ca-carbonates). Focusing on more humid systems, we have extensively explored the role of iron minerals on modulating carbon dynamics. We've found that iron minerals can indeed contribute significantly to the protection of OM against decomposition or correlate with OM abundance in soils, but the relationships are context dependent. In cases when soils are exposed to redox fluctuations, the SRO iron phases can stimulate OM decomposition as they provide an excellent electron acceptor for OM oxidation, and in some cases, more crystalline iron minerals appear to provide greater protection of OM. This helps explain the general observation that oxalate extractable Al is often more strongly correlated with OM abundance than oxalate extractable Fe. However, discrete SRO Al phases are often not identified and rather likely represent Al substitution in SRO minerals or Al-OM complexes—which might also reflect mineral weathering by organic acids rather than mineral protection of OM. Lastly, we find that the route of formation for the Fe-based MAOM is important, with rates of formation, the balance of Fe and C, as well as the degree of aging all critical determinants of the MAOM reactivity. Low-crystallinity, organic-rich Fe-MAOM phases are likely a persistent feature in most soils and an important route for MAOM formation. Overall, we suspect that the more persistent MAOM in soils is likely part of composite structures of low-crystallinity Fe, crystalline-Fe, Al, and clays in structurally complex association with OM.

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Probing the chemical environment of Al and Si in secondary silicates by X-ray photoelectron spectroscopy

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Weathering of primary aluminosilicates produces secondary silicates that control important environmental processes such as the binding of contaminants and organic matter (OM). Possible products of aluminosilicate weathering comprise short-range ordered aluminosilicates (SROAS; imogolite / allophane group), clay minerals (phyllosilicates) and amorphous silica ($SiO_{2(am)}$). Among these, SROAS are particularly effective in stabilizing OM due to their reactive surface groups and the potential for OM occlusion during their formation. Previous studies have shown that the surface reactivity of SROAS is governed by Al speciation and that their structure can be altered by interactions with OM. However, the weathering reactions that determine the structural characteristics of secondary silicates remain poorly understood, as these phases form at mineral-water interfaces that are difficult to study analytically. We tested (1) the potential of X-ray photoelectron spectroscopy (XPS) to reveal the structure of SROAS formed in the absence and presence of OM and (2) whether the technique can distinguish structurally different silicates, based on the binding energies of photoelectrons ejected from Al and Si atoms located in the outermost region of the particles. We analysed three crystalline primary silicates (olivine, epidote, quartz), four vitreous volcanic rocks (two obsidians and two pyroclastics), five clay minerals (halloysite, two kaolinites and two illites), five SROAS (proto-imogolite, Si-rich SROAS, SROAS formed in the presence of different types of OM) and $SiO_{2(am)}$. The binding energies of Si 2s photoelectrons were lowest for olivine and epidote (153.1 eV) and increased in the order SROAS (153.2–153.5 eV), volcanic rocks (153.7–153.8 eV), clay minerals (154.0–154.2 eV) and $SiO_{2(am)}$ (155.2 eV). The same trend was observed for Si 2p photoelectrons. Solid-state ^{29}Si nuclear magnetic resonance (NMR) spectra of SROAS revealed single Si tetrahedra bound to three Al octahedra (local imogolite-like configuration) and poorly ordered Si environments in SROAS. Hence, the Si 2s and Si 2p binding energies correspond to the degree of polymerization of Si as the number of Si-O-Si linkages per Si tetrahedron increases from SROAS to clay minerals to $SiO_{2(am)}$. The binding energies of Si orbitals were similar for SROAS irrespective of chemical composition and OM interference in formation. However, they were distinctly lower than those of volcanic glass, showing that Si depolymerization at mineral surfaces can be detected by XPS. Generally, the binding energies of photoelectrons emitted from Al orbitals varied less than those from Si orbitals. The positions of the Al 2s and Al 2p peaks were located at lower binding energies for volcanic rocks (119.2–119.3 eV; 74.3–74.4 eV) than for secondary silicates (119.5–119.8 eV; 74.7–74.9 eV), possibly due to the predominance of tetrahedral Al in vitreous phases. Secondary silicates, on the other hand, contained mainly octahedral Al with variable contribution of tetrahedral Al; up to 29% of Al in Si-rich SROAS was fourfold-coordinated based on solid-state ^{27}Al NMR analyses. The effect of Al speciation on Al 2s and Al 2p binding energies remained ambiguous for secondary silicates; however, our data indicate that the transition of Al (tetrahedral to octahedral coordination) on glass and feldspar surfaces during weathering is detectable by XPS. Our findings imply that the degree of Si polymerization in alteration layers on mineral surfaces could be analysed by depth-dependent XPS. Moreover, XPS measurements could reveal trajectories of mineral and glass transformation as a function of primary aluminosilicate structure and weathering conditions.

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An investigation into chemical interactions between dissolved organic matter and clay minerals

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The association of organic matter (OM) with minerals has been recognised as the primary mechanism for the preservation of organic carbon in soils[1]. However, the adsorption processes in the organo-mineral associations are still not well understood, particularly the adsorption reactions of different functional groups of OM with various minerals.

To explore these, we extracted dissolved organic matter (DOM) from decomposed plant residues of four common land use systems in Australia, i.e., pine, eucalyptus, pasture, and wheat. Six minerals, including poorly crystalline minerals (ferrihydrite and allophane), metal oxides (goethite and birnessite), and phyllosilicates (montmorillonite and kaolinite), were selected. Batch adsorption experiments of four DOM types were conducted using the selected minerals at pH 4.0 and 10 mM NaCl as the background electrolyte[2]. Adsorption isotherms were obtained based on the equilibrium C concentration and amount of C adsorbed onto different minerals. Carbon near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy with a ZnSe crystal flow-through system were employed to characterise the adsorption mechanisms with minerals.

The poorly crystalline minerals (Q_{max}: 21.4-43.9 mg g^{-1}) demonstrated the highest adsorption capacity for DOM, followed by iron oxides (Q_{max}: 13.5-20.4 mg g^{-1}) and phyllosilicates (Q_{max}: 14.4-15.8 mg g^{-1}), while manganese oxides (Q_{max}: 8.0-10.9 mg g^{-1}) exhibited the lowest capacity. The adsorption capacity and reaction mechanism of DOM varied with its concentration and the surface charge characteristics of minerals. From the C NEXAFS analysis, we found that aromatic C and carboxylic C were preferentially adsorbed by all minerals. However, different minerals exhibited varying adsorption capacities for functional groups. For instance, montmorillonite tended to adsorb more condensed aromatic organic compounds with quinine C and phenolic C, while OM with a higher aliphatic C abundance was more readily absorbed on ferrihydrite. The ATR-FTIR results revealed dynamic changes of adsorbed organic functional groups on mineral surfaces over time (0-140 mins), where the bands of adsorbed functional groups appeared simultaneously but reached saturation at different rates. For instance, in ferrihydrite, which exhibited the highest amount of adsorbed OM, OM with C-H bond rapidly reached an adsorption plateau, while OM with C-O bond continued to accumulate on its surface. This can be attributed to the C-O bonds from carboxyl functional groups underwent ligand exchange with mineral hydroxyls to form strong carboxylate-Fe bonds[3], potentially sustaining the adsorption process.

The findings of our study highlight the crucial role of minerals and OM functional groups in organo-mineral interactions. Different functional groups of OM participate in interaction simultaneously, but certain groups (e.g., C=C, C=O, C-O and C-H) may dominate or play greater role in the adsorption, depending on the organic composition of DOM and the mineral surface characteristics. Our work may therefore provide deeper mechanistic insights into the adsorption processes involved in the long-term preservation of OM in soil environments.

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Soil minerals as boundary condition of microbial carbon use of sorbed organic model compounds

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Sorption strength of organic molecules to minerals is among the boundary conditions that shape the channel for energy and matter use by the microbial community of soil systems. Although the stabilization of organic matter against microbial use and mineralization in soil has been linked to sorption, exact mechanism on stabilization of organic compounds on mineral surfaces remain to be elucidated. Based on the interactions of organic substances, minerals and microorganisms we hypothesized that thresholds of sorption strength of organic monomers to soil minerals control the extent of their microbial processing.

Freundlich sorption isotherms and desorbability (i.e., the ratio of the amount desorbed to the amount sorbed) of uniformly ^{14}C-labeled glucose, acetylglucosamine, phenylalanine, salicylic acid, and citric acid onto goethite, kaolinite, and illite were studied in batch experiments. Monomers adsorbed to minerals were mixed with loamy and sandy arable topsoil and incubated at 25°C. Mineralization of mineral-adsorbed monomers was observed over three weeks, after which the assimilation into microbial biomass, and the ^{14}C remaining in soil were quantified. Additional experiments with isothermal titration calorimetry (ITC) were conducted with unlabeled model organic substances and each mineral to characterize the organic compound-mineral binding thermodynamically.

The adsorption of carboxylic acids onto minerals yielded only for goethite sorption signals quantifiable with ITC for thermodynamic characterization. The adsorption of carboxylic acids onto minerals exceeded that of (amino) sugars and phenylalanine with the overall highest amounts for goethite. Assimilation of monomer ^{14}C into microbial biomass and the microbial carbon use efficiency (CUE) of mineral-adsorbed monomers in both soils increased linearly with the monomer desorbability from mineral phases. Furthermore, the CUEs of monomers adsorbed to goethite were lower than those of the same monomers adsorbed to clay minerals [1].

We conclude that sorption strength and desorbability shape microbial utilization of mineral-bound organic compounds, but no universal threshold for bio-accessibility of sorbed organic compounds was observed. In terms of total amount of carbon retained in the soil, carboxylic acids adsorbed on goethite showed highest values, confirming the significance of oxides for the stabilization of OC within soils.

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Clay interactions with amino acids in marine sediments: Evidence for mineral-modulated organic matter stabilization

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Earthen matrices comprise complex mixtures of minerals and organic matter exhibiting manifold interactions between them. Among these organic constituents, amino acids represent one of the most ubiquitous classes of organic molecules essential for all life on Earth. The universal and abundant presence of amino acids allows us to compare their interactions with minerals across different environments spanning both terrestrial and marine. For this purpose, research teams at ETH Zurich and JAMSTEC have isolated individual amino acids from complex environmental mineral matrices using high-resolution chromatography [1]. Subsequently, amino acid-specific radiocarbon contents were determined via accelerator mass spectrometry providing a measure for individual amino acid turnover times via their radiocarbon ages. Investigations carried out on marine surface sediment showcase direct evidence for the role of phyllosilicates in modulating the preservation of amino acids in the sedimentary record. These preservation patterns reflect molecular-level interactions consistent with laboratory-based experimental sorption studies [2] yet also reveal processes operating beyond the observational range of laboratory experiment timescales. This study makes the case for using naturally occurring amino acids as molecular probes of organic matter-mineral interactions for understanding organic carbon sequestration in natural Earthen matrices.

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Exploring soil mineralogy as an indicator of soil functioning and health

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Understanding soil carbon stability and cycling is crucial for sustainable ecosystem management, particularly in balancing carbon storage and soil health amid climate change. Clay minerals are one of the key carbon-capture materials and sorption to clay materials is assumed to retard the microbial decomposition of soil organic matter (OM). Additionally, different clay minerals have different associations with organic matter, e.g. Illite has a higher adsorption capacity for OM than does kaolinite [1]. Smectite, characterized by its high surface area, is believed to bind with organic material [2, 3]. Moreover, iron oxides can associate with OC to enhance C preservation [4] and reduce microbial-derived C accumulation by inhibiting microbial activity [5]. Therefore, it is crucial to understand how these relationships work in a natural environment and how they are affected by other natural conditions. $\delta^{13}C$ values are typically relatively depleted in living plants and fresh detritus, and progressively enriched with depth in the organic and mineral soil horizons [6]. The $\delta^{13}C$ isotope ratio (‰) variation with depth can be represented by ε, a proxy for soil carbon decomposition [7]. In this study, we use the existing soil survey data from the National Soil Inventory of Scotland (NSIS2) to explore the relationship between soil mineralogy and ε. Our statistical analysis (Pearson's correlation and Principal Component Analysis, PCA) on soil mineralogy from grassland and arable lands suggests that more reactive clays, such as smectite, illite, and illite/smectite, correlate with lower ε values, indicating reduced carbon degradation rates and greater carbon stability. Conversely, soils dominated by more crystalline minerals show higher ε values, reflecting faster carbon decomposition and lower carbon retention. These findings highlight how soil mineralogy, together with land use and pH, influences soil carbon cycling and decomposition rates. This research underscores the importance of understanding clay-organic matter interactions to inform sustainable land management and enhance soil-based ecosystem services, particularly in arable and grassland soils with lower organic matter content. Further research is needed to refine mineralogical analyses in organic-rich soils and assess how mineral-driven carbon stabilization can mitigate climate impacts while maintaining soil health.

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Multiple K-bearing minerals in soil distinctively react with two non-exchangeable potassium extraction tests

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Nonexchangeable potassium (Nex-K), which is slowly released from mineral structure, is a key component for long-term potassium (K) fertility of agricultural soils [1]. Two major tests for extracting Nex-K from soils, the boiling nitric acid method (Nex-K[HNO_3]) and the tetraphenylborate method (Nex-K[TPB]), are widely used, but have not been carefully validated from which minerals in soil Nex-K has been extracted. The objective of this study was to determine K-bearing mineral contents and to reveal their contribution to the Nex-K release potential for agricultural soils.

Soil samples (0–15 cm depth) were collected widely from 322 agricultural fields in Japan. In these soils, the contents of major minerals, including K-bearing minerals, i.e., trioctahedral micas (Micas[Tri]), dioctahedral micas (Micas[Di]), and K-feldspar, were also determined by X-ray powder diffraction (XRPD) analysis using full-pattern summation method [2]. The Nex-K(HNO_3) and Nex-K(TPB) contents were obtained by subtracting the exchangeable K content extracted with 1 M CH_3COONH_4 from the phytoavailable K content extracted with 1 M HNO_3 and combined reagent (0.1 M NaTPB/1.7 M NaCl/0.01 M diNa-EDTA), respectively.

On average, Japanese agricultural soils showed relative abundance of K-feldspar (5.7 wt.%) and Micas(Di) (2.7 wt.%), compared with Micas(Tri) (0.3 wt.%). Although Micas(Tri) was less abundant in soils, its contribution to the Nex-K content—calculated by the standardized partial regression coefficient using multiple regression analysis—was so high, i.e., 91% to Nex-K(HNO_3) and 27 % to Nex-K(TPB). The high contribution of Micas(Tri) to Nex-K(HNO_3) reflects high susceptibility of Micas(Tri) to the structural dissolution by the attack of H_3O^+, which mimics the release of organic acid by plant roots [3]. Mineralogy-based soil categorization by cluster analysis revealed that most of the soils in granitic bedrock areas were grouped into one cluster, in which the soils showed relatively high Micas(Tri) content and also high Nex-K(HNO_3) content. Thus, better understanding of the geologically oriented soil mineralogy allows for estimating the spatial distribution of the potential of soil as a long-term K reservoir.

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Stepwise expansion of micaceous interlayer space changes affinity to cesium

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Micaceous minerals are minor in quantity but are ubiquitously present in most soils. Partial expansion from 1.0 to 1.4 nm in their interlayer spaces increases the number of selective adsorption sites for alkali cations, especially for cesium ion (Cs^+). This site is termed frayed edge site (FES). Although the theoretical definition of the FES is clear, details of the layer expansion impacts on increasing the number of FES remain elusive.

The ion exchange reaction from potassium ions (K^+) to cesium ions (Cs^+) was investigated by both chemical experiments and simulations with stepwise changes in the layer expansion of micaceous minerals. In the chemical approach, various levels of layer expansion were induced by the removal of interlayer K^+ using sodium tetraphenylborate (NaTPB) in three types of micaceous minerals: biotite, muscovite and illite [1,2]. The degree of layer expansion was determined by X-ray diffraction analysis. The number of the FES at each expansion step was estimated by a batch experiment. In the simulation, we evaluated the standard Gibbs free energy for the Cs^+ exchange reaction between the FESs of K^+-fixed muscovite-type mica models and bulk water ($\Delta\Delta G^\circ r$), expanding the d_{001} spacing from collapsed to fully expanded conditions.

In the chemical experiment, the estimated number of the FES for biotite-type micas gradually increased with the release of up to 50% of the K^+ from interlayer sites but then decreased with the further release of K^+, up to full expansion [2]. Thus, co-existence of both non-expanded and expanded interlayers is confirmed to be critical to maximize the number of the FES in micaceous minerals. In the simulation, Δd at the negative minimum value of $\Delta\Delta G^\circ r$, indicating the energetically most stable state for adsorbed Cs^+, was 0.24 nm, corresponding to the interlayer distance of 1.273 nm at the wedge-shaped part of FES [3]. Thus, our studies offer structural insights into FES, highlighting the critical role of the wedge- shaped part of FES in Cs^+ stability.

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Role of nanoscale soil minerals in stabilization of organic carbon in acidic Ultisols of humid tropical India

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This research was aimed to evaluate the role of nano sized (< 0.1 µ) crystalline phyllosilicates and non-crystalline oxides/hydroxides as seat of organic carbon (OC) stabilization in some Ultisols of humid tropical (HT) India. Notably, higher OC sequestration was observed in the soils of the HT climate in comparison to soils from arid and semi-arid environments. Therefore, in this study, representative Ultisols under forest cover with only acidic pH (3.8-5.39) were collected from both surface and sub-surface horizons from four benchmark soils of India. The area received 3000-4000 mm mean annual rainfall (MAR). Two Ultisols (P1 and P2) exhibited Andic properties and were developed from non-volcanic materials in the Nilgiris, southern India. The other two (P3 and P4) were developed from Granite Gneiss rocks in Meghalaya plateau, north-eastern India. The weighted mean value of OC in 0-30 cm was higher in P1 (10.24 %) than P2 (4.82 %), P3 (2.2 %) and P4 (1.01 %). These soils displayed varying amount of nano size (< 0.1 µ) soil clays within the clay (< 2 µ). P3 and P4 Ultisols have higher amount of nanoclays (15-25 %) than P1 and P2 Ultisols (7-20 %) within clay. Sub-surface soils (30-100 cm) contain higher amount of nanoclays (7-30 %) than surface soils (0-30 cm) (7-20 %), indicates a preferential downward movement of nanoclays. The P1 and P2 soil nano-clays were dominated by kaolin (50-70 %), followed by gibbsite, chlorite and hydroxy interlayered vermiculite (HIV), whereas the P3 and P4 soil nano-clays dominated by kaolin (>70 %), followed by gibbsite (20-50 %). The content of non-crystalline oxides/hydroxides (ammonium oxalate extractable) were significantly higher at 0-30 cm in P1 and P2 than P3 and P4. The hydroxy interlayered crystalline phyllosilicate nano clays, were significantly positively correlated (HIV r= 0.52*), chlorite (r= 0.74*) and kaolin (r= 0.47*) with the SOC content. The non-crystalline nano clays viz., oxalate extractable oxides have shown a highly significant positive correlation (r= 0.89*) with SOC content. The findings demonstrate that enrichment of organic carbon (OC) is related with acidity of soils. The acidity in soils breaks crystalline nano-clay minerals to amorphous oxides, which then get entrapped in the interlayers of crystalline nano size phyllosilicates, transforming them into highly active kaolin and other hydroxy interlayered minerals. As result, nanoscale amorphous minerals and other hydroxy interlayered nano minerals together emerge as more active surface for stabilizing OC in these Ultisols under abundant vegetation complemented by high annual rainfall. Thus, OC sequestration is primarily influenced by non-crystalline nano minerals rather than crystalline ones. Understanding these pedogenic processes in Ultisols may help in devising effective management strategies to enhance SOC levels for sustainable biomass production.

Keywords : Nano minerals, Organic carbon stabilization, Humid tropical soils, Ultisols, Gibbsite, Amorphous oxides, Kaolin, Hydroxy Interlayered minerals.

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Tropical climates, soil clays and landslide susceptibility

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Of the >70,000 landslides triggered by Hurricane María, prevalence was highest where soil parent material is granodiorite. Near headwall scarps where landslides were initiated, slip surfaces tended to be shallow (typically ≤ 60 cm) and soils were mobilized rapidly and with long runout distances [1]. The relationship of soil mineralogy to landslide susceptibility on this tropical island was studied by soil mineralogical analysis (bulk and clay fractions) combined with soil geochemistry (bulk fraction) and field observations to test the hypothesis that clay-rich subsoil horizons overlain by less-weathered and more permeable horizons function as slip planes when saturated by intense rainfall events [2]. Soil pits were excavated to depths of ~200 cm in Ultisols on an undulating plateau (5-15^{o} slopes) and to ~ 100 cm in Inceptisols on steep slopes (36-43^{o}) that flank the plateau, and selected pits were located adjacent to scarps from previous landslides, enabling sampling of soil profiles downward through extrapolated slip surfaces. Increased storm intensity due to warming seas makes understanding of landslide triggers especially relevant in this hurricane affected region.

Results from X-ray diffraction (XRD), X-ray fluorescence (XRF) and thermogravimetric analysis (TGA) indicate that soils are heterogeneous, often with subsoil horizons enriched in clay minerals and immobile elements (Al, Fe, Ti) relative to overlying soil horizons. In particular, Inceptisols on steep slopes often contain smectite-rich horizons at 30-60 cm depth that contain 15-25% more clay than overlying more-granular horizons, and these clay-rich horizons are prime slip surfaces. The presence of more deeply-weathered clay-rich horizons at depth is somewhat anomalous and relevant to understanding landslide risk given that tropical soils typically are more deeply-weathered in shallow horizons (e.g. A or B-horizons) and less-weathered in deeper horizons (e.g. C-horizon or saprolite). Field observations and mineralogical-chemical analysis indicate that (A) some of the clay-rich subsoils are created when a prior landslide buries a smectite-rich AB-horizon under permeable colluvium [2], and (B) other clay-rich subsoils may be due to higher chemical weathering rates along joints in the granodiorite that accelerate clay formation along planar features in the subsurface [3]. Where clay-rich soil horizons occur beneath more-permeable overlying horizons, rapid infiltration and absorption of water by smectite-rich subsoil horizons cause decreased shear strength and increased landslide susceptibility. Current work consists of expanding analysis into other soil parent materials (extrusive volcanic rocks, sedimentary rocks) and pairing these results with soil moisture and precipitation monitoring by a team of researchers from University of Puerto Rico at Mayaguez (https://derrumbe.net/) to determine if there are moisture thresholds in the clay-rich subsoil horizons above which landslide risk increases significantly.

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Clays in the Critical Zone: How fast and how long do they hang around?

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From above the treetops to below the Earth's surface where meteoric waters exert their influence, rocks react with acids and water to produce clays, solutes, and bicarbonate. This is the critical zone (CZ) and it is one of the most rapid clay-forming environments on Earth. Yet, volumetrically, most of the clays on Earth are not found in the CZ. Instead, they predominantly occur in ocean sediments, sedimentary rocks, and altered crystalline rocks [1]. The clay minerals in the CZ must form rapidly on geologic time scales, and their residence time appears to be relatively short due to erosion and rejuvenations from weathering. This aligns with 19th-century geologist Grove Karl Gilbert's insight that, despite geologically fast erosion rates of soils from the continents, a regolith persists on most of the land [2].

Our studies on the formation of clays in the passive margin of the USA's southern Piedmont (currently with a temperate–subtropical climate) examine the distribution of clay mineral types across size fractions at various depths in weathering profiles (>10 m) derived from granitic parent material. By analyzing these soils using cosmogenic nuclide abundances (^{10}Be and ^{26}Al) and radiation-induced defects (RID) in kaolinites, we can constrain landscape erosion rates and estimate clay residence times in the CZ. The accumulation of kaolinite in the clay fraction of the B-horizon (i.e., gained from the A- and C-horizons) and kaolinite formation and loss in the sand fraction of the C-horizon (i.e., feldspar and mica hydrolysis) reveals the dynamics of lessivage (in the broadest sense). RID age dating of kaolinites and ^{14}C dating of gibbsites in Piedmont weathering profiles suggests they record a range of formation ages from recent to 3 Ma. Long-term erosion rates in the CZ at our study site, based on *in situ* quartz ^{10}Be from rivers and soil profiles, average ~7 m/Ma [3]. This contrasts sharply with modern erosion rate estimates, which are two orders of magnitude higher [4]. The distribution of clay mineral assemblages in Piedmont regolith is also influenced by land use (i.e., vegetative type and rooting depth). Cultivated land, secondary pine forests, and old-growth hardwoods each have abundant clay horizons with characteristic differences, in part related to greater rooting depths, respectively and thus demonstrating how biota plays a crucial role in landscape evolution and the exogenic cycling of elements.

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LECTURE THEATRE 7 – SESSION 17

Industrial Applications of Clays

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How can the use of pre-consumer wastes from industrial minerals production help meet future customer demand?

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The mining industry has historically generated large amounts of mineral waste from the extraction, processing and use of mineral resources. Waste rock, tailings and by-products have, until recently, been deemed unprofitable or unsuitable for commercialisation. Despite the many challenges associated with the mining industry, holistic efforts are currently being implemented by Imerys to re-evaluate and repurpose waste material into valuable resources. Here, an overview is provided on waste management, sustainability and circular economy approaches aimed at reintegrating mineral waste in the production chain, with a particular focus on kaolin waste material. Practical examples, currently implemented by Imerys, are discussed, such as the recovery of waste kaolin into polymer applications, the production of high performing calcined kaolin from waste feed sources, the use of unkaolinised granite for lithium extraction, and an array of materials from different mining sources for potential use as matting agents in paints.

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Redefining the terminology of bentonites based on geological and mineralogical criteria and the industrial practice

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Bentonites are important industrial clays, consisting mainly of smectite, that originally were linked with alteration of volcanic glassy igneous material, usually a tuff or volcanic ash. Due to their significant physical and chemical properties, bentonites find numerous industrial applications such as the drilling industry, foundries, iron-ore pelletization, civil engineering, adsorbents, filtering, decolorizing and clarifying, and nanocomposites among many others. However, because several bentonites utilized by the industry do not have a volcanic origin, the restriction of bentonites to the alteration of volcanic glassy rocks raised the need for a more generic definition. Hence, the most widely accepted definition of bentonite today is a clay consisting essentially of smectite-group minerals, regardless of the mode of occurrence or origin [1]. However, this definition imposes several restrictions, which render its applicability questionable in several aspects. First, it ignores the importance of bentonites as industrial clays, although initially the term was introduced to describe a clay with certain physical properties. Then, the second part of this definition is redundant because smectites form at a variety of environments through different mechanisms. Third, the attribute "essentially" is ambiguous, because a) it is too vague to be considered from an industrial perspective and b) it excludes *a priori* clays consisting of 50-60% smectite that nevertheless might be suitable for some applications after mild processing, and thus are considered bentonites by the industry, and which have a market share. Hence, it is necessary that the term bentonite embraces the industrial component along with the geological one.

There are additional controversial aspects on the existing bentonite terminology. The first refers to the extension of the term bentonite to include materials that contain mixed layer illite-smectite (I/S) or kaolinite, instead of smectites, i.e K-bentonites, illitic bentonites or kaolinitic bentonites, the latter also known as tonsteins. These terms that are commonly used by sedimentologists, should be eliminated and be replaced by the terms illitic volcanic clays and kaolinitic volcanic clays respectively. The second controversial aspect refers to the characterization of bentonites according to the dominant exchangeable cation. While the term Ca- or Na-bentonite refers to materials containing smectites with exchangeable Ca or Na respectively, the term K-bentonite refers to materials containing mixed layer I/S or illite as was noted before, and the term Mg-bentonite characterizes bentonites containing trioctahedral smectites, namely, hectorite, saponite or/and stevensite. For the latter materials the term bentonite should be used in a similar manner as for their counterparts with dioctahedral smectites, possibly, but not necessarily, with an attribute about the trioctahedral nature of smectite e.g. bentonite with trioctahedral smectites or bentonite with hectorite (or saponite, or stevensite depending on the smectite-type present). Therefore, the term Mg-bentonite should be restricted to bentonites with Mg exchangeable cation, similar to their Ca- and Na-counterparts. Finally, characterization of a bentonite using the name of smectite mineral present e.g. hectorite for the bentonite from Hector, California or stevensite for the bentonite from Rhassoul, Morocco are not appropriate because they denote a clay rock with the name of a mineral, although the clay contains abundant impurities (e.g. calcite in Hector). In conclusion, a more appropriate definition for bentonites would be "*clays containing minerals of the smectite group as the main constituents that may have the potential, in the natural state or after minor processing, for use in industrial applications, due to the physical and chemical properties of smectite*".

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The importance of particle aspect ratio in industrial applications of clay minerals and its measurement

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For many industrial applications, clays are chosen in preference to other minerals as a result of the lamellar shape of their particles. Key examples in which clays are used where particle aspect ratio (AR), defined as the ratio of diameter to thickness, correlates strongly with performance include the reinforcement of plastics [1], barrier coatings [2] for packaging and coatings for paper printed at high speed by rotogravure and offset methods [3].

Methods for the direct measurement of AR of clay minerals are not well established. The most common indirect method used involves the determination of particle size distributions by two different techniques, laser diffraction and sedimentation, and comparison of the results. For disc-shaped particles with AR>5, laser diffraction is sensitive to the actual diameter of the particles, whereas sedimentation is sensitive to the product of the diameter and thickness; thus as AR increases, so does the ratio between the apparent median diameter (d50) of the particles by the two techniques. This approach assumes that the d50 value is representative of the whole sample, and that AR is constant across the size distribution, which is unlikely to be the case. Furthermore, for larger particles (>50µm) the interpretation of sedimentation times using Stokes' Law can be problematic due to the onset of turbulence, and the strong scattering from larger particles may obscure the signal from finer ones in laser diffraction measurements. Electron microscopy shadowing techniques may be used instead to measure individual particles; however, measurement of a sufficient number of particles to be representative of a sample is very time-consuming.

In the 1990s, English China Clays (now Imerys) developed an instrument to determine AR from the change in electrical conductivity of particle suspensions between flowing conditions, when the particles align with the flow, and quiescence, when their orientation is random [4]. Using the 1920s theory of Fricke, AR can be calculated from the conductivity change at a specific volume fraction. Use of the instrument was successfully implemented for measurement of kaolin for paper coating.

An alternative theoretical approach to suspension conductivity was developed by Derjaguin and Dukhin in the 1970s, which was exploited by Weber et al [5] to calculate AR of kaolin particles by measuring conductivity of a stirred suspension as a function of background conductivity by titration with KCl solution and comparison with a blank. In this paper we describe a different approach, whereby the conductivity of stirred suspensions of particles at different volume fractions in a constant background solution is used to determine AR, using the same theory. The AR is shown to be in agreement with the original instrument, and an excellent predictor of stiffness in polypropylene.

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Investigation of Thermal and Mechanical Properties of Pyrophyllite-Impregnated Natural Fiber Fabrics

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Pyrophyllite, typically found in association with metamorphic rocks and hydrothermal veins, is widely utilized in global industries due to its low cost, favorable mechanical properties, and excellent thermal resistance. It plays a significant role in the production of refractories, heat-resistant ceramics, paints, paper, fiberglass, cosmetics, plastics, rubber, fertilizers, and insecticides.

Detailed mineralogical, crystallographic and geochemical studies based on scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses on samples from various locations of the Pütürge region of Malatya, where hosts the majority of pyrophyllite deposits in Türkiye, revealed that the samples include pyrophyllite, quartz, muscovite, kaolinite and illite with varying percentages of iron, magnesium and titanium. Based on their pyrophyllite content and elemental suitability for industrial applications, the samples were classified into low, medium, and high-quality groups.

In an effort to develop eco-friendly insulation materials, fine-grained high-quality pyrophyllite powders with uniform particle sizes were impregnated into natural fabrics, namely jute, cotton, linen and wool, and thermal and mechanical performances of the resulting composites were examined. The fabric samples were mercerized in an alkaline solution to enhance surface reactivity and to promote better interaction with the binder solution. Using the dip-coating method, the fabrics were immersed in a pyrophyllite-rich binder solution and subsequently subjected to a short-time thermal treatment.

Post-treatment analyses revealed that the pyrophyllite-impregnated fabrics exhibited a significant loss of elasticity, observable darkening in color, and minor fiber degradation due to chemical abrasion. However, bonding between pyrophyllite particles and the fabric fibers substantially enhanced the thermal resistance and flame retardancy of the fabrics. These findings indicate that pyrophyllite-impregnated natural fiber fabrics are better suited for applications in eco-friendly thermal insulation panel production rather than for use in the textile or apparel industries.

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LAPONITE® 7007 – Introducing powerful new 'special agent' for rheological applications and beyond

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Discovered by the clay science pioneer - Dr. Barbara S. Neumann, the LAPONITE® brand of synthetic clay products has recently celebrated 60 years of commercial success, cutting edge performance and continuous innovation [1]. Familiar to most of clay scientists, this wonder material is undergoing a true renaissance by greatly expanding the range of applications to new areas, well beyond the classical rheology of coatings and paints. We observe an explosion of interest in LAPONITE® in biomedical applications, 3D printing, energy storage, catalysis, intumescent and antistatic coatings, surface wetting control, and many more [1-4]. It builds on unique properties of LAPONITE®, including fast formation of extremely clear dispersions, powerful rheology with tuneable pseudoplastic or thixotropic behaviour, particularly in combination with organic polymers and other particulates; the list goes on. The exciting new and existing applications are supported by traditionally high purity and reproducible properties of these synthetic clays manufactured on a large industrial scale.

Building on the historical success of LAPONITE®, BYK is introducing a completely novel, 'special agent' material LAPONITE® 7007. Commercially launched at the European Coating Show earlier this year, the product heralds a new chapter in the LAPONITE® story.

LAPONITE® 7007 shares the hectorite-like structure with the rest of the LAPONITE® products, including the conspicuous high purity, fast dispersion, well-established regulatory, toxicological and environmental profiles, and so forth. Where LAPONITE® 7007 stands apart is a step change in rheological power and ease of formulation. In this presentation we shall discuss some of the extraordinary properties of this novel product developed by the R&D department at BYK Widnes, UK:

- Higher rheological effectiveness;
- Significantly reduced sensitivity to electrolytes, surfactants, and pH value;
- Improved dispersion stability in low electrolyte systems;
- No breaking down of the network structure-forming mechanism in more demanding systems extending the scope of formulation;
- Excellent dispersion storage stability at higher product loadings.

Samples of the new LAPONITE® 7007 will be made available on request for select industrial and academic partners via BYK website (www.byk.com).

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Potential of kaolin clay in reducing methanogenic microbial activity in cattle

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Introduction: Methane (CH_4) is a potent global warming greenhouse gas, and ruminants like cattle and sheep are the major source of this emission. By enteric fermentation in the cattle rumen, methanogenic archaea, bacteria, and a few protozoa produce CH_4 through a process called "methanogenesis", which a ruminant emits to the atmosphere through belching. Therefore, interfering with this process, mainly by feed supplements, presents a promising way of reducing this emission [1]. Adding kaolin clay, mainly kaolinite, to a cattle diet shows great potential in achieving this gas inhibition, often through interacting with rumen methanogenesis [2]. Kaolin clay is often a matrix of platy kaolinite and tubular halloysite and studying this mixed species without much purification as methane abatement diet supplement is much needed. And this ought to be with deep understanding of the mechanistic insights of kaolin-ruminal microorganism interactions. Therefore, this study has been conducted to explore how kaolin clay interacted with the rumen ecosystem during methane reduction. **Methods:** Kaolin clay (halloysite: kaolinite ~40% each) was sourced from the west coast of Australia (deposit: Cloud Nine, Western Australia). The viable ruminal fluid was collected from the slaughterhouse with proper animal ethics [3]. An *in vitro* experiment was conducted using the ANKOM system to simulate real rumen conditions. Physicochemical parameters such as dissolved oxygen, oxidation-reduction potential, pH, electrical conductivity, and volatile fatty acids were measured to assess rumen activity. Clay-microbial interactions were investigated using microscopic techniques, and microbial profiling was performed from the 16S rRNA sequencing of the ruminal sample. **Results:** The supplementation of kaolin clay in cattle diet significantly ($p<0.05$) reduced ruminal CH_4 production (over 22%) without affecting the physicochemical parameters or volatile fatty acid profiles. Additionally, bacterial diversity and operational taxonomic unit profiles remained largely unchanged between control and clay-supplemented groups. Notably, interactions between the clay and microbes, especially with a key methane-producing microbe *Methanobrevibacter ruminantium* and nematode, revealed evidence of microbial attachment to the clay and biofilm formation.

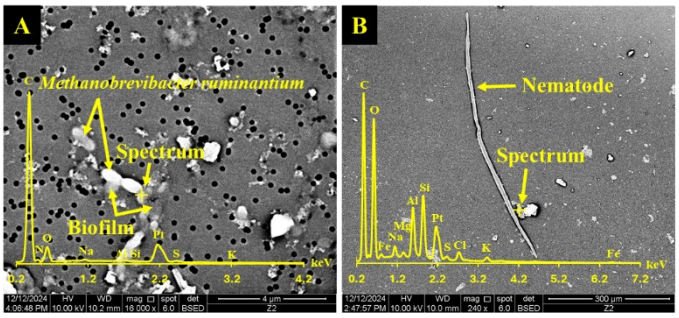

Figure 1. Microscopic images showing the attachment of ruminal microbes onto kaolin clay, where (A) and (B) represent archaea and nematodes' attachment, respectively.

Conclusions: The kaolin clay in the cattle diet appears to interfere with the methanogenic microbial activity, specially M. ruminantium and their symbionts. Clay might have promoted biofilm to the functional shift of their methanogenesis without changing the rumen fluid conditions. As a geophagic material, halloysite-kaolinite mix may be a potential diet supplement for methane abatement.

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Dry processed Westerwald Saprolithe Clays as a new filler for waterborne adhesives and further applications

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Wet processed kaolin products are well-known fillers in waterborne adhesives especially for paper industry. Usually, these fillers consist of a high amount of kaolinite minerals and low amounts of accompanying minerals like other clay minerals, feldspar and quartz. In the Westerwald region there are some primary deposits of deep weathered Devonian shales [1]. They mainly consist of high amounts of Illite / Mica and Quartz. Kaolinite exists only as an accessory mineral.

Table 1: Comparison of the mineralogical composition Kaolin France / Saprolithe Böhmsfund quarry

	Kaolin from France	Capsil 2004R extra (Böhmsfund)
Quartz	6,7	37,6
Plagioclase	-	1,8
Potassium Feldspar	-	2,7
Orthoclase	-	-
Chlorite	-	-
Illite	10,3	31,4
Kaolinite	79,9	25
Anatase	2,6	-
Rutile	0,5	1,5

Although the mineral composition is completely different compared to established kaolin fillers, the properties of these Saprolithe clays are very close to the performance of kaolin. Due to dry processing, the quartz content is not degraded during processing. High plastic clays can be used to compare the rheological properties of these fillers as shown in Figure 1.

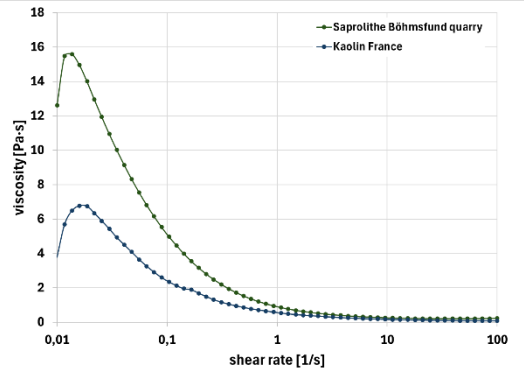

Image 1: Comparison of rheological properties Kaolin France / Saprolithe Böhmsfund quarry

Due to the endless possibilities of blending saprolite and plastic clays, the rheological properties of dry-processed fillers can be optimized to meet customer requirements. The presentation will give an overview of the possibilities offered by dry processing and blending of saprolithes and plastic clays, with an outlook on their applications.

[1] Felix-Henningsen P. (1990) Relief Boden Palaeoklima 6

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LECTURE THEATRE 3 – SESSION 33

Mechanical and Mechano-chemical Activation of Clays

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Mechanochemical activation of kaolin with the addition of different abrasive pozzolans and its effect on the pozzolanic reactivity

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In our research, the mechanochemical activation of kaolin was combined with the addition of different pozzolanic materials (silica fume, diatomaceous earth, and trass) to enhance the structural amorphization of kaolinite and increase its pozzolanic activity. The mixtures of kaolin and pozzolanic materials in the mass ratios of 25:75, 50:50, 75:25, and 100:0 were activated by high-energy dry grinding. The activated mixtures were investigated by X-ray diffraction, Fourier transform infrared spectroscopy, thermal analysis, scanning electron microscopy, as well as by the determination of the specific surface area. To characterize the pozzolanic reactivity, the compressive strength of binders was tested, in which 10% of ordinary Portland cement (OPC) was replaced with mechanochemically activated mixtures.

The addition of pozzolanic materials significantly accelerated the amorphization of kaolinite, which can be attributed to the action of amorphous silica, hydrous silica, or glassy grains as grinding bodies. The effect of these amorphous abrasive grains on the mechanochemical amorphization of kaolinite was found practically the same as that of the crystalline quartz grains. The partial substitution of OPC by the mechanochemically activated mixtures increased the compressive strength of the binders due to the higher pozzolanic reactivity caused by the enlarged reactive silica and alumina content. The strength data showed that the nearly complete (~90%) amorphization of kaolinite in ground mixtures is preferable to the complete amorphization for efficient production of highly pozzolanic cement substitutes, due to the high amount of amorphous phase and the relatively weak particle interactions.

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Characterisation of the Iron-rich clay soils subjected to the intense grinding process

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This study deals with the evaluation of the characteristics of the milled laterite clay from the tropics. For the synthesis, various milling cycles were applied to the soils under the configurations (grinding duration: 20, 40 and 60 min, and grinding velocity 5, 10 and 20 Hz). The testing of the sample was conducted in this study, which includes X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), porosity, DTG-TG and BET-specific surface area as well. The findings revealed that the milling process proved beneficial for enhancing the features of the soils. In particular, prolonged grinding at high velocities (60min and 20Hz) induced the triggering of the amorphisation of the laterite soils and was responsible for the progressive dihydroxylation of the goethite to hematite. The process appeared to be a sustainable way to activate the laterite clay in civil engineering applications and eventually boost the soil's role in the economic growth of the region where they are abundantly found.

Keywords**:** Laterite-clay, milling process, amorphisation, tropics, morphology features

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Mechanical activation of halloysite-rich kaolin for slow-release phosphate fertiliser

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Phosphate fertiliser is essential for plant growth, but its wastage during surface runoff and leaching in the soil profile leads to reduced efficiency, water pollution and extra costs [1]. This issue has been addressed with the formulation of slow-release fertilisers, especially using carrier materials [2]. However, significant challenges remain in finding the right carrier at a reasonable cost. Considering this, we tested the effects of mechanical activation on a halloysite-rich kaolin clay to maximise its retention and release properties for phosphate fertilisation. The changes of halloysite nanotubes (HNTs) were studied for dry (A: clay only) and wet (B: slurry of clay + potassium salt of phosphate, KH_2PO_4) ball milling at varying duration (e.g., 1–8 h). X-ray diffraction (XRD), scanning electron microscope (SEM), and surface area analyses were performed to understand the nature of crystal damage occurring during milling. Aqueous-phase extraction was used to measure the retention and release behaviour of phosphate ions using ion chromatography analyses [3]. We then used high-resolution transmission electron microscopy (TEM-EDX) to map out elements, including P and K, in the matrix for the different preparation methods.

The optimal retention and release behaviour resulted after ~3–5 h of dry milled materials with ~40% phosphate released after the first wash, followed by ~5% in two successive washes. However, the same milling time of wetted co-fertilised material released more phosphate after the first wash (~50%) and significantly less during subsequent washes. We attribute this improved retentive behaviour to the increase in edge sites for enhanced phosphate adsorption on the edges of fractured halloysite tubes, although eventual aggregation of amorphous material led to a loss of retentive sites during overgrinding. These findings give us the choice of fertiliser in terms of the release of nutrient. This also provides an opportunity to optimise grinding parameters for halloysite-rich kaolin clay phosphate fertilisers for use in soil-plant systems.

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Mechanochemistry: A unique tool to boost the potential of natural minerals

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Mechanochemistry utilizing forces of high-energy ball milling is a great tool for both mechanical activation of minerals and for the preparation of their nanocrystalline synthetic analogs [1-3]. This lecture provides an overview of this exciting field. In the first part, it will focus on basic principles, historical overview (Fig. 1a), current state-of-the-art, *in situ* monitoring techniques and scalability. Within the second part, three case studies will be shown, namely:

(i) removal of heavy metals using mechanically activated eggshell waste highlighting the role of calcite-aragonite minerals phase transformation (Fig. 1b) [4,5];

(ii) mechanochemical synthesis of a nanocomposite containing mineral chalcopyrite and its synthetic analogue for the thermoelectric (waste heat to electricity conversion) application (Fig. 1c) [6];

(iii) *in situ* X-ray diffraction monitoring of feldspar mineral mechanical activation (Fig. 1d) [7].

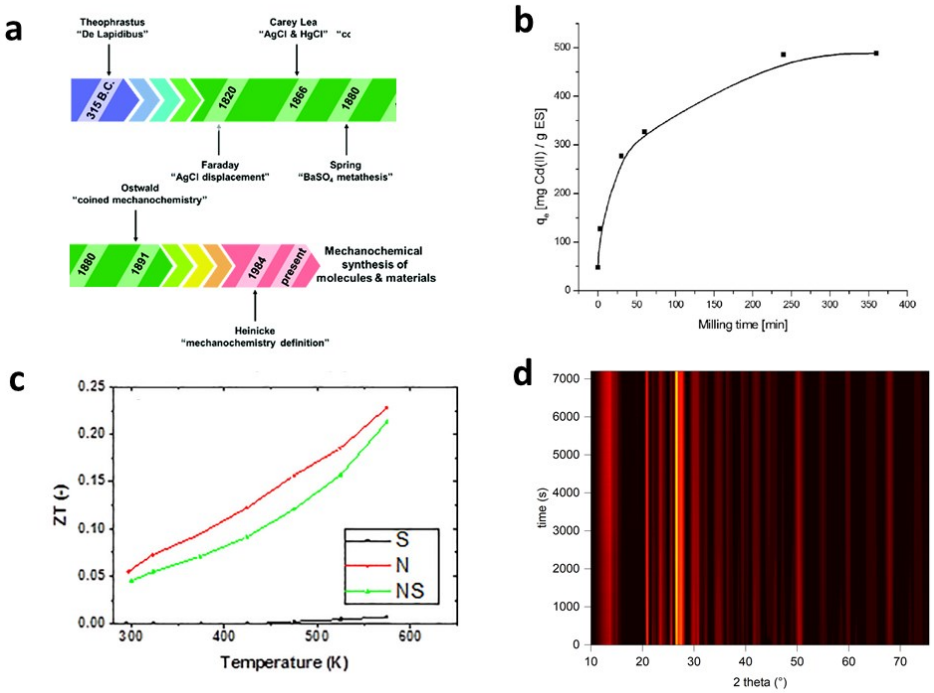

Fig. 1: Lecture overview. Reprinted with permissions from Refs. 3(a), 4(b), 6(c), 7(d) from the Royal Society of Chemistry and Elsevier.

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Mechanochemical Activation of Mine Tailings as Alternative Secondary Cementitious Materials

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Cement clinker production is estimated to contribute a significant amount (8-10%) of the total anthropogenic CO2 emissions. For decades, one of the main mitigation strategies has been the use of supplementary cementitious materials (SCMs), as a proven method for moderating CO2 emissions of concrete and construction sector in general [1]. The mining industry has been generating vast amounts of waste, posing a serious threat to the environment. The current disposal methods of these industrial wastes are directly connected to soil degradation, water contamination and occupation of valuable land [2]. Mechanochemical activation (MCA) processing induces structural disorder, relaxation and mobility, along with amorphization and improved chemical reactivity in solid materials treated with high energy grinding [3,4].

The present experimental study explores the potential of mine tailings as partial substitutes for Portland cement through mechanochemical activation (MCA). The chemical composition, the microstructure, the reactivity, the physical and mechanical properties of mine tailings, before and after mechanochemical activation, were studied. Physical and mechanical properties of cement-tailings mortars were measured and compared to cement or cement-based mortars. The replacement of cement was up to 20% as per current regulations. The findings of the study demonstrate that mechanochemically activated mine tailings can serve as a viable and sustainable cement replacement but also contribute to mitigating both the carbon footprint of cement production and the environmental problems associated with the mining industry.

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Mechanochemical Activation of Phyllosilicates: Efficient utilization of Agitator Ball Mills for large scalable Industrial Applications

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The effect of high energy milling, known as mechanochemical activation (MCA), on phyllosilicate rich materials has been in the focus of several studies in recent years. It has been shown that MCA can be a promising alternative for the activation of clays to be used as reactive supplementary cementitious materials (SCMs). In this context, the focus so far has been the investigation of the effects regarding the milling parameters on the pozzolanic reactivity, the compressive strength of the product and the raw material selection [1, 2, 3, 4]. The milling parameters for planetary ball mills or other mills on a laboratory scale have already been investigated by several studies [5, 6]. A scale-up of this process is indispensable for it to become applicable for industrial use.

Therefore, this study investigates the MCA of two phyllosilicate-rich raw materials on a pilot scale, using a dry agitator ball mill with a grinding chamber volume of up to 40 liters. The two materials from German deposits contain illite-smectite and kaolinite in one case and high contents of muscovite and chlorite in the other. The availability of 2:1 and 2:1:1 phyllosilicates is dominant in the northern hemisphere, so that the use of these raw materials is beneficial from an economical point of view. The comparison between the agitator ball mill in lab and pilot scale and a planetary ball mill in lab scale is intended to evaluate a scale up for the MCA process as alternative for thermal activation. The two raw materials are extensively characterized and the change of particle morphology during the MCA process is investigated. The research investigates the influence of different milling parameters and mill types and sizes on the degrees of amorphization and dehydroxylation. The effectiveness of the agitator ball mill can be shown by comparing the degree of pozzolanic reactivity (R^3-Test) achieved in relation to the degree of activation during the milling process and the amorphization. This study demonstrates the potential of MCA treatment using agitator ball mills, knowing that the mechanisms of an agitator ball mill can be scaled up for industrial application.

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Comparative study of the mechanochemical and thermal activation of natural mixed clays and their performance in a low-carbon binder

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The mechanochemical activation (MCA) of clays is a promising route for developing supplementary cementitious materials (SCMs) with a significantly reduced carbon footprint. Unlike traditional thermal activation, which requires high temperatures (typically 600–900°C) and results in substantial CO_2 emissions, MCA involves high-energy grinding to induce structural disorder and enhance pozzolanic reactivity/amorphization without the need for calcination. One of the MCA key advantages, besides reduced CO_2 emissions, is the ability to activate a variety of clays with different mineralogy, including kaolinite type clays, illite, smectite, mixed-layer clays as well as low purity clays containing secondary phases such as quartz, limestone etc. The activation of mixed clays is very difficult to achieve by calcination alone, so MCA offers the possibility of using a much wider range of clay-based materials.

This work compares the impact of thermal and mechanochemical activation on natural mixed clays from Northen region of France as well as their reactivity in low carbon binder formulations. Different techniques such as XRD, SEM, Zeta potential measurements have been used to follow the chemical and structural transformation of clays under calcination and MCA treatments. In addition to the improved workability demonstrated by rheological measurements, the reactivity assessed by the R3 test and compressive strength displayed higher levels of performance for MCA clays compared to thermal activation.

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Bridging the Gap: Meca-clay - Scaling Up Mechanochemical Clay Activation from Lab to industry

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Many industry sectors are trying to electrify their manufacturing for climate neutrality. In 2020, the German cement industry required an average of 868 kWh of energy to produce one ton of cement (759 kWh thermal + 109 kWh electric = 868 kWh/t). The thermal energy consumption of cement production is nearly seven times higher than electrical, but due to high CO_2 emissions, research is exploring ways to change this ratio. Reducing the clinker factor in cement represents the most effective solution toward climate neutrality in cement production. The clinker factor defines the future capacity of Portland cement clinker lines, impacting investment and production costs for CO_2 capture technology (CCUS plants). These technologies are necessary, as the decarbonization of limestone in clinker production will remain the decisive factor in the GWP (Greenhouse Warming Potential) of Portland cement, and thus also in concrete, for many decades. It is therefore important to minimize all raw material-related decarbonization steps, e.g. by using secondary cementitious material (SCM) with less or no CO_2, such as activated clay. In this context, the use of mechanochemistry to produce SCMs represents an interesting manufacturing concept for the construction materials sector.

Why does mechanochemical activation play almost no role in the production of building materials so far? The reason is relatively simple, the process technologies must be economically viable at large scales. However, research on mechanochemically produced or optimized building materials currently relies on small laboratory mills with batch mode processing. Mechanochemistry is in most cases carried out with "from the shelf" high energy mills, operated in a kind of "stop and go" operation, often in a "black box" manner. This approach is hardly suitable for optimizing industrial production of mass building materials.

Industrial grinding systems are designed for high throughput and low energy consumption, especially in fine grinding, which is already industrially established in some fields of application. Although comminution to the nanometres range leads to products with new properties, the market is limited to chemical additives or refractory materials, where low production capacities are less problematic than for mass cement. To use dry mechanochemistry in cement production, existing grinding concepts must be adapted or new equipment and process technology developed. However, the necessary interdisciplinary cooperation is not common in the existing scientific mechanochemical research scenario. On the product side, the complexity of the underlying physical, chemical and mineralogical changes along with the engineering subprocesses, requires an elaborate and work intensive experimental program to optimize the final product quality.

The installation and operation of continuous flow high-energy mills, even of medium size, usually cannot be retrofitted in existing laboratory buildings due to machine weights, vibration, dust and noise. Another challenge is suitable raw material preparation, as crushing, drying and pre-grinding several hundred kilograms of wet raw clay for larger pilot scale tests. Adequate raw material preparation (e.g., crushers), storage and drying capacities (e.g. flash driers or drum driers), must also be provided.

Therefore, the pilot plant built by the SCHWENK building materials group for the mechanochemical production of its new binder Celitement® provided a unique combination of various technologies for the industrialization of mechanochemistry. The mechanochemical activation of calciumsilicate hydrates from the Celitement development was successfully transferred to the activation of clay.

This keynote lecture will give an insight in a novel binder production concept called meca-clay, exploring the chemical, mineralogical, and physical knowledge of building materials through this emerging and innovative technological approach. It may open new and future-proof business concepts in cement. The types and operating principles of stirred agitated bead mills used for dry fine grinding have been optimized for clay activation. The FOAK (First Of A Kind) ALLMECA-project for mechanochemical clay activation in SCHWENKs Allmendingen plant will be presented.

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Evaluation of different process conditions for mechanochemical activation of clays from mining waste

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The mining sector is vital to the global economy, with Brazil ranking among the world's top mineral producers. However, mining is also one of the largest global generators of waste [1, 2]. A significant portion of this waste originates from weathered mafic and schist rocks, primarily composed of silica, iron, and alumina, forming minerals such as kaolinite, muscovite, and illite, which can be used as precursors for pozzolanic materials for cement. In this context, utilizing clays from mining tailings is a promising alternative due to their abundance and suitable properties, allowing their transformation into high-value components for concrete and other construction materials. Clays must be activated to become amorphous and acquire pozzolanic activity for use as Supplementary Cementitious Materials (SCM), substituting part of cement. The traditional method is calcination at 700-800°C, usually relying on fossil fuels.

A potentially more sustainable alternative is mechanochemical activation, which utilizes high intensity grinding to induce molecular transformations in the particles. This process can be fully electrified, making it environmentally advantageous, especially in countries with a renewable energy matrix, such as Brazil [3]. Furthermore, mechanochemical activation enables the activation of materials not effectively activated by thermal methods [4]. Phases commonly found in mining tailings, such as quartz and iron, can enhance the process by acting as grinding media [5]. This study evaluated the effect of process parameters, such as rotation speed, grinding time, and ball mill filling degree, on the mechanochemical activation of four mining wastes with distinct geological characteristics and one flotation-produced tailing collected from Brazil's most active mining regions: Serra de Carajás and the Quadrilátero Ferrífero. The samples were ground in a high-energy ball mill at 200, 400, and 600 RPM for 30, 60, 120, and 180 minutes, with ball mill filling degrees of 1:3, 1:10, and 1:25. The activation efficiency was assessed using thermogravimetric analysis, the R^3 test [6] and by the pozzolanic activity index [7]. The evaluated clays contained kaolinite ranging from 6.5% to 76.3%, with one sample having 69.8% muscovite. A wide range of phases that could act as grinding media was also assessed, with quartz content varying from 0 to 48.1 and iron phases varying from 8.3 to 36.1. The differences in mineralogy led to distinct grinding behaviors. At grinding speeds below 600 RPM, the dehydroxylation of kaolinite and muscovite was inefficient. At 600 RPM, effective activation required at least 120 minutes of grinding. The ball mill filling degree influenced not only the conversion efficiency but also the rate of accumulated heat gain in the R^3 test. Clays with higher kaolinite content exceeded 90% pozzolanic activity (the minimum required by Brazilian standards [7]) after 120 minutes of grinding, while the others required 180 minutes with a pozzolanic activity of up to 106%.

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Relationships between milling input energy and chemical reactivity for mechano-chemical activation of clays

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Mechano-chemical activation is of rapidly growing interest for producing cementitious precursors from clays. The most widely used grinding apparatus for laboratory-scale studies is the planetary ball mill. Whilst several parametric studies have already been published, it is still largely unknown whether activation efficacy (commonly assessed via the pozzolanic reactivity) is critically dependent on any individual milling parameter, or whether trade-offs are possible between different parameters. We used a first principles approach previously applied to alloy amorphization to estimate the energy of an individual collision event, and the total milling input energy [1]. Using a combination of original data and literature data, we obtained a set of nearly 100 datapoints. Rapid increases in the reactivity as supplementary cementitious materials were generally observed for <10 kJ/g of modelled milling energy input, with a plateau beyond this value. Chemical reactivity exhibited a logarithmic dependence on modelled energy input, with clays consisting of a 1:1 clay mineral tending to have higher reactivity than those consisting of a 2:1 clay mineral or a mixture of clay minerals. No strong trends were observed with individual collision energy, albeit with some indication that a minimum collision energy threshold may exist <0.0001 J. Reasonable agreement was found in trends between modelled input energy and measured energy consumption, albeit with some scatter. Whilst this approach contains known simplifications around the types of forces considered, it is useful for investigating the efficacy of different milling parameters in a more systematic way and hence reducing reliance on trial and error approaches.

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Performance of thermo-mechanically activated Finnish clay: Analysis of reactivity, chemical and mineralogical changes

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Cement production is projected to grow primarily in non-OECD countries while scenarios predict expected consumption in Europe and other OECD countries dropping by 1% between 2015 and 2050 [1]. This drop does not negate the GHG emissions that would still be contributed by the projected 10% cement consumption for OECD countries hence the incorporation of supplementary cementitious materials (SCMs) to reduce these emissions is still important [1]. Conventional SCMs such as blast furnace slag and fly ash are limited in availability especially in the Nordic regions [2]. The investigation in non-conventional SCMs by Adediran [3] highlighted the reactive nature of materials available locally, such as Finnish clay. The Finnish clay showed pozzolanic reactivity with a cumulative heat release of 200.5 J/g SCM and bound water of 6.08 g/100g dry paste. This clay mainly comprising of illite also exhibited a relatively high 28-day compressive strength of 55.1MPa [3]. It shows the potential for local clay as an SCM for the Nordic region, however, there is limited studies available on this material [4]. It is likely that with optimised activation, the reactivity of the Finnish clay can be enhanced. 2:1 clays like illite may be difficult to fully activate thermally, however, studies have shown that mechanical activation may be suitable option [5]. The main aim of this study is to determine the activation process that is suitable for enhancing the reactivity of the Finnish clay and determine the mechanism contributing to the reactivity by exploring the parameters used in the activation processes. Finnish clay with 22% of illite content was thermally and mechanically activated using different parameters such as the temperature (450°C, 650°C and 850°C), dwell time (2hr and 3hr) and among others. The results were compared with laboratory grade metakaolin as reference sample, along with existing data on conventional SCMs from literature. Mineralogical and chemical changes were observed to understand the effect of pretreatment on the clay.

Thermo-mechanically activated clay exhibited reactivity above 160 J/g and 4.5 g/100 g dried paste for R3 isothermal calorimetry and bound water tests respectively which align with results seen in literature [6], [7]. The reactivity of the samples increased with increasing temperature from 450°C to 850°C, however the opposite effect was observed for the dwell time with the sample calcined at a higher dwell time (3hr) having a lower reactivity than the samples calcined for 2hr. The TGA-DSC results showed three distinguishable weight loss events in the raw clay after heating from 40°C to 1200°C. The curve shows a sharp peak at low temperature (<200°C) indicating an episode of dehydration. At higher temperature (>350°C), the sample exhibited another weight loss which can be attributed to the dihydroxylation reaction of the clay minerals. The third peak at higher temperature corresponds to a weight gain event with the effect associated with the formation of new phases through recrystallization. Curiously, there was an increase in the particle size of the samples calcined at 850°C due to agglomeration.

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Mechano-Chemical Activation of Low-Purity Clays

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Low purity clays are highly abundant globally, and their mineralogy and properties vary depending on their geographical location. Clays are widely used for construction materials manufacturing, including production of masonry products and Portland cement. In the case of cement-based materials, low purity clays are used for clinker production, but also as cement replacements (also referred to as supplementary cementitious materials (SCMs)) in Portland blended cement concrete, or as sole precursors for alkali-activated cements (AACs) manufacturing. When used as SCMs or precursors for AACs production, raw clays need to present a poorly-crystalline structure to be sufficiently reactive, which means that an activation treatment (e.g. thermal, chemical or mechanical) is required prior to their used. In the case of low purity clays, conventional thermal treatments (e.g. calcination) are not always effective to induce the structural changes required to achieve sufficient reactivity for cement-based materials applications, therefore alternative treatments need to be adopted instead.

Mechano-chemical activation (MCA) is an activation process that involves grinding of a material until its specific particle size limit is reached, which means that further comminution (particle size reduction) is no longer possible. Instead, a further input of grinding energy can lead to plastic deformation of particles. The increased surface area, combined with the destruction of the crystalline lattice structure of the minerals in the particles, creates highly chemically reactive materials. In the context of construction, the application of MCA to enhance reactivity of a range of resources (including low-purity clays) is limited, despite the significant potential to capitalise on the minerals processing expertise of the cement sector.

In this presentation a brief overview on the effectiveness of MCA of low purity clays with a variety of origins and consequently mineralogy and compositions, as well as highlighting existing knowledge gaps and research needs for positioning MCA as a suitable technology for the widespread use of mechano-chemically activated low-purity clays in cement-based material products manufacturing.

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Mechanochemical activation of low-kaolinitic clays and basaltic fines

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Cement is often partially replaced with supplementary cementitious materials (SCMs) to reduce the CO_2 emission caused by its production. However, there is a shortage of typical SCMs, such as fly ash, slag, and silica fume. Multiple alternative SCMs exist. However, most of these need to be activated before being used, as they would be inert otherwise [1–3].

Mechanochemical activation (MCA) is one way of activation. It is performed by exposing materials to high-energy grinding. In this work, we focus on the effect of MCA on different materials, mainly basaltic fines (BF) and a low-kaolinitic clay (LC). BF are commonly found in large volumes as waste from aggregate, granule, mineral-asphalt mixtures, and other industries [1,2]. LCs are usually not valorised, especially in the case of limestone calcined clay cement (LC^3), where a typically recommended minimum kaolinite content is 40% [4], which cannot be met in many regions of the world.

Grinding for 30 min at 400 rpm with a ball-to-powder ratio (BPR) of 20.6 caused an increase in reactivity seen from the Modified R^3 test. BF and LC showed increased heat release of 2594% and 771%, respectively. The Brunauer–Emmett–Teller Specific Surface Area (BET SSA) decreased in the case of LC by 60.2 % and increased in the case of BF by 284.8 %. Clear amorphization was observed from the X-ray Diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) data.

Cement paste specimens blended activated BF and LC showed an increase in the cumulative heat release at 168 hours, and a lower calcium hydroxide content compared to the cement pastes with the raw counterparts. The mortar specimens showed increased compressive strength and bulk resistivity when cement was blended with activated LC and BF. The slump flow of the mortar with activated LC showed an increase of 487 % compared to the raw counterpart. The slump flow did not change in the case of BF after activation.

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Reactivity, dissolution and hydration of mechanochemically activated clay minerals as supplementary cementitious materials

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Clays are a promising source of raw material to produce supplementary cementitious materials (SCMs) for low-carbon concrete. They require activation to enhance reactivity, and thermal activation (i.e., calcination) is most widely used for kaolinite-rich clays. However, kaolinite-rich deposits are not widely available in relatively cold and dry regions (e.g., the UK), where clays rich in 2:1 clay minerals are more common [1]. These 2:1 clay minerals exhibit limited reactivity after calcination [2]. Alternative activation methods for low-kaolinite clays are therefore required. Mechanochemical activation, using intense grinding, appears to be a promising alternative. The amorphization of minerals induced by intense grinding has long been recognized, and this has been increasingly investigated for SCM production in recent years [3-5]. While promising results have been reported, fundamental understanding from a mineralogical perspective has remained relatively limited.

This work has investigated the reactivity, dissolution, and hydration of mechanochemically activated high purity clay minerals, to assess their suitability for use as SCMs. Binary blends with limestone additions have also been characterised. High purity (>90%) clay minerals including kaolinite, illite, muscovite, montmorillonite, and chlorite, were subjected to intensive grinding for varying durations (5 – 60 min), using a planetary ball mill. Thermally activated samples were also prepared and studied for comparison. Samples were characterised using XRD, the R3 reactivity tests, and dissolution experiments. In addition, hydration of ternary blends of limestone-activated clay minerals-Portland cement was characterised using isothermal calorimetry.

XRD analyses showed progressive amorphization of all clay minerals during grinding. This is different from the mineralogy-dependent behaviour observed in thermal activation. R3 tests confirmed that all the clay minerals became reactive after mechanochemical activation, with reactivity ranking in the order kaolinite > mica > montmorillonite > chlorite. Dissolution experiments in pH 13 NaOH solution under far-from-equilibrium condition showed considerable release of Si and Al, and the dissolution parameters correlated well with R3 tests. The hydration of limestone-activated clay minerals-Portland cement binders aligned with the reactivity and dissolution findings. Enhanced clinker hydration and the peak corresponding to formation of carbonate-AFm was noticed. The research demonstrates that mechanochemical activation is a viable alternative activation method for low-kaolinite clays, and the potential of limestone-mechanochemical activated clays to form binary SCMs.

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Under the microscope: How mechanochemically activated shale behaves in hydrated blended cement systems

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During the Late Ordovician, geographically, the future site of The City of Toronto was a very different place. At that time, the region was dominated by an equatorial shallow sea, part of a basin being fed by sediments from the eroding Taconic Orogeny. Today this pile of lithified marine mud is known as the Georgian Bay Formation, and it is the first bedrock encountered during any deep excavation in Toronto. For example, the southern portion of The Ontario Line, an upcoming subway expansion project, is expected to generate up to 2 million tonnes of ground-up Georgian Bay shale - a material commonly referred to as tunnel boring machine (TBM) muck. During construction of a recently completed tunnel, part of Toronto's new Don River Wet Weather Flow System, this muck was dumped into Lake Ontario to build up a new shoreline, now known as the Ashbridges Bay Landform. These circumstances initiated this research to explore whether there might be better uses for TBM muck, applications that could promote a more circular economy, as opposed to filling up a glacial lake that is sacred to many, and represents about 1.5 % of the world's fresh surface water volume. Specifically, we investigated methods to convert clay minerals in the shale into beneficial amorphous aluminosilicates that could help make concrete more durable. Thermal treatment (calcination) has been used in North America for over 80 years to activate shales. However, calcination does not work well for all clay minerals, including illite, the clay mineral that makes up two thirds of the Georgian Bay shale. We explored an alternative approach, feeding the shale into a vertical attrition mill. Shale processed in the attrition mill exhibited a dramatic boost in pozzolanic reactivity compared to its furnace-calcined counterpart. In this study, we take a more forensic approach, slicing through mortar cubes made with blended cements, and utilizing scanning electron microscopy to take a closer look at how this activated shale interacts with both Portland and Portland-limestone cements.

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Enhancing the Reactivity of Low Purity UK Clays through Mechanochemical Activation

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The need to reduce CO_2 emissions in the construction industry has accelerated the exploration of different supplementary cementitious materials (SCMs) as replacement to conventional Portland cement in concrete production. Clays are being considered as a promising alternative to conventional SCMs (e.g. blast furnace slag from iron making or fly ashes from coal combustion) due to their global abundance. In their natural form, clays lack the chemical reactivity (also referred to as pozzolanic activity) required for their use as SCMs, and therefore clays need to undergo an activation treatment. While thermal treatment (calcination) is an effective method for enhancing the pozzolanic activity of clays, it is not always effective particularly for low-purity non-kaolinitic clays—which are the most abundant clay types in the UK and Europe.

This study investigated the effectiveness of mechanochemical activation (MCA) to induce chemical reactivity of three low purity UK clays, containing less than 5 wt.% of kaolinite. MCA takes place during high energy grinding, and it is defined as the process in which mechanical energy induces physical and structural changes in different materials. MCA was carried out using a planetary ball mill, whose processing parameters were optimised to achieve amorphization and high chemical reactivity of the treated materials. It was used a ball to powder ratio of 25, 20 minutes of grinding and a speed of 500 rpm. Untreated, calcined (at 800^{o}C) and mechanochemically activated clays were characterized by laser diffractometry, X-ray diffractometry and thermogravimetric analysis. The chemical reactivity of untreated, calcined, and MCA-treated resources was evaluated through the R^3 isothermal calorimetry reactivity test. Results reveal that mechano-chemically treated UK clays yield reactivity values ranging from 300 to 400 J/g of SCMs, while the calcined ones achieved values ranging from 60 to 270 J/g of SCMs. This demonstrates that MCA is an effective treatment that significantly enhances the reactivity of the mixed clays evaluated compared with calcination, despite their illitic nature.

Keywords**:** mechanochemical activation, UK clays, low purity clays, SCMs

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LECTURE THEATRE 4 – SESSION 30

Clays in Geotechnics – Problems and Applications

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Micro- and Nano-scale investigation into the origins of sensitivity in clay

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Sensitive clays, primarily found in formerly glaciated regions in the northern hemisphere such as Scandinavia and Canada, exhibit a dramatic loss of shear strength upon remoulding at their natural water content. This behaviour is quantified by the sensitivity index [1], which compares the undrained peak shear strength of a natural clay in its original, intact condition to its liquid (remoulded) state. The sudden loss of strength in sensitive clay has led to devastating shallow landslides, including the 1977 Tuve landslide in Sweden, the 2010 Saint-Jude event in Quebec, and more recently, the 2020 and 2023 landslides in Gjerdrum, Norway and Stenungsund, Sweden, respectively. Although the geotechnical implications of sensitivity are well-documented, the fundamental physico-chemical and structural mechanisms responsible for such extreme mechanical transition remain poorly understood [2].

This study aims to investigate the structural transitions underpinning sensitivity using a multi-scale experimental approach on intact and remoulded specimens of sensitive clays sourced from diverse locations in the world. The approach combines synchrotron-based phase contrast nano-tomography and X-ray scattering techniques. Nano-tomography scans were acquired to image the microstructure of both intact and remoulded samples of sensitive clays at a pixel size of 50 nm within volumes of approximately 100 × 100 × 100 μm^3. Remarkably, on the scales discerned by this imaging technique, the remoulded samples, despite their near-liquid consistency and vanishing shear strength, retain a microstructure that appears broadly similar to that of the intact state— apart from a minor pore closure and rearrangement of clay constituents.

To explore whether more fundamental structural reconfigurations occur at smaller scales, this study employs Small- and Wide-angle X-ray Scattering (SAXS/WAXS), a non-destructive technique well-suited for probing inter-particle interactions in consolidated clay systems [3]. Across nearly all tested sensitive clays, remoulding leads to the emergence of a distinct secondary peak in the SAXS intensity profiles. This feature suggests the development of a new interlayer *d*-spacing, possibly induced by the changes in the electrochemical environment upon mechanical perturbation. These findings imply that the dramatic mechanical transition from solid to liquid-like behaviour in sensitive clays is not driven by microstructural collapse alone but instead may originate from nanoscopic reconfiguration of interparticle forces and clay-water interactions at the nanoscopic level.

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Coupled geotechnical and electrical investigations to assess marsh soil variability: a case study at Poiré-sur-Velluire marsh (France)

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The clayey soils of the Atlantic marsh site of Poiré-sur-Velluire (Marais Poitevin, France) show numerous heterogeneities at different space scales [1]: (i) vertical and horizontal gradients of salinity, (ii) clay layers in plastic and liquid states in the saturated part, (iii) desiccation cracks of several centimetres width in the unsaturated surface layer and, in particular, (iv) micro-reliefs (often called 'mottureaux' or 'gilgais') which are home of a rich biodiversity. To assess the spatial organisation of these heterogeneities, three techniques were used in this original context: the Panda® light penetrometer, electrical resistivity tomography (ERT) with different inter-electrode distances (Wenner-Schlumberger array with 48 electrodes spaced 20cm to 1m apart), and an electrical profiling device specially designed for the study. These methods were complemented by sampling for soil water content measurements and pedological investigations.

Cross-interpretation of all the geotechnical, geophysical and pedological data has highlighted the relationships between these different heterogeneities:

Horizontal salinity gradients exist at several space scales. On a scale of several hundred metres, horizontal salinity gradients reflect the influence of fresh water coming from the limestone plateaus bordering the marsh via ditches. On a scale of a few decimetres, horizontal salinity gradients exist between the desiccation cracks filled with meteoric water during the wet seasons and the low permeable core of microreliefs. This latter feature suggests that the genesis of microreliefs could be associated with osmotic swelling.

Coupled measurements of water content, Atterberg limits and cone resistance have evidenced vertical gradients in clay density. Layers of low-density clays in a liquid state are overlain by plastic to solid clay layers of higher density. These vertical gradients may also be evidence of hydrodynamic instability at the origin of micro-reliefs.

The combination of penetration and electrical tests made it possible to assess the spatial evolution of the thickness of the soft clays at the site scale.

The high resistivity digitations observed on the ERTs suggest that meteoric water can infiltrate the soft clays via desiccation cracks.

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Wetting-Induced Collapse Behaviour of Loosely Compacted Kaolin Soil: A Microstructural Study

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Ground subsidence encountered in the field is commonly associated with collapsible soils. Intrusion of inundating water into the dry deposits of such soils significantly reduces the soil strength, causing considerable volume reduction and damage to the overlying and nearby structures. Kaolin soils possess significant collapse potential and are widely spread over various regions of South Asia: across China and several parts of India [2,3], especially in Northeast India [5,6]. The kaolin deposits exist up to several meters below the ground surface in dry conditions. As the depth of deposit and mechanical stresses can vary significantly in the field, understanding the influence of natural density of kaolin and the stress state on the wetting-induced volumetric behaviour of kaolin is of utmost importance. Collapse in kaolin is attributed to the alteration in the soil fabric due to the changes in the various inter-particle (microscale) forces caused by water saturation [1,4]. The inundation pressure plays a significant role in the fabric evolution during the wetting process, thus controlling the collapse potential of the compacted kaolin. Microstructural studies on pore-fabric evolution during collapse provide valuable insights into the underlying mechanisms and help better understand the influence of inundation pressure on collapse behaviour. Kaolin soil compacted to a dry density of 1.25 g/cc was used in this work to study the wetting-induced volume change behaviour under different inundation pressures in the range of 10-1600 kPa. The compacted specimen of Kaolin soil exhibited a consistent collapse under all the studied inundation pressures. The collapse potential was observed to be increasing with an increase in the inundation pressure up to a maximum value of 13.85% under 800 kPa and then decreased to 11.7% under 1600 kPa. A microstructural analysis was carried out based on the fabric images and the pore size distributions (PSDs) obtained from FESEM analysis and mercury intrusion porosimetry (MIP), respectively. The PSDs and the soil fabric images of the 'as-compacted' specimen and post-collapse specimen under 400 kPa were analysed to understand the changes in the soil fabric and pores due to wetting. The pore size density curve for the post-collapse specimen was found to be on the finer side with respect to the 'as-compacted' specimen, indicating the reduction of the larger pores during the collapse. The inter-aggregate pores in the range of 0.1- 0.5 mm were identified as the major contributing pore size classes to the macroscopic volume change. Wetting under an inundation pressure results in a reduction of these pore sizes and leads to an increase in the finer pore sizes. The magnitude of inundation pressure influences the amount of reduction of these pores during the wetting process. The collapse potential was directly related to the degree of reduction in the pore volume contributed by these pore sizes.

Keywords—Collapse behaviour, Inundation pressure, Kaolin, Microstructure.

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Impact of Substrate Friction on Internal Non-uniform Deformation and Desiccation Crack Formation in Drying Fine Sediments: An X-ray CT Study

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Desiccation cracks in fine sediments can increase hydraulic conductivity and weaken soil strength, posing challenges to the stability of geotechnical structures. Substrate friction is a crucial factor influencing soil desiccation cracks, as it leads to non-uniform shrinkage and promotes crack formation. This study aims to investigate the impact of substrate friction on internal non-uniform shrinkage and desiccation crack formation in drying fine sediments using X-ray computed tomography (CT) combined with a particle tracking method. Micron-sized glass bubbles are embedded in bentonite pastes as markers to track internal deformation with multiple scans during drying. A sample with sandpaper substrate was dried in a container with grease applied to the inner sidewalls. A hybrid particle tracking method integrating Local Relative Positioning (LRP) and Artificial Neural Network (ANN) is adopted to monitor sample internal non-uniform deformation before and after desiccation crack formation. Preliminary results reveal that sample shrinkage is non-uniform due to substrate friction, leading to a crack generated in the central area of the sample.

KEYWORDS: desiccation cracks; fine sediments; boundary friction; shrinkage; X-ray CT

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Studies of electrochemical properties of compacted clays by concentration potential method

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The time evolution of concentration (membrane) potential upon step-wise changes in salt concentration has been studied for diaphragms made of various strongly compacted clays (montmorillonite, illite, kaolinite) equilibrated with 0.1M NaCl solution. Porous ceramic filters were used to confine the clays mechanically to be able to achieve high extent of compaction (dry density ~2000 kg/m^3).

A theoretical analysis has revealed that the time-relaxation pattern is primarily controlled by the properties of porous filters and only slightly depends on the clay properties. At the same time, quasi-stationary values of concentration potential are directly related to the electrochemical perm-selectivity of clay. This property has revealed considerable differences in the electrochemical behavior of various clays used in this study. This has been attributed to the differences in the micro-structure of clays, in particular to the existence or non-existence of interlayer water where cations may retain some mobility.

It has also been shown that in clays with high electrochemical perm-selectivity, one can expect a strong increase in the diffusivity of cationic (radio)-tracers with decreasing ionic strength of equilibrium electrolyte solution. At the same time, low electro-chemical perm-selectivity means no noticeable dependence of this kind. The correctness of this observation has been corroborated by comparison of our findings with the literature data on the diffusion of cationic radio-tracers through compacted montmorillonite (high perm-selectivity) and kaolinite (low perm-selectivity). To check the self-consistency of our approach, we have also carried out some measurements of diffusion of cationic and anionic radio-tracers through compacted illite. It has been found that the measured effective diffusion coefficients were in excellent agreement with the electrochemical perm-selectivity estimated for this clay from the measurements of concentration potential. Given that the concentration-potential measurements are much less time consuming than direct measurements of radio-tracer diffusion (and require no classified laboratory) using them as a substitute can be of considerable practical interest.

Based on the observed correlations and postulated mechanisms, for less compacted clays, we expect similar behaviour (possibly, in contact with somewhat less concentrated electrolyte solutions). This can be potentially useful for (in situ) monitoring of condition of clay-based geotechnical barriers.

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Novel perspectives on the transport and mechanical properties of pollutant containment systems comprising enhanced bentonites

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The prolonged exposure of engineered bentonite-based barriers to contaminated liquids, which have high ionic strength and/or low monovalent-to-multivalent cation ratio, is known to suppress the osmotic swelling potential and increase the hydraulic conductivity of these barriers from one to several orders of magnitude. The evidence of such adverse effects caused by the interaction with liquids with aggressive chemistries, commonly referred to as chemical or hydraulic incompatibility, has thus stimulated the development of enhanced bentonites (EBs), which comprise natural bentonites (NBs) amended with cyclic organic carbonates (e.g., Multiswellable Bentonites, MSBs) or anionic polymers (e.g., Bentonite Polymer Composites, BPCs, Dense Prehydrated Geosynthetic Clay Liners, DPH-GCLs, and HYPER Clays, HCs).

With a view to elucidating the mechanisms responsible for the improved chemical compatibility of EBs relative to unenhanced NBs, Guarena et al. [1] carried out a critical review on the available literature pertaining to the laboratory assessment of the semipermeable, diffusive, and hydraulic properties of EBs, which was interpreted through a theoretical framework for the coupled chemo-hydro-mechanical behaviour of semipermeable porous media. On the basis of such a critical review, enhanced osmotic swelling, which was originally suggested by Scalia et al. [2] as one of the three possible mechanisms believed to influence the behaviour of EBs, was discounted as a factor that contributes to improving the sealing ability of EBs. In the case of MSBs, this conclusion was further corroborated by a greater compressibility relative to NBs subjected to comparative hydraulic conductivity tests, thus suggesting that cyclic organic carbonates act as inhibitors of osmotic swelling. Intergranular pore clogging, which causes the conductive pores to be more tortuous and meandering, was confirmed as the primary mechanism that controls the hydraulic conductivity of BPCs upon permeation with aqueous solutions with high ionic strength. The low hydraulic conductivity exhibited by DPH-GCLs upon exposure to concentrated electrolyte solutions was finally attributed to an enhanced dispersion of the bentonite fabric, which is an additional mechanism relative to those described by Scalia et al. [2] and is ascribed to the combined effect of prehydration with the polymeric solution and preconsolidation through vacuum extrusion.

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Polymer-modified bentonite-silt composites to improve the hydro-mechanical properties of landfill mineral sealings

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Compacted clay layers are widely used in landfill barrier systems, relying on low-permeability soils to prevent leachate migration. When locally available soils like silts or low plastic clays lack sufficient sealing properties, bentonite is added to enhance impermeability due to its swelling capacity and self-healing properties. The additional use of polymers shows significant potential in further modifying bentonite-silt mixtures, maintaining low permeability while improving mechanical properties. The functionality of the sealing system is influenced by the ratio of silt and bentonite mass fractions within the soil-polymer mixture and their interactions. An increased bentonite fraction enhances the sealing function, whereas a higher silt content reduces the costs. While the interaction between bentonite and polymers has been widely studied, little is known about the effect of an increased silt content on hydro-mechanical properties.

This study systematically investigates the hydro-mechanical behaviour of polymer-modified bentonite-silt composites. The polymer Xanthan gum (XAN) and polyacrylamide (PAA) were tested in mixtures of bentonite with 30% or 70% silt, respectively. Oedometer tests were performed in the saturated state to assess stiffness and flexibility, and permeability was estimated using Terzaghi's theory. The adsorption behaviour of the polymer-modified bentonite-silt composites was characterised by determining the specific surface area (SSA), cation exchange capacity (CEC) and water absorption capacity according to Enslin-Neff.

The results indicate that polymer modification increases compressibility in silt-dominated mixtures (see Fig. 1a), whereas the opposite effect is observed in mixtures with lower silt content (see Fig. 1b). In addition, the findings indicate that PAA and XAN modification reduces the swelling index of the soil mixtures. Overall, creep behaviour was found to be influenced by the bentonite/silt mixing ratio and the polymer type. For silt-dominated mixtures, the PAA-modification significantly increased the creep index, whereas the Xanthan modification had a minor effect. Hydraulic conductivity was reduced by addition of PAA and XAN polymer in silt-dominated samples by reducing flow paths, while it slightly increased in bentonite-dominated samples. These findings highlight the potential of polymer additives for optimizing the hydro-mechanical properties of bentonite-silt composites in landfill sealing applications.

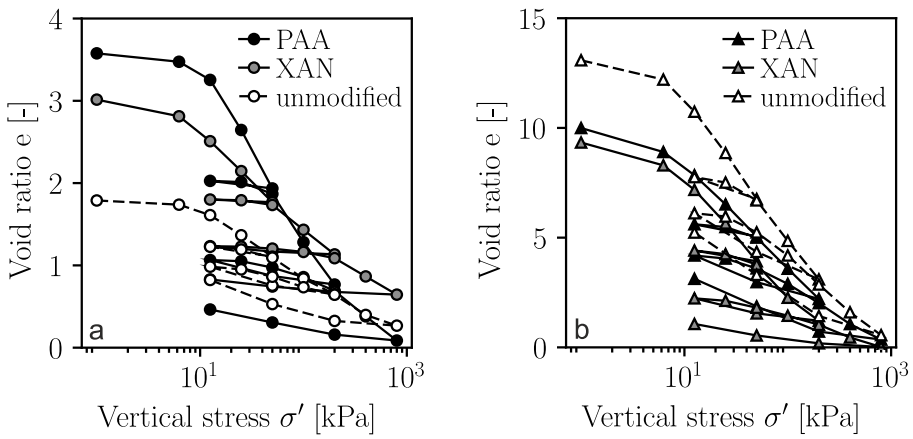

Fig. 1: Results of the oedometer tests for (a) silt-dominated and (b) bentonite-dominated samples

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Montmorillonite and kaolinite as a novel bio-inspired material for the attenuation of viral pathogens and salt leachates

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Owing to the expanded healthcare services, pandemic events (like COVID-19), increased patient load, and technological advancements in medical diagnostics, there is an upsurge in the generation of biomedical waste (BMW). The conventional and improper disposal of such waste through incineration and unplanned dumping in isolated areas poses health risks through the passive transmission of diseases. Therefore, there is an urgent need for a proper containment facility to arrest the leachate produced by these BMWs. The leachate from BMW includes viral pathogens, harmful volatile contaminants, heavy metals, and salts. In the present study, the effectiveness of montmorillonite and kaolinite-based materials to contain such leachate from BMWs was explored for the first time. The attenuation capacity of such materials in the presence of high ionic strength salt leachates, human viral pathogens, and volatile contaminants present in BMWs was assessed. The diffusion rates and the fate of these contaminants over a period of 50 years were also evaluated. The study reveals that kaolinite could attenuate the studied viral pathogens more effectively than the montmorillonite material. However, a layered system of kaolinite-montmorillonite was found to be more effective in inhibiting the passive transmission of the contaminants. The study proposed an alternative disposal facility having a barrier made of the kaolinite-montmorillonite layer that has a thickness of 2-3 mm. Such a containment facility can prevent the transport of viral pathogens and other harmful contaminants effectively over a period of 50 years, thereby maintaining the sustainability goals.

Keywords: Montmorillonite, Kaolinite, Viral pathogens, Salts, Diffusion

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Modified Clay Precursors for their Evaluation as Alkaline Binders for the Stabilization of Marine Sediments

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Mechanical stabilization of dredged marine sediments is a well-established method to manage the large volumes excavated from port areas annually—about 200 million m³ per year in Europe alone [1]. Directive 2008/98/EC [2] promotes the reuse and recycling of dredged sediments to minimize environmental impact and risks to human health. However, upon that, significant treatments are required to enhance their properties. These include the use of traditional binders such as cement. Yet, the growing global demand for cement and its considerable carbon footprint [3] have intensified the search for environmentally sustainable alternatives. In this context, alkaline binders–namely alkali-activated binders (AABs), including geopolymers–have emerged as promising low-carbon substitutes. These binders offer comparable mechanical performance while significantly reducing CO_2 emissions. For these reasons, AABs are increasingly being explored for eco-friendly soil improvement techniques [4]. Alkali-activated binders are inorganic binders produced through the reaction of aluminosilicate precursors with an alkaline activator. Their synthesis typically involves materials such as industrial by-products or natural clays, which, after suitable mechanical, thermal, or chemical modifications, become reactive in alkaline environments. This study focuses on optimizing the pretreatments of a common illitic clay, which may be more readily available than pure clays such as kaolin–widely studied as precursors for alkali-activated materials. Pretreatments play a crucial role in evaluating these clays as potential precursors, as they enhance reactivity by increasing the amorphous phase content and specific surface area. The tests involved heat treatments at 700, 800 and 900 °C, high energy grinding and combinations of the two. A chemical-mineralogical and geotechnical characterization of the clay was carried out, along with an analysis of the modifications induced by each treatment. Results of pretreatments show that over 50% amorphous content can be achieved starting from nearly 100% crystalline material. Alkaline activation pastes were prepared for each pre-treated clay using sodium hydroxide solutions at different molarities, aiming to reduce costs and environmental impact. Two curing conditions (room temperature and 50 °C) were tested to assess the effect of temperature on geopolymerization. Thermally treated clays yielded the best results as precursors, while mechanically treated ones showed poor workability and compromised final integrity with NaOH alone. Preliminary tests helped define mix designs and conditions for evaluating pre-treated clays as binders for stabilizing dredged marine sediments.

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Fix clay with clay

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Natural clays are commonly stabilised with cement and lime-based binders to improve their inferior geotechnical engineering properties. Applications include settlement control of embankments on soft soils, as well as basal stabilisation of deep excavations. As the construction industry seeks to minimise the environmental impact of cement production, calcined clays have emerged as a promising low-carbon alternative, effectively serving as a partial replacement for traditional binders. Clays are naturally abundant, widely available, and inexpensive. When thermally or mechanically activated, they demonstrate pozzolanic reactivity in an alkaline environment, making them a valuable resource for sustainable construction. While much of the focus has been on using calcined clays as a partial replacement for cement in concrete, they also show considerable potential in other applications, such as stabilisation of soft soils.

In the Nordic countries natural sensitive clays, which often possess high water content, high sensitivity, and low strength and stiffness, are dry mixed with traditional binders such as lime and cement to improve their mechanical properties. The incorporation of calcined clay into these binders can provide the necessary alumina and silica to enhance secondary pozzolanic reactions, improving strength and durability while reducing dependence on cement. However, as opposed to other Supplemental Cementitious Materials such as Ground Granulated Blast furnace Slag (GGBS) and Cement Kiln Dust (CKD) [*e.g.* 2], the use of calcined clays in binders for ground improvement is novel.

This study thus explores the effectiveness of using these calcined clays to stabilise soft natural clays, presenting a novel approach to "fix clay with clay". This study incorporates a multi-scale approach to optimise the maximum replacement of calcined clays by capturing the evolving properties at the material scale (submicrometre) and relating these processes to improvements in mechanical properties at the laboratory scale (decimetre). The experimental approach combines Electrical Impedance Spectroscopy (EIS) with miniature Cone Penetration Tests (CPT) to investigate the early-stage curing and strength development as a function of time in a series of binders. Both lime-based and cement-based binders with different proportions of calcined clay were studied and compared to the lime-cement control. Furthermore, select alternative binders that offered the most equivalent performance to the control samples were studied in more detail using traditional geotechnical tests. Finally, synchrotron-based phase contrast nano-tomography and X-ray scattering techniques were employed to study the microstructural differences between the lime and cement-based binders.

[1] Kirsch, K., & Bell, A. (Eds.). (2012). *Ground improvement*. CRC Press.
[2] López Ramírez, A., Zhang, Y., Forsman, J., & Korkiala-Tanttu, L. (2024). Stabilization of soft clay with sustainable binders for dry deep mixing design. *Geotechnical Testing Journal*, *47*(1).

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Stability and Solubility of Mg-Hydroxy-Interlayered Smectite (Mg-HIS)

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In construction, smectite-rich soils must be stabilised, often using cementitious binders [1]. Magnesium-based binders (MB) could offer a novel and environmentally friendly alternative to traditional CaO-based binders. Indeed, when MB hydrates in the presence of smectite, it induces the formation of magnesium-hydroxy-interlayered smectite (Mg-HIS)—a modified smectite where the interlayer space is filled with oligomeric Mg-hydroxyl species [2].

Mg-HIS exhibits significantly reduced cation exchange capacity, specific surface area, and—most importantly—swelling and shrinkage potential, making it particularly suitable for construction applications. Despite its promising properties, little is known about the long-term stability of Mg-HIS. If Mg-HIS is thermodynamically unstable, it and may revert to common smectite over time, with unforeseen consequences.

This study aims to investigate the stability and solubility of Mg-HIS by (i) monitoring its structure and the solution at equilibrium up to 1 year, and (ii) developing a thermodynamic model to predict its stability.

Preliminary results suggest that Mg-HIS remains stable for at least nine months, although minor analytical changes indicate possible activity of the Mg-hydroxides within the interlayer. While the nature of this activity is not yet fully understood, it may involve gradual polymerisation of the oligomers over time. Modelling efforts indicate that Mg-HIS can be treated as a distinct phase with its own solubility product constant (log K_s). The derived log K_s is slightly higher than that of saponite, aligning well with the observed linear trend between log K_s of clay minerals and their corresponding cation ratios.

[1] S. Haas and H. J. Ritter, “Soil improvement with quicklime–long-time behaviour and carbonation,” *Road Mater. Pavement Des.*, vol. 20, no. 8, pp. 1941–1951, 2019, doi: 10.1080/14680629.2018.1474793.
[2] W. J. Zucha, E. Bernard, R. Kuhn, M. Plötze, and A. Puzrin, “Effects of MgO-based cementitious binder on smectites,” *Appl. Clay Sci.*, vol. 265, p. 107677, Mar. 2025, doi: 10.1016/j.clay.2024.107677.

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Soft Calcite from mussel shells: a bio-derived additive for the geotechnical enhancement of marine clays

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Marine dredged sediments, mostly rich in clay minerals, pose significant challenges in geotechnical engineering due to their complex properties and variability. This study shows preliminary experimental results on the treatment of dredged sediments using a peculiar needle-like form of calcite, called Soft Calcite (SC), obtained by a controlled dissolution of the aragonitic layer from *Mytilus Galloprovincialis* sp. shells [1]. When used as a partial replacement for cement, this material can play an active role in the chemo-mechanical stabilization of sediment mixtures. Recent research [2] highlights that biogenic calcium carbonate in mussel shells is more liable to decomposition than lithogenic sources, making it more reactive in hydration reactions with sediment silica and cement minerals. Builds on these findings, here we discuss the results of three different treatments of mussel shells to obtain the SC in a more sustainable and scalable way. These treatments were designed to enhance the reactivity of SC and its effectiveness in the mechanical improvement processes of soft marine sediments. To assess the role of different treatments, SC was subjected to thermogravimetric analysis (TGA), X-ray Diffraction (XRD) and total organic carbon (TOC) measurement. The efficacy of SC can be attributed to three main factors: (i) the higher specific surface area compared to traditional Portland cement, promotes hydration product precipitation and nucleation; (ii) the unique morphology of the SC prismatic needles, which are integrated into the mixtures forming a 3D scaffolding microstructure, as revealed by SEM images and synchrotron nano-computed X-ray tomography (Syn nCT), facilitates the formation of a reticulated network that better hosts CSH gel during cement hydration; and (iii) the impact of different treatment time on the consistency index, water content, and strength of the sediment-cement mixtures prove the persistence of SC after 28-days of curing, which further strengthens the mixture by filling the matrix.

The innovative properties of this material, including its ability to capture and retain harmful pollutants [3], suggest its potential for use as an effective barrier in port areas, addressing both the stabilization of dredged sediments and the remediation of polluted environments.

[1] Murphy J. et al. (2020) Matter 3:2029-2041
[2] Petti R et al. (2024) Géotechnique 0:1-20
[3] Topić Popović N. et al. (2023) Appl Sci 13(1):623

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Soil-Contaminant Interaction: Influence of Elevated Temperatures

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Attempts were made to investigate the changes undergone by the soils, when they interact with contaminants whose attributes are chemical concentration, pH and temperature by employing state-of-the-art techniques such as X-ray diffraction, Nanoindentation, Laser scanning diffraction, zeta potential device and a calorimeter in tandem. The utility of these techniques for establishing physical, chemical and mineralogical changes occurring in the soil, development of the residual normal and shear stresses on the surface of their particles, changes in their hardness, residual modulus and resistance to indentation when exposed to elevated temperatures has been demonstrated. Efforts have also been made to establish relationships between soil-specific parameters (viz., clay content, specific surface area, cation exchange capacity, zeta potential, percentage organic matter) and the heat of wetting, which has been found to be an important parameter that quantifies physico-chemico-mineralogical characteristics of the soil.

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LECTURE THEATRE 5 – SESSION 38+43

Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies

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Microwave-Assisted Synthesis of advanced NiFe Layered Double Hydroxides from MOFs for Environmental Remediation

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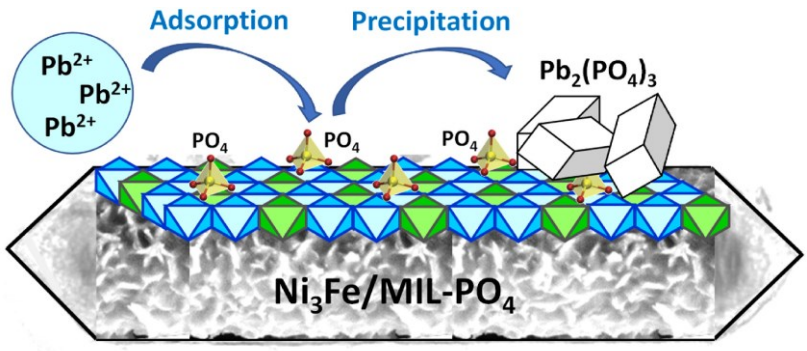
Recent advancements in environmental remediation techniques have highlighted the importance of developing efficient and scalable materials for the degradation of hazardous contaminants. In this context, the microwave-assisted synthesis of NiFe Layered Double Hydroxide (LDH) has emerged as a promising approach for the production of highly crystalline, monodisperse nanoparticles, offering significant advantages over traditional methods. This study presents the synthesis and characterization of NiFe LDH derived from the conversion of MIL-88A, an iron-based metal-organic framework (MOF), using microwave (MW) irradiation. The microwave-assisted method is demonstrated to provide enhanced crystallinity, structural integrity, and uniform rod-like morphology compared to the conventional hydrothermal synthesis, as confirmed by X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Optimal synthesis conditions at 110°C for 30 minutes yielded high-quality MIL-88A crystals with smooth microrods, setting the stage for the subsequent conversion to NiFe LDH.

The catalytic performance of Ni3Fe LDH/88A was evaluated for bisphenol A (BPA) degradation, [1] demonstrating a remarkable efficiency of 81% within 10 minutes, significantly outperforming other materials such as Ni_3Fe LDH/COP and the precursor MIL-88A. The enhanced activity of Ni_3Fe LDH/88A was attributed to the activation of persulfate (PS) by the Ni^{2+}/Fe^{3+} system, with kinetic modeling revealing a higher rate constant (0.153 min^{-1}).

In addition to its catalytic applications, the study also investigates the use of functionalized NiFe LDH materials for the removal of lead (Pb) from contaminated water. [2] By converting MIL-88A(Fe) into NixFe LDH and functionalizing it with phosphate anions, the resulting material demonstrated high selectivity and adsorption capacity for Pb^{2+}, with a maximum adsorption capacity of 538 mg/g, surpassing other reported adsorbents. The fast adsorption kinetics and high selectivity of NiFe-PO4 LDH for Pb^{2+} highlight its potential for water treatment applications. This dual approach, encompassing both catalytic degradation and adsorption for environmental cleanup, underscores the scalability, versatility, and effectiveness of NiFe LDH materials for sustainable and efficient environmental remediation processes.



Pb^{2+} capture by 3D $Ni_3Fe/MIL\text{-}PO_4$

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[2] Li M. (2024) Chemosphere 364: 143070

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Mineral-based advanced oxidation processes for enhancing the removal of antibiotic resistance genes from domestic wastewater

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Clay minerals with their unique 2D-structure exhibit properties that make them ideal for interactions with a range of organic and inorganic contaminants. With their permanent negative excess charge, they can sorb cations including radionuclides and heavy metals; their electron-rich surfaces can contribute to specific electron-donor-acceptor interactions with electron-poor aromatic compounds such as nitroaromatics; and structurally bound ferrous iron (Fe(II)) in clay minerals can contribute to the redox transformation of both organic and inorganic pollutants, for examples chlorinated solvents, chromium or technetium. More recently, clay mineral Fe(II) has been implicated to reduce dissolved oxygen to reactive oxygen species that, in turn, were capable of oxidizing organic contaminants and metalloids and have been connected to antimicrobial effects. Reactive oxygen species (ROS) commonly comprise superoxide radical, hydrogen peroxide and hydroxyl radical, with the latter also being the main oxidant in advanced oxidation processes (AOPs) used in water treatment in some countries and proposed for tertiary/quaternary wastewater treatment to remove recalcitrant organic contaminants and antibiotic-resistant bacteria and genes (ARGs). However, most of the studies investigating mineral-based AOP used idealized or highly simplified aqueous media, and it remains unclear whether and to which extent application in wastewater treatment or remediation is feasible.

Here, we provide a proof-of-concept study for the use of clay mineral-based AOPs for removing ARGs from real wastewater treatment plant effluent. We used the Fe-bearing clay mineral nontronite NAu-1 either to catalyse the activation of H_2O_2 (H_2O_2/NAu-1) or, after reduction of its native structural Fe(III) to Fe(II) (rNAu-1), to produce ROS during Fe(II) oxygenation. We then monitored the abundance of selected ARGs (*tet*M, *tet*Q, and bla_{OXA-10}), *int*1 (a mobile genetic element), and 16S rRNA gene (as a measure of total bacteria) associated with the native bacterial communities in authentic wastewater effluents during treatment and compared our results with the efficiencies of conventional UV and H_2O_2/UV technologies.

Our results demonstrate that H_2O_2 activation with NAu-1 was more effective in removing ARGs compared to conventional approaches and AOPs such as UV irradiation alone or in combination with H_2O_2. Gene removals in H_2O_2/NAu-1 treatment increased with greater H_2O_2 doses and contact times, and we found pseudo-optimal conditions of H_2O_2 dose (0.26-10 mM) and contact time (4-8 h) that led to maximum removals of 1.2-2.3 log units. At longer contact times of 24 h, bacterial regrowth occurred as H_2O_2 became depleted. During treatment with rNAu-1, ARG removals were highest (up to 2.9 log units) and fastest (0.5 h) and suppressed bacterial regrowth over 24 h. Concomitant oxidation of clay mineral Fe(II) and minimal release of metals to the aqueous phase are consistent with a removal mechanism based on extracellular ROS production and bacterial inactivation. Surprisingly, we found similar gene removals with rNAu-1 also under anoxic conditions, where Fe(II) oxidation was minimal. However, release of Fe(II) to the aqueous phase was substantial and we hypothesize that microbial metal uptake and/or synergistic interactions with wastewater constituents, probably organic material, led to the observed gene removal.

Taken together, our results show that mineral-based AOPs have potential for ARG removal in tertiary wastewater treatment and remediation due to elevated removals and low chemical and energy demands.

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Exploring oxidative pathways in iron redox-mediated chlorinated contaminant degradation

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The Fe(II)/Fe(III) redox cycle plays a crucial role in degrading contaminants in environmental systems. Mineral-bound Fe(II) is involved in reductive contaminant degradation pathways and can additionally cause oxidative transformation. While reductive dechlorination and reaction pathways have been extensively studied over time, relatively fewer studies have focused on quantifying abiotic dechlorination processes through oxidative pathways. Recent studies have demonstrated that contaminants could be degraded by hydroxyl radicals (•OH) produced during the oxygenation of Fe(II)-bearing sediments.[1] Furthermore, a recent study reported that the half-life of trichloroethylene (TCE) abiotic dechlorination in sediments decreased from 60 years under anoxic conditions to just 3 months under oxic conditions, primarily due to •OH production and subsequent TCE oxidation.[2] These reports highlight the importance of oxidative pathways in contamination degradation and the need for further research to better understand these mechanisms for environmental remediation. Thus, this study investigates the potential of low Fe-content clay minerals to degrade dichloroethenes (DCEs) under controlled oxic conditions, aiming to evaluate their effectiveness in oxidative degradation processes.

Oxidative degradation of cis- and trans-DCE (DCEs) at pH 8 was investigated, using the Fe(II)-bearing clay mineral SWy-3. We have designed a closed reactor setup to control loss of the highly volatile DCEs and provide sufficient oxygen to completely oxidise Fe(II). Parallel batch reactors were set up with benzoic acid as a scavenger to quantify the production of •OH. Additionally, a comparative investigation on product formation was carried out using equivalent concentrations of aqueous Fe(II), added as $FeCl_2$ to study oxidation in a homogeneous system. Reactant DCEs were monitored over a week using GC-MS like in our previous work[3] and a HPLC method was established to identify and quantify degradation products (dicarboxylic acids: acetic acid, oxalic acid, glycolic acid, glyoxylic acid and formic acid). Formation of CO_2 as final mineralization product was measured with CG-MS after Fe(II) oxidation in the clay mineral (via Mössbauer spectroscopy) and aqueous solution (1,10-phenanthroline method) had stopped.

Results from ongoing experiments will be presented to evaluate the oxidative degradation of DCEs by Fe(II)-bearing clay minerals under controlled oxidising conditions. The study will highlight the extent of •OH production and its role in DCE transformation. Comparative analysis with $FeCl_2$ systems will provide insights into the efficiency of mineral-bound Fe(II) in promoting oxidative pathways. These findings will contribute to a better understanding of abiotic dechlorination mechanisms and their potential applications in environmental remediation.

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2. Schaefer, C. E., Ho, P., Berns, E. & Werth, C. Mechanisms for Abiotic Dechlorination of Trichloroethene by Ferrous Minerals under Oxic and Anoxic Conditions in Natural Sediments. *Environ Sci Technol* **52**, 13747–13755 (2018).
3. Entwistle, J., Latta, D. E., Scherer, M. M. & Neumann, A. Abiotic Degradation of Chlorinated Solvents by Clay Minerals and Fe(II): Evidence for Reactive Mineral Intermediates. *Environ Sci Technol* **53**, 14308–14318 (2019)

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Coarse-grained simulation of colloidal self-assembly, cation exchange, and rheology in Na/Ca smectite clay gels

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Clay minerals—layered silicate nanoparticles that constitute roughly half of the mineral mass in soils, sediments, and sedimentary rocks—are a critical building block of the Earth's subsurface. A key aspect of these materials is their control over fluid flow, solute migration, and solid mechanics in many systems. The aggregation of clay platelets strongly impacts associated transport and mechanical properties. Unfortunately, experimental and computational characterization of clay aggregation is inhibited by the delicate water-mediated nature of the process and by the wide range of spatial scales involved, from 1-nm-thick platelets to flocs with dimensions up to micrometers or more.

In this work, we utilize a new coarse-grained molecular dynamics (CGMD) model to predict the microstructure, dynamics, and rheology of hydrated smectite clay assemblages as a function of particle diameter (6 to 25 nm) and the proportion of Na vs Ca exchangeable cations. Simulated systems have dimensions up to 0.1 μm and contain up to 2,000 clay particles. We monitor the assembly and growth of clay tactoids (i.e., stacks of parallel clay platelets) and aggregates (assemblages of tactoids) as a function of simulation time, exchangeable cation type, and clay platelet diameter. Equilibrated configurations are analyzed to predict structural properties including tactoid size and size distribution, basal spacing, counterion distribution in the electrical double layer (EDL) around tactoids, and the modes of clay association. Finally, non-equilibrium simulations are carried out at different shear rates to predict the rheological properties of smectite gels. Our results demonstrate new potential to characterize and understand clay aggregation in dilute suspensions and gels on a scale of thousands of particles with explicit representation of counterion clouds and with accuracy approaching that of all-atom molecular dynamics (MD) simulations.

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Osmotic swelling mechanism of clay soils from marsh: the spectacular case of 'mottureaux'

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Within the Marais Poitevin (France), the second largest wetland area in France, the 'Michel Brosselin' National Natural Reserve is a unique conservation site to study the evolution of the clay soils of the wet meadows, which have almost disappeared as a result of cultivation. The exceptional character of this landscape is linked to the abundance of 'mottureaux', mounds of several decimetres in diameter that can rise to more than 40 cm above the surface. On the surface, the mottureaux form a wide variety of patterns over dozens of hectares, as previously described by Fernand Verger [1], but their morphogenesis remains unexplained. At the plot scale, mottureaux appear to be a self-organizing system. However, the hypothesis of morphogenesis by self-organization contrasts with the current hypothesis of mottureau formation proposed in the literature [2], which is based on the filling of shrinkage cracks by surface aggregates during runoff, a mechanism that does not a priori induce surface organization. This observation led us to formulate a new hypothesis about the driving force at the origin of the formation of these mounds, which could be the osmotic swelling of the soil, a simple physico-chemical process which occur when different chemical and mineralogical conditions are satisfied.

The osmotic swelling hypothesis implies three conditions: i) a high proportion of swelling clays (smectites) in the soil, ii) a sufficient proportion of sodium (Na) adsorbed on the surfaces of the clays and iii) a sufficiently low salinity of the soil to not inhibit swelling. The results obtained in this study show that: i) the soils are very clayey (clay fraction >45 wt%); ii) the proportion of smectites is relatively low (<30 wt%) compared with soils of the same classification (Vertisols), indicating that the quantity of smectites alone cannot explain the emergence of mottureaux; iii) the clay surfaces have a sufficiently high proportion of exchangeable sodium (ESP>15%) to activate osmotic swelling (at a depth of 20/40 cm). The three criteria that allow the osmotic swelling are reunited and can validate our hypothesis of the driving force of the formation of mottureaux in this pedological context and environment. Nevertheless, the activation of this mechanism requires to consider hydric dynamics involving mixtures of rainwater coming from the soil surface and seawater coming from deep fossil water table. The activating parameter can be obtained by considering a simple qualitative indicator of the hydric dynamics of the mottureaux: the ratio between the exchangeable sodium and exchangeable calcium (Ca) ratio (Na_{ech}/Ca_{ech}), which in the medium to long term reflects the competition between the infiltration of fresh water brought by rainfall (Ca input) and the upwelling of saline water from the deep fossil water table located at depth (Na input alone). The ratio Na_{ech}/Ca_{ech} shows that in areas with mottureaux, the infiltration of fresh water in depth allows the salinity to be lowered, which is not the case in the areas without mottureaux, where the saline water from the surface inhibit the osmotic swelling.

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Competitive adsorption of Cs and Sr onto a soil clay fraction

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In context of nuclear sites remediation and environmental monitoring, multi-contamination by radionuclides is frequently recorded in soils, sediments and aquifers. Moreover, subsequently to the Chernobyl and Fukushima accidents, Cs and Sr have emerged as the main radionuclides encountered in contaminated soils. Understanding and predicting the retention of trace elements in these environments is essential for selecting effective remediation strategies. This retention is partly governed by chemical sorption phenomena on mineral surfaces, especially on clay minerals, which are known to possess negative surface charges compensated by cations. Based on previous studies, competitive adsorption occurs between trace metal elements with similar chemical properties, including valence and hydrolysis behaviour [1-2]. Consequently, Cs and Sr are expected to behave independently each other, such as mono-elemental contaminant. However, to date, no studies have examine this behavior in a multi-contamination context. The aim of this study is to evaluate this assumption by investigating the Cs and Sr retention behaviours in a multi-contamination scenario, focusing on pure illite and smectite, and on a soil clay fraction containing 78 % illite and 8% smectite.

Batch experiments were performed with Ca-illite, Ca-montmorillonite, decarbonated and raw clay fraction extracted from a soil in 10^{-3} mol.L^{-1} $CaCl_2$ or in 10^{-3} mol.L^{-1} $CaCl_2$ and 5 10^{-4} mol·L^{-1} HCO_3. Cs and Sr were simultaneously introduced in each batch. Concentration isotherms were determined by fixing the concentration of one competitor (Cs at 10^{-10} mol.L^{-1} or Sr at 10^{-4} mol.L^{-1}) while varying the concentration of the other. Competitive adsorption was evaluated using a macroscopic multi-site ion exchanger model [3], which simulated the adsorption and desorption of Cs and Sr based on the sorption properties of pure smectite and illite.

The results show that Cs adsorption on Ca-illite and Ca-smectite is not influenced by the presence of Sr, suggesting independent retention of Cs under these conditions. In contrast, Sr adsorption on the clay minerals is slightly reduced in the presence of Cs, with competition between Cs and Sr for adsorption sites being well-represented by the model. When applied to the decarbonated and carbonated soil clay fractions, simulations considering both Cs and Sr simultaneously are in good agreement with the observed adsorption isotherms. These results indicate that Cs and Sr multi-contamination can be accurately modelled by considering both contaminants. While Cs adsorption can be modelled independently of Sr, this is not the case for Sr, which shows a clear competitive behaviour. This study highlights the importance of understanding competitive adsorption dynamics in multi-contaminant systems.

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[2] Marques Fernandes M and Baeyens B (2019) Appl Geochem 100:190-202
[3] Latrille C and Bildstein O (2022) Chemosphere 288: 132582

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Clay mineral contributions to metal mobilization in high- and low-temperature altered subsurface basalts for engineered reactive transport

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Identification of mineral sources of cations that are incorporated into carbonate mineral structures or conserved is needed to achieve commercial-scale carbon sequestration and critical minerals recovery in basaltic and other mafic/ultramafic reservoirs. This study aims to isolate the source and mechanisms of metal ion-leaching (e.g., iron, manganese) from primary and secondary minerals in naturally altered basalts by identification and characterization of pore-lining clay minerals. Historically, primary silicates (e.g., pyroxene, glass) have been studied as the main contributor of cations for carbonate mineralization after CO_2 injection in basalt formations. However, natural dissolution of primary silicates over geologic timescales results in secondary minerals and phases (e.g., smectite, palagonite), which alter pore structures and concentrate metal cations in secondary minerals. This work investigates secondary minerals in two altered subsurface basalt formations as sources of cations incorporated into secondary carbonate minerals: Newberry Volcano (Oregon, USA), a basaltic formation altered by CO_2-rich hydrothermal fluids, and the Grande Ronde Group, a basaltic formation altered by meteoric fluids which hosted the first-of-its-kind Wallula Basalt CO_2 Injection Project (WBIP; Washington, USA). Mineral analysis of the natural (Newberry Volcano) and engineered (WBIP) secondary carbonates in basalts reveal a pattern of initial calcium-manganese-iron ankerite cores, followed by calcium-manganese siderite minerals coating the initial ankerite core.

This study uses subsurface core collected from Newberry Volcano by the United States Geological Survey and pre- and post-injection rock samples (core and cuttings) from the WBIP borehole provided by Pacific Northwest National Laboratory to investigate mobilization of metal cations from clay minerals into porous media from CO2-rich fluids and eventually immobilization into carbonate minerals. Various methods were used to identify cation location and concentration in minerals from the Newberry and Grande Ronde Formations including whole rock digestion (which quantified the total amount of metal ions present in the rock) and microprobe mapping (which identified primary and secondary minerals with detectable amounts of manganese). Clays carefully removed from Grande Ronde basalt vesicles from representative cuttings samples were separated by particle size for X-Ray Diffraction and High Resolution-Transmission Electron Microscopy analysis to identify clay type and cation hosted in secondary minerals.

The study reveals that manganese is hosted in pyroxene, glass, and secondary clay minerals. At least two different clay minerals, with varying concentrations of iron and manganese, are identified in both basalt formations. Preliminary results indicate clay minerals serve as first-order cation sources for secondary carbonate mineralization and provide diffusive pathways for CO_2 migration.

This work supports that secondary clay minerals will play a critical role for carbon mineralization and critical minerals recovery in subsurface basalts and other mafic/ultramafic formations. These clays are found in abundance within structural/matrix and pore- and fracture-lining morphologies and increase mineral surface area and, as shown in this work, the accessibility of metal cations. Understanding secondary minerals in Newberry and Grande Ronde Formations and metal ion leaching mechanisms in CO_2-rich environments will: 1) enhance our understanding of clay minerals in basalt formations, 2) provide insight into future production and storage projects in subsurface basalts, and 3) inform geochemical and reactive transport models for engineered subsurface injection and recovery processes.

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Probing the Surface Bridging Hydroxyl sites of aluminum oxide by ^{19}F Solid-State NMR Spectroscopy

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The structure and chemical reactivity of mineral surface hydroxyl groups play critical roles in interfacial processes [1]. Conventional experimental techniques, such as infrared spectroscopy and X-ray photoelectron spectroscopy, are unable to differentiate short-range ordered structures like terminal hydroxyl (η-OH) and bridging hydroxyl (μ_2-OH), thereby hindering quantitative analysis. Although surface complexation model (SCM) or density functional theory can distinguish between chemically distinct sites in theory, experimental validation is still needed. Solid-state nuclear magnetic resonance (ss-NMR) spectroscopy has emerged as a powerful tool for probing surface sites, and with advanced pulse sequences, it can effectively resolve different surface hydroxyl groups.

In this study, γ-alumina, featuring six distinct surface hydroxyl sites which encompass all structural types of aluminum-bound hydroxyl sites found in clay minerals (fig 1a), was employed as a model mineral. Using ss-NMR techniques, including Transfer of Populations Double Resonance (TRAPDOR) and Heterogeneous Multiple Quantum Correlation (HMQC), we investigated the fluoride adsorption behavior of these sites. Single-pulse and HMQC (fig 1b) experiments revealed that two types of surface hydroxyl groups bound to octahedral aluminum (Al chemical shifts (δAl) between 0–6 ppm) participate in fluoride adsorption. TRAPDOR (fig 1c) experiments further distinguished these as η-OH (δF= −156 ppm) and μ_2-OH (δF= −135 ppm). By deconvoluting the fluoride spectra, we quantitatively differentiated the adsorption capacities of these hydroxyl groups under varying pH conditions. Additionally, surface potentiometric titration data were fitted using the SCM, and the theoretical predictions aligned well with the quantitative results from ss-NMR (fig 1d), enabling accurate determination of the equilibrium constants (log K) for reactions at distinct hydroxyl sites. Our NMR findings confirmed that the two adsorption sites in the SCM correspond to η-OH and μ_2-OH groups, advancing our understanding of fluoride adsorption mechanisms on aluminum oxide surfaces.

Contrary to conventional assumptions [2-3], our results reveal the non-negligible reactivity of μ_2-OH relative to η-OH in surface adsorption process. The observed fluoride displacement of multiple hydroxyl species at ambient conditions enables highly sensitive solid-state NMR characterization of diverse hydroxyl site configurations. This methodology can be readily extended to investigate various clay mineral surfaces.

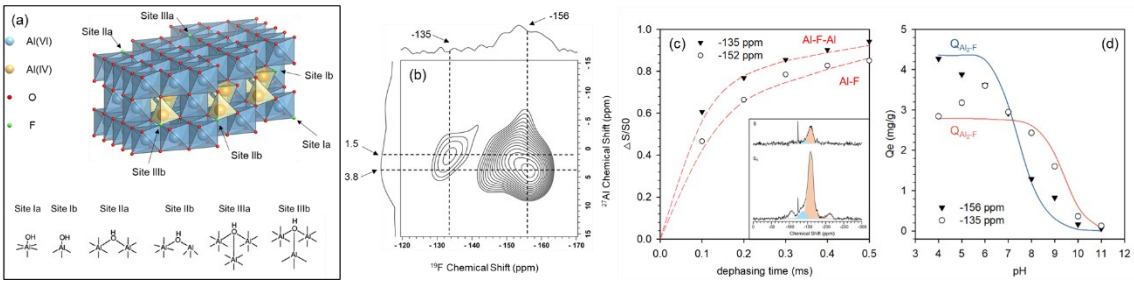

Fig.(a) Structure of γ-alumina and six hydroxyl groups; (b) $^{19}F\{^{27}Al\}$ HMQC spectra; (c) $^{19}F\{^{27}Al\}$ TRAPDOR spectra; (d) ^{19}F NMR peak deconvolution integrals and SCM-derived site-specific adsorption capacities (Qe).

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Stability of Fe^{II}-Fe^{III} hydroxyphosphate formed by anionic exchange of a hydroxychloride green rust precursor

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Green rust (GR) is a monometallic layered double hydroxide (LDH) characterized by the formula $[Fe^{II}_{1-x}Fe^{III}_{x}(OH)_2]^{x+}((x/n)\ A^{n-},\ m\ H_2O)^{x-}$, where A^{n-} is an anion and the layer charge *x* is close to 0.25-0.33. The high Fe^{II} content in GR facilitates its transformation into ferric phases upon exposure to air, which occurs through the transport of electrons and H^+ within the oxyhydroxy-layers. These peculiar properties led to recently hypothesize that GR served as key interfacial element of mineral structures on the early Earth, potentially contributing to the emergence of life [1]. In the proposed model, the transport of phosphate species (PO_4) through GR's interlamellar spaces was considered to generate a vectorial excess of polyphosphates induced by coupling to electron transfer between reducing and oxidizing species present on opposite sides of a GR nanocrystal. This work is devoted to studying the conditions of formation of hydroxyphosphate green rust ($GRPO_4$) starting from hydroxychloride GR (GRCl) as a precursor. In a previous study [2], the precursor was shown to be stabilized either in the presence of an excess of aqueous Fe^{II} or when small concentration of PO_4 was added in the initial solution (molar ratio PO_4 : Fe = 0.1).

Aqueous suspension of GRCl stabilised by PO_4 was subjected to the addition of increasing amount of PO_4 in order to force anionic exchange between Cl^- and PO_4. New small angles XRD diffraction peaks were detected only for PO_4 : Fe ratio higher than ~ 0.7. The corresponding interlayer distance of the new lowest angle peak was ~1.1 nm, a value very close to that measured previously for hydroxysulfate GR. However, the XRD pattern of the Fe^{II}-Fe^{III} hydroxyphosphate ($GRPO_4$) did not exhibit the high angle diffraction peaks usually observed for LDH. The XRD diffraction peaks of GRCl almost vanished for
PO_4 : Fe = 1.33, the critical value corresponding to a full transformation of GRCl into $GRPO_4$. For higher PO_4 amounts (PO_4 : Fe = 2.3), XRD as well as the Raman and Mössbauer spectra suggest a possible mineralogical transformation of $GRPO_4$ into a new phase. Cl- anions initially present in GRCl were fully released in the aqueous phase according to ionic chromatography. The concentration of phosphate measured in solution represented only ~75 % of the expected values for $GRPO_4$, which supports the formation of additional iron phosphate. In conclusion, the reactivity of GRCl with phosphate occurred in 3 steps as a function of increasing amount of PO_4 : (i) adsorption of PO_4 on the GRCl surface, (ii) anionic exchange of Cl^- by PO_4 species leading to the formation of $GRPO_4$ (iii) a mineralogical transformation $GRPO_4$ into an iron phosphate sequestering significantly higher amount of PO_4 compared to GR.

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Enhanced H_2S removal in greenhouse gases using copper-modified naturally occurring zeolite from Mangatarem, Philippines for waste to energy applications

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Hydrogen sulfide (H_2S) is a common and corrosive byproduct in methane generated from animal waste farms, posing risks to equipment integrity and safety. Copper-enhanced zeolites offer an effective solution for removing H_2S from biogas streams, thereby improving methane quality for waste-to-energy applications. Incorporating copper into zeolites enhances their capacity to adsorb and catalytically convert H_2S, protecting generator sets from corrosion and equipment failure during energy conversion processes. This application not only safeguards infrastructure but also promotes cleaner, more efficient biogas utilization in power generation. Using copper-modified zeolites for H_2S removal advances sustainable waste-to-energy practices by ensuring reliable, high-quality methane feedstock while mitigating environmental and operational hazards associated with sulfur compounds.

This study explores the modification of natural zeolite sourced from Pangasinan, Philippines [1], for optimized hydrogen sulfide removal. The raw zeolite (NW-Z) was characterized for its chemical composition and thermal stability. Acid treatment increased the Si/Al ratio and surface area by 32.5%, as confirmed by BET analysis, thereby enhancing porosity. Subsequent cation exchange was performed by soaking acid-treated zeolite (HC-Z) in varying concentrations of NaCl across different durations, with NaCl for 24 hours exhibits the highest copper uptake, as determined by atomic absorption spectroscopy.

The sodium-exchanged zeolite (Na-Z) was then impregnated with copper via immersion in $CuSO_4$ solution, followed by thermal oxidation at 400°C and 800°C to stabilize the copper species [2]. Phase analysis (XRD) identified CuO formation, with a higher CuO content (8.84%) at 400°C compared to 7.81% at 800°C. FTIR spectroscopy revealed structural stability at 400°C, whereas higher temperatures induced significant structural changes. Gas adsorption tests at ambient conditions demonstrated that the CuZ-400°C sample exhibited superior H_2S removal efficiency, surpassing unmodified NW-Z and CuZ-800°C. Post-adsorption analysis indicated a reduction in CuO content, suggesting that the removal mechanism involves both physisorption and chemisorption processes.

The findings highlight that copper-modified, thermally treated natural zeolite (CuZ-400°C) offers a highly effective, low-cost solution for H_2S remediation. Its potential application extends to environmental management, such as reducing acidity in methane streams to prevent corrosion in generator sets used in animal farming, thereby contributing to cleaner, safer, and more sustainable industrial practices.

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Adsorption of chromate pollutants with polyethyleneimine- and poly(N-butylethyleneimine)-modified montmorillonite using combined theoretical and experimental approaches

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Heavy metals and their oxides, including chromates, can be dangerous for humans and animals, even in low concentrations [1]. They can cause health problems, such as nervous system damage, kidney damage, reproductive issues, and even cancer [1-3]. In addition, these substances can also accumulate in the environment and damage ecosystems [2]. They lead to the contamination of soil and groundwater, which can have long-term effects on plants and animals [3]. Contamination of water sources by hexavalent chromium is a global water-related problem mainly due to various industrial activities, including electroplating, leather tanning, stainless steel production, and other metal processing operations [4].

This work presents a combined study of the adsorption of toxic chromate oxyanions into the interlayer space of modified montmorillonite by two polymers, polyethyleneimine and poly-(N-butylethyleneimine), at both theoretical and experimental methods. The main aim is to provide comprehensive structural research that includes calculating the structural stability and determining the strength of hydrogen bond interactions of the studied systems. Moreover, the measured FTIR spectra were examined in relation to the calculated vibrational modes obtained from the vibrational density of states using the *ab initio* molecular dynamics (AIMD) approach [5] to analyze the overlapped bands in detail.

Acknowledgments: The work is supported by the Scientific Grant Agency VEGA (02/0026/23), EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project No. 09I03-03-V04-00009, and research results were obtained using the computational resources procured in the national project National Competence Centre for High-Performance Computing (project code: 311070AKF2) funded by the European Regional Development Fund, EU Structural Funds Informatization of Society, Operational Program Integrated Infrastructure.

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Clay-based amendments reduce PFAS bioavailability in soil: Dynamics of soil-pore water-lettuce system

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Per- and polyfluoroalkyl substances (PFAS) have been widely detected in soil, air, sewage sludge, sediment, water, plants, animals, and human tissues. Due to their high persistence, these chemicals have become priority contaminants of concern. Clay-based amendments are widely used for PFAS remediation in soil and water. This work aims to study the bioavailability of PFAS (perfluoroalkyl carboxylates and sulfonamides) in soil and pore water with and without adding clay-carbon composites to soil. Lettuce plants were grown in soil that was uniformly spiked (@500 ng/g) with perfluorobutanoate (PFBA, C4), perfluorohexanoate, (PFHxA, C6), perfluorooctanoate (PFOA, C8), perfluohexane sulfonamide (FHxSA, C6) and perfluorooctane sulfonamide (FOSA, C8). The amendments (surfactant-modified montmorillonite (MMMT), montmorillonite-biochar composite (BC-MMT) and surfactant-modified BC-MMT (MBC-MMT) were synthesized, characterized (confirmed through XRD, FTIR, SEM techniques) and applied to the soil @ 0, 0.5, 1.0 and 4.0% (w/w) basis. The application of MBC-MMT @4% significantly reduced the concentration of long chained PFAS (PFOA and FOSA) to 47 and 99 ng/g from 212 and 210 ng/g (wet weight basis) in control soil, respectively. Concentrations of short-chain PFAS decreased from 142-204 ng/g in control soil to 6-20 ng/g for short chain PFAS (PFBA, PFHxA, and FHxSA) at harvesting time (80 days). The decrease in PFAS concentration in the amended soil was observed due to hydrophobic interaction between PFAS and surfactant modified clay-based amendments. However, the concentration of FOSA, PFOA and PFHxA were 241, 265 and 230 ng/g in BC-MMT@1% amended soil which was higher than the control soil (FOSA: 210, PFOA: 212, and PFHxA: 204 ng/g) at 80 days. The soil-pore water analysis in the control soil showed the long chain and short chain PFAS concentration in the range of 0.007-8.3 and 12-34 ng/mL which were reduced to 0-0.001 and 0-12 ng/mL, respectively by soil application of MBC-MMT @4%. The soil-pore water distribution coefficient (log K_d) varied from 1.40-4.45 (long chain PFAS) and 0.67-1.92 L/kg (short chain PFAS) in control soil and increased to 3.18-4.9 L/kg for long chain PFAS (PFOA and FOSA) and 1.12-2.4 L/kg for short chain PFAS (PFBA and PFHxA) in MMMT@4% amended soil. Application of clay-based amendments increased the K_d value with increasing rates of amendments and carbon chain length (long chain PFAS (PFOA and FOSA)). Clay-based amendments hold promise as a low cost strategy to reduce bioavailability of PFAS to plants.

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Clay-based formulation of azoxystrobin to control corn late wilt disease and cotton coal rot disease

Rytwo, G. [1,2], Hadad, A.[1,3], Abramovici, A. [1,3], Levi-Lion, A. [1,3], Dimant, E.[3], Hadari, P. [1,3], Steckler, R.[1] and Degani, O. [1,3]

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Late wilt and coal rot (caused by *Magnaporthiopsis maydis* and *Macrophomina phaseolina*) are growing threats to corn and cotton, respectively, worldwide. In heavily infected areas and sensitive varieties, the diseases can cause total loss of crops [1],[2]. The pathogens are found in both crops, corn and cotton, in a restraining equilibrium, the violation of which can lead to a severe outbreak of diseases. Azoxystrobin (AS) is a widely used efficient fungicide. However, it was reported that AS and its degradation products may leach in soils and are highly toxic, posing a potential threat to vulnerable aquatic environments and drinking water resources [3]. Furthermore, regular AS use requires repeated implementations by spraying or drip irrigation. To overcome the problems, we developed a formulation based on its combination with clay, which was applied by covering the seeds or dispersing it on them, directly into the sowing row.

Various clays and organoclays have been proven in dozens of studies in the past as potential matrices suitable for slow-release protection against leaching, evaporation, or photochemical decomposition of a wide range of pesticides [4]. Some formulations are based on raw clays, whereas others use an "engineered" form based on organic cations, optimizing the active compound's adsorption process, release, and activity. For example, raw sepiolite clay has recently been shown to be effective for the slow release of essential oils to control insects for more than one month [5]. Several raw and organoclays were preliminarily tested for the adsorption of the fungicide. Amounts adsorbed were measured gravimetrically and confirmed by FTIR, whereas amounts released to solution were evaluated by GCMS. Organoclays adsorb AS in large quantities but not significantly larger than montmorillonite and sepiolite. Due to the more straightforward preparation procedure, raw clay minerals were preferred for the following pots and field experiments.

Both developed formulations (based AS on sepiolite or montmorillonite) protected the plants at the critical stage of the pathogen's penetration and establishment. In pot experiments in a greenhouse, adding the clay-AS formulation in the sowing hole led to an increase in app. 200% in the weight of shoot and cobs (over 175%) compared to control. In cotton, the clay-AS formulation reduced infestation by 59-92% at midseason.

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LECTURE THEATRE 5 – SESSION 18

Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development

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Paragenetic and non-paragenetic clay mineral assemblages in geothermal prospection

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In many geothermal energy studies, the heterogeneity of clays is neglected despite the basic knowledge that clays in a stratigraphic section are made of weathering products (*in situ* and detrital), early diagenetic processes during a syn-sedimentary phase and late diagenetic processes during low-grade diagenetic to anchizonal thermal alterations. If volcanic and pyroclastic rocks are included also a thermal cooling process with clay mineral formation must be considered. In fault gauche and damage zones compared to the porous or clay bearing host rocks used by hydrothermal systems the non-paragenetic composition of clays under low-grade diagenesis is obvious. If recent bore hole temperatures do not coincide with determined fossil temperatures based on clay mineral indices, assemblage paragenesis and organic matter indices a short duration of same heat flow must be expected. This may indicate a risk in heat exploitation. At higher temperatures it may indicate that the hydrothermal system is not in equilibrium with the geotherm and minimizes energy capture. Nevertheless, it depends on the hydrothermal reservoir and flow rate. In case that all assemblages studied from the gauche to the host rock indicate paragenesis, a steady-state heat flow will be prospected and geothermal use more appropriate. In case the hydrothermal temperature is reflected by host-rock diagenesis and/or metamorphism, a stable heat capture will be promising for a long living extraction system. Case studies will be presented from frontal wedge and orogenic foreland structural units and graben extensional basins.

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Mid-Cretaceous Alpine metamorphism of the Tisza Mega-Unit (Inner Carpathians) constrained by illite K-Ar dating and mineral metamorphic indicators

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Apuseni Mts. represent the biggest exhumed area of two major tectonic blocks of the Inner Carpathians: the Tisza and Dacia Mega Units, with the Biharia Nappe System thrusted over the Codru Nappe System, which in turn is thrusted over the Bihor autochtonous unit. Alpine metamorphism was previously detected in Bihor and Biharia, but not in Codru. This study is aimed at explaining this difference, using tectonically deformed and strongly altered Permian volcanic rocks from the region. Illite/mica is the dominant metamorphic mineral in the altered felsic rocks, while chlorite dominates in the altered mafic rocks. Illite/mica is a mixture of 1M and $2M_1$ polytypes (also 1Md in one sample), perfectly non-swelling, and with the 001 peak broadening below 0.18 $\Delta^{o}2\theta$. EPMA documented two varieties of illite/mica: illite/phengite and illite/muscovite. Combined mineral metamorphic indicators (illite/mica characteristics, presence of epidote, and the absence of metamorphic biotite) restrict the maximum metamorphic temperatures to 250-310°C range, explaining the lack of Alpine ages in earlier studies (temperatures below resetting of old coarse-grained micas, used for dating). Our new K-Ar data constrain the cooling ages of illite/mica in the Codru Nappe System to 117 - 112 $\pm$ 3.2 Ma in the Dieva and Moma nappes, and 102 $\pm$ 3 Ma in the Arieseni nappe. These ages reflect the denudation during eastward advancing of the thrust wedge during the "Austrian" tectonic phase.

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Mutual influence of clay diagenesis and bacterially-induced siderite cementation in Carboniferous strata, Anadarko Basin, U.S.A.

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This study examines the reciprocal relationship between bacterially induced siderite cementation and clay mineral diagenesis in the Carboniferous strata of the Anadarko Basin, USA. While siderite cementation in sandstone has been well studied, its development in mudstone and its interaction with clay mineral transformations remain less understood. We analyzed 40 samples of siderite-cemented sediments, accompanied by adjacent uncemented counterparts, from two cores, employing petrography, X-ray diffraction, Fourier-transformed infrared spectroscopy, electron microscopy, and stable isotope analysis. Results reveal two distinct siderite cementation styles—bands and concretions—with bands restricted to mudstone and concretions occurring in both mudstone and mud intraclasts within sandstone. The spatial distribution of these cementation forms suggests a strong affinity for clay-rich domains. Microscopic evidence of bacteria-derived nanoglobules indicates a biotic origin for the early stage of siderite formation, driven by microbial Fe-reduction near the sediment-water interface. These Fe-rich nanoglobules evolve into Mg-enriched rhombohedral siderite during a subsequent, deeper diagenetic stage (~1.1 km depth), likely of abiotic origin. The presence and morphology of siderite cement exert a notable influence on clay mineral diagenesis, particularly illitization. Siderite concretions are associated with localized increases in alkalinity and K-ion availability, creating favorable microenvironments for illite formation. In sandstone-rich facies, porosity and permeability enhanced fluid-rock interaction, whereas in mudstone-rich facies, fine-grained sediment and organic matter played a more prominent role. Where mudstone and sandstone are closely interbedded, illitization appears spatially undifferentiated, likely due to fluid mixing and bioturbation. These findings point out a dynamic interplay between microbial processes, siderite precipitation, and clay mineral transformations during eogenesis, and they highlight the importance of incorporating these feedbacks into diagenetic models aimed at predicting reservoir quality in siderite-rich formations.

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A new depositional and diagenetic hypothesis for Mg-clay minerals in the Pre-salt Tupi Field, Barra Velha Formation, Santos Basin (Southeastern Brazil)

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The Barra Velha Formation (BVF) is the main reservoir of the Pre-salt Oil system in the Santos Basin (Southeastern Brazil). The main mineralogy of the rocks composing this formation are calcite, Mg-calcite, dolomite, clay minerals and quartz. The clay minerals identified in the BVF were talc, kerolite, stevensite and saponite. This study proposes a new depositional and diagenetic hypothesis involving the clay minerals of the BVF.

For the purpose, samples and thin sections a well core were studied, applying techniques such as X-ray diffractometry (XRD) and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS).

XRD results indicate two principal phases of clay minerals: talc and Mg-smectite. From the quantification of these phases, three clay minerals assemblages have been identified. Assemblage 1 has a predominance of talc, with Mg-smectite occurring at concentrations below 20%. Assemblage 2 is dominated by Mg-smectite, while talc may be present in quantities below 20%. Assemblage 3 contains both talc and Mg-smectite, each one with more than 20% in concentration. Mg-smectite was defined as saponite according to the Al content in the chemical composition. The most widely accepted model for the origin of Mg-clay minerals from the Brazilian Pre-Salt is the direct precipitation from a precursor gel. In this neoformation model, pH and salinity would be the main factors to define whether talc or smectite would be deposited. A pH (~8) favours the precipitation of talc, whereas a pH (~10) promotes the formation of Mg-smectite. However, the coexistence of talc and saponite in the same sample would not be hydrochemically feasible under the same conditions.

This suggests that neoformation controlled solely by hydrogeochemistry may not fully explain the formation of these clay minerals. To address this issue, representative thin sections of each clay mineral assemblage were analyzed using SEM-EDS and a new depositional and diagenetic hypothesis is proposed. Saponite forms through the transformation of pre-existing detrital clay minerals, while talc subsequently forms as a product of the diagenetic alteration of saponite.

This model accounts for the coexistence of talc and saponite by introducing a sequential transformation pathway rather than direct precipitation under identical conditions. Scientific arguments support this model. First, the substitutional texture observed in samples containing both talc and saponite strongly suggests a transformation process rather than simultaneous precipitation, which would not be feasible in the current model. Second, talc does not exhibit a chemical composition close to its ideal formula, $Mg_3Si_4O_{10}(OH)_2$. The presence of aluminum, which cannot be accounted for by direct precipitation, suggests the involvement of precursor materials in its formation. Third, an analysis of saponite crystals and their zoning reveals that the inner regions are richer in aluminum compared to the outer regions or even the borders. Lastly, the presence of residual detrital clay minerals floating within talc-dominated regions further supports the idea of a transformation process. This study provides a new perspective on the genetic aspects of clay minerals from the Pre-salt and advances the understanding of Brazilian reservoirs.

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Partitioning behavior of rare earth elements in hydrothermal chlorite

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Rare earth elements (REE) consist of the 15 lanthanides along with Sc, and Y. They play an important role in the transition to a green, low-carbon economy and development of innovative technologies. As these technologies achieve wider adoption, demand for REE is expected to rise. To identify new resources and to ensure adequate supply for present and future uses this research investigates the nature of the association of REE and hydrothermal chlorite. More specifically it examines if REE are present as adsorbates, structurally integrated, or a combination of both, and further reports on the mechanisms for recovering REE hosted by chlorite. X-ray diffractometry analysis, magnetic separation, hand picking, scanning electron microscope-energy dispersive spectrometer, laser ablation inductively coupled plasma mass spectrometry, leaching experiments, and inductively coupled plasma optical emission spectroscopy are being undertaken on a range of hydrothermal chlorite collected from the obducted oceanic crust from the Dinarides. The analysis revealed distinct speciation of chlorite, including mixed-layered chlorite-smectite and discrete chlorite. The mixed-layers exhibited higher REE content compared to discrete chlorite. The former has been associated with low-temperature conditions and water-to-rock ratios, whereas the latter forms at higher temperatures and water-to-rock ratios. Ongoing leaching experiments aim to quantify the recoverable REE present as adsorbed species, while structurally bound REE remains non-leachable. Further investigations will evaluate the surface properties of different chlorite species, including surface area, cation exchange capacity, and surface charges, as these factors influence chlorite reactivity and its interactions with REE in hydrothermal systems. Molecular dynamics simulations will complement these analyses, providing insights into adsorption patterns, atomic density and the potential for structural incorporation of REE in chlorite.

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LECTURE THEATRE 6 – SESSION 19

Industrial Applications of Clays

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Application of the vO-D probe to vermiculites

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Vermiculites are expandable clay minerals with a layer charge (LC) between 0.6 and 0.9 e^- per $O_{10}(OH)_2$ formula unit (p.f.u.), commonly forming during weathering or in low-temperature hydrothermal systems at the expense of mica or chlorite. As LC is used to define this mineral, its precise measurement is highly important. However, vermiculites, especially from weathering environments, are usually present as one of the phases in the complicated mixture, which makes their LC measurement challenging. The vibrational OD method, which utilizes the position of a sharp, high-frequency vO-D band in the Fourier Transform Infrared Spectrum (FTIR) of D_2O-saturated smectite [1], may offer an appealing solution to the problem of vermiculite LC measurement. However, the OD method was tested and calibrated only for dioctahedral smectites with the LC between 0.2 and 0.6 e^- p.f.u.

In this contribution, examples of the application of the OD method to natural and synthetic vermiculites are presented and discussed to assess the degree to which this method can be used to probe the LC of high-charge expandable clay minerals. Three sample sets were investigated: (i) vermiculite-rich 0.2-2 µm size fraction of an alpine soil (Podzol) from the Tatra Mountains (Poland); (ii) soil fraction from the same region which had undergone various degrees of potassium fixation; and (iii) a set of synthetic saponites with the LC between 0.4 and 1 e^- p.f.u. [2].

The FTIR spectra of all investigated samples displayed changes in the OD stretching region that were correlated with the presence and LC of the vermiculitic component. Furthermore, vO-D exhibited shifts correlated with the K content or LC value for sample sets (ii) and (iii), which proves that vO-D can be used as a LC probe even for vermiculites. In the case of sample set (i), vO-D was present in all but the least weathered sample and also displayed shifts consistent with the sample composition (vermiculite ± mica-vermiculite vs. mica-vermiculite + mica-smectite) determined with the X-ray diffraction. The calibrations developed in [1] seem to be applicable only to the low part of the vermiculitic LC. A new LC calibration is required for samples with LC greater than approximately 0.7 e^- p.f.u., possibly due to the changes in the H-bonding network of the interlayer water.

This work was partially supported by the Polish National Science Centre [grant number: UMO-2016/23/N/ST10/01388]

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Inferring the position of interlayer cations and their effect on smectite properties from spectroscopic measurements of a D_2O-saturated interlayer

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Once their interlayer H_2O is replaced with D_2O, smectite or its interstratified variety exhibits a distinctive envelope of the O-D stretching vibrations in the Fourier transform infrared (FTIR) spectrum. The sharp, high-frequency water stretching band (νO-D) originates from OD groups involved in weak H-bonds with the siloxane surface. The strength of these bonds depends on the charge present on the siloxane surface. The position of νO-D linearly correlates with smectite layer charge (LC) values determined independently using the structural formula method or the alkylammonium method. The calibration forms the basis of the spectroscopic LC determination technique, known as the OD method [1]. The OD method returns total LC regardless of whether the charge originates from octahedral or tetrahedral substitution.

Beyond its use in LC determination, the νO–D band also provides valuable insights into the interlayer environment, cation positioning, charge origin, and changes therein, which can be tracked using various experimental setups.

LC is calculated from νO-D under the assumption that interlayer cations are located in the middle of the fully expanded interlayer. Experimentally, this is achieved by performing FTIR measurements under relative humidity ≥60% on samples saturated with cations of high hydration enthalpy (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, Li^{+}). This configuration maximizes the charge contrast between the interlayer and the 2:1 layer, resulting in the highest effective LC. However, when cations bind directly to the siloxane surface—as is typical for K^{+} and other low hydration enthalpy cations—they partially neutralize the 2:1 layer surface charge, reducing the effective LC. A similar reduction occurs during mild drying of montmorillonite saturated with small cations (for Li^{+} at ~60°C or even lower, Mg^{2+}, Fe^{2+} at ~100°C). At higher temperatures, cations migration into the 2:1 layer result in their fixation either within the ditrigonal cavity or in octahedral vacancies (the Hoffmann-Klemen effect). Contrary to common assumptions, beidellite also shows a degree of Li^{+} and Mg^{2+} fixation at >110°C and >200°C, respectively. This is often misinterpreted as evidence of octahedral charge in the Greene–Kelly test and similar protocols (e.g., [2]). Moreover, the high precision of the OD method enables detection of LC variability caused by subtle changes in the oxidation state of structural ^{VI}Fe.

Here, we demonstrate how measurements of effective LC – in conjunction with other tests – can be applied to monitor the aforementioned subtle changes in the interlayer environment and 2:1 layer charge. Shown are the experimental, tentative criteria for distinguishing the position of interlayer cation—whether within the 2:1 layer or at the siloxane surface—following heat-induced migration. The position of the fixed cation governs the reversibility of fixation under different post-heating treatments: low-energy wetting removes inner-sphere adsorption; cation exchange can reverse fixation in the ditrigonal cavity; however, fixation in octahedral vacancies is irreversible unless strong treatment is applied. Additionally, we discuss a homogeneous *versus* heterogeneous model of interlayer cation fixation.

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[2] Malla PB and Douglas LA (1987) Clays and Clay Minerals 35(3): 232-236

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Layer Charge measurements for the industrial characterization of bentonite: The past and future of the OD method

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The OD method for measuring the layer charge (LC) of dioctahedral smectites (Kuligiewicz et al. [1]) has conceptual roots in an earlier evaluation of the 'activation' of raw bentonite (i.e. its industrial scale exchange to the Na-form) 25 y ago by near-infrared (NIR) spectroscopy. This presentation is about the NIR-background and the future perspectives of the OD method for high-throughput industrial application.

NIR probes the overtones and combinations of the vibrational modes involving O-H with no direct interference from the anhydrous part of the structure nor from anhydrous accessory minerals. The NIR spectrum of the O-H bonds can be used as a non-invasive proxy of clay mineralogy, octahedral sheet and interlayer composition, level of hydration, as well as a variety of technologically important properties of industrial samples (the latter after suitable chemometric calibration).

Two matching sets of non-purified Milos bentonites, ground and equilibrated at ambient humidity, were studied by NIR. One set preserved the natural interlayer cations (mostly Ca^{2+}, Mg^{2+}) and the other was subjected to Na-activation. The two most dominant NIR features of dioctahedral smectite are due to the interlayer H_2O combination mode at ~5250 cm^{-1} and the AlAlOH stretching-bending combination mode of the octahedral sheet at ~4525 cm^{-1}. Both give sharp bands, accurately isolated by 2nd derivatives. The position of the AlAlOH combination was variable but did not depend on interlayer cation type, whereas the H_2O combination mode depended on both, the position of the AlAlOH mode and the nature of the interlayer cation. Na-activation shifted the H_2O combination to higher frequencies and could be used as a semiquantitative indicator of activation progress, but the magnitude of the shift depended on the position of the AlAlOH mode. These observations could be rationalized if the position of the AlAlOH mode was a proxy for layer charge, thereby determining both the position of the sharp interlayer H_2O mode and its shift upon Na-activation.

The mid-infrared attenuated total reflectance (ATR) spectrum of bentonite, subjected to in situ mild H/D exchange, separates the aforementioned cation-dependent combination mode of H_2O into a cation-independent stretching (νOD) and a cation-dependent bending fundamental (δD_2O). It is the former that was calibrated against LC in the OD method [1]. Armed with this calibration and years after the original NIR study, it became possible to measure directly the LC of the raw and activated bentonites. These data were then used to develop a chemometric methodology that predicts the LC of raw bentonite based on its NIR spectrum and the results of OD but requiring no H/D exchange [2]. Removing this last obstacle from the widespread application of layer charge measurements in industry opens up new exciting possibilities. Among them comes the evidence that some bentonites undergo a significant reduction of LC over a period of months after sampling.

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A Molecular View on the Effects of Smectite layer charge

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Smectite clay minerals play a fundamental role in numerous natural and environmentally relevant processes, including nutrient retention, environmental remediation, and serving as waste liners for isolating contaminants, due to their swelling and high adsorption capacity. The unique properties of smectite minerals arise not only from their large specific surface area (approximately 750 m^2/g) but perhaps more importantly from their negative layer charge, which facilitates intercalation of cationic solutes and solvent molecules. Although both the surface area and surface charge properties are intrinsically coupled to the unit cell, mainly the latter property show large variation between differently sourced smectite clay minerals, and hence greater influence on other types of warranted physical properties.

To quantify this crucial charge property, researchers have traditionally employed cation exchange capacity (CEC) measurements that rely on different smectite–cation interactions [1]. These methods provide an estimate of the surface layer charge, since the interlayer surface area and its associated charge overwhelmingly dominate over edge sites. More recently, the so-called O–D method has gained traction because it does not depend on specific smectite–cation interactions but instead reflects the basal surface layer charge alone [2]. The divergence between traditional CEC methods and the O–D method has come under increasing scrutiny, particularly in light of concerns about cation fixation in smectite layers and its implications for clay barriers in nuclear waste disposal.

This research aims to investigate the role of smectite layer charge, the basis for the O–D method, as well as the potential for cation fixation, from a molecular perspective. This is accomplished by molecular dynamics (MD) simulations using a new general forcefield called MINFF [3], which incorporates additional angle constraints to realistically represent the distorted ditrigonal cavities characteristic of smectite clay minerals. Because MD simulations can capture the hydrated structure of smectite layers, they can also be used for one-dimensional X-ray diffraction (1D XRD) modelling. In this study, we evaluate the performance of the new force field and examine the effects of varying smectite layer charge and cation fixation using 1D XRD modelling. This is achieved through our MATLAB implementation of Reynolds' recursive algorithm (same as in the Newmod software), which allows for modelling of both custom silicate layers and interlayer phases based on MD-derived density profiles.

This work ideally offers a pathway toward linking molecular structural properties of smectites with experimental XRD, and ultimately, toward better predicting clay behaviour in engineered barrier systems. The methodology developed here also provides a foundation for future exploration of dynamic processes such as structural rehydration or the effects of varying layer charge, at elevated temperatures [4].

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Homoionic trans-vacant and cis-vacant montmorillonites: A density functional theory study

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Swellable clay minerals, known as smectites, are very important in soils and sedimentary rocks. They are also crucial for geotechnical applications, such as the engineered barrier system (EBS) in radioactive waste deposits, and various industrial uses due to their abilities in cation exchange, hydration, and swelling. The hydration of smectites can have both negative and positive effects. Negatively, it can cause borehole instabilities or retain water for plants. Positively, as the main constituent of bentonites, smectites enhance hydraulic barriers in shafts and drifts, which are part of the EBS in underground mines or waste disposal facilities. Thereby, montmorillonites that are dioctahedral smectites are most common.

Numerous experimental studies on the hydration of homoionic smectites can be found in literature. However, structural heterogeneity of natural dioctahedral smectites [1,2] is the source of uncertainties in the interpretation of experimental data. Hence, computational studies are especially useful to understand the influence of structural features on the hydration and swelling of smectites [3]. Thereby, many studies were performed for Na-saturated trans-vacant dioctahedral smectites.

The present study is a continuation of [4,5] and focuses on montmorillonites (sensu stricto). Layer charge was varied between 0.125 and 0.5. Three different octahedral structures (tv Mgcis, cv Mgcis and cv Mgtrans) and four different interlayer cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) were considered. The electronic structure, atomic geometry, and total energy of montmorillonite models were calculated by Density Functional Theory (DFT) as implemented in the Vienna Ab Initio simulation package (VASP version 5.3.4) and dispersion correction (DFT-D3) was applied.

DFT calculations confirmed that cis-vacant (cv) octahedral sheets are preferred over trans-vacant (tv) octahedral sheets in montmorillonites independent of the position of the Mg^{2+} substitution in the cv structures. The basal space of the anhydrous homoionic montmorillonites correlated with the layer charge and the ionic radius of the interlayer cations although their position is different in dependence of size and charge. Variation in the basal space resulted in different specific densities of the montmorillonites, which needs to be considered for calculation of porosity and saturation in compacted bentonites, e.g. in the EBS. Bulk modulus also varied with the structure of the montmorillonites being highest for Na-saturated tv and cv montmorillonites at a layer charge of 0.5 and lowest for K-saturated tv and cv montmorillonites at a layer charge of 0.125.

Part of this work was funded by the German Federal Ministry BMUV (contract 02 E 12001A) and a BIB MORA-LPDP Scholarship, Republic of Indonesia.

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Determination of the presence and magnitude of tetrahedral layer charge of swelling clay minerals by intercalation of glycerol

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Layer charge of swelling clay minerals is an important property that governs hydration and intercalation reactions within the interlayer space. However, determining the layer charge is not trivial with many existing methods either being laborious or yielding average values that do not account for the diversity of complex mineral mixtures. Here, we present an approach to determine the layer charge of swelling clay minerals by exploiting the variation in glycerol orientation within their interlayer space as a function of relative humidity.

For this purpose, we mixed Ca-saturated swelling clay minerals with 30% v/v glycerol and 1 mM $CaCl_2$ solution and shaked it for 24 h at 90 °C to maximise glycerol intercalation. We analysed oriented slides using X-ray diffraction along a desorption-sorption H_2O isotherm. We assessed the method using six saponites, two hectorites and one stevensite, all synthesized with controlled layer charges spanning both the smectite and vermiculite groups. We observed that, in saponites, glycerol molecules orient parallel to the clay layers at low rh (layer-to-layer distance d ~ 18 Å) but perpendicular at high rh (d ~ 16 Å). The difference between d at 90% and 5% rh (Δd_{GLY}) increases as the layer charge increases, and can be used as a proxy for the amount of tetrahedral layer charge. Conversely, when layer charge originates in the octahedral sheets, there is no change in glycerol orientation.

To validate this method, we applied it to 23 smectite and vermiculite samples with known composition and layer charge [1-3] with reasonable success. For example, we measured layered charge per formula unit of 1.02 for NAu1 nontronite (100% tetrahedral layer charge) compared to the published value of 1.05. We were also able to detect tetrahedral substitutions in samples where only 13% of the layer charge originates from these sheets (*e.g.* SCa1 montmorillonite). Lastly, we were able to determine the contributions from the tetrahedral sheet to the layer charge and estimate its magnitude in complex mixtures of swelling clay minerals from temperate climate soils [4] and hydrothermally altered magmatic rocks [5].

Our results suggest that the intercalation of glycerol can be used for the determination of tetrahedral layer charge of swelling clay minerals, even when swelling layers are interstratified with non-swelling components, and/or in complex mixtures with other clay minerals.

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Thermal effects on smectite's interlayer water stability under constant relative humidity conditions

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The hydration state of smectites is influenced by interactions between interlayer water, exchangeable cations, and external factors such as relative humidity (RH) and temperature. While RH is a well-established factor in controlling water content, the impact of temperature changes on water adsorption isotherm remains less understood. This study investigates the thermal stability of interlayer water in smectites by varying temperature under fixed RH conditions.

The temperature-dependent behavior of homoionic smectites was examined by equilibrating them at fixed RH levels and monitoring changes in basal spacing (d_{001}) using X-ray diffraction (XRD). Additionally, gravimetric measurements were employed to assess total water content. The XRD data revealed a consistent reduction in d_{001} values with increasing temperature, despite constant RH, indicating a progressive decrease in interlayer thickness.

Progressing from 10°C to 80°C at 30% RH Na-smectite exhibited the most significant change, with d_{001} dropping from 15.5 Å to 9.9 Å. In contrast, Ca- and Mg-smectites showed more gradual interlayer collapse, with d_{001} values decreasing from 16.2 Å and 17 Å to approximately 12 Å, respectively. The extent of d-spacing reduction was found to be cation-dependent, with divalent cations maintaining larger interlayer spacings than monovalent ones at comparable conditions, reflecting their stronger hydration energies. Interestingly, the adsorbed water content measured at 10°C, 20°C, and 40°C (on the basis of dry mass obtained by dehydration at 200°C for 15 hours) also decreased, with Na-, Ca-, and Mg-smectites showing a reduction in water content from 20.6% to 10.8%, 28.1% to 19.0%, and 29.6% to 19.1%, respectively [1].

Although, for a given 30% RH the absolute water content in air increases with temperature (from 2.82 to 87.28 g/m³ at temperatures between 10°C and 80°C), the reduction in interlayer water content and d-spacing with rising temperature is counterintuitive. This suggests that the increasing temperature overwhelms the swelling effect of the higher absolute water content in equilibrium with smectite. The interlayer thickness is almost directly proportional to the gravimetrically-measured, indicating that the density of water in the interlayer space remains almost constant, similarly to the properties of bulk water. These results underscore the destabilizing effect of temperature on interlayer water, even at constant water vapor pressure, leading to measurable dehydration. The findings offer valuable insights into smectite hydration thermodynamics, with implications for understanding natural thermal gradients in clay-rich environments and for applications involving thermally exposed clays.

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LECTURE THEATRE 6 – SESSION 21

Impact of temperature on bentonite barrier systems based on findings from in situ experiments in the context of radioactive waste disposal

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Review of changes on clay mineralogy and pore water chemistry produced at temperatures below and above 100°C in large-scale and laboratory tests

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One of the most important design variables for a geological nuclear waste repository is the temperature limit up to which the engineered barrier system (EBS) and the natural geologic environment can be exposed. Most repository concepts establish a design criterium of 100°C for the maximum temperature in the clay barrier at the bentonite/canister interface for avoiding bentonite alteration [1,2]. This conservative criterion ensures that no adverse temperature-induced effects, such as illitization and/or chloritization of the smectite clay mineral, dissolution of carbonates and cementation by precipitation of SiO_2 will occur. These effects would affect to the bentonite properties, leading to a reduced swelling, loss of plasticity, increase of hydraulic conductivity and diffusivity.

However, the 100°C criterion may be not cost-effective, especially when considering size optimisation: waste package spacing and distance between geological galleries for a given amount of heat-emanating waste [3]. For this reason, the possibility of allowing the maximum design temperature to reach values well above 100°C is being explored. Nevertheless, possible changes in deep geological repositories (DGR) designs must be based on that the performance targets for the engineered barrier safety functions are fulfilled, even at an elevated temperature, and confirming that the repository ensures post-closure radiation safety.

Significant research efforts world-wide have increased our knowledge and understanding of how underground disposal systems will function over very long periods of time [4]. Experimental and modeling studies on the occurrence of irreversible temperature-induced effects and related performance impacts have been achieved at temperatures below and above 100°C, not only at laboratory scale but also by means of large scale *in situ* tests in underground research laboratories (URLs).

In this work, a review of studies performed at laboratory and in large-scale *in situ* tests at below 100 °C (e.g. FEBEX in situ experiment [5, 6]) and above (e.g. ABM5 Heater experiment [7]), are described. Results are focused on geochemical, mineralogical, clay mineral alteration, macroscopic physical-chemical properties (CEC, BET, SA), as well as pore water chemistry changes and associated mechanical changes, since these are relevant for the bentonite performance with respect to its barrier roles. In addition, the impact of a high temperature on bentonite and couplings between the thermal, hydrological, chemical, and mechanical (THMC) processes are analysed from modelling studies, considering also the interaction between the EBS and host rock under various scenarios [8, 9].

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Iron reduction in bentonite in field experiments

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Most national programs for the final disposal of highly radioactive waste rely on some type of geological disposal. All concepts rely on the multi-barrier-principle where a series of engineered and natural barriers will work together to contain and isolate used nuclear fuel to protect people and the environment. In many concepts, bentonite is used as an engineered barrier. Bentonite is primarily chosen for its very low hydraulic permeability when saturated, which ensures that diffusion is the main transport process through the barrier. Another important property is its swelling pressure, which allows bentonite to self-seal.

Additionally, bentonite is a natural material that has remained stable over millions of years. This long-term stability is critical, as the barrier needs to maintain its protective properties for up to a million years.

Even though the bentonite has been stable in the mine, the stability in a repository environment needs to be confirmed. One way of doing this is by large of medium scale tests of the repository components in underground research laboratories. In several field tests the reduction of Fe(III) to Fe(II) in the smectite has been observed after the exposure to repository conditions, including heating. Hydromechanical testing of the reduced samples show no significant changes in the important properties compared to references samples. This may indicate that the process is of limited concern for repository performance. However, it is still important to understand the underlying mechanism to be able to predict to consequences over longer timescales.

A number of potential mechanisms for the reduction have been identified:

- Reducing species (Fe^{2+}, HS^-) in the local groundwater
- Interaction with the copper heater
- Leaking electrons from the power supply
- Microbial reduction
- Interaction with pyrite originally present in the bentonite

Of these mechanisms the pyrite reaction seems to be the most plausible. Iron can be reduced according to the reaction:

$$14\,Fe^{3+} + FeS_2 + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16H^+$$

In the full scale Prototype repository test at the Äspö underground laboratory in Sweden an increase of Fe(II)/Fe(total) from about 30-35% to 40-45% was observed. The Prototype repository was dismantled in two campaigns the first at ~10 years and the other at 23 years and no difference in iron reduction as a function of time was observed. The content of pyrite in the bentonite should be sufficient to account for this reduction. The amount of reduced sulfur in the bentonite has been measured and it seems to be a reduction compared to the original content. The content is however close to the detection limit, which makes it difficult to draw any firm conclusions.

The overall interpretation is that iron in smectite is reduced by pyrite at elevated temperature. The reduction does not progress with time and therefore it is likely that some type of (redox) equilibrium is reached. The magnitude of the reduction is limited and will not have an effect of the hydromechanical properties of the material. This is however only a preliminary interpretation and there could be other processes involved as well.

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Bentonite Erosion and Piping Test (BEPT) Preparation considering Heating Effect in KAERI Underground Research Tunnel (KURT) in South Korea

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Understanding bentonite erosion and piping under disposal conditions is critical for evaluating the long-term integrity of the bentonite buffer. The pressure difference between groundwater inflow and the swelling bentonite significantly influences the performance of the engineered barrier system (EBS). Elevated groundwater pressure can lead to the formation of piping channels within the bentonite or gap-filling materials [1–3]. Conversely, significant swelling may result in the intrusion of compacted bentonite into fractures within the host rock [4]. Previous field studies on erosion and piping have typically followed a standardized procedure: (1) borehole drilling and flow analysis, (2) site selection, (3) test design, (4) instrumentation and bentonite installation, (5) groundwater inflow, (6) erosion and piping monitoring, (7) evaluation and assessment, and (8) dismantling. However, these studies have primarily focused on the hydro-mechanical interactions between groundwater and the bentonite buffer. In actual disposal conditions, the decay heat generated by radioactive waste alters the temperature distribution between the buffer and the surrounding rock. Furthermore, desiccation cracks can develop from the canister-buffer interface toward the outer buffer. These thermal and desiccation effects can significantly influence the evolution of erosion and piping phenomena, but have not been adequately considered in previous field-scale tests.

In South Korea, the only underground research tunnel dedicated to geological disposal studies is the KAERI Underground Research Tunnel (KURT), established in 2006 and expanded in 2015. KURT consists of six research galleries, and the Bentonite Erosion and Piping Test (BEPT) is planned to be conducted in Gallery II. Two existing boreholes have been used to assess groundwater flow direction and rate, and two additional boreholes have been drilled to verify these data. Based on these results, the final site for BEPT has been selected, and supplementary injection and monitoring boreholes have been drilled. The test specimens are designed to be 200 mm in diameter and 1,000 mm in total height. A heater is installed in a mandrel approximately 75 mm in diameter. Measurement sensors are installed in bentonite and their cables are connected to surface through the mandrel at center. The sensor configuration includes four total pressure sensors, two relative humidity sensors, and two temperature sensors distributed along the specimen height. Additionally, 12 electrodes are embedded at the mid-height of the specimen to measure electrical resistivity. Not only wired THM sensors but wireless THM sensors will be also tested under high-temperature and high-pressure conditions to simulate decay heat and swelling pressure effects. Installation of BEPT will be conducted in second half of 2025 and the test will be continued until 2029.

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First H-and O-stable isotope results from the Alternative Buffer Materials experiments: Tracking structural isotope exchange in smectite during bentonite-water interactions from 70-250°C

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The Alternative Buffer Materials (ABM) 2 and 5 intermediate field experiments, conducted at the Äspö Hard Rock Laboratory in Sweden, were designed to investigate the stability of different bentonite materials of interest as buffers around canisters containing spent nuclear fuel in long-term underground Deep Geological repositories. The ABM2 and 5 experiments consisted of compacted bentonite discs stacked vertically around a central heating system emplaced in a host-rock borehole. This experimental configuration was intended to simulate the heating that occurs during radionuclide decay in order to evaluate bentonite buffer performance and stability up to 250°C. ABM2 was considered a low-temperature experiment reaching a maximum temperature of 140°C and underwent an emplacement time of ~7 years. ABM5 was a high-temperature experiment with a maximum temperature of 250°C and an emplacement time of ~5 years.

Samples from five different bentonite materials from the ABM2 and 5 experiments were obtained in order to track the structural stable hydrogen (H)- and oxygen (O)-isotope exchange between smectite and water over the thermal gradients observed in both ABM systems. The ABM experiments provided a unique opportunity to track isotopic exchange between smectite and water in a long-term, imperfect, natural but still semi-controlled environment or "living laboratory". This work aimed to both understand the bentonite-water-thermal interactions occurring in the complex ABM systems while also gaining insight into outstanding, decades-old, questions in the scientific literature regarding smectite structural H- and O-isotope exchange in a natural environment. H-isotope analysis was done using a modified High Temperature Elemental Conversion Analysis coupled with an Isotope Ratio Mass Spectrometer (IRMS) procedure following Kanik et al. [1] and the classical silicate fluorination method after Clayton and Mayeda [2] was used for O-isotope analysis with off-line IRMS.

H-isotope compositions between the ABM2 and ABM5 packages showed clear differences while O-isotope compositions showed similar trends between the two ABM packages. In both ABM packages H- and O-isotope exchange was more progressed at higher temperatures but the mechanisms for H- and O-isotope exchange proceeded differently. H-isotope compositions nearly reached modeled equilibrium values at temperatures between 130-150°C in the absence of any smectite alteration, which suggests proton exchange as the exchange mechanism. The calculated percentage of exchanged oxygen showed that the O-isotope compositions were far from reaching equilibrium and were more resistant to exchange than hydrogen. A two end member mixing model was used to calculate the percentage of O-isotope exchanged and a dissolution/re-precipitation mechanism involving fine smectite is considered as a possible mechanism.

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What can we learn from cation exchange studies of buffer materials in in-situ tests' (ABM-1, -2 and -5) after heating from 140 °C to 250 °C?

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Bentonites as candidate materials for High-Level Radioactive Waste (HLRW) repositories are investigated with respect to long term stability as buffer material [1-3]. In-situ tests were conducted in rock laboratories such as the second phase of the 'Alternative Buffer Material test' (ABM) in Äspö, Sweden where different bentonite buffer materials with various exchangeable cation populations were packed vertically on each other with an iron tube as heater in the centre [4]. We report on changes of cation exchange data of the whole packages ABM-1, ABM-2, and ABM-5, the latter being heated up to 250°C [6].

Direct comparison of extracted exchangeable cations is a challenge because boundary conditions varied between the different packages. All three packages were heated in different steps and to different peak temperatures . Heating started after water saturation (ABM-2 and -5) or directly from start (ABM-1). Bentonites were naturally saturated with water by typical fractures in the crystalline rock mass, with fractures at different positions relative to the bentonites. Partly an artificial water saturation system was used. In ABM-2 monitoring for water pressure in the galleries above the experiments showed pressure drops possibly indicating so-called boiling of water in the sand filter around the blocks [5]. Here possibly water has left the system to the rock and was filled up again in cycles.

During heating groundwater entered the blocks for water saturation from the rock side to the heater. In contrast to expectations, only a minor CEC decrease of, on average, 1.8 meq/100 g was detected in ABM-5, although processes depending on high temperature were expected to alter the swelling properties of smectites that can be followed analytically by reducing bentonite CEC values and by layer charge differences [7]. In ABM materials, exchangeable cations were redistributed between the different (mostly bentonite) materials. In contrast to the former experiments ABM-1 and -2, however, in ABM-5 the average exchangeable Na^+ occupation of the reacted material was much closer to the reference materials and exchangeable Ca^{2+} gains were lower at 250°C compared to only 140°C maximum temperature. That could help understanding so-called selectivities between mono- and bi-valent cations at different temperatures. Exchangeable Mg^{2+} loss was comparable to ABM-2. How does this fit together? The presentation will give an overview about possible reasons for these differences.

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Mineralogical and Chemical Transformation of Ca-Bentonite at High Temperatures: A Long-Term Evaluation

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The current safety-considered design temperature requirement for buffer material in a high-level radioactive waste disposal is 100 ℃. However, in the case of South Korea, which has a territory with limited space and a high population density, increasing this design temperature could significantly reduce the overall area of the disposal site. Therefore, this study aims to investigate any changes in bentonite as a buffer material through mineralogical and chemical assessments under high-temperature conditions (up to 200 ℃) with highly concentrated KCl solution (1 M).

The study used Ca-type bentonite and experimentally evaluates key factors resulting from the solid transformation of montmorillonite, a primary mineral in bentonite, into illite or interstratified mineral form. Various analyses, including supernatant and XRF for interlayer ion exchange amount of bentonite under each experimental condition, XRD for mineral analysis, Electron Probe Microanalysis (EPMA) for the chemical composition of altered clay, and TGA for changes in moisture content, have been conducted.

Within the experimental results obtained, the concentration of K^+ ions appears to be the major alteration factor during high-temperature treatment of bentonite. However, more data collection on alteration samples is necessary to derive more accurate alteration factors. The evaluation methodologies developed in this study will be applied to ongoing long-term and short-term thermal alteration experiments to continually gather experimental results and serve as key fundamental data for interpreting physical performance changes in altered buffer materials.

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LECTURE THEATRE 7 – SESSION 27

Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces

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Element partitioning between clay minerals and fluids: a molecular dynamics simulation approach

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The partitioning of elements between clay minerals and fluids plays a crucial role in geochemical cycling and the metallogenic processes of critical metals. While field sampling and laboratory analyses provide essential geological and geochemical data, such as elemental composition, mineral structure, and thermodynamic properties, the underlying atomic-scale mechanisms remain poorly understood. To address this issue, recently we developed a molecular dynamics (MD) based method to quantify the partitioning, enabling the direct comparison with experiments. We first established a framework for Na^+/K^+ cation exchange between montmorillonite interlayer and surrounding fluids, revealing how partitioning relates to the variation in water activity and ionic activity ratios. We investigated Li^+ partitioning in clay minerals, providing insights into the formation mechanisms of clay-type lithium deposits and examined Rb^+/Cs^+ exchange with Na^+, providing implications for nuclear waste disposal and soil remediation. We also explore elemental partitioning related to other clay minerals, such as palygorskite and sepiolite. The potential applications and future development of this method will be discussed.

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Hydrogen-Induced Swelling in Clay Minerals: Molecular Insights into Caprock Integrity for Subsurface Hydrogen Storage

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Hydrogen is a clean, renewable alternative to fossil fuels that can help reduce greenhouse gas emissions, particularly CO_2. Geological formations offer promising options for large-scale storage, but ensuring caprock integrity is critical to prevent leakage and ensure long-term safety [1]. A significant yet often overlooked factor in caprock integrity is hydrogen-induced swelling in clay minerals present within the caprock [2]. Smectite clays like montmorillonite have layered structures consisting of aluminosilicate sheets separated by zero (0W) to three (3W) layers of water [3]. When hydrogen molecules are intercalated into the interlayer nano-space of clays, they can induce changes in the structural properties, such as the expansion or shrinkage of interlayer pores, which in turn can impact the mechanical response of the caprock. Using Molecular Dynamics simulations, we examined how hydrogen intercalation in dry to fully saturated interlayers affects the swelling behaviour of these clays. We focused on how hydrogen changes the transition between hydration states (e.g., from 0W to 1W and 1W to 2W), and why these changes occur. Finally, we evaluated the elastic and plastic responses of clay minerals to H_2-induced swelling. Our findings shed new light on the molecular mechanisms underlying this phenomenon and highlight their implications for maintaining caprock integrity in hydrogen storage environments.

Acknowledgement: The Clay Minerals Group (CMG) of the Mineralogical Society of the UK and Ireland has partially funded this work through a “CMG Research Grant.”

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Molecular dynamics to resolve mechanistic ambiguities in Cs adsorption on todorokite

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Radioactive cesium (137Cs), a highly volatile and mobile contaminant from nuclear accidents and improper waste disposal, migrate through soil systems, posing significant environmental risk. Todorokite, a tunnel-structured manganese oxide abundant in soils, has been taken attention for its role immobilizing this radionuclide. The oxide features 6.9 Å × 6.9 Å sized nanotunnels, with both (100) and (010) external surfaces and these nanotunnels serving as potential binding sites. Previous studies suggested a two-site surface complexation model for Cs^+ on todorokite, with EXAFS analysis indicating the formation of outer-sphere (OS) complexes. However, ambiguities persist regarding the roles of nanotunnels versus external surfaces and the precise nature of Cs^+ coordination. This study employs classical molecular dynamics (MD)-based free energy calculations to resolve uncertainties regarding the Cs^+ adsorption mechanism. We computed potentials of mean force for Cs^+ and Na^+ as functions of their relative positions from aqueous solution toward the todorokite surface or throughout the nanotunnel. From these calculations, we derived selectivity coefficients between Na^+ and Cs^+ for each plausible binding site. Nanotunnels exhibited strong preference for Cs^+ over Na^+, whereas (100) and (010) external surfaces slightly favored Na^+ over Cs^+. These results align with the selectivity coefficients reported in the two-site complexation model proposed based on isotherm data. Nanotunnels most likely correspond to the strong affinity site and external surfaces correspond to the weak affinity site in the complexation model. Further MD simulations revealed that inside the nanotunnels, Na^+ formed both OS and inner-sphere (IS) complexes, but Cs^+ predominantly formed IS complexes due to steric hindrance. Even on the external surface, IS complexes of Cs^+ were predominant, conflicting with prior EXAFS interpretation. MD simulations predicted the averaged Cs–O distance of IS complexes on the (100) surface to be close to that of Cs^+ in aqueous solution, demonstrating that IS complexation of cation with surface does not always lead to reduction of its averaged bond distances compared to aqueous cation. MD simulations also predicted the Cs–O distance of IS complexes to be shorter inside nanotunnels than on external surface, a feature not identified in the EXAFS analysis. The absence of such a shorter distance in EXAFS analysis is attributed to the use of high concentration of Cs^+ in sample preparation, under which condition IS complexes on external surfaces dominate over those within the nanotunnels. Our study indicates at trace levels, nanotunnels drive Cs^+ selectivity of todorokite through IS complexation. Incorporating atomistic MD simulations to surface complexation models will enhance the multiscale prediction capability for radionuclide migration in soil systems.

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Atomistic computational modelling of thaumasite and its aqueous interfaces

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Thaumasite, $Ca_3[Si(OH)_6](CO_3)(SO_4)\cdot 12H_2O$, is a hydrated calcium silanol-carbonate-sulfate natural mineral with a columnar crystal structure. The columns of stacked silicon and calcium hydroxide polyhedra $[Ca_3Si(OH)_6^{4+}$ are running parallel to the *c* lattice vector of thaumasite [1] and are interconnected through a network of hydrogen bonds (H-bonds), facilitated by H_2O molecules, SO_4^{2-} and CO_3^{2-} anions that occupy the intercolumnar spaces within the crystal. From the crystallochemical perspective, the thaumasite crystal structure is extremely unusual because all Si atoms in the hydroxide columns are octahedrally coordinated by hydroxyls [2]. Under normal conditions, the crystal chemistry of silicon-oxygen compounds is dominated by the tetrahedral SiO_4 coordination of silicon atoms, while the octahedral SiO_6 coordination is only found in minerals under extreme conditions of temperature and pressure, such as existing in the Earth's mantle [3]. Silica atoms in 5-fold and 6-fold coordination can also be occasionally found in silica glass, or as an intermediate species in the process of aqueous dissolution of phyllosilicates [4]. Thus, thaumasite represents a very rare example of a crystal in which silicon is octahedrally coordinated under ambient temperature and pressure, far away from these harsh conditions. In addition to its importance in mineralogy and crystallochemistry, thaumasite is also of considerable interest in the chemistry of cement and concrete because its formation can cause significant damage to concrete due to the expansion of the cement matrix in the process of so-called "sulfate attack" [5].

Here we use classical molecular dynamics (MD) computer simulations with the ClayFF-MOH force field [6] to quantitatively investigate the structural, vibrational, mechanical and thermodynamic properties of thaumasite. Additionally, for a more detailed examination of the structure and dynamics of intracrystalline H-bonds in this material, path integral MD technique was applied. The results of classical MD simulations demonstrate good agreement with available experimental data and DFT calculations. Mineral-water interfaces for the (1 0 0) and (0 0 1) surfaces of thaumasite were also simulated and compared with the aqueous interfaces of a similar columnar crystal of ettringite, $Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O$ [7]. The interfacial energies for hydrated (1 0 0) and (0 0 1) thaumasite and ettringite crystal faces provide new insights on the atomistic scale solubility mechanisms of these minerals. The simulations also confirm the possibility of thaumasite epitaxial growth on the surface of ettringite [8].

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Atomistic insight into the effects of actinyl-ligand interactions on the actinyl retention by clay minerals

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The safe and reliable storage of high-level radioactive waste (HLW) requires a deep understanding of the interactions between the radionuclides present and other species in the surrounding environment. Several countries have chosen to store HLW in deep geological repositories with clay minerals acting as a natural barrier to surround the waste canisters. In France, the chosen storage site is rich in Callovo-Oxfordian clay rock (COx), which contains illite, smectite, and interstratified illite-smectite clay minerals. As the waste canisters eventually degrade, small organic molecules (particularly carboxylates) are expected to be released in addition to the waste. The formation of actinyl-carboxylato complexes may prevent the retention of actinyls by the clay barriers, lowering its effectiveness. It is therefore important to study these systems on an atomistic level to predict the long-term behaviour of the clay barrier at preventing radionuclide migration.

We use classical molecular dynamics (MD) computer simulations to study how the clay-actinyl interactions are affected by malonate and carbonate ions. The actinyls of choice are uranyl(VI) and neptunyl(V) – UO_2^{2+} and NpO_2^{+}, respectively. The clay mineral model is a *cis*-vacant smectite with isomorphic substitutions in both tetrahedral and octahedral layers and the structural formula of $Na_{0.75}[Si_{7.75}Al_{0.25}][Al_{3.5}Mg_{0.5}]O_{20}(OH)_4$. Malonate is a dicarboxylic acid that is unique in its ability to form both side-on (chelate) and end-on complexes with actinyls. Carbonate ions were also included due to the presence of calcite in the geological storage conditions.

Our simulation results illustrate a much greater tendency for uranyl to both adsorb on the clay surfaces and form complexes compared to neptunyl, owing to uranyl's higher charge. Equilibrium simulations reveal a concentration-dependent influence of the ligands on uranyl adsorption. Higher concentrations of ligands generally resulted in lower uranyl retention on the clay surface. To calculate the free energies of adsorption and complexation, we also carried out potential of mean force (PMF) calculations. These results provide both thermodynamic and kinetic explanations for the differences exhibited by the actinyls. Furthermore, the energetics of the two different actinyl-malonate binding modes were sampled.

This study provides a quantitative atomistic-level insight into the complex interplay of interactions between actinyls, anionic ligands (malonate and carbonate) and clay minerals. By combining equilibrium MD simulations with free energy calculations, and comparing the results to available experimental data, we are able to predict the effects of such ligands on the clay barrier's effectiveness on actinyl retention.

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Frontiers of multiscale modelling of retention and transport in clays: Surface reactivity to chemical thermodynamics

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Clay minerals are inherently multiscale materials with high surface reactivity and complex hierarchy of pores. Their fundamental building blocks, the TOT layers, stack to form interlayer pores accessible for diffusive transport of water and cations. In compacted clay systems, these stacks contribute to the complex network of pores combining interlayer and interparticle porosity thus enabling transport of solutes and solvents. The chemical reactivity of clay minerals is primarily governed by permanent structural charge and pH-dependent protolysis of surface functional groups, resulting in complex, chemistry-dependent surface speciation and competitive sorption. Given the complexity of the system not a single experimental or modelling approach is capable of describe whole range of relevant phenomena in a single setup. A multi-methodological approach is needed to integrate composition-specific surface reactivity of clay minerals with the complex pore structure and the interactions across scales. Recently, coupling ab initio simulations, spectroscopy, and wet chemistry has particularly successful in elucidating sorption mechanisms and mineral dissolution processes [1-2]. Laboratory investigations of ionic diffusion and large-scale pore scale transport modelling supported by molecular simulations account for electrostatic interactions, solvent structuring, pore connectivity in the system and thus able to explain effect background electrolyte composition on diffusion of ions in clays, often referred to as surface diffusion [3].

This contribution aims to review recent advances in modelling the reactivity and transport of clay systems, with particular focus on clay mineral dissolution, sorption and transport phenomena. Connections to spectroscopic characterization and macroscopic modelling of reactive transport are also discussed. The integration of molecular-level insights with thermodynamic and pore-scale models offers a comprehensive understanding of sorption and transport phenomena in clay rocks at saturated and partially saturated conditions [4-6].

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Bridging the Gap between Molecular Simulations and Surface Complexation Modeling for Heterogeneous Surfaces: A Case Study with Uranium and Arsenic Adsorption on Clay Minerals

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Among all natural sub-micro sized phases, clay minerals are ubiquitous in soils and sedimentary rocks in nature as well as in engineered environments, and while clay minerals' adsorption properties have been studied extensively, their unique level of surface reactivity heterogeneities necessitate further investigation at the molecular level to understand and predict the influence of these heterogeneities on their macroscopic properties. In this study, we investigated the surface structures and desorption-free energies of U(VI) species (UO_2^{2+}) and As(V) species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) complexed at different edge surface reactive sites of a cis-vacant montmorillonite layer using first-principles molecular dynamics (FPMD). We show that U(VI) forms bidentate and tridentate complexes on montmorillonite edge surfaces, whereas As(V) monodentate complexes are the most stable. Then we constrained a state-of-the-art surface complexation model (SCM) with surface acid-base chemistry and surface complexation properties obtained from the molecular-level simulation results. While our results highlighted the complexity of the interfacial chemistry controlling the complexation of inorganic contaminants on clay mineral surfaces, they also evidenced the reliability of an integrated workflow using modern multi-scale simulation techniques to address the challenge of predicting the heterogeneities in mineral surface reactivity.

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Harnessing Machine Learning Models for Predicting Pore Size Distribution in Clays

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Pore Size Distribution (PSD) is a fundamental microstructural property that significantly impacts the hydro-mechanical behavior of soils, particularly clay materials. The evolution of pore structure in clays depends on variety of factors such as clay mineralogy, pore fluid chemistry, compaction state, overburden load, clay fabric etc. These factors collectively influence the arrangement, size, and volume of pores, which are directly linked to the engineering behavior of clays [1]. Therefore understanding PSD characteristics of clay is essential for accurately assessing the soil behavior under varied engineering applications. Although several advanced experimental methods exist for quantifying PSD, they are often invasive, require specialized equipment, and are limited in their ability to capture the full range of pore sizes [2]. The advancement of machine learning (ML) techniques has led to growing interest among researchers. The development of ML-based models facilitates the prediction of PSD characteristics across diverse soils, taking into account the factors influencing them and effectively capturing the complete range of pore sizes.

The present study aims to develop ML based models that provide a non-invasive, accurate, and efficient approach to predict PSD characteristics in clays. The experimental data obtained from mercury intrusion porosimetry (MIP) for three clayey soils namely sodium bentonite, calcium bentonite, and kaolinite subjected to various compaction states (wet of optimum, dry of optimum, and optimum conditions) prepared using diverse pore fluids, including water, NaCl (0.01M and 1M), and $CaCl_2$ (0.01M and 1M) were utilized. A comparative analysis was performed using three ML algorithms, Feedforward Neural Networks (FNN), Convolutional Neural Networks (CNN), and Random Forest Regressor to predict PSD [3]. Model performance was assessed by predicting PSD for individual scenarios, as well as visualizing predicted versus actual values for specific soil-pore fluid-compaction combinations. Results indicate that ML approaches effectively capture non-linear variations, offering accurate predictions across diverse soil and pore fluid conditions. The analysis indicates that the Random Forest Regressor model achieved superior prediction performance, with the highest R^2 value of 0.993 and the lowest Mean Squared Error (MSE) value of 0.145 during the training phase.

This study integrates ML-driven insights with experimental findings, promising broader applicability with enhanced accuracy paving the way for innovative soil behavior modelling. In the future, this work can be extended by validating the developed models using diverse soil samples from various geographical regions. Incorporating such data, with its inherent noise and variability, will strengthen the model's robustness and enhance its generalization capabilities.

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Multi-scale simulations of the retention and aggregation of organophosphate esters (OPEs) with clay-organic complexes

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Clay-organic complexes, as the major substrate in surface environment, play an essential role in the retention of organophosphate esters (OPEs). Due to the complexity and heterogeneity of clay-organic aggregates, the molecular-level understanding of the interactions between OPEs and clay-organics has not been elucidated. This work systematically investigates the dynamic retention and aggregation behavior of three types of OPEs (TBEP, TCEP and TCP) with kaolinite-organic complexes by molecular dynamic (MD) simulations and density function theory (DFT) calculations. Flexible (SRFA) and rigid (WFA) molecular structures of organic matters are considered. Results demonstrate that both SRFA and WFA can act as bridges to connect the hydroxyl surface of kaolinite and OPE aggregates. The flexible SRFAs tend to fold themselves, thereby providing hydrophobic sites for OPEs. The aggregates of WFA are divided into several parts and attach to outer surface of the OPE polymers, as the rigid WFA cannot undergo conformational changes. According to DFT results, OPE oligomerization is primarily driven by vdW interaction attributed to their typical hydrophobic nature, supplemented by weak electrostatic forces from minor hydrophilic moieties. This work reveals that the transport and bioavailability of OPEs are significantly reduced by forming OPE-NOM-kaolinite co-aggregates, and provides a quantitative understanding of the environmental processes of OPEs at the molecular and electronic scales.

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Surface complexation of rare earth elements on clay minerals and iron (oxyhydr)oxides: Insight from first principles simulations

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Rare earth elements (REEs) are of critical importance to modern high-tech and green-tech industries and have been recognized as strategic materials worldwide. Among different REEs deposits, regolith-hosted deposits (e.g. ion-adsorption deposits, IADs) and deep-sea mud have received unprecedented attentions due to their high concentration of REEs and especially the enrichment of heavy REEs (HREE). Clay minerals and iron (oxyhydr)oxides (e.g. goethite) were found to play a key role in the enrichment of REEs in these deposits. How REEs interact with clay minerals and iron (oxyhydr)oxides is therefore essential to the understanding of REEs enrichment in these deposits. It was believed that REEs are adsorbed as outer-sphere complexes on clay basal surfaces but many studies supported the existence of inner-sphere complexes. However, the nature of such inner-sphere complexes is still unclear. The complexation mechanisms of REEs on goethite also remain largely unexplored, especially in the deep-sea hydrothermal environment.

In this study, by using the first principles molecular dynamics technique, we investigated the microscopic complexation mechanisms of REEs on clay edge surfaces and goethite surfaces. The possible complexation sites for REEs on clay edge surfaces and goethite surfaces were first derived based on the calculated acidities. Then, by taking Sc^{3+}, Y^{3+}, and La^{3+} as model REE cations, the complexation structures and free energies of REEs on clay edge surfaces and goethite surfaces were determined, based on which the atomic level complexation mechanisms were derived. The species and structures of REEs complexes established in the present study form a reference structure set and could improve the interpretation of experimental data. The findings in this study enable an in-depth understanding of REEs fractionation and enrichment in regolith deposits and deep-sea muds.

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Unravelling smectite clay nanoparticle aggregation: microstructure, dynamics, and coupled material properties

Warren Huff Clay Science Pathway Award 2025

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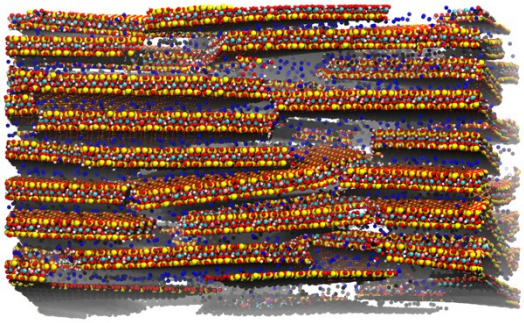
Clay aggregation refers to the process by which individual clay particles bind together to form larger, more stable structures known as aggregates. Understanding this process is crucial for applications in agriculture, environmental remediation, and geotechnical engineering, as it directly influences the coupled thermal, hydraulic, mechanical, and chemical (THMC) properties of soils, geofluids, sediments, sedimentary rocks, and engineering materials. A fundamental challenge in studying clay aggregation is its strong dependence on factors such as temperature, solid fraction, saturation, clay type, and the nature of exchangeable cations. This sensitivity remains incompletely understood due to the difficulty in characterizing the complex microstructures of hydrated clay nanoparticle assemblages and their interactions with water across length scales ranging from nanometers to micrometers.

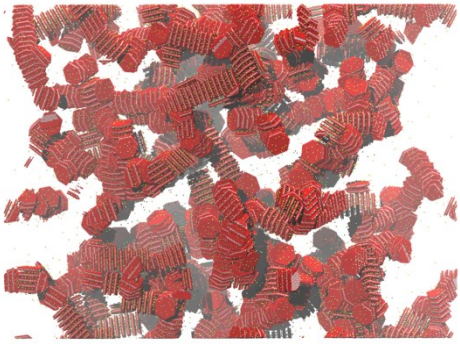
This work addresses these challenges through a two-part study. In the first part, we employ large-scale all-atom molecular dynamics (MD) simulations to examine a hydrated Na-montmorillonite assemblage consisting of 27 clay nanoparticles. Simulations span a wide range of temperatures (298–373 K) and dry densities (781–1,827 $kg \cdot m^{-3}$), yielding predictions for various THMC properties of water-smectite mixtures, including heat capacity, thermal conductivity, thermal expansion coefficient, suction, hydraulic conductivity, and the self-diffusivity of water and Na ions. In the second part, we extend this framework using a new coarse-grained molecular dynamics (CGMD) model to simulate the self-assembly of up to 2,000 smectite particles with diameters of 6, 12, and 25 nanometers. These simulations explore the effects of Na and Ca counterion fractions on clay aggregation and provide insights into structural properties such as the number of platelets per tactoid, tactoid size distribution, clay basal spacing, counterion distribution, modes of particle association, and rheological properties.

Our findings demonstrate that properties predicted by our MD models align closely with experimental observations and theoretical models, underscoring the critical role of nanoscale features in influencing the macroscale behavior of clay materials. This work bridges the gap between the microstructural characteristics of hydrated smectite assemblages and their macroscale properties, revealing the emergence of complex structural and rheological properties at scales involving thousands of clay particles. These insights advance our understanding of clay colloidal aggregation and provide a foundation for studying natural and engineered processes involving clay-based materials in complex environments.

All-atom MD simulations of a large-scale smectite clay assembly



Coarse-grained MD simulations of large-scale smectite clay aggregations



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LECTURE THEATRE 7 – SESSIONS 3+16

Sorption and intercalation in layered materials: from origins of life to material science

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Role of Layered Minerals in the Emergence and Preservation of Proto-Proteins and Detection of Extraterrestrial Biosignatures

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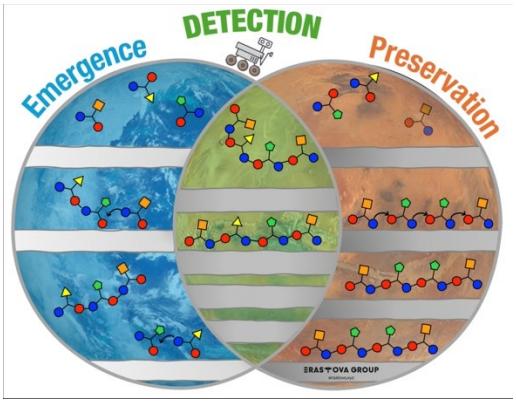

The origin of life remains one of the central enigmas in science, probing how inanimate matter transitioned into living systems. This talk explores the key role of layered minerals in prebiotic chemistry and biosignature preservation, integrating insights from space missions, laboratory experiments, and molecular modelling.

Clay minerals are hypothesised to have concentrated organic species, catalysed polymerisation reactions (e.g., peptide-bond formation), and shielded proto-biomolecules from harsh early Earth or extraterrestrial environments, making clay mineral-rich sights a priority for the search of extraterrestrial biosignatures. However, minerals' potential as primitive genetic materials remains limited due to their inability to sustain long-term information replication. Instead, we propose that minerals can transcribe environmental cycles (e.g., tidal or seasonal changes) into molecular sequences, allowing formed polymers to remain mobile and chemically active rather than overly protected, which would hinder their functionality.[1]

Leveraging statistics obtained from high-throughput molecular dynamics simulations, we bridge experimental gaps by providing insights into mineral-organic interactions under conditions unattainable in the lab, such as geological timescales or extraterrestrial settings like Mars. Our findings demonstrate that both smectite clays and layered double hydroxides can selectively adsorb amino acids and catalyse peptide formation, yet with very distinct mechanisms.[2,3] The produced polymer composition and yield are dictated by the mineral structure and environmental factors, which we discuss. While a peptide preserved within a clay may appear as a biosignature, we argue that such mineral-formed peptide is only a biosignature-lookalike. Based on statistics collected from our simulations, we are able to propose an approach to identify whether the mineral-encapsulated peptide is a pseudo-biosignature during space missions, based solely on its amino acid composition.

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Understanding the adsorption of amino acids onto montmorillonite clays through molecular simulations

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Clay minerals have a track record of long-term preservation of organics, making clay-rich soils of interest to Martian missions.[1] Amino acids are among the building blocks of life, easily synthesised, and commonly found in space.[2] However, their ubiquity means that, even preserved on extraterrestrial rocky bodies, amino acids alone do not constitute a biosignature. Clay minerals are not only capable of adsorbing amino acids, but also polymerizing them into a peptide,[3] which makes the identification of a true biosignature even more difficult.

In this case, one must find routes to distinguish these pseudo-biosignatures from true ones, that would have emerged and functioned elsewhere and only later preserved by the clay. In view of sample return missions, one must find a route to discard the samples containing pseudo-biosignatures.[4] Ideally, we must do so by only knowing the retained amino acid distribution and the mineral structure, as this is the data we realistically could obtain.[5]

To this end, we have studied the adsorption of 20 proteinogenic amino acids onto montmorillonite clay (SWy1) in the presence of 4 cations. The knowledge of the selectivity of the mineral toward adsorbed species allows us to suggest the composition of a polymer generated by this mineral surface. Anything matching the predicted composition can be confidently discarded as a pseudo-biosignature. On the other hand, the presence of amino acids that are unlikely to be adsorbed by this mineral under the given conditions will suggest the sample should be investigated further and potentially returned to Earth for in-depth studies. [4]

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Mineral-mediated RNA evolution

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Constraining the environmental conditions that allowed relevant chemical reactions in living beings is crucial to understanding the emergence of life. The data has revealed that a frozen Earth surface dominated during the emergence of life [1]. Contrary to intuition, ice-mediated reactions accelerate in the eutectic phase of water ice through freeze concentration [2]. Additionally, on a frozen Earth surface, continental runoff and geothermal fluids contained supersaturated concentrations of dissolved silica and mineral particles, where essential biomolecules could have interacted. Among these key biomolecules, ribonucleic acids (RNA) have been highlighted for their widespread presence, as well as their capacity to catalyse self-replication and carry genetic information [3].

Taking a multidisciplinary approach, we are exploring the potential of mineral surfaces to bind and release RNA strands in a controlled manner through pH shifts induced by periodic temperature fluctuations, similar to those found in natural systems. Our ongoing experiments show that freezing and thawing cycles of biological and geochemical relevant buffer solutions (e.g., bicarbonate, phosphate) can shift the pH by up to four units. This process not only promotes RNA duplex strand denaturation but also alters the pH-dependent surface charges of minerals, ultimately allowing us to control the adsorption and desorption of negatively charged RNA molecules. By coupling these two mechanisms with the presence of a self-replicating ribozyme, a more complex RNA molecule capable of catalysing the formation of complementary RNA strands, we aim to promote the synthesis of new RNA strands in an open-ended manner [4].

Complementarily, using cryo-transmission and scanning electron microscopy analyses in the eutectic phase, we aim to characterize interfaces, pores, and bubbles as potential microenvironments and compartments capable of forming protocells. This compartmentalization could eventually sustain replication and evolution of newly formed RNA strands.

the expectation is that our results will not only reconcile prebiotic conditions, components, and chemical processes that contributed to the evolution of primordial biomolecules but also provide insights into the interplay between the eutectic phase present in ice water, silicate-based minerals, and RNA, with potential extensions in geoscience, materials science, and medicine.

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Competitive Sorption of H_2O and CO_2 in Clay Mineral Interlayers

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The first-reported competitive CO_2-H_2O sorption isotherms on a naturally occurring expandable clay mineral (SapCa-2 Saponite from Ballarat, California) are reported using controlled-environment X-ray diffraction (XRD) combined with ATR-FTIR spectroscopy and gravimetric sorption methods. Our data for Na-, K- and Cs-exchanged saponite illustrate the influence of the exchangeable cation on CO_2-H_2O sorption. In a recent study, CO_2 (p/p_o = 1.0) was observed to intercalate into the interlayer region of Cs-saponite at low RH (~1% RH), resulting in a surface loading of CO_2 of 1.1 $mmole_{CO2}/g_{clay}$ [1]. In contrast, CO_2 was unable to access the interlayer region of K-saponite at low RH, and some interlayer H_2O was required for CO_2 sorption to occur. K-saponite was able to sorb about 0.8 $mmole_{CO2}/g_{clay}$ at 10-20% RH [1].

In this study, we obtained complementary controlled-environment XRD data of oriented deposits of Cs- and K-saponite in the presence of N_2 and CO_2 with controlled humidity. The observed *d*(001) of Cs-saponite at low RH in N_2 was 11.2 Å. In the presence of CO_2 (p/p_o = 1.0) at low RH, *d*(001)-value increased to 11.8 Å. The change in *d*-value was reproducible, switching between N_2 and CO_2. At high relative humidity in a CO_2 atmosphere, the *d*(001) of Cs-saponite increased to 12.3 Å. The *d*(001)-value of K-saponite in N_2 at low RH was 10.6 Å reflecting the smaller size of the K^+ ion. In agreement with the recently published FTIR and gravimetric data, CO_2 did not intercalate into K-saponite in the absence of interlayer H_2O, resulting in a *d*(001) of 10.6 Å. Exposure of K-saponite to 15% RH in N_2 resulted in a *d*(001) of 10.9 Å. K-saponite exposed to CO_2 with 15% RH did not expand initially (*d*(001) of 10.9 after 1.5 hours), but overnight exposure resulted in expansion to 11.4 Å.

These results of differential CO_2 interlayer access can be partially interpreted based on the resultant *d*(001) values. At low RH, Cs-saponite has a *d*(001) of 11.2 Å compared with a value of 10. 6 Å for K-saponite. A more compelling argument is based on thermodynamic considerations of cation-CO_2 and cation-H_2O free energies of solvation. In all cases, the free energy of solvation by H_2O is favoured over CO_2. However, the difference becomes smaller as the ionic radius of the cation increases (Na to Cs). Thus, the competition between CO_2 and H_2O becomes more favourable for CO_2 on Cs-saponite compared with K-saponite.

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Hybrid clay pigments: the influence of lamellar clays and intercalation on structural properties

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Clay-based materials are widely used as hosts for organic and inorganic materials, particularly in the development of hybrid pigments [1]. In this study, two clay minerals, saponite (industrial synthetic clay) and montmorillonite (synthetic montmorillonite) , were investigated for the synthesis of stable hybrid pigments [2]. The objective was to compare **two intercalation strategies** to determine the most effective approach for obtaining a stable pigment with enhanced colour stability that could be further used in applications such as paintings, cosmetics and so on.

Organic (Cetyltrimethylammonium bromide - CTAB, β-cyclodextrin - β-CD) and inorganic (aluminium and zinc salts) compounds, known to interact with dyes, were intercalated using two different strategies: (i) pre-modification of montmorillonite before dye adsorption and (ii) simultaneous insertion of all components [3].

Characterization techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray fluorescence (XRF), revealed that pigments synthesized via the second approach exhibited higher intercalation efficiency and stability, with increased d_{001} distances. In contrast, pre-modified clay composites faced steric hindrance, limiting further dye insertion. Fourier-transform infrared spectroscopy (FTIR) confirmed interactions between the clay and the intercalated species, while adsorption kinetics and isotherm studies highlighted significant differences between clays. Notably, montmorillonite showed a greater dye adsorption capacity, whereas among saponite composites, Zn-Sap exhibited the highest dye uptake. Stability assessments by observing the dye releasing revealed that the most stable pigments were those incorporating the surfactant (CTAB), both in saponite- and montmorillonite-based systems. Additionally, Sap-(Al-Bet) also exhibited remarkable stability, suggesting that interactions with the aluminium component contribute to a reinforced hybrid structure.

These findings underscore the impact of molecular arrangement in hybrid pigment design. By identifying the most effective intercalation strategy, this study provides insights into optimizing pigment synthesis for **potential applications in various fields**.

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Luminescent pigments based on organically modified smectites: structural and spectroscopic characterization

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Pigments with luminescent properties were designed based on organoclays with specific organic cations functionalized with a laser dye, rhodamine 6G (R6G). Pigments were synthesized using smectite exchanged with tetraoctylammonium and tetraoctylphosphonium cations, with surfactant loadings ranging from 0 to 100% of the smectite's cation exchange capacity (CEC) and R6G concentrations from 0.001 to 0.08 mmol/g. Some pigments based on saponite exhibited luminescence even without modification. On the other hand, materials prepared from montmorillonite had to be modified to achieve at least weak photoactivity of the dye. By a suitable choice of parameters, it was possible to prepare pigments that absorbed and emitted light at variable wavelengths [1]. UV-visible absorption and fluorescence spectroscopies were most suitable for the characterization of the dye in the pigments. The predominance of smectites and organic surfactant and very low amounts of luminophore in the solid pigments presents challenges in characterizing the interaction of luminophore molecules by other analytical methods. In this context, a suite of characterization techniques was used to evaluate the structural and compositional changes in the studied systems. X-ray diffraction (XRD) revealed that the incorporation of surfactant cations significantly influenced the interlayer spacing (d001), with basal spacing increasing from 1.2 nm in pristine clays to ~2.6 nm in fully exchanged samples. Co-intercalation of dye and surfactants resulted in broader diffraction peaks, suggesting reduced structural ordering due to dye cations inclusion. The effect of the dye was best detectable at its highest concentrations (0.08 mmol/g).

Infrared (IR) spectroscopy confirmed the presence and gradual incorporation of surfactant cations through increase in the intensity of C–H stretching and bending vibrations. At higher dye concentrations (0.08 mmol/g), characteristic R6G bands such as C=O and aromatic C–H vibrations were clearly detectable, despite some overlap with surfactant bands. At very low concentrations (<0.005 mmol/g), the absorption bands of dye diminished significantly. Additionally, a broad band around 3440 cm^{-1}, absent in pure R6G, suggested hydrogen bonding interactions between dye molecules and interlayer water, as band weakened with increasing surfactant content, *i.e.* with growing hydrophobicity of samples.

Acknowledgement: The authors acknowledge financial support from Slovak Grant Agency VEGA No. 2/0161/25 and the Slovak Research and Development Agency projects Nos. APVV-21-0302 and APVV-22-0150.

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FRIDAY

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LECTURE THEATRE 1 – SESSION 32

Sustainable and eco-friendly clay-based materials

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Eco-friendly clay-based bricks using Construction and Demolition Waste

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Construction and demolition waste (CDW) is a worldwide problem. In EU-28 this kind of waste constitutes 35% of the special waste produced. In general, CDW mineral fraction is very heterogeneous (mortar, ceramics, concrete, rocks, natural gravel, masonry, sand, soil, etc.) and depends on the characteristics of each construction. For suitable recycling, it is necessary to separate specific materials such as plastic, timber, soil, plaster, composites, paints and dangerous substances such as mercury, lead or asbestos. These substances, if present impart hazardousness to the CD.

Considering that the EU recovery rate of CDW has reached 90% [1] although there are wide variations between EU countries. In line with the EU legislation, this study proposes the recycling of three different CDW typologies (from tiles, cement and bricks) into a commercial brick body by total substitution of the sand. The recycled aggregates were physically and mechanically pre-treated in a plant and showed a particle size range between 0-4 mm.

A commercial brick body (90 wt% clay /10 wt% sand) was used as a reference and the mixes were prepared with the total replacement of sand by the recycled aggregates. Brick samples were extruded with variable water amounts (20-22%) to obtain a suitable plasticity, dried for 12h at 105°C and fired in an electrical kiln (thermal cycle: 10 h; Tmax: 1020°C and isotherm: 2.5 hs) simulating a typical brick-making process. The specimens were characterised following the technical rules. In particular, linear shrinkage (LS%) and flexural strength on dried green pieces and (24h-immersion) water absorption (WA%), linear shrinkage (LS%), flexural strength, colour test, efflorescence and Hg-porosimetry on fired pieces.

The brick samples with recycled aggregates as received showed an increase of "calcinelli" to the reference. For this reason, further experiments were conducted using the aggregates sieved below 1mm. For these mixtures, the defect was eliminated. Regarding the tests after drying the recycled aggregates provoke a slight decrease in LS% values while the cement sand improves the mechanical resistance in green.

Fired bricks showed similar LS% and WA% and high flexural strength values (up to 18%) to the reference. Mercury intrusion porosimetry tests highlighted a slight increase in total porosity except for samples prepared with cement sand. Besides, from an aesthetical point of view using CDW the efflorescence is decreased. Finally, based on the results obtained, the recycled aggregates studied can be used to replace natural sand.

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Recycling Aggregate Washing Sludge into Ceramic Applications: A Case Study of the Marrakech Region, Morocco

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The exploitation of quarries and the production of aggregates are vital and inescapable sectors for the socio-economic development of countries on a global scale. However, the clayey sludge resulting from this exploitation is increasingly being dumped in nature, presenting a significant threat to the environment and adding an economic burden to the industry. The Marrakech region, renowned for its historical ceramic tradition, utilizes local clay deposits. However, due to their poor quality, artisans frequently blend them with imported clays from other regions to improve workability and performance. Given this backdrop, this study focuses on the characterization of clay-rich sludge from the Marrakech-Tensift region to explore its potential reuse in traditional ceramics and earthen construction. A total of fifteen samples were obtained from various quarry sites along the main tributaries of the Tensift basin. The physical properties of these sludges were determined through particle size distribution and plasticity limits analysis. The chemical composition was assessed using XRF, total organic content analysis, and calcimetry, while the mineralogical composition was determined by X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR).

The results indicated that the primary oxides in the samples were SiO_2 (56–77%) and Al_2O_3 (9–14%), with trace amounts of the remaining ones. Quartz, feldspars, and clay minerals were the dominant mineral phases, accompanied by minor quantities of calcite and hematite. Among the clay minerals, illite was the most abundant, followed by kaolinite and chlorite, with smaller amounts of smectite, vermiculite, and chlorite-smectite mixed-layer minerals. Regarding plasticity, the clays exhibited low to medium plasticity. Additionally, the study revealed significant grain-size variability, suggesting that certain modifications are necessary to optimize their properties.

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Hydrothermally treated sewage sludge as a substitute for clay in the synthesis of ceramic bricks

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In the pursuit of sustainable construction materials, the integration of waste by-products into traditional manufacturing processes offers significant environmental benefits. This study explores the production of bricks using a mixture of natural clay and biosolid waste, aiming to reduce energy consumption during firing and promote the reuse of waste materials. The biosolid waste derives from the hydrothermal conversion of sewage sludge carried out at the FREEDOM HT plant (LIFE19 ENV/IT/000165, https://life-freedom-project.eu/), which is directly connected to the civil WWTP in Cassano d'Adda, Italy. The sewage sludge was treated at 220 °C for 30 minutes, with pre-heating and cooling times of 20 minutes each.

The resulting product was successfully used to replace 10, 30 and 50 wt% of an industrial illitic clay in the production of bricks. The obtained raw ceramics were heat treated in an industrial brick kiln at 900 °C. The ceramics obtained, including those with the highest percentage of added cake, have good chemical and physical characteristics. All samples were characterized by X-ray powder diffraction, X-ray fluorescence, and scanning electron microscopy.

In the ceramic samples, alkaline feldspars appear to be zoned, showing a Na-rich core and a K-feldspar-like rim, resulting from the reaction between the original albite and the clay mineral breakdown products. Na-K substitution in feldspars can therefore be used as an indicator of the sintering process and allows to monitor the thermal effect induced by the biosolid. Results indicate a kinetic effect, suggesting that the cake locally allows the temperature to rise, triggering the substitution.

To ensure environmental safety, leaching tests indicated that the bricks are safe for construction use and do not pose a significant risk of groundwater contamination and do not introduce new environmental hazards, thereby supporting sustainable waste management.

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Thermophysical and mechanical performances of eco-friendly clay bricks from northeastern Morocco

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The buildings sector is one of the most energy-consuming. Therefore, eco-friendly construction materials emerge as an essential solution to reduce the environmental footprint of this sector.

This research aims to the valorisation of clayey samples from northeastern Morocco in ecological clay bricks by optimising firing conditions. For this purpose, clayey samples were characterized using different methods including X-Ray diffraction, X-ray fluorescence, grain size analysis, Atterberg limits, and Simultaneous Thermal Analysis. The raw samples were used to formulate bricks which were dried and fired using direct and stepped firing processes. Water absorption, density, thermal conductivity, ultrasonic pulse velocity, and mechanical strength were measured to assess the influence of the heat treatment on bricks.

The results indicate the presence of quartz, calcite, illite, and kaolinite in the raw materials. The clayey fraction is greater than 45% and the plasticity index ranges from 28 to 34%. The stepped firing process significantly improves mechanical strength of the fired bricks by 20% but it slightly influences the thermophysical properties.

The stepped firing treatment investigated enhances brick durability and contributes to reduce environmental impacts of building materials.

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Hydrothermal synthesis of zeopolymers from kaolin and construction wastes

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The adoption of Hydrothermal Treatment (HT) to promote simultaneous zeolitization/geopolymerization of components – including mixtures of clay and wastes – has emerged as a promising technology to produce innovative sustainable advanced materials [1,2], here called zeopolymers (zeolite/geopolymer composites). This study aimed to develop zeopolymers from mixtures of Construction and Demolition Waste (CDW) and kaolin. This process is based on the alkaline HT of spherical granules of Ø ~10 mm, previously fired at low temperatures (600 °C). Different mixtures of kaolin and CDW (0 - 100%) and NaOH solution concentrations (2, 4 and 6 M) were studied. The HT was carried out at 90°C for 24 h, adopting a liquid/solid (L/S) ratio of 8 mL/g. Before and after the HT, the granules were characterized, focusing on crushing strength, density, water absorption, as well as on mineralogical evolution through XRD-Rietveld.

HT led to reducing water absorption and increasing density. Despite this, the zeopolymerized aggregates were *lightweight*. Although a reduction in the mechanical strength was observed when adding CDW and decreasing NaOH concentration, all values were suitable, ranging from 1.88 ± 1.13 MPa to 5.44±1.33 MPa for formulations containing 100% CDW and 100% kaolin, respectively, which are in the same order or even higher than those of commercial lightweight aggregates [3]. Regarding the mineralogical changes produced after the HT, a decrease of the amorphous phase favoring the crystallization of zeolites was observed. The highest zeolite formation (~22% of zeolite A) was obtained for the mixture containing 37.9% CDW, using 4 M NaOH solution, showing benefits of incorporating CDW in the developed materials. This is could be a technological advantage, as zeolites present high adsorbent capacity, permitting the use of the produced materials as lightweight aggregates with decontaminating capacity. These results showed that it is possible to produce zeopolymers from clay and CDW, leading to energy and material savings, fostering the circular economy.

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Low T fired clays with dolomite addition: sustainability in ceramic industry

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In the last few decades, international policies have encouraged sustainable development and environmental protection in the industrial cycles [1,2]. Ceramic industry has been adopting innovative strategies to ensure eco-efficient processes [3], such as the production of quality ceramic products fired at low temperature [4]. In this line, the use of dolomite may entail a potential green-solution, as the firing at low temperature of dolomite-rich clays gives rise to a semi-hydraulic material able to harden [5].

Several technological properties of clayey pastes made out of kaolinitic-rich clays outcropped in the Region of Coimbra (Portugal) with the addition of the 5, 10 and 20% of micronized dolomite and fired at 750, 850 and 900 °C were assessed. Dolomite addition provided the improvement of the technological performance of the clay pastes, in that lower linear shrinkage and mass loss were recorded, reducing in turn the porosity and water absorption values and increasing the flexural strength of the testing probes. Two important issues should be highlighted: i) such better behaviour was achieved when adding the lesser quantities of dolomite, whereas the addition of 20% of dolomite yielded totally undesirable results, and ii) very similar results were attained in the testing probes fired at 850 and 900 °C.

Both issues suggest that dolomite addition may entail a sustainable and eco-friendly measure for ceramic industry, since a low quantity of dolomite improves the mechanical and hydric behaviour of kaolinite-based ceramic products fired at low temperatures (850 °C). The next steps should be the assessment of the technological performance of such kaolinitic-rich clays with dolomite addition and fired circa of 800 °C and by using other magnesia-rich compounds. Definitely, dolomite addition may provide green-solutions towards the design of eco-efficient materials in the ceramic industry, reducing CO_2 emissions and energy consumption.

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Behaviour of calcined and uncalcined Tunisian clay in the cold consolidation process by alkali activation

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Two illite-kaolinite clays from Zemlet El Beida deposit in the Gabes region, Tunisia, have been studied [1]. They differed in the position of the mineral beds and in the main principal minerals: one clay, BHG_2, is rich in hematite (12 wt% of Fe_2O_3) and the second, BHG_5, is rich in calcite (23wt% in CaO). In the first case, the illite/kaolinite ratio (by weight) was 61/39, while in the second clay it was 79/21.

In order to better exploit their plasticity (plastic index=20-22%; liquid limit= 45-48%) for the production of building materials, the two clays were cold consolidated at room temperature after mixing the as-received powders with NaOH solution [2]. The alkali activation was also tested on calcined clays fired at 550, 750 and 950 °C for 4 h, i.e. soon after the main thermal events of dehydroxylation of fillosilicates, loss of CO_2 from the carbonates and recombination of oxides, respectively. The overall reactivity of the clays was directly related to the total cation exchange capacity (CEC) and specific surface area of the unfired and calcined clays.

The formation of the aluminosilicate network was detected in the consolidated materials at each NaOH concentration (10, 12, and 14 mol/L) by the shift of the characteristic absorption band around 1020 cm^{-1} using the Fourier Transform Infrared (FTIR) spectroscopy.

Thermal activation at 750°C slightly increases the mechanical performance measured as compressive strength. At higher calcination temperatures, zeolite crystallisation occurs due to the low reactivity of the crystalline phases produced by the recombined oxides.

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Clay influence on compaction and strength of unfired sediment bricks

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Based on particle size, dredged sediments and natural soils generally consist of four main components: clay, silt, sand and gravel. In unfired earth materials, clay and silt provide binding properties, whereas sand and gravel act as fillers. A sufficient proportion of clay is necessary to achieve optimal material stiffness and strength [1]. Amounts of 10 to 22% and 5 to 15% are recommended for compressed earth blocks and rammed earth, respectively [2–4]. Depending on its nature and proportion, clay may offer several advantages or disadvantages concerning the physicochemical and geotechnical characteristics of raw sediment or soil, as well as the strength and durability of material. For instance, an adequate amount of clay and water contributes to the soil's plasticity and material's strength. Conversely, low or excessive clay content results in adverse effects, such as cracks, swelling, accelerated deterioration of earth materials due to excessive rain, reduced material tensile and compressive strengths, etc. The influence of clay on the engineering properties of unfired earth materials has been widely studied, but further research is needed due to the variability in clays and sediment characteristics. Combining low-clay soils with pure clays or clayey soils can enhance the plasticity (cohesion, moulding) and densification (compaction, kneading, pressing, etc.) of materials. In this context, sediment dredged from the River Seine in a town near Rouen was reused in unfired earth bricks production. Given its low clay content (less than 3%), the sediment was mixed with other locally available resource, such as excavated clayey soil, to improve its properties. This article presents key findings highlighting the effect of excavated clayey soil (ECS) on the compaction parameters, including optimum moisture content (OMC) and maximum dry density (MDD), as well as the strength of sediment bricks. In the mixtures, the dredged sediment was replaced with ECS at 10wt.% and 20wt.%, while the control sample made of 100wt.% sediment was used for comparison. The compaction test was carried out using the miniature Proctor on both sediment and ECS separately at various water contents, maintaining the same compaction energy of 600kN.m/m^3. The flexural and compressive strength tests were conducted on air-dried sediment bricks (cured for 3 weeks), with dimensions of 4×4×16cm^3 and 4×4×4cm^3, respectively, using a tabletop precision universal tester (Shimadzu, Autograph AGS-X series), at a loading rate of 0.5mm/min. Since clays have a high surface area, which creates intermolecular forces that attract water molecules, the excavated clayey soil needed less water to reach the MDD than the sediment. For ECS, the MDD of 1863kg/m^3 was reached at an OMC of 13%. In contrast, for the sediment, the MDD was 1470kg/m^3 and was achieved at an OMC of 22%. As expected, the addition of the sediment to the soil rich in clay enhanced the mechanical performance of the bricks. The sediment bricks containing 10wt.% and 20wt.% exhibited flexural strengths (R_f) of 0.95 and 0.99MPa, respectively, while the reference sediment bricks showed the R_f of 0.5MPa. Following the addition of ECS, the compressive strength of the reference sediment bricks (1.9MPa) substantially increased, reaching 3.29MPa and 3.43MPa for bricks with 10wt.% and 20wt.% excavated clayey soil, respectively. Based on these results, the combination of excavated clayey soil with the sediment from the River Seine was beneficial, as it improved the strength of unfired sediment bricks, while promoting sustainability in construction and the circular economy.

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Effect of prolonged curing of compressed lime-stabilized clays from the Far North Region of Cameroon on their physical, mechanical and mineralogical characteristics

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This study focuses on aims to make the long-term physico-mechanical and mineralogical characterization of lime-treated blocks of clay materials from the Far North of Cameroon. The formulated blocks were stabilized at 6, 8, 10 and 12% and cured at 21, 28, 100 and 365 days, prior to the determination of their physical, mechanical and mineralogical characteristics.

Apparent porosity, linear shrinkage and water absorption decrease with increasing stabilization rate and curing time. Compressive strengths gave values greater than 2 MPa at 28 days for all specimens, satisfying the requirements of the Cameroonian compressed earth blocs standards.

Compressive strength equally increases with increasing stabilization rate and curing time, reaching maximum values of 15.5 MPa (365 days cured 12% lime-stabilized sample SZ) and 19.9 MPa (365 days cured 12% lime-stabilized sample SDo) in their wet and dry states respectively.

Powder X-ray diffractograms reveal the occurrence of new mineral phases including calcite, vaterite, portlandite, thaumasite, stratlingite, ettringite, ankerite and tricalcium silicate. These results are confirmed by the Fourier Transform Infrared Analysis, with the appearance of new vibration bands 2929 and 2848 cm-1 related to C-H bonds and the vibration band around 1425 cm^{-1} characteristic of carbonate formation (calcite). These new mineral phases appeared from early curing periods, with no evolution due to prolonged curing.

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Sediments as renewable raw earth for producing unfired bricks and mortars

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The texture of fine sediments, whether from rivers, harbours, waterways or dam reservoirs, contains clays in varying quantities depending on the source from which they are extracted. These clays confer certain properties to sediments, such as plasticity and cohesion. Additionally, the clay minerals present and associated oxides can contribute to reactive or binding properties. This research focuses on the oxides present in fine sediments, with a view to proposing low-CO_2 blended cement formulations incorporating calcined sediments and other industrial by-products such as slags or ashes. Although the flash-calcination technique for dredged sediments is promising as it reduces the temperature required for calcination, it is still an energy-consuming process [1]. Consequently, cements mixed with flash-calcined dredged sediments cannot be fully considered as eco-friendly cements. The presence of clays in sediments gives them plasticity and even cohesion, depending on their water content. This plasticity allows for a certain workability, enabling them to be shaped. Sediment-based unfired earth bricks are therefore conceivable, as their suitability has been demonstrated in recent projects using dredged river sediments. Whether or not these sediments are suitable for the manufacturing of unfired earth bricks needs to be verified by means of reference charts covering plasticity and particle size distribution. Corrections can be achieved by incorporating additions of clay particles (lack of plasticity) or coarse elements (granular correction). These additives are mainly sourced from waste soils excavated from temporary deposits. Once shaped, these sediment-based bricks are air-dried, making them eco-friendly. These sediment-based bricks are designed to meet specific strength requirements, depending on the application: filling material, earthen bricks, earth walls. During the shaping process, green bricks can be pressed, compacted or kneaded, all of which densify them. However, the introduction of natural fibers provides shaped bricks with mechanical reinforcement, giving them a ductile behavior whose toughness indexes can be used to assess their improvement. Bricks reinforced with waste plant fibers are still eco-friendly, while increasing their mechanical strength and conferring hygroscopic and thermal properties. Raw sediments can also be used to produce sediment-based mortars. Depending on their composition, sediment-based mortars can partially replace the sand or hydraulic binder used in traditional mortars. According to the quality and quantity of clays contained, sediments can be reused directly as unbaked bricks or mortar reinforced with plant fibers. This is a renewable resource, considered as a waste product, which can be combined with other waste products, such as plant fibers, to produce an eco-friendly material. First, a methodology is presented for the production of unfired sediment-based bricks reinforced with waste fibers. Two case studies are reported using local materials: river sediments and short oil palm fibers (case 1, [2]) or flax tow fibers (case 2). The methodology includes material characterization (sediments and fibers), sediment suitability, definition of optimum moisture content, compaction of the sediment mixture, control of fiber distribution and orientation using digital imaging, and strength-optimized testing. Once brick production protocols have been defined, strength properties (flexural and compressive) are evaluated in order to optimize fiber content and length according to the standards. In both case studies, the strengths obtained are discussed regarding the different influences. A case study (case 3, [3]) on the production of a sediment-based mortar without fibers is also presented. The methodology followed is similar: sediment characterization, suitability tests, strength optimization according to sand and/or cement substitution.

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Reusing excavated Finnish clays in sustainable construction: A laboratory study on compressed earth blocks

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Large quantities of potentially reusable clay are generated as by-products from construction and civil engineering projects, often ending up in urban landfills. However, locally excavated clays have significant potential as valuable materials for construction, offering an opportunity to reduce waste and promote sustainability. Furthermore, clay masses already deposited in landfills could be repurposed for new products if their properties and suitability as raw materials are thoroughly understood. Finnish clays, rich in illite and chlorite minerals, are typically fine-grained with a high water content. Despite this, there is limited research on the effective utilization of excavated Finnish clays in construction. Expanding knowledge in this area could facilitate broader applications of clay, contributing to the transition toward a circular economy.

Compressed Earth Blocks (CEBs) are innovative and sustainable building materials made by compacting soil, particularly clay-rich earth, into dense blocks [1,2]. CEBs present an eco-friendly alternative to traditional building materials like bricks and concrete, utilizing locally sourced soil with minimal environmental impact. They also help reduce carbon emissions and energy consumption, as no firing process is required.

This study explores the potential of using excavated surplus clay, sand, crushed concrete, and fly ash to produce compressed blocks at a small scale in the laboratory. The properties of the clays, including oxide and mineral composition, water content, and Atterberg limits, were analyzed. The influence of compression pressure (17, 33, and 50 MPa) on the compressive strength of the samples after 7 and 14 days was assessed. Both natural wet clay (30-40% water content) and dried clay were tested. Wet clay limited the clay content to approximately 30 wt%, while dried clay allowed up to 70 wt% in the mix. The morphology of the compressed samples was examined using light microscopy and scanning electron microscopy (SEM).

The compression pressure applied during sample preparation significantly influenced compressive strength. In clay/ash mixtures, increasing the pressure from 17 to 50 MPa enhanced strength from 10 to 25 MPa. In contrast, hand-rammed samples exhibited a much lower compressive strength of approximately 4 MPa. Samples made from wet and dry clay with crushed concrete showed similar strength at equal moisture content. However, fine fly ash was unevenly distributed in the wet clay, leading to lower strength than in dry clay. The impact of the clay content on strength was low. These findings provide valuable insights into the incorporation of higher clay content in compressed earth blocks and will be further validated through large-scale applications.

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Improvement of characteristics of subbase layer materials in rigid pavement using natural aggregate and cement

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Clayey materials of the Sudano-Sahelian zone of Cameroon are generally of swelling nature and their geotechnical properties are limited by their low bearing capacity when they are used as road infrastructure platforms. This study examines the contribution of untreated gravelly materials (GNT 0/31.5) and cement in improving the bearing capacity of materials on a section of existing road on which the roller compacted concrete (RCC) will rest. After description, eleven pits approximately 1.20 m deep showed that the subbase course of approximately 25 cm is made up of clayey sand and reddish to yellowish sandy clays. Identification (particle size analysis, plastic limit), mechanical (modified Proctor, CBR) and deformation (deflection, plate) tests were carried out according to NF P standards. The 30% mixture of GNT was carried out without the addition of cement, and subsequently six experiments were developed with 20% and 25% GNT, with a cement variation of 2, 2.5 and 3%. Structural damage to the pavement was recorded with an average deflexion strain of 38.4 mm and 1.1 mm by plate test. Materials from the subbase course contain on average 24% fine particles (< 80µm) with an average plasticity index of 15%. The average maximum dry density is 2.14 g/cm^3, with an average swelling of 0.03% and an average CBR index of 27%, i.e. below the recommended value (35%). The addition of 30% GNT cancels out the swelling, improves the bearing capacity from 27 to 100% and reduces the fine particle contents and plasticity to 20.7% and 5%, respectively. The addition of cement further enhances the geotechnical properties of the studied clay materials. With 20% GNT, the CBR bearing capacity increases to 260, 330 and 435 with 2, 2.5 and 3% cement, respectively. At 25% GNT, it is 320, 340 and 360% at 2, 2.5 and 3% cement. Adding 30% of aggregate is an environmental benefit to be encouraged in improving the poor bearing capacity of clay soils. The choice to stabilize with a low rate of cement (2 to 3%) will depend on economic choice and durability.

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Recycling marble waste clay powder for cement mixes

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The manufacturing of building materials is associated with a high carbon footprint and results in the emission of greenhouse gases that contribute substantially to climate change. The production of mortars also has environmental impacts as it involves the extraction of virgin raw material, the use of cement as a binder, and significant water consumption. Therefore, reducing or replacing sand and cement would make it possible to limit the pollution associated with the production of cement mixes, steering toward sustainable materials with similar performance. Following these key principles, and in accordance with the requirements of the 2030 Agenda [1], the use of waste materials could be considered, in a circular economy system, to reduce the environmental cost of transporting secondary raw materials while maximizing the potential benefits. The present research investigated the mechanical strengths of mortars, at 28 and 240 days, made by replacing sand and cement with waste materials from two important productive areas in Apulia, the limestone processing [2] and the olive-oil field. Several conglomerates were made by partially or fully replacing sand with pitting, an agricoltural bioproduct, and partially replacing cement with limestone or marble saw powder, known as marmettola [3]. Pitting is the main waste material from olive oil production, obtained by separating olive pits from olive pomace. Marmettola is a material that can be assimilated, granulometrically, to clay with a behavior close to that of a binder. Mechanical strength data for 28 days show that as the amount of waste materials increases, flexural and compressive strengths progressively decrease. In the former case, they decrease with percentages that are around 100% if only part of the aggregate is replaced and with percentages of around 200% if even part of the binder is replaced by the marmettola. Regarding compressive strengths, partially substituting only the aggregate, results in a decrease in values of about 100%; if the marmettola is also used, the strengths decrease by about 160%. Even after 240 days, the mechanical strengths show a similar trend, observing their decrease as the content of pitting and/or marmettola increases, respectively. The flexural strength is reduced by about 80% if only the aggregate is replaced by the pitting and by 220% if also part of the cement is replaced by a clay material such as marmettola. Contextually, compressive strength is reduced by about 130%, both when only the aggregate is replaced by the pitting and if also part of the binder is replaced by the marmettola. A comparison of mortars with the same content of pitting and different amounts of marmettola (0 g in the former case and 100 g in the latter) exhibits lower mechanical strengths at 28 days if the latter is added. For mortars with a pitting content of 100 g, the difference between the flexural strength values is 5%, in contrast, for mortars with 350 g of pitting replacing the same aggregate content, the difference is about 65%. Similarly, compressive strength highlights a difference between values of 40% for mortars with the addition 100 g of pitting and about 80% for mixes with 350 g of pitting. Concerning mechanical strengths for 240 days, it is found that, for the same mixes, flexural strength increases by 8% in mortars in which 100 g of cement is substituted for the same amount of marmettola and decreases by approximately 65% if the mortars are made with 350 g of pitting and 100 g of sand. Compressive resistance always exhibits a decrease in values of about 45% by substituting 100 g of marmettola for the binder, regardless of the content of pitting in the mortars. Therefore, the study revealed that replacing part or all of the aggregate with pitting and even part of the binder with marmettola significantly influences the mechanical performance of the mortars, both at 28 days and at 240 days. However, in general, the strengths are such that these innovative and sustainable mixes cannot be considered compatible with structural applications.

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Durability and Resilience of Geopolymers Incorporating Iron Mine Tailings

Santos A.[1], Pinho T.[1], Andrejkovičová S.[1], Rocha F.[1], Almeida F. [1]

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In recent years, there has been an increase of research on the properties of geopolymers, with metakaolin commonly used as the primary precursor [1]. Research have demonstrated that this material produces building materials with favourable properties. However, metakaolin is expensive and a finite resource. Therefore, it is crucial to identify alternative precursors that can partially or fully replace kaolin without compromising the final properties while also being by-products that contribute to sustainability. A key requirement for these alternative precursors is a high silica and alumina content, and one potential source is mine tailings. The exploitation of mining tailings can improve waste management, prevent environmental pollution and have the potential to increase economic viability.

In addition to energy efficiency and sustainability in the production of materials without sacrificing properties, durability remains a key factor influencing the continued use of conventional building materials [2]. As a result, research on the durability of geopolymers remains an open and evolving field. Recently, the incorporation of recycled materials and industrial by-products as precursors in the development of high-value geopolymers has gained increasing attention, particularly to enhance resistance to freeze-thaw cycles and chemical attacks.

This study investigates the mechanical properties and durability of geopolymers based on metakaolin with the incorporation of tailings. The objective was to evaluate the effects of introducing six different types of mine tailings in varying proportions to develop more sustainable geopolymers by reducing metakaolin consumption. Kaolin sourced from São Vicente da Pereira was calcined at 700°C for four hours to obtain an amorphous, more reactive clay. The mine tailings were collected from three different mining in Portugal, to enable an assessment of the potential of various iron mine tailings as alternative precursors. To evaluate the durability and resilience of geopolymers containing mine tailings, six different tests were conducted: freeze-thaw cycles, water immersion, seawater immersion, exposure to hydrochloric acid (5%), exposure to sodium sulphide (3%), and an accelerated aging chamber test. The variations in compressive strength (CS) before and after each test were analysed [3].

The results for geopolymers incorporating iron mine tailings indicated that, prior to testing, the CS ranged between 29 and 40 MPa. Among the durability tests conducted, immersion in sodium sulfide resulted in the smallest reduction in CS, ranging from 1.5% to 19%. This minimal decrease can be attributed to the solution's pH, which is close to 12, aligning with the natural alkalinity of geopolymers. Conversely, the freeze-thaw cycles test led to a significantly reduction in CS, varying from 10% to 27%. Additionally, certain formulations were unable to endure the full cycle of freeze-thaw exposure, resulting in fracture and rendering them unsuitable for subsequent CS testing. The formulations that obtained the lowest reduction in most of the tests were the geopolymers with the tailings from the Moncorvo Mine, which is composed of 65% hematite and 32% quartz. This research was supported by GeoBioTec (UIDB/04035), FCT scholarship (UI/BD/152214/2021) associated with DOI:10.54499/UI/BD/152214/2021 and research scholarship (80/2024/BI/AgendasPRR).

[1] Bumanis et al. (2022) Minerals, vol. 12, no. 9, pp. 1–12.
[2] Min et al. (2022) *Case Stud. Constr. Mater.*, vol. 17.
[3] Zhang et al. (2022) *Constr. Build. Mater.*, vol. 318, p. 126052.

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LECTURE THEATRE 3

Panel-led discussion: Questions concerning clay minerals in radioactive waste disposal

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LECTURE THEATRE 4 – SESSION 14

Materials via Ordered Interstratifications

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Colloidal system of dye-sandwiching clay bilayers: liquid crystallinity and photonic applications

Nakato, T.[1*], Watanabe, T.[1], Mouri, E.[1], Harada, T.[2], Shintaku M.[2], Suzuki, Y.[2], Kawamata, J.[2], Miyata, H.[3], Yamauchi, Y.[3], and Breu, J.[4]

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Colloidal clay nanosheets obtained by delamination layered crystals of smectite-type clay minerals in water form liquid crystals because of their shape anisotropy. Loading of organic dyes onto the liquid crystalline clay nanosheets will enable novel photonic materials where photofunctions of the loaded dye are controlled by the liquid crystallinity of the clay nanosheets. However, adsorption of organic dyes onto the nanosheets renders the nanosheet surfaces hydrophobic and consequently colloidal stability of the nanosheets is lost. This drawback was overcome by sandwiching the guest organic dye molecules between two clay nanosheet, which enables retention of the hydrophilicity of the clay surfaces exposed to the solution [1]. Employment of the second-stage intercalation compound incorporating the guest molecules in every other interlayer space enables the formation of bilayer-type clay nanosheets sandwiching dye molecules between a pair of the clay silicate layers upon delamination in water.

We prepared the bilayer-type clay nanosheets of synthetic fluorohectorite clay (FHT) sandwiching cationic stilbazolium dye (St^+). The dye-sandwiching clay nanosheets formed stable aqueous colloids, which showed colloidal liquid crystallinity. The liquid crystalline clay nanosheets responded to an applied AC electric field to be aligned parallel to the electric field. Assembled structure of the dye-sandwiching clay nanosheets under the electric field was characterized by aligned discrete clay platelets. The electric alignment of the clay nanosheets induced alteration of light absorption of the sandwiched St^+ molecules, which verifies a strategy of constructing stimuli-responsive photonic materials of clay–organic hybrids, as illustrated in Figure 1 [2].

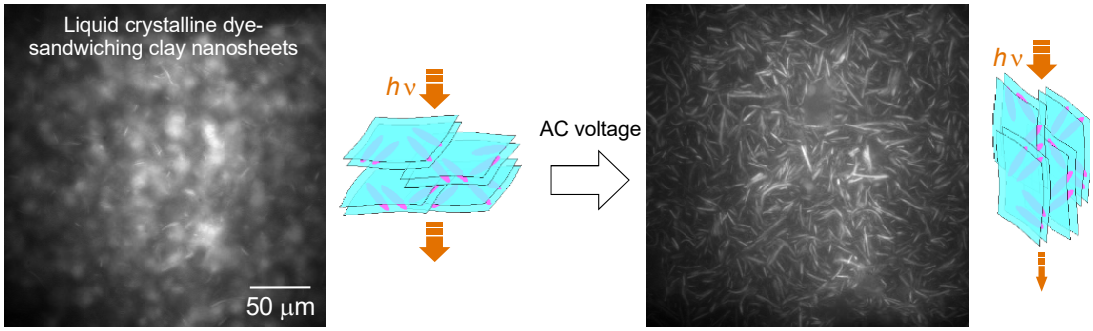

Figure 1. Fluorescence optical microscope images and schematic representation of the liquid crystalline sandwich-type clay-dye hybrid before and after the electric alignment.

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The Multiple Ways to Break Symmetry during Partial Ion Exchange for Making Ordered Interstratifications

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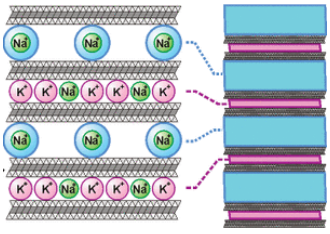
Ordered mixed-layer materials with strictly alternating interlayers of hydrated and collapsed interlayers (R1, $\omega_{hyd} = \omega_{col}$) are known for a long time as the natural mineral Rectorite. Rectorite shows a regularly interstratified sequence of illite- and smectite-like layers.[1] It is generally accepted that the regular alteration of hydrated and nonhydrated interlayers coincides with alternating pronouncedly different densities of interlayer cations. This interlayer ion variation in turn is thought to be the consequence of an ordered stacking of polar lamellae. Each 2:1 layer in the stack is identical and contains an aluminum-rich and an aluminum-poor tetrahedral sheet.

With the emergence of melt-synthesized hectorites, first introduced by Corning, the number of reports of ordered interstratifications suddenly increased substantially.[2] As hectorites resemble symmetric 2:1 layers, it became clear that the reason for the alternating densities of interlayer cations cannot be a polar structure.



Rather than polar silicate layers, a uniform charge density as found with melt-synthesized smectites or selected natural vermiculites is key. With these upon partial ion exchange an ordered redistribution of differently sized interlayer cations leads to ordered structures. Multiple ways driving this break of symmetry along the stacking direction exist: Bulky organocations with equivalent areas smaller than the charge density of the clay, condensation of highly charged hydroxy islands, variations of solvation energies and/or substantially different selectivity of incoming cations for the interlayer.

Ordered interstratifications are only known for graphite intercalation compounds and for 2:1 layered silicates while offering a huge potential for appealing materials properties. Nanoparticles [3] or hydrophobic dyes [4] may be encapsulated between a silicate sandwich. They may be converted to Janus-platelets [5] or to ferronematic [6] or structurally coloured [7] suspensions.

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[2] Ijdo, W. L., Lee, T., Pinnavaia, T. J. Adv. Mater. 1996, 8, 79.
[3] Loch, P.; Hunvik, K. W. B.; Puchtler, F.; Weiß, S.; Seljelid, K. K.; Røren, P. M.; Rudic, S.; Raaen, S.; Knudsen, K. D.; Bordallo, H. N.; Fossum, J. O.; Breu, J. Spontaneous formation of an ordered interstratification upon Ni-exchange of Na-fluorohectorite. Appl. Clay Sci. 2020, 198, 105831.
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[6] C. F. Dai, O. Khoruzhenko, C. Zhang, Q. L. Zhu, D. Jiao, M. Du, J. Breu, P. Zhao, Q. Zheng, Z. L. Wu, Angew. Chem. Int. Ed. 2022, 61, e202207272.
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Orderly Interstratified Layered Ruthenic Acid as a Precursor of Ruthenium Oxide Nanosheets with Double-Layer Structure

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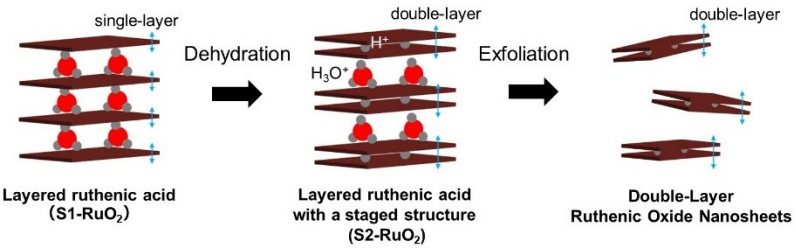
As a novel strategy for synthesizing inorganic nanosheets, the utilization of a phenomenon where the interlayer environment of layered compounds changes periodically to form superlattice structure, known as ordered interstratification or staging, is attracting considerable interest. Owing to the periodic stacking of two types of interlayers with different reactivities, the layered compound with a staged structure will exhibit site-selective intercalation. In other words, such staged layered compounds can serve as precursors of unique nanosheets with multi-layer structure through chemical exfoliation process. Using this approach, nanosheets with double-layer structure have been synthesized from certain types of clay [1], layered double hydroxides [2], and graphite [3]. To synthesize multilayer nanosheets from various layered transition metal oxides with attractive functionalities, a method for preparing staged layered metal oxides needs to be developed. We previously reported that the dehydration of layered ruthenic acid, derived from layered potassium ruthenate, proceeds layer by layer, resulting in the formation of a stage 2 phase (S2-RuO_2) with alternating hydrous and anhydrous interlayers [4]. In this study, we evaluated the dehydration behaviour of layered ruthenic acid and the ion-exchange reactivity of S2-RuO_2 to demonstrate the feasibility of preparing double-layer nanosheets using S2-RuO_2 as a precursor (Scheme 1).



Scheme 1. Schematic illustration of the formation of layered ruthenic acid with a stage 2 structure and the utilization as a precursor of nanosheets with double-layer structure.

The dehydration behavior of fully hydrated layered ruthenic acid (S1-RuO_2) under constant temperature and humidity was evaluated by XRD. The basal spacings of S1-RuO_2 and fully dehydrated layered ruthenic acid are d = 0.789 nm and d = 0.456 nm, respectively. Upon gradual dehydration, a new diffraction peak appeared at d = 1.24 nm along with its high-order diffractions, indicating the formation of S2-RuO_2 [4]. The phase composition was dependent on humidity; high humidity favored the formation of S1 and S2 phases, while low humidity promoted complete dehydration. These results suggest a stepwise equilibrium process from S1 to S2 to fully dehydrated RuO_2. To exfoliate S2-RuO_2, cetyltrimethylammonium (CTA^+) was intercalated selectively into the hydrous interlayers, forming an intercalation compound with an expanded basal spacing of d = 2.72 nm. Dispersion of this compound in organic solvent yielded nanosheets with a bimodal thickness distribution at 0.8–0.9 nm and 1.3–1.4 nm. Given that crystallographic thickness of single-layer ruthenic oxide nanosheets is approximately 0.5 nm, these values correspond to single- and double-layer nanosheets, respectively. Both types were obtained in comparable yields. These results demonstrate that periodic modulation of interlayer hydration is a promising strategy for the synthesis of double-layer nanosheets.

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Bright, Non-Iridescent Structural Colors from delaminated Ordered Interstratified Clay Nanosheets

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[2]University of Bayreuth, Germany

Recent advances in clay mineral colloids reveal a straightforward route to bright, non-iridescent structural colors using double-layered (DBL) nanosheets. The key lies in ordered interstratification: By partially exchanging the interlayer cations (e.g., Na^+, replaced e.g. with Cs^+ or NH_4^+), each pair of clay sheets forms a stable 2-nm DBL instead of a single 1-nm sheet. This thicker lamellar unit provides greater refractive index contrast, producing significantly brighter structural colors compared to single-layer systems.

In aqueous suspensions, these DBLs undergo repulsive osmotic swelling, spontaneously forming a nematic phase. The container geometry (e.g. flat cuvettes or cylindrical capillaries) imposes subtle confinement, creating domains of co-planar nanosheets that reflect specific visible wavelengths. By adjusting clay concentration (or ionic strength), one can fine-tune the interlayer spacing and thus the reflected color. Notably, the inherent partial disorder in these nematic stacks (from slight nanosheet wrinkling, turbostratic shifts and/or orientational distribution of nematic domains) naturally suppresses iridescence—ensuring the color is angle-independent.

While these photonic dispersions remain stable in water, embedding the DBLs into hydrogel or maybe biopolymer matrices represent a logical next step to produce fixed pigments for industrial applications. Such fixation would preserve the tuned interlayer spacings, enabling scalable fabrication of non-toxic, non-bleaching colorants for coatings, packaging, or cosmetic formulations. This simple yet powerful approach exemplifies how ordered interstratification in clays—combined with clever container confinement—can underpin a new generation of sustainable structural colors.

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LECTURE THEATRE 4 – SESSION 24
Greenhouse Gas Remediation

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Functionalized Smectites for CH_4-CO_2 Gas Separation in Biogas Upgrading

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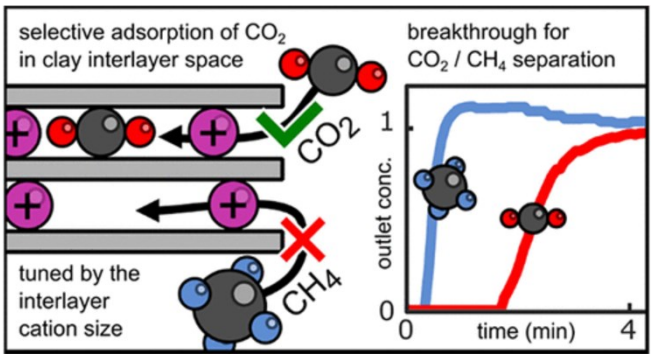
Layered swelling clay minerals such as montmorillonite and bentonite have large internal surfaces where substantial amounts of gas can adsorb provided that the gas molecules can access the confined space of the interlayer galleries. The width of this space can be tuned by exchanging the cations in the galleries that compensate the negative charge of the aluminosilicate layers. We show that the sorption capacity for CO_2 at near-ambient pressure can be increased by more than an order of magnitude upon exchanging the natural Na^+ cations by bulkier Cs^+ or by hydrated Ca^{2+} and Mg^{2+} ions [1]. All these three cations also lead to a selectivity of approx. 30 for CO_2 vs. CH_4 sorption thus enabling efficient separation of these two gases in a pressure/vacuum swing adsorption (PSA) process (see [2] and figure below). Competitive adsorption of water with CO_2 and the relevance of keeping Ca^{2+} and Mg^{2+} ions hydrated highlights the relevance of controlling the humidity of the input gas in practical applications such as biogas upgrading [3].

A numerical analysis of the PSA process allows to trace the evolution of the CO_2 and CH_4 concentrations within the reactor with time and suggests that CH_4 and CO_2 recovery and purity better than 95% can be achieved in a continuous operation mode with two sorption columns in parallel in a single adsorption stage at an energy consumption of approximately 0.1 kWh/Nm^3 of biomethane [4]. Higher purity levels can be achieved with two (or more) consecutive sorption stages. This makes our material an attractive alternative to currently dominant membrane-based separation technology for biogas separation from anaerobic digestion processes of various forms of biological waste.



Left: Sketch of smectite layers with cations of suitable size to permit CO_2 adsorption in clay galleries and prevent CH_4 adsorption. Right: measured breakthrough curves of a 50-50 CO_2-CH_4 mixture through a montmorillonite-filled sorption column.

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[2] Mendel N. et al. (2023) Ind Eng Chem Res 62:17883-17892
[3] Mendel N. et al. (2025) J Phys Chem C 129:6953-6966
[4] Mendel N. et al. (2025) Ind Eng Chem Res (accepted for publication)

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Hybrid mineral composites obtained by heterocoagulation, as effective nanomaterials for CO_2 capture

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Due to the concepts of Green Chemistry, efforts should be made to use renewable raw materials and carry out catalytic processes to reduce the level of greenhouse gas emissions to the atmosphere and even more to convert CO_2 into more desirable products in industrial and environmental applications.

This project aims to develop innovative hybrid mineral composites (anionic-cationic mineral brushes) with a basic character, active in the capture of CO_2 from flue gases. In this project, we focused on the preparation and modification of hydrotalcite precursors, their derivatives obtained by thermal treatment, and hybrid, anionic-cationic mineral brushes generated on a phyllosilicate matrix – smectite, acting as a structure-forming platform. Our research focused on a detailed analysis of the structural modification of the mineral composites and its effect on the development of enhanced CO_2 sorption capacity.

First of all, a series of anionic layered double hydroxides (LDH), with a hydrotalcite structure $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][An^{-}]_{x/n}\cdot mH_2O$, differ in Mg/Al compositions, ageing time, degree of crystallinity and grain size, controlled by the synthesis conditions, were obtained and characterised using XRD, FTIR, SEM/EDS, and N_2 adsorption/desorption methods for structural-sorption correlation. The results obtained provided the basis for the synthesis of anionic-cationic mineral hybrids. The in-situ spectroscopic methods with the CO_2 probe molecule were used to gauge the quality and quantity of the generated basic centre. The obtained results were comparatively investigated to estimate the temperature range, strength, and stability of those centres with the Temperature-Programmed CO_2 Desorption method (TPD-CO_2). The influence of the synthesis parameters on the nature of the generated basic centres, their strength, CO_2 adsorption/desorption process kinetics and sorption capacity was investigated.

The synthesised precursors had a crystalline structure characteristic of hydrotalcite with R3m rhombohedral symmetry and crystallite sizes of 10, 20 and 30 nm, dependent on the crystallisation time. The crystallites of the resulting MgO oxide were in the range of 3-6 nm. FTIR spectroscopic studies of the anionic hydrotalcite-like precursors and their mixed oxides exhibited that CO_2 reacts with the O^{2-} and OH^- to form carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. Carbonates and bicarbonates are already formed at low CO_2 vapour pressure, and there is no preference as to which O^{2-} or OH^- basic centres react with CO_2 first. Increasing the ageing time of LDH precursors affected their crystallinity and dense packing in the grain, consequently reducing the availability of the generated basic centres and the number of OH- groups. Calcination increases the basicity of hydrotalcite; the O^{2-} centres have a higher strength than the OH^- groups. Calcined samples, derived mixed oxides, form more carbonates than their precursors due to the greater number of available O^{2-} centres. LDH synthesis with the use of the 'high surface area method' resulted in a 30 % increase in BET and a doubling of basic centres.

Increasing the Al content in the octahedral layer of the Mg/Al-LDH structure resulted in an increase in the concentration of the basic centres O^{2-} and OH^-. Consequently, the highest sorption values of CO_2 molecules on the surface of the resulting oxide sorbents were exhibited by MgAl-2:1 material.

Acknowledgements: Research funded by the Development Project of the ICSC PAS No. 2/PR-MZ/2024

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A permselective membrane for size-sieving based H_2/CO_2 separation

Lukas Federer[1], Ingmar Pietsch[1], Felix Uhlig[1], Max Stevenson[1], Daniel Friedrich[1], Josef Breu[1]

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Hydrogen (H_2) plays a central role in the green deal of the European Union.[1] The total annual demand for H_2 was estimated at ~90 million tons in 2022 and is still rising.[2] The only way to produce clean (green) H_2 is electrolysis.[3] However, the majority of H_2 comes from sources that require a separation step. The largest proportion of world's H_2 is still produced from fossil fuels.[4] Besides the chemically produced H_2, also biomass derived H_2[5] and geological H_2 resources[6] are affected by this need of purification. The most common commercial processes used for H_2 purification are pressure swing adsorption and fractional distillation. A major drawback of these processes is the high operation costs due to high energy consumption. Another issue is the lack of purity of H_2.[7] A majority of applications require a H_2 purity of at least 99.99%, so it is difficult or even impossible to use the so obtained gas in certain H_2 economy applications.[8] Continuous separation processes via permselective membranes are significantly more energy-efficient.[4,7] Membranes that are permeable for H_2 but impermeable for larger relevant gas molecules like CO_2, CH_4, CO and N_2 are needed. We fabricated a clay-based permselective membrane for efficient H_2 purification by tailoring the interlayer gallery height of the silicate enabling size-sieving based separation of H_2.[9] 1D dissolution of sodium fluorohectorite yields an aqueous nematic suspension of monolayer nanosheets[10] enabling simple membrane fabrication by spray coating. These nanosheets show a uniform thickness of 1 nm and remarkable aspect ratio[11], thus self-assembling into defect-free films when spray-coated onto porous substrates. Monodomain Bragg stacks with uniform interlayer spacings are obtained by perfectly textured restacking of individual nanosheets.[9] Monolayers seem to be crucial for fabrication of perfectly ordered membranes, as different preparation methods published (e. g. vacuum suction or *in-situ* growth) did not result in perfect ordering.[12] Subsequent ion exchange of the interlayer cations, $[Na(H_2O)]^+$, with less hydrophilic and thus non-hydrated guanidinium cations, leads to collapsing of the interlayer gallery to a uniform height of 2.9 Å. Thus, the gallery height matches the kinetic diameter of H_2 and is significantly smaller compared to other relevant gas species, for instance CO_2. Using a Wicke-Kallenbach cell, we observed a near-perfect size-sieving based separation of H_2 and CO_2 (4:1 ratio), mimicking a typical feedstock found with steam reforming of methane, at ambient conditions. The H_2 permeance through the obtained tortuous path in our membrane was reduced to 3 GPU (1 GPU = 10^{-6} cm^3 cm^{-2} s^{-1} $cmHg^{-1}$).[9] We are confident that the H_2 permeance may be improved in future work by optimizing the thickness of the membrane, aspect ratio of the clay nanosheets and roughness of the substrate.

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Natural kaolin minerals with varying iron contents reduced cattle's enteric methane generation

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Background: Methane (CH_4) is a potent greenhouse gas (GHG), and its largest emission (~77%) comes from the enteric fermentation of ruminant animals (e.g., cattle, sheep). It occurs as animals burp while grass and other feedstuffs undergo fermentation in the rumen, the first digestive compartment, Beauchemin [1]. Reducing this CH_4 emission is crucial for GHG mitigation and minimising input gross energy loss caused by carbon and hydrogen loss. Technologies, including chemical additives or vaccination, face challenges such as toxicity and unfavourable on-farm adaptation, Beauchemin [1]. Natural kaolin clay, a low-cost and biocompatible feed additive, offers a promising alternative. This is because of its assemblage of platy kaolinite and hollow tubular halloysite structure, antimicrobial properties, and its legacy in predominant natural consumption by grazing animals, a practice called 'Geophagy'. Additionally, iron (Fe), a common kaolin impurity, involves a purification cost for specific applications. Interestingly, structural iron in the kaolin may provide two key benefits in animal feed: (1) by addressing nutrient/iron deficiency, and (2) suppressing methanogenesis by influencing electron transfer to consume hydrogen, a raw material for CH_4 generation. Therefore, valorising naturally deposited kaolin clays (without purification) for livestock CH4 mitigation, and improving animal husbandry is a promising approach, but not well studied, which is the motivation for this research.

Methods: Two raw kaolin clays, iron-poor (Kao) and iron-rich (KaoFe), were collected from the Cloud Nine deposit, Western Australia, and underwent detailed characterisation. Viable, debris-free rumen fluid (RF) from grass-fed cows was collected using standard methodology, Fortina [2], with animal ethics approval. RF was diluted (1:3) with McDougall's buffer and mixed with 2 g dry matter (DM) (1 g forage, 1 g grain) containing 5% kaolin clays, and ran an *in vitro* animal model, ANKOM [3]. *In vitro* digestibility (IVD), and different biochemical parameters were also assessed after this fermentation.

Results and discussion: Minerals characterisation showed that Kao contains approximately 76% kaolinite and 20% halloysite, while KaoFe holds 69% kaolinite and 27% halloysite. Additionally, 3.75% Fe oxides (predominantly Fe^{2+}, approximately twice the amount of Fe^{3+}), 3.59% K_2O, and traces of mica/illite were also found in KaoFe. Regardless of the CH_4 generation by basal diet matter, only 5% inclusion of clays showed 23% and 37% less CH_4 emission than the similar experimental conditions in the control group without adding clays. The IVD, co-efficient of fermentation efficiency (CFE), crude protein (CP), and ammonia nitrogen (NH_3-N) generation showed no significant differences between clay-treated and control groups, which indicates the clay's non-toxic nature in the rumen. Strong correlation among numerous biochemical parameters in different treatment groups suggests that clay inclusion in the basal diet increased hydrogen sinkers (consumers), such as propionic acid and methanogen inhibitory ions, such as Al^{3+}, Si^{4+}, Fe^{2+}/Fe^{3+}, and K^{+}. And the inclusion of KaoFe sample contributed to more of these, resulting in a strong relationship with the decreased CH_4 generation.

Conclusion: This study highlights the potential of natural kaolin clays to reduce CH_4 emissions from cattle burps without affecting gut compatibility or digestibility, with a particular focus on the role of iron impurities in lowering enteric methane. This offers a promising strategy for valorisation of natural clay for GHG mitigation and sustainable livestock farming.

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LECTURE THEATRE 5 – SESSIONS 8+9

Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential

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Experimental Investigation of Li^+ Adsorption by Chlorite

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Lithium (Li) is a critical metal element widely used in new energy, new materials, the defense industry, and many other high-tech fields[1]. With the rapid development of lithium-ion batteries in electric vehicles and energy storage systems, the consumption of Li is growing exponentially[2]. Clay-type Li deposits, characterized by their wide distribution, large reserves, and low mining costs, have emerged as a significant potential source of Li resources[3]. Chlorite is a primary host mineral for Li in clay-type Li deposits[4], but the Li sequestration mechanism by chlorite remains unclear. This study investigated the adsorption of Li^+ by chlorite through batch adsorption experiments and spectroscopic methods. The effect of chlorite chemical composition, adsorption time, pH, and ionic strength on the adsorption process was examined. The adsorption mechanism was studied by X-ray photoelectron spectroscopy (XPS), solid-state nuclear magnetic resonance (NMR), and thermogravimetric-differential scanning calorimetry (TG-DSC).

The results indicated that the adsorption of Li^+ by chlorite samples reached equilibrium within 48 hours. High-iron chlorite (14.74 wt.% Fe_2O_3) exhibited higher Li^+ adsorption amounts compared to the low-iron sample (1.55 wt.% Fe_2O_3), probably due to the larger CEC value of the high-iron chlorite. The adsorption of Li^+ by chlorite is pH dependent, and the pH edges included two distinct parts: slow increase of Li^+ adsorption below pH ~9.0, and sharp increase of Li^+ adsorption above pH ~9.0. Higher ionic strength promoted the adsorption of Li^+. Acid-base titration experiments revealed a point of zero charge (PZC) of ~9 for the chlorite. Therefore, at pH < 9, chlorite carried positive charges, generating electrostatic repulsion against Li^+. Increased ionic strength weakened this repulsion due to the shielding of Coulombic forces, facilitating Li^+ adsorption. After the adsorption of Li^+, the dehydroxylation temperature of the brucite-like layers in chlorite decreased significantly, and the binding energy of the Mg 1s XPS peak declined most obviously compared with that of other elements such as Al, Si, and Fe. The ^{7}Li-NMR spectrum of the adsorbed samples (with an initial Li^+ concentration of 2000 mg/L) displayed a chemical shift of −0.72 ppm, indicative of six-coordinated Li[5]. These findings suggested that Li^+ may be incorporated into the structure of chlorite, by replacing Mg in the brucite-like layer. This study provided experimental insights into the sequestration mechanisms of Li by chlorite and offered a scientific foundation for the mineralization of clay-type Li deposits.

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Distribution, mineralogy, and formation environment of lithium- rich clays in the Salar de Pastos Grandes

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By 2050, the projected growth in Li-battery manufacturing is expected to require an annual Li production that is twelve times the current rate, involving extraction of over 25% of the world's known Li reserves [1]. Closed-basin brines are becoming an increasingly important Li resource, favored for their relatively lower cost and reduced environmental impact compared to traditional hard-rock mining [2]. Located in the Central Andes of South America, the so-called "Lithium Triangle" contains the majority of these brine-hosted Li deposits, accounting for over half of the world's known Li reserves [3,4]. Accurate assessments of the Li reserves, accumulation timescales, and resource lifespans require a detailed understanding of the processes governing Li accumulation. Although there is broad consensus regarding felsic volcanics as a source of Li to these basins, the intrabasinal processes that influence modern Li distribution and concentration remain poorly understood [5,6]. Clay-brine interactions represent one such key process, given that Li-rich clays are found in volcano-sedimentary basins worldwide and act as secondary Li sources to brine systems [7,8]. Although Li-enriched siliciclastic sediments have been recorded in Lithium Triangle brine resources, studies characterizing the clay assemblages and clay-Li associations are extremely limited in this region.

This study focuses on the geochemical characterization of the sedimentary infill of the Salar de Pastos Grandes, Argentina. We specifically focus on defining the spatiotemporal variations in the Li-rich clay mineral assemblage. Samples were collected from industry sediment cores and Miocene-Pleistocene lacustrine sediments that crop out at the basin margin. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to determine the bulk and clay mineralogy and morphology of a suite of claystones, mudstones and interbedded Li-rich ashes. Elemental geochemistry, including lithium concentrations, of the clays are used to investigate the timing and formation conditions of clay formation and lithium enrichment. Preliminary data shows remarkably high lithium concentrations (~2000 ppm) in clay and ash rich lacustrine units beneath the main brine aquifer—the highest lithium concentrations recorded in basin fill sediments in Lithium Triangle to date. The clay mineral assemblage is dominated by a varied assemblage of illite and smectites that are intercalated in the mudstones, but do not appear interlayered. Preliminary geochemical data demonstrates a correlation between Mg and Li that supports a lithium enrichment in the smectite component of the clay component while SEM analysis supports a detrital origin of illite. Further results from ongoing mineralogical and geochemical analyses will be presented.

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Utilizing stable isotopes to identify the formation processes responsible for lithium enrichment in clay deposits of the Western United States

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Lithium (Li) bearing claystones are increasingly attractive exploration targets for diversifying critical mineral supply chains for green energy technologies. Diverse mineralogies and ore grades within and between clay deposits is important for the identification of optimal processing technologies and warrants further research to understand the underlying mechanisms controlling the distribution of Li within these deposits [1]. We summarize the occurrence and distribution of Li within the recently discovered Li-bearing mudstones of Barstow, California, USA, and place the deposit into the context of other known volcano-sedimentary Li deposits [1,2]. We characterized the bulk ore and clay fraction mineralogy and bulk elemental chemistry via X-ray diffraction and ICP-OES respectively. We measured the oxygen and hydrogen isotope composition of the clay fraction ($\delta^{18}O_{clay}$, δD_{clay}) and the carbon, oxygen, and carbonate clumped isotope composition of the coeval carbonate minerals ($\delta^{13}C$, $\delta^{18}O_{carb}$, Δ_{47}) to infer environmental conditions (i.e., temperature) and processes driving Li enrichment during clay formation. Measurement of $\delta^{18}O_{clay}$ utilized laser BrF_5-fluorination of clay pellets, normalized to clay mineral society hectorite and kaolinite standards SCHa-1 and KGa-1b [4]. Bulk mudstone Li concentrations range from 20 to 2,500 ppm, and the most enriched samples correspond to a greater proportion of smectite, relative to illite, chlorite, and kaolinite. The most common accessory minerals found within the Li-enriched mudstones are analcime, calcite, dolomite, and feldspar. Bulk mudstone Li concentrations covary with the oxygen isotopic composition of the carbonate phases ($\delta^{18}O_{carb}$; 17–35‰ VSMOW) similar to results from recent studies of claystones from Clayton Valley, Nevada, USA [3]. Smectite $\delta^{18}O_{clay}$ values mirror paired carbonate trends and contain an evaporitic slope in $\delta^{18}O$-δD space, suggesting both minerals formed from the same evolving evaporatively enriched water reservoir. Calculated smectite formation temperatures range from 17–51 ºC and carbonate clumped isotope formation temperatures range from 15–50 ºC, indicating that low temperature processes drive Li enrichment. The combined geochemical and stable isotope results suggest that between 19 to 13 million years ago, evaporation of ephemeral underfilled to perennial balance-filled lake waters led to the Li enrichment of pore waters and subsequent Li-smectite authigenesis in the Barsow basin. We speculate the primary source of Li to ancient lake/pore waters came from the weathering of ash falls to the lake and aqueous Li weathered from coeval felsic volcanic rocks surrounding the Barstow basin. Evidence for Li-rich hydrothermal contributions to lake/pore waters is minor. Our study suggests that other deposits set in nearby extensional regimes may have had similar paleoenvironmental controls on the low-temperature formation of authigenic, Li-rich smectite.

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Mineralogical Insights in the Recovery of Lithium from Clays of the Thacker Pass Deposit (Nevada, USA) by Acid Leaching

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Volcano-sedimentary deposits have been gaining importance as an alternative source of lithium. The Thacker Pass deposit within the southern end of the McDermitt caldera, in northern Nevada in the United States, represents a prime example of this type of deposit [1]. It is the largest known lithium deposit in the United States and one of the largest in the world. Lithium is found at Thacker Pass within a sedimentary clay-rich sequence with illite and smectite-like clays as host minerals. Gangue minerals such as carbonates and silicates are also present in the deposit [2]. With sulfuric acid (H_2SO_4) as lixiviant, Lithium Americas Corp (LAC) has found that the average yield for lithium extraction from materials with lithium-rich smectite is 79%, whereas the yield for lithium-rich illite is 87%. Additionally, LAC has also found that the lower extraction yields are correlated with higher magnesium contents [3].

In this study, two leaching feeds containing both types of clays at Thacker Pass, and their separated <2µm and >2µm fractions were evaluated. The extent of dissolution under two sets of experimental leaching parameters was assessed by means of chemical analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and mineralogical analysis by Fourier-Transformed Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD).

The separation process proved to be effective in recovering clay fractions without major lithium losses (<6%) or structural modification, thus, offering a unique possibility to study the leaching behaviour of lithium-rich clays in materials different than the Clay Minerals Society Hectorite (SHCa-1) [4][5]. Additionally, XRD on oriented slides in <2 µm showed that one sample was an illite/smectite (10/90) mixture, while the second sample was classified as pure Illite.

The <2µm fraction of both materials showed a similar leaching behaviour under both experimental conditions, while their parental feeds showed a preferential leaching of lithium in illite-rich clays at low sulfuric acid concentrations. Mineralogical analysis of the residues left after leaching suggested that carbonates in the parental feeds control the extent of lithium recovery by selective protonation in the first stage of leaching at low sulfuric acid concentrations. The results of this study complement the knowledge of the chemical path of the leaching system, not only in terms of bulk chemistry, but also in relation to the mineralogy of the clays.

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Using airborne and orbital imaging spectroscopy to differentiate lithium bearing hectorite from spectrally similar phyllosilicates - results and on-going difficulties

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Lithium has been designated as a critical mineral by the U.S. Geological Survey (USGS) due to its importance to the United States economy and over-all risk to supply. The Airborne Visible/InfraRed Imaging Spectrometer (AVIRISc) and the Earth Surface Mineral Dust Source Investigation (EMIT) imaging spectrometer, currently deployed on the International Space Station, are being used to identify and characterize potential new sources of lithium on Earth. Challenges have been identified, however, in mapping lithium bearing deposits using remotely sensed data, including similarity in spectral features among certain phyllosilicates and areal mixing of minerals. Spectral-based mineral maps generated using expert systems such as the USGS's Mineral Identification and Characterization Algorithm (MICA) use spectral feature matching of diagnostic absorption features to identify the spectrally dominant mineralogy in each pixel of an imaging spectroscopy data set. Hectorite (a Li-bearing smectite), saponite (a non-Li bearing smectite), and sepiolite and vermiculite (non-Li bearing phyllosilicates) have a primary absorption in the shortwave infrared centered near 2.31 µm caused by a combination of the OH stretch and octahedral cation (primarily Mg^{2+})-OH bend fundamental absorptions. MICA analysis using the 2.31 µm feature was able to map distributions of hectorite in Amargosa Valley, NV, however, confusion with these other spectrally similar minerals was identified. These confusions were confounded by areal mixing of a range of minerals at the spatial resolutions of the airborne and orbital imaging spectrometers used to collect these data. Similar results were obtained using imaging spectrometer data collected over the Barstow, CA. area. For AVIRISc data covering a hectorite mine near Hector, CA, we found that MICA was able to identify hectorite without significant false positives for saponite, sepiolite, or vermiculite. In this contribution, we elaborate on these findings – presenting spectral-based mineral maps, X-ray diffraction analysis, and bulk chemistry results.

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Critical Mineral Potential of Clays and Clay-Rich Materials, Southeastern USA

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Samples of various clays and clay-rich materials (Table 1) were collected from sites located in the Southeastern United States and characterized for their rare earth element + yttrium + scandium (REE+) and lithium (Li) contents, bulk chemical composition, and mineralogy. Elemental mapping was conducted by µ-XRF for selected samples.

The average REE, REE+, and Li concentrations of the clays and clay-rich materials are shown in Figure 1.

Kaolin had the highest average REE and REE+ concentrations, at 420.4 ppm and 461.0 ppm, respectively. Coal processing waste had the highest average Li content (332.5 ppm). Kaolinite was the most abundant mineral constituent of both materials, averaging 75% and 22% in kaolin and coal processing waste, respectively.

The REE ore potential of the collected materials was assessed using the method of Seredin and Dai [1], which is based on the ratio of critical REE to excess REE+Y. Sixty six percent of the collected samples classify as "Promising". Despite their lower REE and REE+ concentrations, shale and two bauxitic clay samples had the highest ore potential due to their higher CREE contents. Underclay and coal processing waste exceeded the 120 ppm Li economic grade.

Material	Number of Samples
Coal Underclay	15
Coal Roof Rock	13
Coal Processing Waste	3
Kaolin	3
Bauxitic Clay	17
Illitic Clay	2
Ball Clay	13
Bentonite	2
Shaley Sandstone	4
Organic/Ferruginous Shale	19

Table 1. Samples collected for characterization.

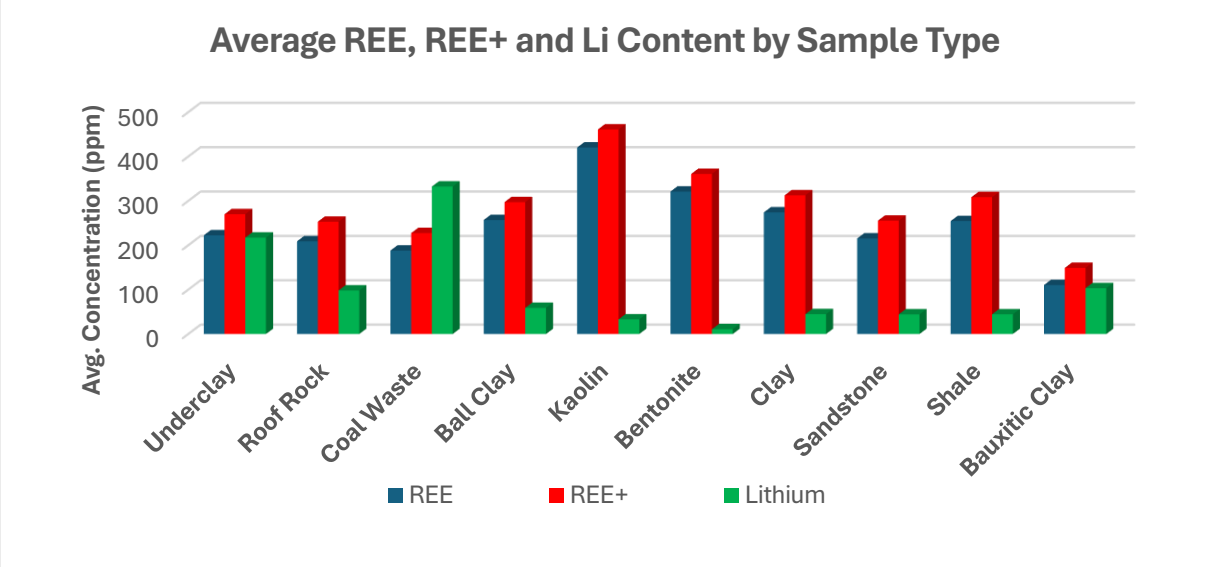

Figure 1. Average REE, REE+, and Li contents of the characterized clays and clay-rich materials.

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REE elements geochemistry in the present-day acid-sulfate types alteration from the active hydrothermal systems, São Miguel island, Azores Archipelago

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Acid-sulfate alteration is comprised by clays, sulfate, sinter, and native sulphur minerals crystallized as neoformation products from the dissolution of primary minerals during water–rock interaction.

Samples were collected from the active hydrothermal systems of São Miguel island, Azores Archipelago. Kaolinite, halloysite-7 Å, and opal-A occur in assemblages with alunite. High amounts of high-field strength elements (HFSE) and rare earth elements (REE) were measured in acid-sulfate rocks. The Nb vs. Ta and Zr vs. Hf show a positive trend and widely scattered relationships, suggesting a large fractionation during acid-sulfate alteration. Higher ΣREE amounts (up to 934.5 ppm) were found in clay-sulfate assemblages and lower ΣREE amounts in sinter (opal-A + sulfate, 169.05 ppm) than fresh rocks (up to 751.2 ppm). The acid-sulfate rocks reveal a distinctive "*gull-wing*" chondrite-normalized pattern with a negative Eu anomaly and light- and heavy-REE "*wings*" similar to the "*gull-wing*" pattern of fresh rocks. The Eu/Eu* shows a large fractionation of acid sulfate rocks from 0.16 to 0.78 with respect to fresh trachyte products (0.10–0.38). The variation of (La/Sm)N and (La/Yb)N ratios show a large fractionation of light-REE and heavy-REE. The Y vs. Dy and Y vs. Ho show a very good positive correlation coefficient and a large Y fractionation in acid-sulfate rocks with respect to fresh trachyte rocks. The results obtained are compared with the data from the near-vent hydrothermal metalliferous sediment core from the Lucky Strike site (the Mid-Atlantic Ridge) and Aeolian Archipelago (Volcano and La Solfatara).

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Controls on cold-climate critical minerals: Rare earth elements in supra-permafrost sediments of three brine ponds in Wright Valley, Antarctica

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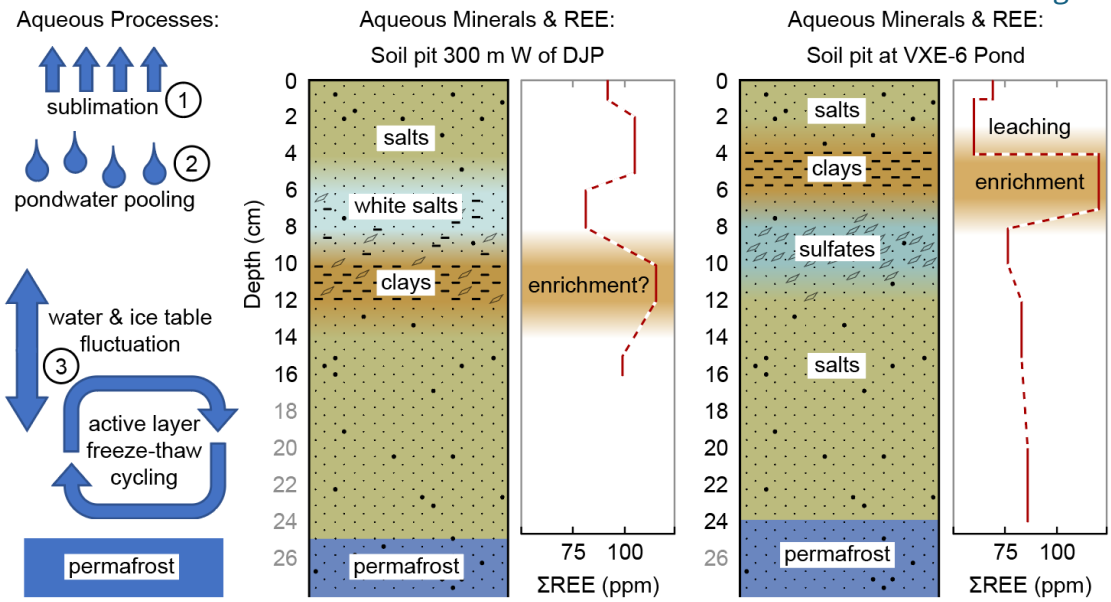
Rare earth elements (REE) are a group of metals considered critical minerals for the energy transition and for numerous advanced technologies essential to modern society. However, despite continually increasing resource demand, REE accumulation processes (especially low-temperature processes) remain understudied and relatively poorly understood. To aid in closing this knowledge gap, we investigate polar-region weathering profiles and REE behavior in the shallow, supra-permafrost regolith of three brine ponds (Don Juan Pond, VXE-6 Pond, and Brine Pond #1) in Antarctica's McMurdo Dry Valleys (MDV). We characterize REE distributions at five soil pit sites across the three brine pond basins. At the scale of an entire basin (i.e., at 100-m-scale) across three Don Juan Pond (DJP) soil pits, we document decreasing REE abundances toward the pond center (with the center of DJP being the most REE-depleted site in this study). This is compatible with an overall cross-basin trend of increased chemical leaching with increasing proximity to the center of DJP. At the scale of individual sediment profiles (i.e., at cm-scale) among all five soil pits, we document two soil pit locations where relative REE enrichment occurs at a clay-rich sediment horizon: at the soil pit 300 m W of Don Juan Pond, the clay-enriched 10–12 cm depth interval has ΣREE ~17% higher than average for the soil pit, and at the VXE-6 Pond soil pit, the clay-enriched 4–7 cm interval has ΣREE ~46% higher than average. The clay-enriched, REE-enriched horizons are compatible with zones of active chemical alteration and concentration due to intermittent aqueous activity including supra-permafrost freeze-thaw cycling, brine pond activity, and possible surface meltwaters. Overall, this work demonstrates the potential for limited water availability (and attendant leaching, aqueous alteration, and clay formation) in cold desert regions to nonetheless influence the mobility and concentration of regolith-hosted REE in the shallow subsurface. While MDV regolith-hosted REE are far below economic concentrations, Antarctic permafrost- and brine pond-associated geochemical processes may be relevant to understanding REE behavior (and REE accumulation) in desert and cold regions elsewhere on Earth, as well as to guiding future in-situ resource utilization in analogous planetary environments such as on Mars.


Aqueous Processes:
sublimation
1
pondwater pooling
2
water & ice table fluctuation
3
active layer freeze-thaw cycling
permafrost
Aqueous Minerals & REE:
Soil pit 300 m W of DJP
Depth (cm)
salts
white salts
clays
permafrost
enrichment?
75 100
ΣREE (ppm)
Aqueous Minerals & REE:
Soil pit at VXE-6 Pond
salts
clays
sulfates
salts
permafrost
leaching
enrichment
75 100
ΣREE (ppm)

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Effect of clay mineralogy on REE recovery from regolith-hosted REE deposits

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Regolith-hosted rare earth element (REE) deposits are the most important sources of the world's heavy (H)REE supply. Up to 80 – 90% of the bulk REE in the regolith are hosted in clay minerals through adsorption. Kaolinite and halloysite are often found to be the main clay minerals in these deposits [1,2], however, they could be of significantly varying physical and chemical properties among different deposits. It is expected that these variations contribute to the variation in the style of REE adsorption, affecting the recovery in mining practice. In this study, three well characterised REE-ore samples from South China, with different REE composition and with clay minerals of different properties are leached with a range of common electrolyte solutions (NH_4, Na, Mg and Ca sulphate or chloride salts) at different starting pH (4 and 7) and initial concentrations (0.05, 0.1 and 0.5 M) to investigate the effect of clay mineralogy on REE recovery.

Preliminary results show that there is no significant variation on recovery using different starting pH and initial concentrations of Mg or NH_4-salts to leach the samples from the Bankeng LREE deposit. However, recovery is lower for HREE, especially those runs starting in neutral pH and with the NH_4-salts, on the samples from the Zudong HREE deposit. Moreover, on the Zudong samples, positive Y anomalies develop in leachates from runs starting at neutral pH, particularly on the sample with higher proportion of kaolinite but lower of halloysite. On the other hand, negative Y anomalies are observed for the runs starting at pH 4 for the same sample with the same concentration of the lixiviants. Exceptions are the runs with K salts that positive Y anomaly is shown in the leachate regardless the starting pH of the runs.

In the Zudong HREE deposit, as the bulk regolith do not show any obvious Y anomalies for all studied samples and the variation of Y anomaly is dependent on the kind of cation and the starting pH, it is likely to be caused by the variation of the initial Y, Dy and Ho contents and/or variation in the occurrence form among these elements on the clay minerals. The lower recovery of HREE in runs starting at neutral pH indicates that the adsorbed HREE, at least partially, occur in a relatively strong form than hydrated free cations [3]. As ionic radii of the HREE are smaller and the hydration shells thus larger, the electrostatic force between hydrated HREE ions and the clay mineral surface should be weaker than that of the LREE. Perhaps intercalation in interlayers of halloysite would contribute for additional electrostatic bonding to the adsorbed HREE, affecting the recovery at higher pH. For the Bankeng LREE deposit, likely all REE are adsorbed on the clay minerals in the same form such that the REE recovery is consistent largely regardless of the starting pH and initial concentration of the lixiviant used.

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Ion-sorbed Rare Earth Elements in Kaolins and Bauxite ore deposits, Western Georgia, Upper Coastal Plain, USA

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World-class kaolin ore deposits are found in the late Cretaceous and the early Tertiary sedimentary rocks in the upper Coastal Plain in Georgia. These kaolin deposits are formed by the sedimentological processes followed by in-situ chemical weathering which result in lenses or beds of kaolin clay. The kaolin ore, and bauxite lenses where present, are expected to contain enrichments of the REE given apparent insolubility of the mineral hosts containing them. Three hypotheses have been advanced to explain the occurrences of the REE in these mined kaolins and bauxites. H1 – REE are present in primary minerals (inheritance). H2 – the REE are sorbed onto mineral surfaces (ion-sorbed REE). H3 – some combination of H1 and H2 [1-4]. The REE are "critical" metals as they are vital constituents for many technologies. These kaolin and bauxite deposits represent novel resources of the REE.

Lenses of bauxite (3-4 m) are found within kaolin ore lenses (~ 9 m) in the sand-dominant Nanafalia Formation of the Wilcox Group (Paleocene-Eocene) western (Andersonville, GA) Upper Coastal Plain. The bauxite-kaolin lenses are found within micaceous sands in Oconee Group (Cretaceous-Paleocene) in the central Upper Coastal Plain (Wilkinson, GA). Combined sedimentological and subsequent weathering processes produced both these kaolin-bauxite ore assemblages [4,5]. The fraction of ion-exchangeable REE were different in these two sections. Eleven to 33% of the REE was exchangeable REE in the lower bauxite and kaolin at Andersonville. The highest fractions of exchangeable REE (2.5-9.3%, leaching efficiency) were observed in the upper kaolin in the Wilkinson section. The leaching efficiency for the remaining bauxite and lower kaolin were < 2.5 % at Wilkinson [5]. The fractions of exchangeable REE differed considerably between Andersonville and Wilkinson sections. Possible reasons for this difference include proximity to Fall Line and hydrologic recharge area [6] leading to lower exchangeable REE at Wilkinson [7]; a greater supergene enrichment of the REE at Andersonville.

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Clay mineralogical and geochemical characteristics of a lateritic profile within the Karakaya Complex, Biga Peninsula, NW Türkiye

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The present study addresses clay mineralogy and geochemical characteristics of a lateritic profile formed within the Triassic Karakaya Complex. This complex is situated to the west of Geyikli village (Balikesir) on the Biga Peninsula, northwest Türkiye. The study area mainly consists of the Karakaya Complex, including metasandstone, phyllite, metavolcanics, marble, and serpentinites, which were later intruded by Early Miocene Şaroluk granitoids and Hallaçlar volcanics. The Karakaya Complex has undergone significant chemical weathering throughout time, leading to the formation of a lateritic weathering profile. This lateritic profile is categorized as a Ni-Co laterite, according to geochemical data revealing significant amounts of Ni ranging from 1576 to 2373 ppm and Co from 1807 to 2576 ppm in most samples. Conversely, some samples exhibiting lower amounts of Ni and Co have been thought to represent either a siliceous cap or weakly developed saprolite units.

X-ray diffraction (XRD) analyses reveal that the clay mineralogy of the studied lateritic profile mainly includes kaolinite, illite, and residual quartz. Post-treatment analyses using ethylene glycol (EG) and thermal heating (350–550 °C) confirm that expansive clay minerals such as smectite and chlorite have not occurred. Instead, the profile is dominated by non-expanding clays, particularly kaolinite and illite. These mineral assemblages indicate an advanced stage of weathering and the presence of strongly leached, well-developed kaolinitized zones within the profile.

Integrated mineralogical and geochemical data show that the investigated lateritic profile shows typical weathering-related zonation. The results highlight the possible enrichment of transition metals during Lateritization and the role of feldspar-rich metaclastic rocks within the Karakaya Complex as a suitable lithology for the formation of clay phases.

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Concentration and distribution of critical metals in laterites, bauxites and red muds

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Chemical weathering leading laterites and bauxites also enriches in metals considered as critical for the European Union, including alkaline earth metals (Be, Sr), transition metals (Sc, V, Co, Nb, Hf, Ta, W), other metals (Ga, Bi), metalloids (Ge, As, Sb) and rare earth elements (REE). In addition, bauxite residues (red muds) from the Bayer process also provide a valuable source of these metals [1], whose economic importance comes from applications in green energies and the manufacture of non-polluting vehicles. This work evaluates the concentration and distribution of critical metals in lateritic levels and karst bauxite deposits (Lower Cretaceous, NE Iberia), and in bauxites and red muds from alumina producers.

The laterites are mainly formed by kaolinite, illite, smectite, quartz, hematite and goethite and the bauxites are mainly formed by boehmite, kaolinite, hematite, goethite and gibbsite [2,3]. X-ray diffraction (XRD) analyses were conducted in the bauxites and red muds to determine their mineralogy. Geochemical analyses of 25 laterites, 22 karst bauxites and 3 bauxites and their corresponding red muds were carried out by inductively coupled plasma mass spectrometry (ICP-MS). In addition, 4 laterites and 4 bauxites with higher critical metal content were selected to identified by field emission secondary electron microscopy (FESEM) and transmission electron microscopy (TEM) which mineral phases host the critical metals.

The average critical metals content in the red muds (2152 ppm) is double the average found in the original bauxites from the companies (1146 ppm), reflecting a double enrichment factor of critical metals in bauxites residues. The critical metals have in general a good positive correlation with boehmite, calcite, diaspore and hematite in the bauxites, whereas the correlation is also good with diaspore, hematite, anatase, nyerereite and ussingite in the red muds. This reflects that after alumina extraction, the critical metals concentrate in those minerals resistant to the Bayer process and the new ones formed through this process.

Karst bauxites have a higher critical metal content (1302 ppm) than laterites (722 ppm), indicating that intense chemical weathering increases metal concentration. In the laterites, transition metals, other metals, metalloids and the REE correlate with kaolinite, goethite, and hematite, while alkaline earth metals associate with illite. TEM results revealed up to 100 nm monazite, xenotime, zircon, lanthanum oxide and cerium oxide particles adsorbed on the surface of kaolinite. This would indicate that both Fe oxides and clay minerals control the distribution of critical metals in the laterites [4]. In karst bauxites, transition metals and metalloids correlate with hematite and goethite, likely adsorbed onto them. REEs do not correlate with bauxite-forming minerals but occur in phosphates and zircons that were not detected by XRD, but observed by FESEM. Phosphates are enriched in light REE (La, Ce, Pr, Nd and Sm) and/or heavy REE (Gd, Dy, Er and Yb) and Y, while zircons are enriched in Y.

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An uncommon occurrence of Ni-Co-Mn-Fe-rich nodules hosted in Plio-Pleistocene palygorskite and palygorskite-smectite continental deposits of west Macedonia, Greece

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Fe/Mn nodules have been described from lacustrine, soil, shallow marine, but mainly from deep-sea environments [1,2,3,4]. In the Pacific Ocean, mineable Mn-Ni-Co-Fe-rich nodules form significant deposits, due to the increased demand of Mn, Ni and Co for the batteries of EV cars. In continental deposits, such enrichments are almost absent [4,5,6].

In the Ventzia Basin, western Macedonia, northern Greece, a thick fluvial Plio-Pleistocene succession hosts commercial lacustrine-palustrine clay deposits composed of palygorskite and palygorskite/smectite, overlying altered ultrabasic rocks of the Vourinos ophiolite complex and the clastic Tsotyli formation. In four mining areas of the Ventzia basin, medium-hard nodules were detected randomly scattered in the clayey matrix, ranging from 1 to 5 mm in diameter [7,8].

XRD, XRF and SEM-EDS analyses of the nodules revealed that their clayey groundmass is mainly composed of palygorskite, talc, amphiboles and serpentine [7]. Metallic grains occur scattered within the groundmass, composed of asbolane, birnessite, hematite, goethite and amorphous phases. In the bulk pellet samples, Mn, Ni, Co and Fe content is 13.3%, 2.64%, 0.66% and 12.7%, respectively, whereas in the metallic micro-grains of the pellets the range is 8.79-32.34% for Mn, 2.70-8.85% for Ni, 0.73-6.30% for Co, and 5.63-22.65% for FeO. SEM studies of polished cross-sections of the nodules reveal an onion-like feature, where bright and dull bands alternate. Stromatolitic structures were observed denoting a water born environment of formation [9]. Partially decomposed nodules, glued in a new nodule reveal reworking features. Bacterial-like accumulations are clearly visible within the nodules providing additional evidence for biological activities within the basin.

Presence of metallic nodules is interpreted as a relevant indicator of groundwater level changes and early diagenetic processes that could be linked to climatic fluctuations due to the Lower Pleistocene glaciations [4]. It is suggested that these nodules were formed diagenetically from late-stage Mn-bearing fluids. As palygorskite was formed during diagenesis from a smectitic precursor [8], it is suggested that the excess Ni and Co which was released during smectite to palygorskite transformation was incorporated into the ferromanganese nodule structure through sorption by the Mn-rich phases. It is concluded that during dry periods, Mn-Ni-Co-Fe-rich residual fluids accounted for the deposition of these metals precipitated as nodules under fluctuating redox conditions in pore spaces and voids within the clayey sediments. Biological activity played an important role as well. The almost solely source for Mn, Ni, Co, and Fe was the ultrabasic substrate of the basin.

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LECTURE THEATRE 7 – SESSION 36

Clay Materials in Healthcare Technologies

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Nanoclay-Mediated Crystal Engineering in Biofunctions to Balance Antibacteriality and Cytotoxicity

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The crystalline phase of metal oxides is a key determinant of the properties and functions of nanomaterials. Traditionally, research has focused on replicating the crystalline phases found in bulk materials, with limited attention to phase diversity due to difficulties in controlling crystal phase and structure. Here, we focuses on three core strategies for nanoclay-based composites: 1) Crystalline phase engineering: Talc-mediated interfacial engineering modulates the crystalline phases of metal oxides (e.g., MnOx) to optimize oxidase activity. For instance, in the M/T-190 composite, talc induces the formation of Mn_3O_4-MnOOH interfaces, enhancing oxygen radical generation by modulating charge distribution and d-band center alignment. This achieves a 99% broad-spectrum antibacterial rate (against *Escherichia coli* and *Staphylococcus aureus*) while maintaining 84% cytocompatibility. 2) Dispersion optimization: Talc-supported ZnO nanoparticles mitigate agglomeration and improve monodispersity, leveraging non-covalent interactions to disrupt bacterial membranes and amplify physicochemical synergistic antibacterial effects. 3) Composite doping: Ag^+-doped Ag-ZnO/talc systems synergistically boost reactive oxygen species (ROS) production, inducing bacterial membrane damage and nucleic acid leakage, alongside low cytotoxicity (cell viability >80%) and dermal safety. Biosafety evaluations confirm their wound-healing promotion and long-term antibacterial stability (e.g., Ag-ZnO/talc coatings retain activity for two months). These strategies balance antibacterial performance and biosafety through precise regulation of nanoclay-metal interfacial interactions, providing a theoretical and technical foundation for developing advanced antibacterial dressings, medical coatings, and tissue engineering materials.

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Effect of Montmorillonite Modification on Its Antibacterial Mechanism

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Contamination and associated infections caused by pathogenic microorganisms have long been recognized as a serious threat to human healthcare quality. With the rapid spread of antimicrobial resistance due to the overuse of antibiotics [1], there has been a growing interest in developing novel antibacterial agents based on inorganic materials [2]. Clay minerals, abundant in nature, have shown promise not only as drug carriers [3], but also as versatile components in pharmaceutical formulations [4], sorbents for toxic materials in water treatment [5], and most importantly as antibacterial agents[6], all due to clays' chemical reactivity. This newfound understanding positions clay minerals as key players in the quest for effective and sustainable solutions in combating complex bacterial infections.

We aim (i) to explore the generation of reactive oxygen species (ROS) through the iron-induced Fenton reactions [7, 8] particularly when Fe(II) is present in the exchangeable cation position or in the lattice structure; (ii) to investigate the potential oxidation of bacteria by the presence of mineral impurities in clay such as pyrite [8], and (iii) to study the potential release of mineral-bound bactericidal metals from clays such as Copper (Cu), Zinc (Zn), Silver (Ag) [9, 10].

To fulfil these objectives, we employed cation exchange modification on natural montmorillonite, microbiological assays and physico-chemical analysis to characterise the underlying antibacterial mechanisms.

Understanding these mechanisms is crucial for optimizing and controlling clays' antibacterial properties.

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Layered Clay Minerals in Cancer Therapy

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Cancer is one of the deadliest diseases, and current treatment regimens suffer from limited efficacy, nonspecific toxicity, and chemoresistance. With the advantages of good biocompatibility, large specific surface area, excellent cation exchange capacity, and easy availability, clay minerals have been receiving everincreasing interests in cancer treatment. They can act as carriers to reduce the toxic side effects of chemotherapeutic drugs, and some of their own properties can kill cancer cells, etc. Compared with other morphologies clays, layered clay minerals (LCM) have attracted more and more attention due to adjustable interlayer spacing, easier ion exchange, and stronger adsorption capacity. Therefore, the structure, classification, physicochemical properties, and functionalization methods of LCM are summarized. The state-of-the-art progress of LCM in antitumor therapy is systematically described, with emphasis on the application of montmorillonite, kaolinite, and vermiculite. Furthermore, the property-function relationships of LCM are comprehensively illustrated to reveal the design principles of clay-based antitumor systems. Finally, foreseeable challenges and outlook in this field are discussed.

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Biosafety of clay materials as biomedical nanocarriers

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Because of their unique layered structure, high specific surface area and controllable ion exchange ability, clay minerals have attracted great attention in the field of tumor drug nanocarriers and have shown great potentials [1,2]. As natural nanomaterials, clay minerals such as montmorillonite, kaolinite and halloysite can efficiently load tumor drugs through intercalation and adsorption, but their biosafety is highly dependent on mineral intrinsic properties [3]. Factors such as interlayer size, edge surface and structural defects of clay minerals directly affect the drug loading and release kinetics. However, excessive structural defects could lead to the delamination or disintegration of the carrier material in physiological environments. The surface and interface characteristics of clay minerals play a critical role in determining biocompatibility, as hydroxyl groups and charge distribution on the mineral surface significantly affect the interactions with biomolecules [4]. By regulating mineral phase transformation, its biosafety could be deeply governed. During phase transformation, structural distortion and a reduction in surface hydroxy-group density occur, which may directly affect its toxicity and blood compatibility. Notably, when the mineral phase transforms into an amorphous form, its sharp edge structures will possibly destroy the cell membrane and increase the hemolysis rates [5]. Future development needs to built up a balance between drug loading efficiency and biosafety, such as the construction of core-shell structures or the directional modification of surface groups, to provide new strategy for the precise design of intelligent anti-tumor nanocarriers.

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RENOVITE®: A Novel Injectable Clinical-Grade Nanoclay for Targeted Biomedical Applications

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Introduction: Nanoclays (NC) are layered silicates with high aspect ratios and permanent negatively charged surfaces. Their inherent negative charge and cation-exchange capacity enable efficient interactions with biomolecules, creating opportunities for regenerative medicine and drug delivery applications[1]. Certain synthetic hectorites such as Laponite form delaminated dispersions in water and generate gels due to charge interactions between the particles. These colloidal gels are highly sensitive to changes in ionic concentration, pH, and the presence of organic compounds. RENOVITE®, a proprietary analogue of synthetic hectorite clay, has been designed with an optimized magnesium-to-lithium ratio[2], which enhances clay gelation in physiological fluids compared to the commercial synthetic hectorite, Laponite™ (XLG).

Results and Discussion: RENOVITE® was synthesized via a controlled hydrothermal process. Elemental composition was confirmed using ICP-OES. Structural properties were characterized through XRD and FTIR, confirming the hectorite analogue. SAXS and TEM were used for particle size analysis. SAXS revealed the disc-like structure of the nanoparticles, with an average radius of 15.22 ± 0.60 nm and a thickness of 1.43 ± 0.12 nm. Zeta potential measurements using a Stabino™ II device with acid titration demonstrated a 50% decrease in negative zeta potential for RENOVITE® between pH 8 and pH 5, with particle agglomeration occurring at a physiological pH of 7.33, in contrast to XLG, which agglomerated at a lower pH of 5.9. Polyelectrolyte titration to determine the surface charges of NC revealed a slightly higher charge of XLG as compared to the RENOVITE®. Rheometric analysis revealed an associated increase in the storage modulus of 17144.0 ± 427.7 Pa following serum exposure, signifying enhanced gel stiffness under physiological conditions (Figure 1).

Conclusion: RENOVITE® is a clinical-grade injectable nanoclay gel that provides a stable, localised matrix at physiological pH, offering an effective solution for targeted biomedical applications.

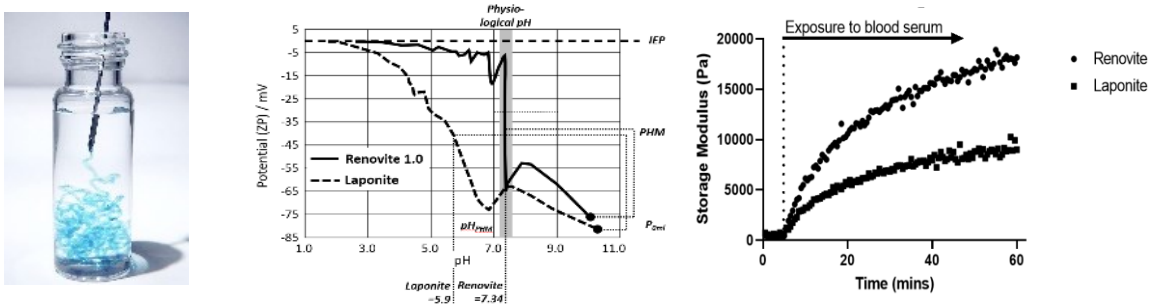

Figure 1: Injectable NC (left), zeta potential measurement against pH sweep (center), and storage modulus (Pa) of nanoclay gels (right).

[1] Mousa, Mohamed, et al. *Biomaterials* 159 (2018) 204-214
[2] US20240216287A1(2023), Richard Oreffo, Jonathan Dawson, Mohamed Mousa, Allison Shaw, Agnieszka Janeczek

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Preparation and performance modulation of kaolin-based antimicrobial materials

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This report explores the biological effects and mechanisms of action of kaolinite, leveraging its natural physical and chemical properties, such as its layered structure, negatively charged surface, and hydrophilicity[1]. The antimicrobial properties of kaolinite-based composites were modulated through surface interface modification, functional assembly, and other technical methods, using kaolinite as a matrix. ZnO/Kaol composite antimicrobial materials were synthesized via interfacial modulation[2]. The antimicrobial efficacy against Escherichia coli and Staphylococcus aureus was assessed, and theoretical calculations were employed to elucidate the mechanism of reactive oxygen species generation by ZnO/Kaol-15. Additionally, the interactions between the materials and bacterial cell membranes were investigated using the Riemannian molecular dynamics calculation system. The embedded ZnO/Kaol was prepared by utilizing kaolinite as a carrier, activated through high-energy mechanical ball milling and subsequent calcination. The in vitro antimicrobial activity of ZnO and its interfacially embedded ZnO/Kaol composites was compared. The antibacterial mechanism was further explored through theoretical calculations. The piezoelectric properties of embedded ZnO/Kaol were systematically characterized and evaluated for biosafety, and the antimicrobial performance of the developed piezoelectric antimicrobial masks was investigated.

[1] Xue Y et al. (2024) Adv. Mater. 2024, 36, 2308726.
[2] Ji H et al. (2024) Adv. Funct. Mater. 2024, 2407875.

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Facet engineering modulates d-π* hybridization for boosting antimicrobial activity

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Reactive oxygen species (ROS) have been growing as an emerging "hot" topic in antimicrobial applications. However, optimizing antimicrobial activity by enhancing ROS generation remains a formidable challenge. Here, using bassanite as a proof of concept, we propose the facet engineering of bassanite matrix can enhance the ROS generation efficiency via tuning the d-band center of Cu atom. Theoretical calculation and experimental investigations reveal that the d-band center of Cu atoms is significantly shifted upward when Cu doped into the (204) facet of bassanite compared to the (400) facet. A higher d-band center facilitates adsorption and activation between Cu and O2 through the formation of stronger d-π* orbital hybridization, resulting in increased ROS production. Through engineering, the material exhibits better antimicrobial activity when Cu doped into the (204) facet, which presents a clear potential in construction materials and personal protection. This work shed light on designing new materials with high antimicrobial activity and the application of facet engineering.

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Clay-based nanostructured systems for the controlled delivery of chlorhexidine

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Clay minerals, used in human health since prehistoric times, are well-established carriers for therapeutic agents. Their ability to assemble bioactive molecules enables the development of hybrid materials with improved stability and controlled drug release profiles [1-3]. This work presents nanostructured materials composed of montmorillonite (MONT) and sepiolite (SEP) clay minerals, assembled to chlorhexidine digluconate, a broad-spectrum agent well known for its remarkable bactericidal and fungicidal properties.

Chlorhexidine (CHX), widely used in dental care and wound disinfection, exhibits distinct interaction mechanisms with the two clay types here considered. In montmorillonite, CHX intercalates into the layered silicate as confirmed by an increase in basal spacing observed through X-ray diffraction (XRD), whereas in sepiolite, CHX adsorbs onto the external surface of the fibrous silicate particles. The resulting hybrids were characterized using XRD, IR (ATR and FTIR) and UV-Vis spectroscopies and CHN elemental chemical analyses, confirming the successful adsorption and the molecular organization of the drug on the clay surfaces.

This study also considers composite materials incorporating CHX-clay minerals in both chitosan and cellulose films. The resulting biocompatible films with the CHX drug-loading capacity of the clay minerals, were characterized by various physicochemical techniques, including IR, fluorescence X-ray, Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDX). The mechanical properties have been measured and antimicrobial experiments have been carried out against Staphylococcus aureus. In the case of chitosan-based materials, it is also important to consider the benefits provided by the barrier properties and antimicrobial nature of this biopolymer.

The resulting nanostructured materials show great potential for biomedical applications such as wound dressings, antimicrobial coatings, or drug delivery membranes, offering sustained CHX release in a suitable form for topical or clinical use.

In summary, the clay-CHX nanostructured biohybrid materials developed in this work represent promising platforms for the design of novel antiseptic delivery systems, aligning with the growing interest in functional clay-based biomaterials and their advanced applications.

Acknowledgements: Funded by AEI, Spain & ERDF A way of making Europe, EU (project PID2022-137889OB-I00) and by CSIC (PIE project ref. 202460E199).

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[2] Carretero M et al. (2013) Dev Clay Sci 5: 711-764
[3] Ruiz-Hitzky E et al. (2019) Clays Clay Miner 67: 44-58

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Deep detoxification of secondary aluminum dross treated by carbide slag

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3 million tons of secondary aluminum dross (SAD) is generated in China annually[1]. SAD includes highly reactive AlN and Al, which can react readily with H_2O to produce corrosive or flammable NH_3 and H_2. This may present a potential explosion risk. NH_3 can irritate the skin, eyes, and respiratory system, posing serious health risks. Additionally, it can also react with acidic gases like SO_2 in the atmosphere to form aerosolized ammonium salts, contributing to atmospheric pollution. On the other hand, the easily soluble fluoride (e.g., NaF, KF) and chloride compounds (e.g., NaCl, KCl) in SAD can leach into the surface or underground, causing significant damage to surrounding soils and contaminating water resources. The particle size of SAD is typically less than 200 μm, and a significant amount of dust is generated during its loading, transportation, and storage, leading to a substantial increase in PM2.5 levels, often exceeding safety standards.

The hydrometallurgical process was found to be effective in removing soluble salts, AlN, and Al. However, the formation of $Al(OH)_3$ hinders the hydrolysis of AlN and Al[2,3]. It can be an effective way to increase hydrolysis rates by adding acid or alkali. However, large amounts of acidic or alkaline wastewater are generated which is difficult to treat. Carbide slag contains around 80% $Ca(OH)_2$, and it is produced about 45 million tons in China. In this work, $Ca(OH)_2$ was introduced into SAD to investigate the mechanism of deep detoxification during hydrometallurgical process. With increasing $Ca(OH)_2$ addition, the Al metal and N removal efficiencies increased. All Al metal and N were removed while 45wt% and 40wt% $Ca(OH)_2$ were added, respectively. The formation of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ due to reactions between $Ca(OH)_2$ and $Al(OH)_3$ under alkaline condition is mainly responsible for deep detoxification. In addition, around 97% soluble F was removed, which is ascribed to the fixation by $Ca(OH)_2$.

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Effect of montmorillonite and sepiolite on the production of virulence factors, eDNA release, and biofilm formation in *Pseudomonas aeruginosa* culture medium

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Pseudomonas aeruginosa is an opportunistic multidrug-resistant bacterium capable of producing multiple virulence factors including pyocyanin and pyoverdine. Pyocyanin facilitates the release of extracellular DNA (eDNA), a major component of *P. aeruginosa* biofilm. Pyoverdine is an iron-scavenging siderophore that plays a crucial role in iron acquisition. Previous studies have shown that clay minerals, such as montmorillonite and sepiolite can selectively bind pyocyanin, even in the presence of different biological compounds including mono- and poly-saccharides, proteins, and DNA. Because pyocyanin and pyoverdine play multiple roles in pseudomonal pathogenesis, such as quorum sensing (QS), biofilm formation, and growth inhibition of other bacteria, sequestering these virulence factors may prove to be a novel strategy for disarming the bacteria. The objective of this research is to develop clay minerals that remove pyocyanin and pyoverdine from cultures of *P. aeruginosa* and to assess 1) their effect on pyocyanin, pyoverdine, and eDNA production, 2) biofilm formation, and 3) antibiotic susceptibility. These results will enable us to evaluate the potential of clay minerals as an alternate approach to antibiotics.

Due to the similar chemical properties of Gallium (Ga^{3+}) and Iron (Fe^{3+}), as well as recent studies on the use of gallium nitrate ($GaNO_3$) to inactivate pyoverdine, Ga-montmorillonite will be employed to specifically adsorb pyoverdine. Na-montmorillonite will be selected in this study due to its high adsorption and selectivity for pyocyanin. Sepiolite is also used in this study as a sorbent mineral because its tunnel is accessible to pyocyanin but inaccessible to large biological compounds. *Pseudomonas aeruginosa* PAO1 will be used as a model strain. Clay samples of different concentrations will be introduced into Luria-Bertani (LB) medium initially containing 10^5 colony forming units (CFU) of PAO1 at various time intervals. Pyocyanin will be quantified via UV-Vis spectrophotometer at 520 nm (OD_{520}) while pyoverdine will be measured using fluorescence spectroscopy. The minimum inhibitory concentrations (MICs) of standard of care antibiotics against PAO1 in either planktonic or biofilm growth modes in the presence and absence of clay will also be assessed using a standard broth dilution assay in Mueller-Hinton.

Preliminary data suggest that clay minerals effectively adsorb pyocyanin and pyoverdine from *Pseudomonas aeruginosa* culture medium. Similar results are also expected from eDNA production due to the reduction of pyocyanin and pyoverdine. Given the strong correlation between these virulence factors and biofilm formation it is expected that clay treatment will inhibit biofilm formation and increase bacterial susceptibility to antibiotics.

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Kaolinite Interface Engineering for Biomedical Applications

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Wound infection and delayed wound healing are significant clinical challenges, exacerbated by the increasing prevalence of antibiotic resistance [1]. Kaolinite, a naturally occurring layered clay mineral, exhibits excellent physicochemical properties, biocompatibility, and potential for antibacterial applications [2,3]. This study leverages kaolinite bio-interface engineering to design multifunctional clay-based materials for combating drug-resistant infections and accelerating tissue regeneration. Through calcination modification, functionalization with zinc oxide, and composite design with nitrogen carbide, the antibacterial mechanisms, wound-healing effects, and structural regulation of kaolinite-based materials are explored. Key findings include the enhanced antibacterial performance and wound healing properties of kaolinite, which disrupt bacterial membranes, reduce exosome secretion, and promote controlled release of zinc ions. In addition, the interfacial polar interactions between kaolinite and nitrogen carbide enhance photodynamic performance, enabling singlet oxygen production even in the dark. These findings demonstrate the potential of kaolinite-based materials in developing advanced antimicrobial agents and wound-healing biomaterials. The study provides theoretical guidance for the high-value processing of clay minerals and developing novel nano biomedical materials, offering innovative strategies to combat antibiotic resistance and improve wound infection management.

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[3] Wang D and Yang H (2024) Appl Clay Sci 259, 107516

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Clay-based systems for stimuli-controlled release of active molecules

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The last few years, the use of stimuli-responsive materials have aroused the interest in various domains, such as in medicine, cosmetics, agriculture… Indeed, this type of materials is able to act as artificial muscles, biosensors, or to deliver active molecules with efficient targeting [1].

Various stimuli are already employed to release a molecule from a carrier material. For example, the variation of pH, light, temperature, magnetic field, ionic strength, or the application of a redox potential, allow a broad range of applications. Spatio-temporal "on-off" action is wanted to deliver on demand [2] and minimise dispersion around the target where it could create damages.

Lots of papers show the ability of clay minerals such as kaolinite, montmorillonite, or halloysite nanotubes for loading molecules. Clays are non-toxic host material, compatible with applications in the field of biology, medicine, pharmaceutical, food processing… They are also cost-effective and eco-friendly materials. Synthetized clays can be functionalised in order to intercalate molecules of interest within the inter-lamellar space.

Nevertheless, studies about stimuli-responsive systems with clays, acting as carrier material for active molecule delivery, are less reported compared to polymeric materials. However, the water-soluble molecules are more efficiently entrapped in clays rather than in polymers [3]. Moreover, polymer carriers are less efficient in preventing the host molecule from degradation, and the release is sometimes too fast and not durable [3]. Having both a protecting effect, and the ability to release the host molecules, remain challenging. In this aim, clay-based nanocomposites are developed and show efficient stimuli-responsive behaviours.

In this presentation, the use and the structure of functionalised clays and clay-based nanocomposites as stimuli-response systems are highlighted.

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[2] Bruneau M et al. (2019) Journal of Controlled Release 294: 355-371
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Clay minerals in the underpainting layers of northwestern European paintings (16th–19th century)

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Clay minerals and clay-based pigments have used early in historical northwestern European paintings, particularly in underpainting layers to build up the painted surface of the panel. Preparatory layers ensure adhesion and surface stability, protect against chemical interactions, and contribute to long-term preservation by providing a smooth, protective base for the paint. These hidden clayey layers suffer from alteration and undergo physico-chemical modifications due to the interactions of chemical species within the mixture and with surrounding environment during natural time. These modifications make difficult to identify clay and clayey pigments, by conventional analytical techniques, in the process of restoration of historical paintings. This study aims to identify the components of hidden underpainting layers through the use of the conventional non-destructive technique FTIR (Fourier-transform infrared spectroscopy).

Specimens of clay-based underpainting layers were prepared following recipes and treatises from northwestern European fine arts dating from the 16th to the 18th centuries [1,2]. Four types of underpainting preparations were made using white clays (kaolin and bentonite) and clay-rich pigments (such as red ochre and raw sienna, rich in Fe and Mn oxides), as well as non-clay pigments mixed with organic binders like siccative oil or animal glue. Organic and inorganic stabilisers, including starch, calcium carbonate, and calcined bone, were also incorporated. The preparations were applied by brush in 2 or 3 layers, depending on the consistency. The prepared specimens were air-dried and subjected to artificial ageing under controlled variations in temperature and relative humidity to simulate natural ageing conditions. Both air-dried and aged specimens were analysed using FTIR and X-ray diffraction (XRD). XRD and FTIR analysis were also performed on powder for the raw materials to monitor chemical and mineralogical changes related to setting and ageing processes.

The O–H, Al–OH, and Si–OH absorption bands of smectite and kaolinite exhibit variations in intensity, and in some cases slight shifts in position, which can be attributed to structural destabilisation of the clay phases during setting reactions. Similarly, the absorption bands associated with organic binders show intensity changes linked to ongoing polymerisation processes.

[1] Wallert A, Hermens E and Peek M (1995) Getty Publications.
[2] Stols-Witlox M (2014), Universiteit van Amsterdam.

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Mineralogy and Geochemistry of the Kaolinite-Alunite Deposit of Madriguera (Segovia, Spain)

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The kaolinite-alunite deposit of Madriguera is located in the province of Segovia, on the northern slope of the Ayllón Mountain Range, where Miocene red gossan breccias and Ordovician-Silurian grey and black slates are exposed [1]. The ore was mined at various times throughout the 20th century, and three quarries are situated between the towns of Nogales and Madriguera. The main objective of this study is to characterize the deposit from a mineralogical and geochemical perspective. This characterization will serve to define mineralogical associations, with the ultimate goal of identifying their corresponding spectral signatures in the visible, near-infrared, and shortwave infrared (VNIR-SWIR) ranges. These signatures can then be used for both exploration and potential future exploitation of the deposit.

For this purpose, 60 samples from the La Tejera and Herreras quarries were analysed using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and VNIR-SWIR spectroradiometry. Prior to analysis, the samples were powdered using an agate mortar. For XRD analysis, the full routine for clay mineral identification was followed, including oriented aggregate preparation, ethylene glycol solvation, and heating at 550 °C. A statistical treatment of the data was done with Past V4.3 and SPSS V13 software.

The mineralogy of the deposit results from the superposition of two alteration processes affecting the Paleozoic rocks: hydrothermal alteration and weathering. These processes altered the original sedimentary-metamorphic minerals—such as quartz, feldspar, and primarily phyllosilicates—leading to the formation of kaolinite, minerals from the alunite-jarosite series, and occasionally graphite. These minerals form distinct mineralogical associations with characteristic geochemical and spectral features that enable their identification by using portable equipment of XRF and VNIR-SWIR spectrorradiometer.

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Spectral and Geochemical Discrimination Between Different Slovak Bentonites

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Various statistical techniques can be utilized to differentiate between different types of bentonites based on their geochemical and spectral signatures. The fingerprinting of bentonites through geochemical analysis using multivariate statistics has proven effective in various correlation studies. In contrast, statistical analysis employing infrared (IR) spectral signatures is less commonly explored despite its potential as a valuable analytical method. This study aims to investigate the valuable chemical and spectral fingerprints of various Slovak bentonites using the whole rock elements and near-infrared (NIR) spectroscopic data to differentiate between multiple groups of samples based on a set of variables that distinguishes these groups.

The bentonite samples were collected from the Michaľany-Lastovce deposit (East Slovakia), Lutila-I, and Bartošova Lehôtka-II deposits (Central Slovakia). Pulverized bulk samples (<250 µm) were analysed using Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and mass spectrometry (ICP-MS). Additionally, these samples underwent measurement through near-infrared spectroscopy (NIR) using FTIR and ASD FieldSpec 4 Hi-Res spectroradiometer. The data was statistically analysed. To determine the geochemical affinities of the samples, dimensionality reduction techniques, including principal component analysis (PCA), linear discriminant analysis (LDA), and t-distributed Stochastic Neighbor Embedding (t-SNE).

For the NIR spectral data, the applied PCA effectively clustered most of the analysed bulk samples into two groups; however, the distinction between these groups could have been more clearly defined. In contrast, LDA successfully categorized the bulk samples into two distinct groups and identified three groups within the clay fraction samples (<0.2 µm) using nine principal components. Furthermore, t-SNE yielded the most remarkable results, distinctly clustering the bulk samples into two well-defined groups and separating the analysed clay samples from the bulk samples into two additional groups.

The results of the PCA and t-SNE analyses on the geochemical data revealed two distinct groups. The Lastovce samples exhibited a higher concentration of Zr than those from Bartošova Lehôtka, which, in contrast, had higher levels of Nb, total rare earth elements (TREE), and relatively higher amounts of rare metals. It is noteworthy to mention, however, that the significant amount of TREE in the studied samples does not imply a uniform distribution; Lastovce samples contained a higher amount of total heavy rare earth elements (HREE), while Bartošova Lehôtka samples were characterized by a higher concentration of total light rare earth elements (LREE).

Multivariate statistical analysis, encompassing both geochemistry and infrared spectral signatures, proves to be an effective method for differentiating between various types of bentonites. Consequently, this approach can offer insights into bentonite composition and the source materials. The presented approach for verifying the origin of bentonites could also be used in the trade of bentonite or other clay raw materials if its origin is essential, as well as its potentiality to search for the origin of clay raw materials in different fields, such as archaeology.

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Determination of KGa-1b and SHCa-1 $\Delta'^{17}O$ and $\delta^{18}O$ via Laser Fluorination of Lithium Fluoride Clay Pellets

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Stable oxygen isotope measurements in silicate clays, such as smectite and kaolinite, are widely used in the geological sciences for understanding processes related to weathering, hydrologic balance, temperature, and geochemical conditions during mineral formation. Despite the wide applicability of oxygen isotope analysis of silicate clays and clay-rich sediments, a consistent sample preparation protocol and the standardization of smectite and kaolinite materials is needed to improve the accuracy and interlaboratory comparisons of clay isotope measurements, especially those made via laser fluorination methods. To address this gap, we summarize the results from Gagnon et al. 2025 [1]. We report oxygen isotope values ($\delta^{18}O$) and triple oxygen isotope values ($\Delta'^{17}O$) for two leached clay reference materials—KGa-1b (kaolinite) and SHCa-1 (hectorite/smectite)—using conventional nickel reaction vessel fluorination combined with dual-inlet isotope ratio mass spectrometry. We also analysed the same materials as LiF-bound pellets using laser fluorination to assess reproducibility and compatibility between techniques, incorporating a standard laser chamber drift correction.

The laser fluorination technique yielded highly precise and reproducible $\delta^{18}O$ and $\Delta'^{17}O$ measurements for the KGa-1b and SHCa-1, aligning with bomb values of $\delta^{18}O$. We stress the importance of proper sample preparation and laser chamber drift corrections using the following newly determined values. We propose that our KGa-1b $\delta^{18}O$ value of 21.4783‰ (±0.2666 [1σ]; ±0.0422 [1SE]) and $\Delta'^{17}O$ value of −0.0735 (±0.0144 [1σ]; ±0.0023 [1SE]) be used as a primary standard, which eliminates the need for additional non-clay silicate standards. When analyzing via laser fluorination, no less than 3 KGa-1b pellets should be analyzed across the beginning, middle, and end of day. These standards should be used to apply a daily drift correction normalized to our accepted KGa-1b value. Additionally, the SHCa-1 $\delta^{18}O$ value of 21.7686‰ (±0.7534 [1σ]; ±0.2271 [1SE]) and $\Delta'^{17}O$ value of −0.1222‰ (±0.0078 [1σ]; ±0.0023 [1SE]) may be used as a standard when analysing $\delta^{18}O$ and $\Delta'^{17}O$ of smectite-rich clay materials. By establishing a methodological framework and reference values that support the use of clay standards in stable isotope geochemistry, this will enable more accurate reconstructions of paleoclimate and environmental conditions from clay-rich sediments.

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Utilization of infrared spectroscopy to study LBL films based on smectite and quaternized chitosan

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Chitosan (CH) is widely known as an antibacterial, biocompatible, and biodegradable polymer. After quaternization of CH, its use is expanded not only due to increased solubility in water but also increased antibacterial activity. TMCH or CH and two smectites with different cation exchange capacities (CEC) were used for the preparation of hybrid systems by the layer-by-layer (LBL) method. The objective of this work was to study the influence of the smectite layer charge on the resulting properties of hybrid systems. TMCH was prepared by a two-stage quaternization reaction of CH with iodomethane. The success of the reaction was controlled by H-NMR and IR spectroscopy in the mid and near IR regions. Two smectites were used for the preparation of hybrid films: Sumecton SA (S; CEC = 0.72 mmol/g) and montmorillonite Lutila from a new Slovak deposit (Lu; CEC = 1.14 mmol/g). The polypropylene glass (PP), used as a substrate for LBL films, was activated by DCSBD plasma for 20 s in ambient air and then put into TMCH or CH solution. After the activation, the PP was immersed in stock solutions of S or Lu and again TMCH or CH, and this was marked as the first layer of the LBL film. Films were prepared by alternating layers of cationic CH and TMCH molecules and negatively charged S and Lu until reaching a total of 40 layers of the LBL film. Infrared spectra were measured by the ATR method after the deposition of each layer. The most significant changes were observed in the 950 – 1100 cm^{-1} region. These changes were attributed to Si-O stretching vibrations of smectites and C-O stretching vibrations of CH or TMCH. The intensity of the bands increased linearly up to 25 layers, after which the growth stopped. For this reason, the PP glass with 20 layers was reactivated by DCSBD plasma. After this step, the layers increased linearly up to the applied 40 layers. As the number of layers increased, the following trend was observed in the intensity of the band region: TMCH-S < CH-S < TMCH-Lu < CH-Lu. To increase the quantity of TMCH in LBL samples, 1 wt. % of CH_3COOH was also used for film preparation. This modification helped to increase the amount of TMCH; the band intensities were approximately the same as those of the CH samples. From these results, the influence of the layer charge on the sample properties is obvious; films prepared with Lu (higher CEC) contained higher amounts of components compared to S. The prepared samples were also tested for the stability of LBL films in water. The samples were immersed in water, shaken for 24 h, and again analyzed by IR spectroscopy. The most intense decrease in the mentioned band area was observed for the Lu samples and the least significant for the S. The antibacterial activity of the prepared samples was also tested. The most pronounced bacterial inhibition was observed for the TMCH-Lu sample and confirmed the substantial influence of layer charge and type of polymer on the resulting properties of the materials.

Acknowledgment: The authors acknowledge the financial support of the Slovak Research and Development Agency (APVV-20-0175 and APVV-21-0302) and VEGA grant agency (2/0161/25).

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Characterization and settling behavior of Alberta oil sands mature fine tailings (MFT)

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The Alberta oil sands deposit represents the third largest reserves of oil on the planet. Commercially, the bitumen is extracted from the oil sands using water-based process. The water-based bitumen extraction produces a large volume of waste, known as tailings. Tailings include a mixture of water, sand, silt, clay and residual bitumen. The tailings are pumped into large settling basins (tailings ponds) where sand fraction settles out rapidly leaving a stable suspension of fine (clay-rich) solids in the middle and water supernatant on the top. The aged stable suspension of fines containing >30 wt% of solids in the middle layer is called mature fine tailings (MFT). The further consolidation of MFT will take several centuries as they slowly dewater and consolidate [1]. The oil sands surface mining in Alberta disturbed about 900 km^2 of land and generated over 1.3 billion m^3 of tailings [2]. Alberta's oil sands operate under a zero-effluent discharge policy thus the tailings which are temporarily stored in tailings ponds must eventually be reclaimed and integrated into mine closure landforms. In order to deal with the massive inventory of MFT and provide a stable landscape in a timely manner, it is essential to investigate composition and settling behavior of MFT.

In the present study MFT sample provided by Syncrude Canada Ltd. was studied. Bulk MFT and various size fractions (>250, 63 – 250, 40 – 63, 2 – 40, <2, 0.2 – 2 and <0.2 µm) isolated from the bulk MFT were examined using X-ray diffraction (XRD), quantitative XRD (QXRD), infrared spectroscopy (FTIR), elemental (CHNS) analysis, thermal analyses (TG, DTG, DTA) and cation exchange capacity (CEC). The settling behavior was investigated in the settling test using the untreated MFT, MFT treated with cyclohexane and MFT treated with bleach. Cyclohexane and bleach were used to extract the residual bitumen from the MFT. The main goal was to evaluate possible changes in the settling behavior of MFT before and after removal of the residual bitumen using different extracting method (solvent-based versus bleach-based). The settling test was performed by the sedimentation of MFT in distilled water, at room temperature for 288 hours. During the test, distinct layers were formed in the settling mixtures. After the test, small liquid samples of settling supernatant collected from each settling layer were analyzed for particle size distribution analyses. The rest of the settling layers was dried overnight (60 °C), passed through a <250 µm sieve and analyzed by XRD, FTIR, CEC and transmission electron microscopy (HRTEM).

This work was supported by the Slovak Grant Agency VEGA (project 1/0306/23).

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Hydrothermal alteration and clay minerals in Palomares fault zone in Neogene volcanic province of the SE Iberian Peninsula (Spain)

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El Arteal and Herrerías are two N12ºE trending fault segments of the Palomares sinistral strike-slip fault zone (Almería), located in the Neogene volcanic province of the southeastern Iberian Peninsula (Spain). This fault zone controls uplift (exhumation) of metamorphic rocks of the Nevado-Filábride and Alpujárride Betic Orogen units, subsidence of the Neogene sedimentary Vera Basin and the occurrence of isolated high-K calc-alkaline and ultrapotassic volcanic rocks from the Miocene [1]. The metamorphic rocks host vein-type mineralizations of base-metal sulphides ± native silver, siderite, barite and hematite linked to subsidiary extensional fractures, which evidence the existence of active fluid circulation, water-rock interaction [2] and possible mobilization of strategic elements.

The aim of this work is studying the alteration processes leading to clay mineral neoformation along the two fault segments as well as the geochemical variations that may be associated. A total of 24 samples were collected sequentially, from unaltered materials in both blocks (taken as reference samples) to samples inside the fault zone. The methodology applied was a mineralogical and quantitative characterization on both the bulk sample and the clay fraction by X-ray diffraction, Scanning Electron Microscopy (SEM), using back-scattered electron (BSE) imaging and major and trace element geochemical analyses.

The mineralogical results in this study identify a significant amount of phyllosilicates (illite-micas and kaolinite) at El Arteal and smectites-illite at Herrerias in the altered fracture zones. Moreover, three mineralogical associations have been detailed in each segment in the fracture zone, which are: In El Arteal fault: (1) illite-muscovite, kaolinite, iron oxides and oxyhydroxides (hematite and goethite) and rutile, (2) halite, illite-muscovite, kaolinite, paragonite and gypsum, and, (3) calcite, halite and illite-muscovite. In the Herrerias fault: (1) smectites, illite-muscovite, paragonite and chlorite, (2) gypsum and (3) iron oxyhydroxides (goethite) and smectite-illite. The geochemical studies identify a generalized enrichment of strategic elements in the altered materials with hydrothermal evidence. The average concentrations of Large-Ion Lithophile Elements (LILE) and some chalcophile elements (Sb and As) are higher than their abundances in the Earth's crust [3] in both faults. An enrichment in Light Rare Earth (LREE) is only shown at El Arteal segment.

This geochemical variation and the mineralogical increase in the altered fracture zone demonstrates the influence of hydrothermal fluids [4] in these two fault segments linked to a geotectonic context with residual geothermal activity and the intrusion of igneous bodies during the Miocene.

Acknowledgements: Study carried out within the framework of the scholarship DIN2022-012822 funded by MICIU/AEI /10.13039/501100011033.

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EvalOpt – Increasing the reliability of quantitative phase analysis by optimising Rietveld refinement results with alternative analytical methods

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The quantification of mineral contents is an important tool for the interpretation of geological or industrial processes. Several approaches allow the quantitative determination of phase contents, among them the Rietveld method [1]. Results from round robin tests show that a successful quantification depends strongly on the skill of users. Although the refinement procedure itself is automatic and therefore user-independent, the results are influenced by the choice of structural models, refineable parameters and limitations of these parameters. All refinement results, even if the result is statistically satisfying, need validation and – if necessary - correction by other techniques [2].

A straightforward approach to check and optimise phase contents is the comparison with independent analytical results. Data from e.g. X-ray fluorescence analysis (XRF) are suitable for this. XRF results have a much higher quantitative uniqueness, but are not sensitive to phase contents. For the comparison, the chemical composition of a mineral mixture can be calculated from the phase contents and the chemical compositions of the individual minerals. Several codes already allow these calculations, partly with the possibility for (manual or automatic) optimisation.

The new software EvalOpt allows the simultaneous evaluation and optimisation of large sample series. A method of linear programming techniques is applied with the goal of an automatic and therefore objective optimisation. The software architecture is flexible enough not only to use data from XRF. In principle, all analytical results which depend on phase contents can be taken into consideration. The actual version allows so far the optimisation by using data from cation exchange experiments and LECO (carbon and sulphur determination) data, in addition to XRF data.

EvalOpt contains a user-friendly graphical interface and tools for input and output routines. Diagrams simplify the interaction and allow the user to identify outliers and the need of intervention. For demonstration, the Rietveld refinements of a large series of geological samples, performed with the software bundle BGMN/Profex [3], will be optimised with EvalOpt.

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Sessions 3+16: Sorption and intercalation in layered materials: from origins of life to material science

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The role of layered double hydroxide minerals in the origin of prebiotic peptides

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Many studies have been performed to investigate minerals as catalysts for prebiotic peptide formation. However, most adsorb molecules via multiple points of attachment, making the polymer inherently hard to remove, and so the question becomes "how did life escape mineral surfaces?".[1] In contrast, layered double hydroxides (LDHs), a rarely studied group of minerals, have been shown to allow mobility in adsorbed molecules as only the negative C-terminus adsorbs.[2] It has been proposed that these minerals could be the origin of prebiotic peptides, through concentrating amino acids and promoting peptide bond formation. However, this has only been shown computationally,[2] with experimental evidence only available for the formation of dipeptides.[3]

Shallow-sea alkaline hydrothermal vents are an often overlooked prebiotically relevant environment, providing hybrid conditions between deep-sea vents and terrestrial springs. Due to tides, these vents are often alternatingly submerged (in freshwater or seawater) and exposed to the atmosphere, providing continuous wetting-drying cycles.[4] Layered double hydroxides are thought to have been widely distributed at these vents on the early Earth, formed through serpentinization reactions or from brucite ($Mg(OH)_2$).[5] Therefore, LDHs at these shallow-sea vents are excellent candidates for the origin of prebiotic peptides, as dehydration of the mineral drives the polymerisation reaction entropically, while rehydration allows for the removal of the formed peptide and repopulation of the amino acids.

We carried out experiments to polymerise glycine using Mg_2Al-LDH. However, unlike previous experiments, we repopulated the amino acids during each rewetting step, which we suspect was the limiting factor in these tests. We believe this is more accurate for origin of life scenarios, as amino acids are thought to have been widely available on the early Earth, through extraterrestrial delivery or endogenic synthesis. Therefore, more amino acids would have become adsorbed onto the mineral surface. While the origins of life have geological timescales at their disposal, neither our lifetime nor laboratory constraints permit us to attempt such slow experiments. Therefore, we also adapted the previous experiments by using a nitrogen atmosphere and a nitrate-intercalated LDH, to ensure maximum adsorption of the amino acid to the mineral surface, so as to increase the possibility for peptide bond formation. We will present the first results of these experiments.

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Eu^{3+} ion as a luminescent sensor for tracking physicochemical changes in nanoclays: A case study on Laponite

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Trivalent lanthanide ions have been widely employed as luminescent probes for the structural analysis of various materials, ranging from natural zeolites to bentonites [1]. Notably, the sharp emission lines of Eu^{3+} luminescence serve as a powerful tool for investigating crystalline structures and monitoring physicochemical changes in clays subjected to different treatments, such as hydrothermal processes.

However, only broad and poorly resolved Eu^{3+} luminescence bands have been observed. These broad emissions, attributed to transitions from the $^5D_0$ excited state, are primarily due to the low crystallinity of clays, which stems from their natural origin. Recently, we have observed a significant enhancement in the photoluminescence of isolated Eu^{3+} ions when incorporated into a family of synthetic high-charge micas [2]. The efficiency of the photoluminescence emitted by these Eu^{3+}-incorporated mica samples exceeded our initial expectations, indicating a promising avenue for further research and development in this area.

Laponite is a synthetic nanoclay with the chemical formula $Na_{0.7}[Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4]$. Its particles are disk-shaped with a high aspect ratio (approximately 25 nm in diameter and 0.92 nm in height) and tend to stack due to attractive electrostatic interactions in the solid state. Its high specific surface area, approximately 370 m^2/g, makes it a material with remarkable adsorption properties [3]. In particular, this synthetic clay could be of interest for the adsorption of actinides under hydrothermal conditions, which requires proper structural characterization.

Here, we present a study on using Eu^{3+} lanthanide ions in contact with Laponite as sensors for monitoring the physical and chemical changes of this synthetic clay under ambient and hydrothermal conditions. The $Eu(NO_3)_3$-Laponite system has been hydrothermally treated in a steel reactor under various times and temperatures. Cation exchange reactions and the generation of new crystalline phases have been monitored by X-ray diffraction. Emission spectroscopy and Eu^{3+} lifetimes were employed to characterize both the cation intercalation process and the associated phase transitions. The results have been compared with those obtained for the high-charge mica family of aluminosilicates.

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Structural and spectroscopic characterization of montmorillonite modified with poly(2-n-alkyl-2-oxazolines)

Pribus, M.[1], Jankovič, L.[1], Kureková, V.[1], Barlog, M.[1] and Madejová, J.[1]

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Poly(2-oxazoline)s (POxs) are non-ionic polymers suitable for different bio-applications. Composites of montmorillonite (Mt) and poly(2-methyl-2-oxazoline) (PMeOx), poly(2-ethyl-2-oxazoline) (PEtOx) and poly(2-propyl-2-oxazoline) (PPrOx) were prepared for the first time and the effect of polymer loadings and the side chain length on the adsorption and structural characteristics was examined. The interlayer space of Mt increased with increasing POxs loading from 0.5 to 5.0 mmol·g^{-1}. Gradual transformation of the polymer chain arrangement from monolayer to bilayer up to pseudotrilayer was observed for individual polymers in dependence on the side chain length. The intensities of the bands related to the vibrations of the C=O and CH groups increased with rising amounts of polymers. A slight shift of the bands position reflected the transition from disordered to more ordered polymer arrangement. The thermal stability of PMeOx-Mt at elevated temperatures was determined by thermogravimetric analysis. The first mass loss (~90 °C) is related to desorption of water. Second and third around 370, 450 °C is attributed to the degradation of intercalated PMeOx. The fourth mass loss of the organoclay, at a temperature of around 540 °C, was ascribed to the oxidation of carbon soot, or the in-situ creation of condensed polymeric species by partial thermal decomposition of polyoxazoline. Unexpected and very high adsorption of POx on Mt interlayer and outer surfaces, markedly exceeding the CEC of Na-Mt, was discovered for the first time. Adsorption isotherms of polymers revealed a sharp increase in adsorption at low polymer loadings. When the surface of Mt was saturated with POxs, a plateau not changing with the loading of the polymer appeared. The high adsorption of various polyoxazolines was found for PMeOx (353 mg·g^{-1}) followed by PEtOx (383 mg·g^{-1}), and PPrOx (355 mg·g^{-1}).

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Preparation and Characterisation of Montmorillonite/Polyquaternium-2 Nanocomposites

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Polyquaternium-2 (PQ-2) is a cationic water soluble polymer and it has been used as a conditioning agent for skin and hair care products such as soaps, shampoos and hair conditioners. In industry, it can be used as a leveling agent in electroplating, for example [1]. Composites of clay minerals with cationic polymers, such as poly(diallyldimethylammonium chloride), polyethyleneimine, and chitosan are frequently and systematically studied systems. On the other hand, composites of montmorillonite (Mnt) and PQ-2 were prepared for the first time and the effect of increasing $n_{PQ\text{-}2}/m_{Mnt}$ ratio on the colloidal properties and structural characteristics were examined.

For dynamic light scattering and Zeta potential measurements a colloidal dispersion of Mnt with various loadings of PQ-2 were prepared, for measurements of infrared (IR) spectra, solid samples with various loadings of polymer were prepared. Zeta potential of Mnt in aqueous dispersion is around - 34 mV. The addition of small amount of PQ-2 polymer led to partial neutralization of negative charge of Mnt, which was manifested as a slight increase in Zeta potential to less negative value. With increasing loading of PQ-2, the Zeta potential is increasing and at $n_{PQ\text{-}2}/m_{Mnt}$ ratio equal to 0.53 mmol·g^{-1}, the Zeta potential of Mnt particles modified with PQ-2 is 0.0 mV and the negative charge of Mnt is completely neutralized. When the loading of PQ-2 is higher than 0.53 mmol·g^{-1}, the colloidal particles have positive charge and system develops an anion exchange capacity.

The characterization of prepared nanocomposites was carried out also by IR spectroscopy in the middle-infrared region. In the spectra of prepared nanocomposites, the changes in the NH stretching region (3150 – 3550 cm^{-1}) were observed. A peak near 3430 cm^{-1} was dominant at low PQ-2 loadings, while with increasing polymer loading, a broad band around 3300 cm^{-1} became stronger and eventually dominant at polymer loading ≥2.0 mmol·g^{-1}. The peak near 3430 cm^{-1} was assigned to free NH groups, and band near 3300 cm^{-1} to hydrogen-bonded NH groups. Significant changes were also seen in CH stretching regions (2800 – 3050 cm^{-1}). As PQ-2 content increased, band intensities rose and shifted to lower wavenumbers. The most significant shift was observed for the $\nu_{as}CH_3$ band from 3030 cm^{-1} (at 0.125 mmol·g^{-1}) to 3013 cm^{-1} (at 3.0 mmol·g^{-1}). The shift indicates the decreasing amount of disorder “gauche” and increasing amount of ordered ”trans” conformers. Modification also affected the vSiO band, with a shoulder at 1086 cm^{-1} appearing due to overlap with the NH_2 wagging band (1120 cm^{-1}) and changes of SiO_4 orientation.

PQ-2 polymer exhibits significant antimicrobial activity against both Gram-positive and Gram-negative bacteria as well as methicillin-resistant *Staphylococcus aureus* [2]. PQ-2 polyelectrolyte immobilized on the surface of montmorillonite could exhibit strong bactericidal activity and it that case the prepared composite nanomaterial would be suitable for the preparation of functional surface with antimicrobial properties.

Acknowledgements: This work was supported by the Slovak Research and Development Agency under contract numbers APVV-23-0635 and APVV-21-0302.

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Infrared spectroscopic analysis of smectite-chitosan nanocomposites

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Clay-polymer nanocomposites with antibacterial properties are frequently prepared using biopolymers such as chitosan (CTS) [1]. The preparation of Clay-CTS nanocomposites involves a reaction in an acidic environment, using acetic acid and citric acid (cross-linker) added simultaneously to CTS solution. This could provide a basis for the later integration of other polymeric species, such as polyvinyl alcohol and polylactic acid, to develop shape memory responsive composite materials. Particular stages of the procedure were studied by infrared (IR) spectroscopy in both the middle and near infrared (MIR, NIR) regions to investigate the possible effects of acidic conditions during preparation on clay mineral structure.

The clay-based composite materials were prepared using four clay minerals, synthetic (SWN Sumecton, Kunimine Industries, Japan and Laponite RD, Rockwood Additives, United Kingdom) and natural (SHCa, USA) hectorites, and montmorillonite Kopernica (Slovakia). The reaction products of the smectites studied with both organic acids were examined first. In the MIR spectra of Kopernica, no significant changes in the main absorption bands attributed to stretching (ν) and/or bending (δ) vibrations of structural O-H or Si-O groups were observed. However, natural and synthetic hectorites showed alteration in their spectra. A decrease in the intensity of ν and δ vibrations of structural OH groups at 3680 cm^{-1} and 670 cm^{-1} due to partial decomposition of the layered structure and removal of central atoms from octahedral sheets was detected. In addition, a new component of Si-O band appeared at 1074 $cm^{-1,}$ and also new band at 800 cm^{-1}. Presence of those bands confirmed formation of amorphous silica upon reaction in all studied hectorites. Contribution of the component at 1074 cm^{-1} varied between samples, and its intensity increased in order SHCa ≈ SWN < Laponite. In NIR spectra, very indicative bands of the amorphous siliceous phase were those connected to Si-OH groups. The first overtone (2ν) near 7320 cm^{-1} and corresponding combination mode (ν+δ) near 4420 cm^{-1} appeared only for trioctahedral smectites (hectorites).

Spectra of composite samples based on smectites and chitosan displayed a wide featureless band in the region 3200 – 2800 cm^{-1} of ν(N-H) and ν(C-H) vibrations and intensive bands at 1431 cm^{-1} and 1601 cm^{-1} attributed to C–N and C=O stretching vibrations [2]. The other bands of chitosan and organic acid were largely overlapped by more intensive bands of smectites. Absorption bands of amorphous silica were also visible in the spectra of clay-CTS composites, showing that the presence of large biopolymer molecules did not hinder the decomposition of the smectite layers. However, the intensity of the bands of amorphous silica (e.g. near 800 cm^{-1}) was lower in comparison to samples when only organic acids were involved in preparation. This observation indicates a lower extent of formation of amorphous SiO_2 and a decrease in decomposition of layers for nanocomposite samples.

IR spectroscopy as a very sensitive experimental method, showed formation of an amorphous phase in clay-based composite samples prepared with chitosan under acidic conditions using organic acids and confirmed alteration in the structure of trioctahedral smectites, while the structure of dioctahedral smectite remained intact.

Acknowledgement: The project is funded by Slovak Academy of Sciences program for PhD students, DoktoGrant No. APP0633.

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Session 4: From Dioctahedral to Trioctahedral Smectites: Where Volcanism meets Weathering, Sedimentation and Diagenesis

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Diagenetic and hydrothermal assemblages at Izu-Bonin rear arc (International Ocean Discovery Program – IODP Site U1437)

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International Ocean Discovery Program (IODP) Expedition 350 drilled Site U1437 in a submarine volcano-bounded basin situated in the modern Izu-Bonin rear-arc, NW Pacific Ocean. Subaqueous volcaniclastic sediments and rocks with a maximum deposition age of 15.4 ± 0.8 Ma were recovered from 0 to 1,806.5 meters below seafloor (mbsf).

In order to document post-depositional processes in such geological setting, we describe mineralogical variations over the entire volcaniclastic succession using optical microscopy, X-ray diffraction, and Electron Microprobe techniques. Four alteration stages (1, 2, 3 and 4) were identified through the occurrence and development of diagenetic background mineral assemblages (smectite ± Na-Ca zeolites ± illite) that were further superimposed by hydrothermal alteration.

Stages 1 and 2 are characterized by diagenetic reactions linked with low fluid/rock interactions that enabled glass devitrification and subsequent lithification under burial conditions. Stages 3 and 4 are characterized by moderate to pervasive alteration processes that are well developed in coarser-grained rocks, and that may be induced by thermal pulses associated with fluid inputs.

Below 1,460 mbsf, infilling and replacement textures overprinted the background alteration and can be directly linked with the development of two hydrothermal mineral assemblages: (i) ordered C/S (chlorite-smectite mixed-layers) ± chlorite ± albite, and (ii) calcite ± chalcedony ± anhydrite ± laumontite. Both assemblages evidence relatively low-temperature (up to 225 °C) hydrothermal activity that affected subaqueous volcaniclastic rocks at Site U1437. These assemblages are comparable with propylitc alteration facies recognized in ore-bearing hydrothermal systems.

The preferential development of alteration mineral assemblages in high-permeability, coarse-grained lithofacies, reflects the significant influence of the physical properties of volcaniclastic rocks with depth on chemical kinetics, in comparison with those imposed by the local geothermal gradient.

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Use of Electron Probe Microanalysis in the Quantitative Analysis of Magnesium Clay Minerals from the Pre-Salt (Brazil): Microsite Evaluation and WDS Compositional Mapping

[1]Da Silva M. D., [1]Gomes M. E. B., [2]Pozo M., [1]Mexias A. S., [1]Bongiolo E. M., [3]Ramnani C. W., Semeler, A.R.[1], Jantsch, L.C.[1]

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The quantitative characterization of clay minerals, particularly magnesium-rich ones in the pre-salt, is challenging due to their reactivity, the coexistence of different mineral species, and diagenetic transformations such as dolomitization and interstratification [1]. We applied electron probe microanalysis (EPMA) for the quantitative analysis of these clays, focusing on selecting suitable microsites and compositional mapping using Wavelength Dispersive Spectroscopy (WDS). Based on mineral assemblage identification, the microsites were classified as follows: (I) pure kerolite; (II) stevensite-rich; (III) mixed-layer K/S; (IV) saponite and detrital minerals. The pure kerolite assemblage comprises, in addition to the clay mineral itself, carbonates, predominantly calcite spherulites and rhombohedral dolomites. Kerolite occurs as homogeneous laminated aggregates, as indicated by Si, Mg, and Ca maps, without significant substitution or alteration. Representative structural formula: $M(_{0.08–0.51})(Mg_{5.46–5.93}Fe^{2+}{}_{0.007–0.031}Al^{IV}{}_{0–0.109})(Al^{IV}{}_{0–0.015}Si_{7.854–8.09})O_{20}(F_{0.7}OH)_4$.

The stevensite-rich assemblage shows a higher proportion of smectites and intense dolomitization and silicification processes, leading to matrix replacement and, in extreme cases, the formation of carbonate lenses concordant with the matrix. Silica mobility and late-stage dolomitization (low Ca) are evident. Representative structural formula: $M(_{0.4–0.87})(Mg_{5.17\text{-}5.64}Fe^{2+}{}_{0.004–0.03}Al^{IV}{}_{0.03–0.16})(Al^{IV}{}_{0–0.05}Si_{7.94–8.08})O_{20}(F_{3.0}OH)_4$.
In the mixed-layer K/S assemblage, the "S" component is interpreted as stevensite. The samples exhibit diffuse reflections in the smectite region, with kerolite present. Compositional maps reveal two distinct and interrelated chemical populations within clay aggregates, suggesting small-scale reactions. Representative structural formula: $M(_{0.18–0.88})(Mg_{5.2–5.88}Fe^{2+}{}_{0–0.04}Al^{IV}{}_{0–0.30})(Al^{IV}{}_{0–0.17}Si_{7.46–8.08})O_{20}(F_{1.0}OH)_4$.

Saponite occurs in distinct microsites, with evident geochemical variations in compositional maps. Al and K are enriched in both the clays and, to a greater extent, in detrital minerals (feldspars, biotite, and muscovite), which are found exclusively in this assemblage (referred to as a mixed matrix, whereas in other assemblages, it is pure). The Mg map distinguishes a Mg-rich phase (saponite) from another depleted phase, enriched in Al, K, and Si (likely detrital clays).
Electron probe microanalysis (EPMA) proved to be essential for in situ chemical analyses, enabling the distinction of clay mineral compositions in complex assemblages. WDS chemical mapping is an effective approach to visualizing element mobility and distribution, clarifying microscale reaction processes, and serving as a reference for determining in situ analysis points.

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Zircon U-Pb geochronology of Sarmatian (Serravallian) bentonite clay from the southern margin of the Pannonian Basin System

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The Ugljevik area is located in the southern marginal part of the Pannonian Basin System (NE Bosnia and Herzegovina). The Paratethys marine transgression reached this region around 14.2 Ma, giving rise to the investigated 4.5 m-thick succession of ooide limestones alternating with marls, deposited in a shallow marine environment. This research focuses on a 4–5 cm-thick layer of bentonite clay deposited between marl layers. The bentonite clay is predominantly composed of montmorillonite, which formed through alteration of volcanic ash in submarine environments. Illite, quartz and calcite (~5%) are present in small quantities, while kaolinite was found in trace amounts only in the clay fraction. Zircons and apatite were present in the silt size fraction. Marl layers contain 40-60% calcite and about 9-10% quartz with smectite as the major clay mineral, while illite and kaolinite occur in smaller quantities.

Previous bio-magnetostratigraphic research determined the maximum age of the bentonite layer to be ~12.5 Ma [1]. According to [2], the bentonite clays from the Ugljevik section are related to the calc-alkaline magmatism of the eastern Carpathian-Pannonian region, particularly the Apuseni Mountains and/or the Eastern Carpathians. Recent U-Th dating on zircons extracted from the bentonite layer established an age of 12.05+/-0.21 Ma. The co-occurrence of benthic foraminifera *Elphidium reginum*, *E. aculeatum* and *Anomalinoides dividens* along with the minute rissoid gastropod *Mohrensternia* cf. *inflata*, palynomorphs *Polysphaeridium zoharyi*, *Tytthodiscus mecsekensis*, *Cymatiosphaera miocaenica* and ostracods *Aurila mehesi*, *Senesia vadaszi*, *Callistocythere postvallata*, and *Cytherois sarmatica* further indicates an early Sarmatian age.

Ongoing research will focus on the geochemical composition of zircon to confirm the source of volcanic ash and establish a connection between the Ugljevik bentonite clay and other early Sarmatian volcanic events in the Pannonian Basin.

This research was conducted as a part of the internal research project „RAMPA“ at the Croatian Geological Survey, funded by the National Recovery and Resilience Plan 2021–2026 of the European Union – NextGenerationEU, and monitored by the Ministry of Science and Education of the Republic of Croatia.

[1] Mandic O et al. (2019) Global and Planetary Change 172: 374–395
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The Universe of Clay Minerals in Basalts – a petrographic approach of some Paraná-Etendeka flows in South Brazil

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The understanding of clay minerals as markers of fluid-rock interaction processes in basalts is of great importance to various fields of geology and their impact on society. This work reviews the clay minerals that occur in basalt of the Paraná Etendeka Magmatic Province in southern Brazil. The basic volcanic rocks of the Serra Geral Group constitute 97.5% of the volcanic pile and cover 1.2 × 10 6 km² in South America, especially in the south-central region of Brazil. The data presented here resulted from the analysis of flow architecture, petrography, and mineralogy of high-TiO2 basalts (Pitanga and Paranapanema) in the north-central region of Rio Grande do Sul – Brazil. For a long time, these minerals have sparked interest due to their association with amethysts in those largest deposits of this type in the world, and for their potential as remineralizers. More recently, they have become protagonists in studies of atmospheric CO2 capture and in the occurrence of large landslides that accompanied the floods of May/2024 in southern Brazil. The term "clays" in basalts is commonly used to refer to brown and occasionally green clay minerals that occur filling vesicles in the vesicular levels from base and top of flows. However, detailed petrographic studies allow the distinction of various phases of smectites and celadonites throughout the profile of these lavas. Iron-rich saponite-type smectites occur generally in the interstitial mesostasis of basalts, where they form microcrystalline associations with K-feldspar and quartz. In thick flows, saponite is the characteristic clay mineral and, chemically, it approaches the field of nontronite. In the central portions of these flows, they are predominantly calcic. In vesicular levels, they are sodium-calcic and associate with zeolites, especially filling vesicles. Celadonite occurs in thin and intensely vesiculated flows. Petrographically, it appears both in the mesostasis and in vesicles, geodes, and fractures. Its crystallization occurs by epitaxial growth from saponite occupying the central portions of large vesicles and in interstitial spaces. In this type of occurrence, it shows temporal association with very fine acicular apatite and constitutes the external coating of amethyst geodes, thus serving as a prospective guide. Locally, in thin and fully vesiculated lavas, there is more than one generation of celadonite: forming large crystals in association with smectites of high crystallinity and specific morphology in "ball of wool"; in a regular celadonite-smectite interstratified, unprecedented in these rocks; and as filaments covering the previous morphologies, always accompanied by cristobalite. The relationship between the occurrence of clay minerals and the internal architecture of flows suggests that the formation of Ca-saponite is temporally and chemically related to late and post-magmatic fluids whose crystallization is conditioned by different cooling rates of the body. Celadonite occurs under conditions of higher fluid-rock ratio, filling porous spaces, which determines its crystallinity. The source of potassium is the alteration of microcrystalline K-feldspar and even glassy portions compositionally similar.

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Session 5: Teaching, History, and Future of Clay Mineralogy (in honor of Dewey Moore and Bruce Velde)

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Combined 3D printing and computer models for teaching clay mineralogy: symmetry, rotation, shifting, and stacking of layer structures

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Imagining mineral structures in 3-D spacing is difficult for most students at the beginning. It is more challenging to imagine the atom arrangement details when discussing about different polytypes of the clay minerals and how the stacking sequence affecting their properties and diffraction patterns. Physical models of minerals can help in comprehending the concepts but unfortunately, they are expensive and limited in varieties. Computer models are great visual aids, but often it is hard to find the hidden symmetries and the relationships of shifting, rotation, or reflections due to busy details in the models. A combined approach of using both computer models and the physical models can make the learning of the structural concepts easier.

We have taken the advantage of 3D printing to generate some basic building sheet structures and glue them to form the common 1:1 and 2:1 layer structures. Both dioctahedral and trioctahedral models are built from these sheet structures. Symmetry evolvement/loss in stacking the sheets and layers can be analyzed and marked on models directly. Distributions of octahedral cations, the magnitudes and directions of relative shifts or rotations of tetrahedral sheets in a 2:1 layer and in sequential layers can be examined. The 12 regular stacking shifts of the trioctahedral 1:1 layers, 6 regular stacking shifts of 2:1 layers in micas can be demonstrated easily with the combined computer and 3D printing models (Fig. 1).

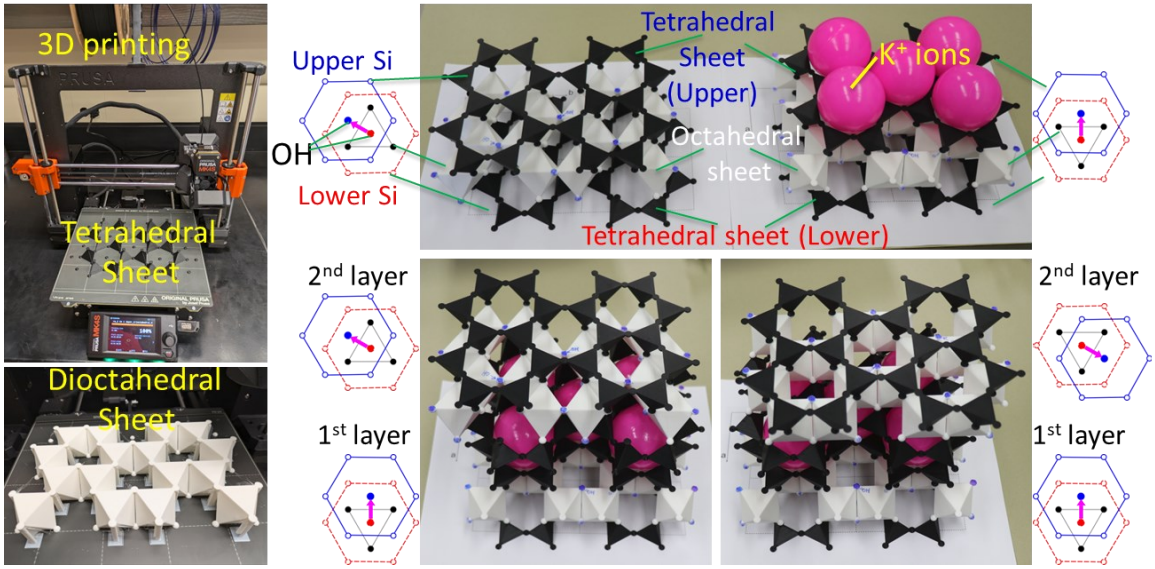

Fig. 1. Tetrahedral and dioctahedral sheet 3D printing and the example 2:1 layer stacking in micas.

Generating ideal 3D printing models also enable the thinking about the geometry relationships of the atoms and polyhedral. The re-iteration of calculating the atom positions and examining the 3D printing models can also enhance the understanding the structures of clay minerals. Some pitfalls in generating and slicing the models before and during the printing will be shared. The major drawback of 3D printing is the time, often more than 10 hours, needed to print one model. It is still challenging to 3D print a complete model with a variety of colors and complex atom arrangements due to the need of supporting during the printing. Scaling down the models will be more practical for students to print their own models.

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Session 6: Origin and Age of Clay Minerals in Soil and Sediment

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Mineralogical and geochemical evolution of Fe- and Al-rich phyllosilicates during the formation of the Baniaka Archean-age iron deposit in South-Eastern Gabon

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Originally anoxic ([1]), the Earth's hydrosphere underwent a gradual increase in its oxygen content (O2) starting in the Archean, closely linked to biological activity. However, the precise details of this oxygenation, particularly its kinetics, are still the subject of debate ([2], [3], [4]). The Baniaka iron deposit, located in southeastern Gabon, offers an exceptional setting for studying the oxygenation state of marine environments during the Archean (2.8–2.7 Ga), along the margin of the Congo Craton. This deposit belongs to the Belinga Group, a sequence of greenstones resting on an Archean charnockitic basement [5].

The study, based on a 179-meter drill core, reveals two main units: a metasomatic basement composed of gneiss and alternating quartzites and amphibolites rich in magnetite, followed by a banded iron formation (BIF). This BIF has a clay-rich base dominated by nontronite, indicating deposition under weakly oxic conditions, then evolves into a banded structure characteristic of chemical sedimentation in an oxidizing environment. The transition between these units is marked by mineral alterations reflecting low-grade metamorphism [6].

The mineralogical composition, notably the presence of phyllosilicates such as chlorite, stilpnomelane, smectite, and kaolinite, as well as the processes of magnetite martitization into hematite, indicate a progressive shift in redox conditions towards a more oxidizing environment. Detrital inputs enriched in kaolinite, P, Cr, and rare earth elements also reflect phases of intense continental surface weathering [7].

Finally, the subsequent migmatitic metamorphism has had little effect on the original mineralogical signature, allowing these mineral assemblages to be used as reliable indicators of the physico-chemical conditions of the Baniaka deposit’s depositional environment.

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The crucial role of textural characteristics in sepiolite crystallinity and rheological properties

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The existence of variations in the sorption and rheological properties of clay raw materials of economic interest depends initially on the type of deposit considered and the genetic conditions of its formation. The aim of this work is to determine the influence of the type of sepiolite formation on the rheology and to correlate it with its compositional and textural features. [1]

Eight sepiolite samples from two different geological contexts have been studied. One related to volcaniclastic deposits (SpV) and the other to sedimentary rocks environments (SpS). The samples have been characterised by X-ray diffraction using scanning electron microscopy (SEM-EDS). Some properties such as specific BET surface area and rheological behaviour have also been determined. The results indicate that all samples show a predominance of sepiolite, although the SpV samples show a higher content of associated minerals which may include quartz, feldspar and calcite. Also, the SpV sepiolite is less well ordered ("crystallinity") than the SpS, as evidenced by the FWHM parameter, crystallite size, and XRD reflections [2] indicating low "crystallinity" sepiolite (LCS).

The study of the microfabric and constituents by SEM shows significant differences between the two groups. Thus, the SpV sepiolite shows skeletal to matrix-skeletal microfabrics with small-sized (<5 µm) and caked aggregates. In contrast, the SpS sepiolite shows a greater variety of microfabrics, mainly of the matrix and glomerular type, locally laminar and skeletal. The sepiolite fibres form aggregates of sizes greater than 5 µm, looser and with development of inter-aggregates porosity. Some samples showing the presence of gel-like films with incipient development of sepiolite.

Higher viscosities (>50.000 mPa·s) were observed in sepiolite SpS samples characterized by larger aggregates of fibres and high specific surface areas (>320 m^2/g). In contrast, samples with smaller aggregates (SpV) and lower surface areas (244 m^2/g) exhibited reduced viscosities of up to 20.000 mPa·s. [3]

It is interpreted that the SpV sepiolite associated with a volcanoclastic environment presents replacement textures with a high content of minerals that do not undergo sepiolitization, which affects "crystallinity" and the development of fibrous aggregates size. In sepiolite linked to sedimentary environments without the presence of volcanoclastic deposits (SpS), the processes of anthigenesis by replacement of magnesian clay minerals or neoformation from dissolution and/or gels and later recrystallization are responsible for its textural and compositional characteristics, favouring the rheological behaviour.

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A new method for measuring the K-Ar age of diagenetic illite

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Scott and Smith [1] discovered six decades ago that nearly all the K^+ of muscovite (< 50 µm) could be replaced by Na^+ through cation exchange in a concentrated NaCl (1.7 M) solution containing Na-tetraphenylborate (NaTPB, 0.3 M), whereas only two-thirds of the K^+ of an illitic clay (< 2 µm) was exchangeable under the same conditions. The illitic clay was "Grundite," a Pennsylvanian underclay produced as a commercial product in Grundy County, Illinois.

McIntosh et al. [2] recently presented mineralogical and K-Ar evidence that both detrital mica and diagenetic illite-smectite are present in Pennsylvanian illitic underclays (paleosols) of the Illinois Basin. Here, we test a hypothesis that one but not both of these components loses all of its fixed K^+ upon extended exchange with Na^+ in a NaCl-NaTPB solution. If so, Na^+–K^+ exchange in the presence of NaTPB should be useful to eliminate all potassium and its associated radiogenic argon from that component, leaving material whose K-Ar age value represents well the other component.

Three size fractions (< 1 µm, 1–2 µm, 2–5 µm) were prepared from each of four middle and upper Pennsylvanian illitic underclay samples [2]. A portion of each fraction underwent Na^+–K^+ exchange in 1 M NaCl–0.2 M NaTPB–0.01 M Na EDTA solution for one hour, another for one day, and another for 22 days. Air-dried, oriented clay samples, prepared for each of the 36 products and for an untreated portion of each fraction, were examined by X-ray diffraction. A 10.0 Å peak associated with detrital mica was originally present in the patterns of all 1–2 µm and 2–5 µm fractions, but that component was not detectable by X-ray diffractometry in portions treated for one day and for 22 days. These preliminary results suggest that the NaCl-NaTPB-EDTA solution may effectively eliminate detrital mica.

Conventional K-Ar analyses of the size fractions and the products of Na^+–K^+ exchange are underway to further test the refined hypothesis that detrital mica, but not diagenetic illite, in the underclays loses all of its fixed K^+ and radiogenic Ar upon extended exchange by Na^+ in a NaCl-NaTPB solution. The measured K-Ar age values of fractions treated for 22 days converge to about 240 million years. Considering published age values, interpreted as indicating protracted diagenesis that extended into the Mesozoic [2], this convergence suggests that the 22-day treatments left K and radiogenic Ar in diagenetic illite but not appreciably in detrital material.

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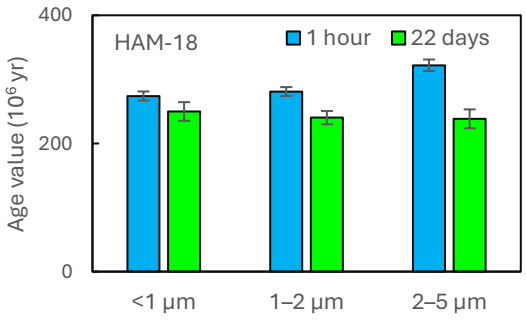

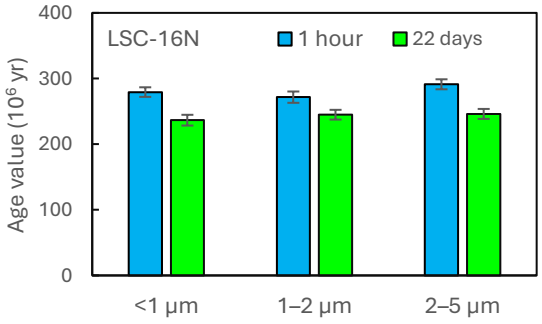

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Investigating $^{40}Ar^*$ loss from hydrothermal illite crystals of different size

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This study aims to test experimentally if the postulated $^{40}Ar^*$ loss from the structure of the finest clay particles [1] can be measured in natural samples. The best samples for studying this potential effect are pure hydrothermal illites from volcanics altered at shallow depths. Crystallization and growth of hydrothermal illite is relatively fast compared to burial diagenesis, so finer particles should be formed practically at the same time as the coarser ones. Illite crystal growth extended in time due to prolonged burial effect, which makes coarser crystals younger [2] can be avoided in these samples. Detrital contamination is absent. In such material, the postulated $^{40}Ar^*$ loss should not be masked by the differences in ages of illite crystals.

In this project, K-Ar ages from different size fractions of hydrothermal illite-smectite and rectorite originating from Neogene volcanic complexes in the Zempléni (Hungary) and the Banská Štiavnica (Slovakia) Mountains were measured. Three samples were analyzed: two (FUZZ-3: trans-vacant illite-smectite, FUZZ-6: cis-vacant illite-smectite) from the Füzérradvány area (Zempléni Mountains) and one rectorite sample from Červená Studňa in the Banská Štiavnica Mountains. Each sample was separated into three size fractions (2-0.2 µm, 0.2-0.05 µm, and <0.05 µm) and subjected to K-Ar dating and XRD measurements.

For both: FUZZ-3 and the rectorite from Červená Studňa, a consistent trend of decreasing apparent age with decreasing grain size is observed (FUZZ-3: from 13.15 Ma to 11.91 Ma; rectorite: from 12.51 Ma to 11.38 Ma). The age of the thickest fraction of FUZZ-3 agrees excellently with U-Pb dating of this tuff: 13.1 Ma [3]. This systematic age reduction in finer fractions strongly suggests significant post-crystallization $^{40}Ar^*$ loss. This loss can be due to recoil effects during ^{40}K decay, where the recoiling $^{40}Ar^*$ nucleus is more easily expelled from the smaller grains at edges and at the external surfaces [1]. Additionally, diffusion may play a more significant role in the $^{40}Ar^*$ loss from these finer fractions over geological timescales, as $^{40}Ar^*$ loss expected from recoil effect is smaller than the measured $^{40}Ar^*$ loss.

The sample FUZZ-6 exhibits a different pattern, with the finest fraction (<0.05 µm) yielding the oldest apparent age (11.87 Ma), as compared to the thickest one (10.77 Ma). This may reflect the illite crystal growth mechanism extended in time [2], due to younger thermal event.

Summarizing: in the studied samples there is a significant decrease of apparent ages in finer fractions, which can indicate $^{40}Ar^*$ loss due to recoil and $^{40}Ar^*$ diffusional loss, although such effect can be masked by a complex hydrothermal history.

Acknowledgements: Authors acknowledge financial support from the NCN: OPUS 2020/37/B/ST10/01697.

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Formation of laterites through the alteration of basalts

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Laterites are widely distributed worldwide in the tropical/subtropical belt, approximately framed between 20°N and 28°S. Laterites are dominant in NE Argentina, particularly in Misiones province. Some authors suggest that these laterites have been developed from the weathering of tholeiitic basalts [1] and others propose an allochthonous “tropical loess” model [2]. In this research, we describe the alteration process of basalts with the crystallization of Mg-smectite and kaolinite. For this study, we sampled from the least altered basalt to laterites with fragments of basalts, laterites with remains or very low proportions of basalt and finally pure laterites.

The combination of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) studies show that the basalt contains pyroxenes, plagioclases, hematite and Mg-smectite. The SEM images show evidences of alteration until the complete replacement of olivine and partially of plagioclase by Mg-smectites. In laterites with fragments of basalts, XRD patterns show the coexistence of Mg-smectite and kaolinite. The SEM also shows the presence of masses of Mg-smectite with hexagonal and rounded morphologies along with accessory kaolinite with irregular shapes. The presence of Mg-smectites and kaolinite showing colloform textures indicates low-temperature formation (Fig. 1). Smectite is surrounded by kaolinite masses, suggesting that the formation of kaolinite took places after that of smectite. In contrast, in those laterites with remains of basalts, the only clay detected by XRD is kaolinite, although SEM suggest also the presence of Mg-smectite in these laterites. Finally, pure laterites are mainly formed by kaolinite, gibbsite, quartz, hematite and goethite.

The textures of the clays suggest that the red laterites in Misiones are the result of an alteration *in situ* of the massive and vesicular basaltic flows occurring in the area. The described textures and sequence from the basalt to the crystallization of Mg-smectite and finally that of kaolinite suggests that the formation of clays took place by a low-temperature hydrothermal alteration associated to the underlying tholeiitic basalts, supporting the autochthonous origin theory. However, it cannot be ruled out that some of the clays were generated by weathering, especially the smaller ones.

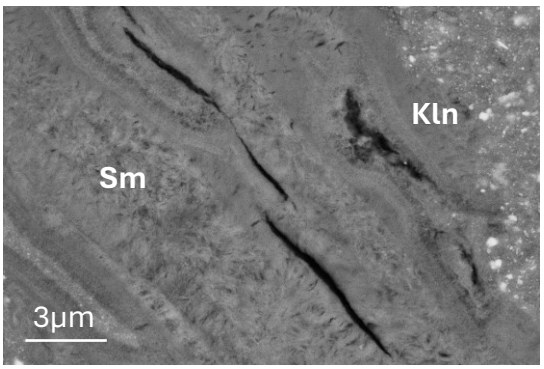

Fig. 1. Textures of hydrothermal clays. Sm: smectite, Kln: kaolinite.

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Clay mineralogy in transitional-continental environments of the Late Triassic: an indicator of the paleoenvironmental impact of the Carnian Pluvial Episode in southeastern Iberia

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At the end of the Triassic, the Peri-Tethys region was dominated by a warm and semi-arid climate. However, during the middle Carnian, a climatic shift towards more humid conditions occurred, known as the Carnian Pluvial Episode (CPE) [1]. This change is documented in sedimentary records across global continental and marine environments, with the expansion of extensive fluvial systems [2] to the west, and the disruption in the development of marine carbonate platform [3] towards the east.

In southeastern Iberia the Manuel Formation, part of the Valencia Group's K2 unit, provides a detailed record of these changes. This unit is dated to the middle Carnian through fossil evidence, derived from palynological studies, and ammonites and mainly shows alluvial, but also aeolian and of continental - marine transition environments.

This unit is stratigraphically divided into three sequences of transgressive-regressive character: K2.1, K2.2 and K2.3 from bottom to top respectively, and may reach up to 220 meters thick in the studied section. These sequences predominantly consist of siltstones and sandstones, interpreted as a braided and meandering fluvial system with a significant development of floodplains where bioturbation, palaeosols and eventually siliciclastic and carbonate lakes occurred [2, 4]. The three sequences show the presence of aeolian deposits and marine influence. The three subunits were clearly controlled by sea level changes.

A detailed clay mineralogy study from 56 samples of the Montealegre del Castillo section in Albacete, in the so-called Meseta Estable of the southeastern Iberia, shows certain mineralogical trends that are repeated according to the different facies. Most samples contain quartz, feldspar (albite and orthoclase), calcite, hematite, and the clay assemblage is formed by illite and Mg-rich chlorite. Compositional differences were identified in the clays, with significant variations between those collected in strictly fluvial facies and those from marine-influenced facies. In samples formed in lacustrine facies containing organic matter, the formation of Mg-rich chlorite is apparently inhibited compared to samples without organic content. This clay mineral assemblage differs from those previously described for the CPE record in purely continental environments, where palaeosols and the presence of kaolinite or smectite were considered as evidence of relatively increased humid conditions [5, 6]. However, the clay mineral associations both in continental and transitional environments suggest that the humidity during sediment deposition was lower than initially inferred. These mineralogical changes provide valuable information about the paleoenvironment, especially regarding moisture levels during deposition. In addition, the magnesium content in the chlorite provides clues about the proximity of the depositional environment to the coastline.

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Mineralogical analysis of egg-bearing palaeosols (External Sierras, Pyrenees, Spain): Insights into Late Cretaceous paleoenvironmental conditions

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This study focuses on sedimentological and mineralogical analyses of continental palaeosols from the Garum Facies (Maastrichtian-Danian) outcropping close to the Loarre village (External Sierras, Pyrenees, Spain) for interpreting the palaeoenvironmetal conditions of their formation. The basal sediments of the Garum facies are composed of reddish paedogenized lutites with intercalations of rare white limestones and brownish sandstones. All these materials represent the last continental deposits close to the K/Pg boundary and host several dinosaur egg accumulations.

Sedimentologic features such as grain size, texture, mottling, rhizolith and ferruginous and carbonate nodules in the palaeosols were characterized. The mineralogical composition of the palaeosols was determined by X-ray diffraction in the whole samples and in the < 2 μm fractions. Thin sections of the palaeosols were also studied by optical microscopy and field emission scanning electron microscopy to characterize their texture and the chemical composition of the clay minerals. In addition, the humidity index was calculated to determine 5 cycles that reflect increases and decreases in the humidity of the environment.

The sedimentary environment suggests the presence of a fluvial system with expansive floodplains, where paleosols developed through subaerial exposure, with occasional ephemeral freshwater lakes. Oxisols, gleysols, protosols and vertisols have been described on well, moderately to poorly drained soils. The ferruginous nodules, rich in iron oxides, suggest fluctuating redox conditions, while carbonate nodules indicate episodes of drier conditions with calcium carbonate precipitation. The presence of several coloured rhizoliths, also points to varying temperature and humidity conditions.

The presence of kaolinite in the palaeosols suggests intense chemical weathering under warm and humid conditions. On the other hand, smectite, formed under seasonal wet and dry cycles, reflects climatic variability. Illite/smectite mixed-layers were also identified, reflecting intermediate weathering conditions, where fluctuations in humidity played a significant role in soil evolution. These clay mineral assemblages provide evidence of alternating wet and dry climatic phases, supporting the interpretation of periodic environmental changes within the study area.

The different types of palaeosols, together with the identified clay minerals (kaolinite, smectite and illite/smectite mixed-layers) reflect alternations of wet and dry periods in warm climates that allowed the pedogenesis. Furthermore, this study confirms that dinosaur eggs and clutches were laid in dry periods, and eventually covered by ephemeral flooding.

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Interstratified Kaolinite-Smectite in the Paris Basin: A new perspective on enhanced chemical weathering during the PETM

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The Paleocene-Eocene Thermal Maximum (PETM) was a short intense warming event lasting approximately 200 000 years [1]. Triggered by a sharp increase in atmospheric CO_2 around 56 million years ago, the PETM is often cited as an analogue to current global warming [2]. It has been associated with an accelerated hydrological cycle and a global, yet not systematic, increase in kaolinite content within sediments [3]. This enhanced kaolinite sedimentation has been explained by two main hypotheses: (1) increased chemical weathering, which facilitated kaolinite formation and transport to basins [e.g., 4], and (2) the reworking of lateritic paleosoils due to a higher frequency of extreme climatic events [e.g., 5, 6]. The latter hypothesis suggests a lag time between kaolinite formation and sedimentation that exceeds the duration of the PETM. Recently, Walters et al. [7] proposed an alternative mechanism based on OH-isotope measurements performed on kaolinites found in marine sediments from the North Sea Basin. They suggested that the transformation of smectite to kaolinite in soils from the basin margins could account for the observed sedimentation patterns, aligning with the timescale of the PETM.

In this study, we investigate clay mineralogy of three terrestrial sections in the Paris Basin (Therdonne, Cachan and Maisse), located on the southern edge of the North Sea Basin, using X-Ray Diffraction (XRD) of the 2 µm fraction and scanning and transmission electron microscopy (SEM and TEM). The three studied sections are tied to the PETM interval thanks to carbon-isotope analysis and palynology.

Our results show the development of interstratified kaolinite-smectite (KS) within two of the three sections. More precisely, an evolutive sequence from smectite-rich KS in calcretes towards kaolinite-rich KS in pseudogley and finally kaolinite, is evidenced in the Cachan borehole. These results are the first observation of the transformation of smectite to kaolinite within PETM sediments and confirm the hypothesis of Walters et al. [7]. The transformation of smectite to kaolinite in soils reflects tropical conditions in the Paris Basin and provides a new perspective explaining worldwide enhanced kaolinite sedimentation in relation to an accelerated hydrological cycle during the PETM.

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Intensified hydrological conditions and environmental changes during the Paleocene-Eocene Thermal Maximum at Modgunn Hydrothermal Vent Complex (IODP Expedition 396)

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Geological records from the Paleocene-Eocene Thermal Maximum (PETM) are considered the closest analogue to earth system response to large and rapid carbon cycle perturbations, providing important context into climate feedback processes essential for understanding anthropogenic climate change. Atmospheric warming exerts a substantial effect on global and regional hydrological cycles, with climate models suggesting a 'wet-get-wetter, dry-get-drier' scenario for the Early Eocene. Geological records from the PETM show significant responses in hydrological and sedimentary systems with enhanced erosion and transport of coarse terrigenous material to the marine basins, globally increased chemical weathering rates, and pronounced seasonality marked by extreme rainfall events. However, these responses exhibit notable regional and temporal variability. The International Ocean Discovery Program (IODP) Expedition 396 recovered an expanded and relatively continuous shallow marine PETM succession from the Modgunn Hydrothermal Vent Complex (HTVC) over a transect of ~500 m on the Norwegian continental margin. The PETM onset and body were captured in boreholes U1568A and U1567B, as identified by the distinct carbon isotope excursion (CIE) and biostratigraphy. From these boreholes, we produced multi-proxy sedimentary and geochemical records, to investigate the hydrological, sedimentological, and environmental response to the PETM, as well as their temporal relationships with the carbon cycle perturbation. These records include X-ray Diffraction (XRD) analyses on bulk and clay mineralogy, major and trace elemental data from core scanning X-Ray Fluorescence (XRF), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and grain size analysis.

Our preliminary results show potential stratigraphic offsets between the climatic feedbacks and the CIE onset at Modgunn HTVC. Detrital smectite dominates the clay mineral assemblage during the Late Paleocene and Early PETM, with kaolinite appearing just prior to the CIE onset. This early increase in kaolinite/illite (K/I) ratio aligns with other North Sea records, suggesting a potential intensification of the hydrological cycle preceding the major carbon cycle perturbation in the North Atlantic. However, we also observe a temporal lag between the rise in K/I and the influx of coarse terrigenous material, with no major change in grain size until later in the PETM. This suggests that different mechanisms may govern variations in these proxies, a hypothesis we aim to explore further. Enrichments in molybdenum and other redox-sensitive indicators point to multiple episodes of anoxic to euxinic conditions throughout the early PETM, likely driven by strong water column stratification and oxidation of organic matter from enhanced seasonal rainfall and runoff. Increased nutrient delivery to the ocean may have promoted seasonal primary productivity and diatom blooms. These records show major environmental changes along the Norwegian margin driven by a strengthened hydrological system during the PETM. However, the exact mechanisms controlling the timing of these climatic responses remain to be fully resolved.

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Assessing the role of clay mineralogy in Blue Carbon storage and stability in Ireland's Offshore Continental Shelf Sediments

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The term Blue Carbon, while not a common term, is simply the carbon captured by the world's ocean and coastal ecosystems.

Blue Carbon habitats, have an innate ability to store excess carbon, either in its organic or inorganic form. This carbon storage potential can be encouraged through management and restoration. Initially, Blue Carbon habitats included coastal and vegetated benthic sediments such as salt marshes, seagrass meadows and mangrove forests. The sediments of continental shelves are now also recognised as a huge carbon sink due to the sheer volume and expanse they cover. With a marine territory greater than ten times that of its landmass, it is important that Ireland explores the Blue Carbon potential of its offshore marine sediments. The QUEST project, funded by the Irish Marine Institute (MI) and Environmental Protection Agency (EPA), aims to quantify, characterise and assess the source, and fate of past and present carbon storage in the coastal and offshore sediments of Ireland so that this important carbon sink can be managed and if possible, increased.

The ultimate sink for Blue Carbon is marine sediment, however, once deposited, the fate of this carbon is variable. Many environmental factors are at play in the stabilisation, transformation, and/or liberation of carbon from sediments. Biological productivity and seafloor-water oxygenation are the most common environmental factors cited for increased organic carbon (OC) storage in marine sediments. In tandem with this, the role of mineralogy as an OC protector and binder is also significant. Clay minerals and Fe-(hydr)oxides have been shown to play instrumental roles in OC preservation and transformation in marine sediments. Building on previous carbon-stock evaluations performed by the QUEST team, an investigation into the role that mineralogy plays in Blue Carbon storage and stability in Irish offshore continental sediments is outlined.

Focus is placed on >5m vibro cores from mud-patch areas, to assess how carbon storage, source and stability has changed throughout recent geological time. Bulk physical and geochemical characterisation of sediment are determined, including particle size analysis (PSA), % total OC (TOC), total nitrogen (TN) and elemental concentrations generated by X-ray fluorescence (XRF). The relationship between PSA, TOC, and total specific surface area (TSSA) is examined to help elucidate the role of clay minerals in carbon storage. From selected depths, the <2µm sediment fraction is separated from the bulk by centrifugation using Stoke's law. Clay mineral identification is conducted by X-ray diffraction (XRD) on the <2µm fraction. Organic matter characterisation through pyrolysis-gas chromatography-mass spectrometry is conducted on the same depths as those selected for clay mineral XRD. Sedimentation rates for the uppermost horizons are estimated using gamma spectrometry (e.g. ^{210}Pb)

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Sessions 8+9: Critical Minerals in Clay-rich Deposits: Processes, Occurrences, and Resource Potential

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Boron, lithium and strontium in the Late Miocene saline-alkaline lake deposits of Karlovassi Basin, Samos Island, Greece

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In the Aegean Sea in Samos Island, Greece, Late Miocene continental volcanic terrain, tuffaceous and clayey rocks are widespread and occur interbedded with evaporites. In west Samos, the Karlovassi saline-alkaline lake basin was filled with a basal conglomerate, limestone, tuffs, Mg-rich mudstone and claystone, and finally a siliceous limestone [1]. The volcanic glass was diagenetically transformed to zeolites, smectite, opal-CT, and the authigenic boron bearing K-feldspar [2,3]. Colemanite, ulexite, celestite and gypsum were deposited with the form of lenses, nodules, or fissure fillings in close association with claystone within the tuffaceous sequence [3,4]. The rocks were classified in three groups, GI- the authigenic K-feldspar-rich tuffs, GII- the zeolite and authigenic K-feldspar-rich tuffs, and GIII- the smectite- and illite-rich claystones/carbonates. Representative samples of the three groups were analyzed by ICP, for major and trace elements; main focus was given on boron, lithium and strontium.

Boron ranges between 540-1460 ppm (GI), 120-600 ppm (GII) and 78-160 ppm (GIII), with their high values related to the abundance of boron-bearing K-feldspar. Lithium values range between 28-340 ppm (GI), 42-310 ppm (GII) and 24-240 ppm (GIII), showing almost equal distribution amongst the three groups. The highest Li content of group GIII (240ppm) was measured in dolomite [1]. According to 175 rock analysis performed by Rio Tinto Exploration back in early 2000s, 13% of the samples have >500 ppm Li, reaching up to 910 ppm in dolomitic claystones. The B:Li correlation coefficient is -0.10 in group GI, 0.60 in group GII and 0.53 in group GIII. The negative correlation of B with Li in group GI can be attributed to their presence in different minerals, in accordance with the Li- and B-rich clayey deposits of Rhyolite Ridge and Bonnie Claire, Nevada, where lithium mineralization is hosted within claystone, and boron is in the form of searlesite [5]. The partial relationship of boron with lithium in groups GII and GIII is attributed to the possible presence of Li-B minerals such as jadarite $LiNaSiB_3O_7(OH)$ that occurs in Serbia. Strontium also shows enrichments, ranging between 44-3900 (GI), 59-2400 ppm (GII), and 97-2200 ppm (GIII), having negative or negligible correlation with boron, B:Sr -0.67 (GI), -0.04 (GII), 0.24 (GIII) due to its presence as celestite and fixing in the clinoptilolite lattice [3]. The rare Sr-borates tunellite and veatchite identified in the western Anatolian borate deposits [6] have not been detected.

Taking into account that Karlovassi closed basin hosts authigenic K-feldspar, zeolites, dolomite, dolomitic marls and magnesian clays, which are promising for Li enrichments [7,8,9,10,11], as well as the Li content in Bonnie Claire, Nevada, and in Bigadic, Western Anatolia [10] that increases bottomward, and in Thacker Pass where Li is enriched in illitic rather than smectitic clays, a thorough borehole investigation is suggested for the Late Miocene clayey and tuff deposits of Karlovassi basin, targeting to the discovery of commercial lithium deposits, along with boron and strontium.

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Session 10: Natural Zeolites: From Geology and Fundamental Science to Applications and Market Challenges

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Sustainable Alternative to Copper-Based Pesticides in Agriculture: The LIFE MICROFIGHTER Approach

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Copper (Cu) is an essential micronutrient for plants [1], but its extensive use as a pesticide in agriculture, particularly in organic and integrated production systems (IPS), has led to its accumulation in European soils [2]. This accumulation poses significant risks to soil biodiversity, water quality, and human health. Despite European Union (EU) regulations limiting copper inputs to 28 kg/ha over seven years (4 kg/ha/year on average), copper-based pesticides remain indispensable for managing fungal and bacterial diseases [3]. The environmental impact is particularly severe in Italy, Greece, France, and Spain, where high Cu concentrations threaten agricultural sustainability.

The LIFE MICROFIGHTER project presents an innovative approach to mitigate these issues by developing and testing a novel Zeo-Biopesticide composed of natural Italian zeolites (potassium chabazite) and a biocontrol microorganism (Pseudomonas sp. DLS65). This alternative aims to control key pathogens affecting grapevine, tomato, and olive, including downy mildew, bacterial speck, bacterial spot, olive knot, and peacock spot. By leveraging the synergistic effects of zeolites and biocontrol agents, the project seeks to significantly reduce or eliminate copper-based pesticide applications in organic and integrated farming systems. The project's key objectives are: i) to reduce copper inputs from an average of 4 to 2 kg/ha/year without compromising crop yield and quality, with the potential for a complete Cu replacement; ii) to demonstrate a decrease in total soil Cu concentration while enhancing soil biodiversity; iii) to raise awareness among farmers, policymakers, and stakeholders about the environmental and health risks of Cu-based pesticides, promoting the Zeo-Biopesticide as a viable alternative; iv) to conduct comprehensive environmental monitoring, life cycle assessment (LCA), and an economic feasibility analysis to assess the long-term sustainability of the technology. To evaluate the impact of the Zeo-Biopesticide, total and bioavailable Cu concentrations in soil are monitored at the beginning and third year of the study using inductively coupled plasma mass spectrometry (ICP-MS). Other physico-chemical soil parameters, including organic matter content, pH, electrical conductivity, and cation exchange capacity, are analyzed to assess their correlation with Cu levels. Spatial distribution maps of Cu concentrations across experimental fields in Italy, Croatia, and Spain (nine sites in total) are created to visualize changes over time. After one year, baseline Cu data and initial distribution maps have been generated. These will be compared with subsequent analyses to determine the Zeo-Biopesticide's effectiveness in reducing soil Cu contamination.

By integrating natural mineral-based strategies with microbial biocontrol, LIFE MICROFIGHTER offers a promising, sustainable solution to Cu overuse in agriculture, supporting environmental protection and regulatory compliance while maintaining agricultural productivity.

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Obtention of Clinoptilolite Nanoparticles via Ultrasonic Cavitation Dispersion

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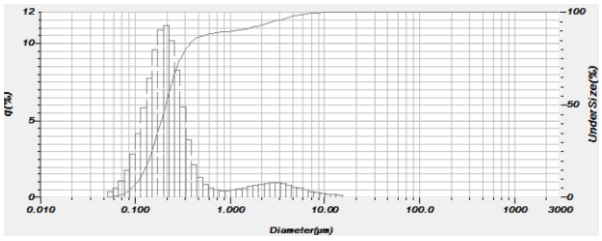
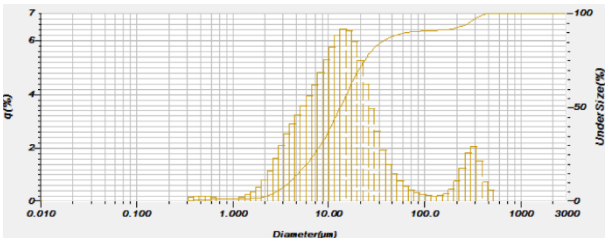
Clinoptilolite, a natural zeolite characterized by its microporous crystalline structure and high ion-exchange capacity, possesses detoxifying, antioxidant, and immunomodulatory properties, rendering it a promising material for advanced medical applications [1]. This study explores the ultrasonic-assisted dispersion of pre-existing nanoparticles within micronized clinoptilolite powder, utilizing cavitation-induced sonication in a deionized water solution (280 mL, 40 kHz, 320 W, 5 minutes) with dimethyl sulfoxide (DMSO, 20 mL) as a co-surfactant [2], [3]. High-intensity ultrasonic energy effectively disrupts particle agglomeration, allowing nanoparticle dispersion into an aqueous suspension, while DMSO lowers surface tension to promote uniform dispersion. Particle size distribution (PSD) analysis of a 50 mL sonicated sample reveals a mean particle size of 210.8 nm, with 50% of particles below this threshold, 10% below 112.4 nm, and 90% below 1.2304 µm. The observed size range, from 58 nm to 15.172 µm, indicates a broad distribution that enhances surface area, enteral and systematic bioavailability compared to untreated samples [4]. The sonication process reduces nanoparticle agglomeration through nanobubble sono-implosion, significantly improving particle dispersion [5]. Clinoptilolite's chemical composition and crystallinity were validated using X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), and petrographic analysis. However, further characterization and optimized preparation methods are needed to fully quantify, isolate, and achieve high-resolution electron microscopy imaging of the nanoparticles. This reproducible ultrasonic DMSO-assisted dispersion method establishes a robust framework for preparing bioactive clinoptilolite nanoparticles, paving the way for advancements in nanomedicine, biotechnology, and potential explorations in quantum biology [6].



Img.1 Clinoptilolite Ultrasonic Treated Samlple



Img.2 Clinoptilolite Ultrasonic Untreated Samlple

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Sodalite and cancrinite for safe entrapment of As and Se

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Selenium (Se) and arsenic (As) are common hazardous pollutants, which pose health risks even at low concentrations. They are present waste repositories and often found in contaminated soils, water and cement. The immobilization of Se and As is challenging, because both elements occur primarily as negatively charged oxyanions, whereas mineral surfaces typically have negatively charged surfaces, resulting in poor retention of these anions [1].

Sodalite (SOD) and cancrinite (CAN) are zeolitic structures with a 4:3:3:12 Na^{+}:Al^{3+}:Si^{4+}:O^{2-} molar ratio that creates a positive charge, which must be compensated by a negatively charged ion. As a result, the framework can encapsulate and stabilize a wide range of anions. Thanks to these extra-framework properties, these zeolites are capable of immobilizing high concentrations of Se or As up to 975 mmol/kg. Both structures can form naturally or be synthesized under hydrothermal conditions in an alkaline environment, typical for cement, and remain stable under most environmental conditions.

The aim of this study is to investigate the formation and stability of Se and As incorporated in SOD and CAN structures and to understand the mechanism of Se/As anion immobilization. The key questions are whether these zeolites can effectively immobilize Se and As, remain stable after anion incorporation, and ensure long-term entrapment without the risk of toxic element leaching from the zeolitic framework. In a first step, a wide range of previously reported synthesis conditions, which can be used to obtain pure, metalloid-free SOD and CAN [2][3], were analysed and further modified to encapsulate anions in these frameworks. Next, the structure and properties of the obtained materials are characterised by a variety of methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) and thermogravimetry (TG). Additionally, anomalous XRD (AXRD) and X-ray absorption spectroscopy (XAS) will be used to pinpoint the structural sites occupied by anions in different oxidation states and to study their local environment and obtain an understanding of the encapsulation mechanism.

A detailed mechanistic understanding of the incorporation of As and Se by zeolites of the sodalite and cancrinite families will help to decide whether these and similar zeolites are suitable as a stable matrices for the immobilization of anionic pollutants.

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Origins of compositional diversity in natural zeolites within the Antrim Lava Group, Northern Ireland, UK

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The Antrim Lava Group comprises voluminous alkaline basalts, less extensive tholeiitic basalts, and inter-flow sediments formed in the Palaeocene between 63.2 and 60.0 Ma [1,4] during early rifting of the North Atlantic. Zeolites and associated minerals crystallized within vesicles during post-eruptive hydrothermal overprinting as the lava pile of >80 flows accumulated. Studies in the mid-20th century [e.g. 7] established geographical patterns in zeolite species distributions which reflect host rock chemistry (alkaline vs. tholeiitic) [5] and coastal vs. inland exposures of the lava pile. Zeolites crystallized from relatively high-salinity hydrothermal fluids, such as phillipsite-Na [2], gmelinite-Na and gobbinsite [6], appear to be spatially associated with coastal outcrops of the Antrim Lava Group. Unusual Mg-rich varieties of chabazite and heulandite are geographically restricted to a coastal location on Islandmagee.

Data presented here as bivariate and ternary compositional diagrams, from EMPA obtained in PhD research in the 1980s and more recent EMPA and SEM-EDS analyses, illustrates a wide heterogeneity in alkaline element chemistry and Si/Al ratios in Antrim zeolites. We explore the extent to which this diversity may be due to ionic exchange with modern seawater in specimens from coastal locations.

Inland and coastal localities of Antrim zeolite specimens are distinguished on previously published discrimination diagrams utilizing graphs of Si/Al vs. (Na+K)/Ca in phillipsite and chabazite associated with freshwater and seawater-influenced environments in Antarctica [2]. A marine influence is also clearly evident in erionite and gmelinite given their wide compositional ranges extending to high ratios of Si/Al and (Na+K)/Ca in specimens from the same localities where phillipsite and chabazite show high ratios. Individual crystals commonly show zonation from Ca-dominant cores to Na-dominant rims, for example changing from garronite in the core to gobbinsite in the rim. Chabazite from Rathlin Island and erionite and cowlesite from the north coast location of Dunseverick have exceptionally high Na contents. We infer that seawater interaction is more rapid and extensive with fibrous zeolites such as erionite than with species that form blocky crystals.

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Synthesizing zeolites from granite cutting sludge

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The accumulation of industrial waste is a serious problem, as it has significant effects on the quality of soil, water, and air. This research addresses the idea of synthesizing zeolites from various types of industrial waste, managing them appropriately, and transforming them into raw materials for new processes at the end of their life cycle. The synthesis will be carried out using a hydrothermal reactor and will focus on the capture and separation of CO_2/H_2, promoting sustainability and the circular economy. Zeolites, characterized by their porous and crystalline structure, formed by a three-dimensional network of [SiO4]4- and [AlO4]5- tetrahedra linked by oxygen atoms, are very useful in catalysis, water treatment, and gas purification. In order to determine whether the product obtained from the synthesis is indeed a zeolite, various characterization techniques will be employed. In addition, the zeolites with the best performance for the aforementioned applications will be identified.[1][2]

The next step was to select the sludge to be valorized; in this research, granite cutting sludge will be used. This sludge was sieved to obtain a smaller particle size and increase its contact surface, reaching 63 µm. [3]

In previous experiments, it was found that zeolitic materials did not form from sludge samples containing iron. Since our sample had a high iron content, an acid pretreatment using aqua regia was carried out to remove it. The acid was diluted by bringing 50 mL to a total volume of 1 L; from this diluted solution, 200 mL were added to 100 g of sample and left to rest for 24 hours. Afterwards, the mixture was filtered and washed until a neutral pH was reached.

Next, the sample was placed in an oven at 70°C for 24 hours. After removal from the oven, an alkaline fusion method using NaOH was applied, and the sample was calcined for 2 hours at 400, 500, and 600°C.

The fused sample was then mixed with 100 mL of deionized water and stirred for 24 hours. After this period, the mixture was transferred to the reactor for crystallization at 180°C for 12 hours and again at 180°C for 48 hours to observe any differences.

Finally, the prepared product was washed several times with deionized water to adjust the pH to approximately 9–10.

The final samples obtained consisted of a liquid phase, which was the washing water; an upper gel with high water content; a compact white central gel; an intermediate gel darker in color than the central gel; and a dark solid that settled at the bottom.

All sample fractions were individually separated and subjected to advanced characterization techniques, including FTIR, XRD, and XRF, among others, in order to verify the formation of zeolitic phases. Preliminary findings are encouraging and support the continuation of the planned research focused on the application of these materials for carbon dioxide (CO_2) capture. [4]

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Session 11: Identification and Characterization of Phyllosilicates on Mars and Other Planetary Bodies through Remote Sensing, Rover Instruments, and Analog Studies

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Assessing the Spectral Response of Secondary Martian Minerals

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Determining the mineral content in samples or terrains during the study of extraterrestrial bodies is crucial for the accurate interpretation of geological processes that have occurred on their surfaces, and spectroscopy in the visible, near-infrared, and short-wave infrared (VNIR-SWIR) ranges plays a prominent role among the remote sensing methods, as it is well known. In the case of Mars, in addition to the primarily volcanic minerals (olivine, pyroxene, and feldspars) there are regions rich in secondary minerals including different clay minerals, carbonates,and/or sulphates such as gypsum and jarosite, which are of particular interest as they indicate the past presence of water on the planet. All these secondary minerals have a good VNIR-SWIR spectral response, and they are easily identified, however the mixtures among them can have non proportional spectral response. As shown by Santamaría-Lopez et al., (2024) and Santamaría-López & Suárez (2024) some of these minerals can even not be identified in certain mixtures, been the detection limit of each mineral varies depending on the accompanying minerals.

In this study, analysis was carried out using a spectroradiometer to examine mixtures of the aforementioned minerals with clay minerals to observe how their spectral responses change as the proportions of their components vary. It was found that clay minerals are easily identifiable even in the presence of high amounts of olivine, pyroxene, and calcite. However, gypsum stands out as the mineral with the most intense spectral response. Clay minerals, on the other hand, cause deviations in the position and a drastic reduction in the intensity of certain absorption features of pyroxene, augite, and especially calcite, making their identification more challenging.

The modification of various absorption features of olivine, pyroxene, and calcite can occur even when the proportion of clays or gypsum are very low. This poses a significant challenge when interpreting geological features of terrains or samples analyzed in situ by rovers. For example, a high clay content derived from feldspars could suggest a volcanic terrain that has been exposed to atmospheric weathering over a long period (i.e., a mature terrain). However, this conclusion could result from an overestimation of the clay content, which, despite being low, can obscure the presence of other minerals.This works offers preliminary results on the detection limits of common minerals in altered Martian rocks.

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Spatially resolved analysis of habitability-related phenomena: Talc-like and associated minerals at different scales

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The origin of secondary minerals depends on both the solutes in the solutions entering the reaction environment and the reactive primary rock-forming minerals that contribute additional solutes to the environment of secondary-mineral formation. Both types of minerals – primary and secondary – can be detected from orbit at ~ ≥ *m-scale* and from advanced landed imagers and imaging spectrometers at ~*sub-mm to 100-10 µm resolution*.

Co-occurrence of any such reactant-product assemblages at spatial resolutions larger than the scale of the individual grains-crystals can occur by any number of processes. These can range from mechanical juxtaposition of genetically unrelated grains to precipitation of secondary minerals onto passive primary-mineral substrates to grain-crystal-scale reaction relationships including reactive interfaces and primary-mineral replacement by secondary minerals at *sub-micron to nanometer scales*.

The environments in which aqueous alteration processes may include source-area (paleo)weathering reactions with surface water; eo-(early), meso-(burial) and telo-(uplift) diagenetic reactions with (respectively) pore fluids immediately beneath the depositional surface, deep basinal pore fluids, and recent-modern groundwater; and neoweathering of exhumed sedimentary rock at the recent-modern surface by recent-modern surface moisture.

Each possible process, each possible paleoenvironment, and each possible environment-process association, can be framed as an hypothesis. To determine which of these processes produced – and by such determination (by testing each hypothesized process) infer – the specific paleoenvironmental formation conditions of any specific assemblage of such minerals requires spatially resolved *in litho* observations *at sub-micron to nanometer scales and spatial resolution*.

This presentation illustrates mineral characterization, identification, and interpretation of talc and talc-like minerals from published case studies at different spatial scales.

Example: Phyllosilicate (including clay) minerals in Mars meteorites: Clay-related products of pre-terrestrial (martian) aqueous alteration of rock-forming silicate minerals in Mars meteorites are mainly Si-Al-Fe(±Mg?) mineraloids consisting of a mixture of multiple poorly, nano- or non-crystalline constituents in varying proportions. Some occurrences contain constituent phases that are sufficiently large and crystalline to diffract X-rays or electrons. Phyllosilicates consist mainly of 2:1 low-layer-charge (collapsed-smectite-like or talc-like) nanocrystalline (commonly operationally amorphous) material; some occurrences contain associated sparse 1:1 serpentine-like material. The hydrous metamorphic alteration that formed talc-like phases in ALH 84001 (orthopyroxenite) (~3.9 Ga, Noachian) [1] indicates that liquid water was present and reacting with rock-forming silicate minerals on ancient Mars.

[1] Steele A et al. (2022) Science 375:172–177

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Session 12: Advances in structural characterization of layered compounds

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Electron diffraction mapping and DFTEM imaging as potential tools to probe layered materials superstuctures and structural defects

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Layer materials are known to present large variations in their crystal structures, such local heterogeneity of chemical composition, regular or random interstratification of polytypic fragments, or ordered or modulated arrangement of mixed-valence metals and/or interlayer cations.

Powder X-ray diffraction (XRD) is one of most widely used technique to investigate order and disorder in layer materials. However, it provides an information averaged over a large number of particles and structural heterogeneities among our within individual particles cannot be assessed.

Transmission electron microscopy in regular (TEM) or scanning (STEM) mode allows coupling chemical and structural characterizations at the particle scale, at the nanoscale or even at the atomic scale. Recording of X-ray emission (STEM-EDX) provides chemical mapping of the local chemical composition while electron diffraction techniques in TEM mode (SAED) allows investigation of the crystal structure of single crystals. Origin of superstructures can be imaged using dark-field TEM (DFTEM) up to atomic scale to reveal local departure to the periodic arrangement of interlayer cations and heterovalent layer cations and compared with HRSTEM images. Structural heterogeneities within individual crystals can be further investigated by recording convergent beam electron diffraction (CBED) signal at the nanoscale using scanning capability of all modern microscopes (using ACOM system or 4D-STEM technique), in order to reconstruct ED maps across a particle. Calculation of orientation maps allows for quantifying for example the local curvature of the thin clay particles. In addition, reconstruction of virtual dark-field images of the mapped area may lead to a better understanding of the local modulations to the averaged structure determined by powder XRD.

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Computational study of 1,10-Phenanthroline trapping by smectites

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1,10-Phenanthroline (phen) is a classic chelating bidentate ligand for transition metal ions that has played an essential role in developing coordination chemistry [1]. Phen is a rigid planar, hydrophobic, electron-poor heteroaromatic system whose nitrogen atoms are beautifully placed to act cooperatively in cation binding. These structural features determine its coordination ability toward metal ions. For instance, an intense luminescence or interaction with DNA can feature metal complexes with phen. Moreover, phen, a widely used chelating compound, is also present in wastewater. Clay minerals are abundant, low-cost materials for environmental applications. Because of their large specific surface area, high porosity, surface charge, and surface functional groups, clay minerals function as adsorbents, filters, flocculants, and carbon stabilisers. Further, the clay minerals' surface can be modified from hydrophilic to hydrophobic, making them suitable adsorbents and carriers of non-ionic organic compounds [2].

In the study, the models of two smectites, montmorillonite (dioctahedral) and saponite (trioctahedral), were used to study the stability of phen-smectite hybrid structures for trapping/immobilising phen from wastewater and potential further technological use (sensors, adsorbents, etc.). The density functional theory (DFT) method with the D3 scheme [3] for dispersion corrections implemented in the VASP program was used for examination. The findings highlight both studied phen-smectite hybrids as stable structures.

Acknowledgement: ES is funded by the EU Next Generation EU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00009.

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Assessment of basic properties of nanostructured anionic layered double hydroxide derived nanocomposites by in-situ CO_2 FTIR sorption

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This research will focus on the design and synthesis of a highly active sorbent material for climate-economic applications. It will contribute to decarbonisation, resulting in a reduction of CO_2 production, in particular in the energy and industrial sectors, and will support climate action in the context of environmental protection.

Given that CO_2 molecules have an affinity to basic catalysts, materials for carbon capture from exhaust gases must be characterised by the presence of basic centres, and the ability to generate centres of varying strength and distribution is of great importance when capturing CO_2 molecules from both cold and hot exhaust gases.

In this project, the nanostructured anionic layered double hydroxides (LDH) and their mixed oxides, characterised by porous structure, different composition and environmental neutrality, were obtained with one-pot synthesis and used to assess the basic properties by in-situ CO_2 FTIR method. For the first time, the qualitative-quantitative studies of the generated basic centres were carried out using in situ spectroscopic methods with the CO_2 probe molecule supported by Temperature-Programmed CO_2 Desorption. The influence of the synthesis parameters on the nature of the generated basic centres, their strength, CO_2 adsorption/desorption process kinetics and sorption capacity was investigated. Using a co-precipitation method, a series of anionic layered double hydroxides (hydrotalcites), with formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][An^{-}]_{x/n}\cdot mH_2O$, and compositions with Mg to Al ratio from 2:1 to 5:1, differ in ageing time, degree of crystallinity and grain size, controlled by the synthesis conditions, were obtained and characterised using XRD, FTIR, SEM/EDS, and N_2 adsorption/desorption methods for structural-sorption correlation.

FTIR spectroscopic studies of the anionic hydrotalcite-like precursors and their mixed oxides exhibited that CO_2 reacts with the O^{2-} and OH^- to form carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. Carbonates and bicarbonates are formed at low surface coverages, and there is no preference which O^{2-} or OH^- basic centres react with CO_2 first. The ageing time and crystallinity affect the availability of the generated basic centres and the number of OH^- groups, of which only some (free OH^- groups) are basic enough to react with CO_2. The decomposition of structural carbonates was practically complete after activation at 400 ^oC. Calcination increased the basicity of hydrotalcite; the O^{2-} centres have a higher strength than the OH^- groups. Calcined mixed oxides form more carbonates than their precursors due to the greater number of available O^{2-} centres. Bicarbonates decompose at lower temperatures than carbonates. Moreover, the 'bidentate' carbonates are more stable than 'bridged' carbonates. The highest concentrations of O^{2-} and OH^- basic centres were exhibited by the layered materials with the highest Al content, indicating an edge effect during the sorption of CO_2 molecules on the surface of mixed oxide sorbents.

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Session 13: Clay Applications in Ceramics

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Shear stability of ceramic slips in solid casting production

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In the production of complex shape ceramic parts with the traditional slip casting process, controlling the rheological properties of the suspension is crucial. Especially when working at low pressure or ambient pressure, thixotropy and the gelation rate of the suspension are extremely important [1]. Effective gelation requires a sufficient concentration of colloidal clay particles in the suspension, which can be characterized by specific surface area. Flocculants and deflocculants added to the suspension also influence the gelation behaviour. A higher colloidal content in kaolinitic clay also promote superior technological properties of the green and fired body [2]-[3], ensuring fewer defect and increasing the product quality. Instead, the presence of non-colloidal filler particles (up to 30% vol.), like quartz or chamotte, can compromise the stability of the suspension leading to settling or segregation phenomena during shear flow [4]. The presence of a composition gradient within the ceramic piece, could result in a differential shrinkage rate for different zones and therefore in the development of internal stresses that contribute to fractures formation in the later firing stages. This project aims to study the static and dynamic stability of clay suspensions for ceramic applications. Specifically, it focuses on developing strategies to minimize particle segregation and ensure uniformity in composition and structure throughout the ceramic products. By analysing the production process, raw clay material and fault-cracked ceramic parts of a local majolica industry, we identify the key parameters that control suspension stability. Rheological measurement together with mineralogical x-ray powder diffraction (XRPD) analysis and particle size measurement of kaolinitic clays are performed. Homogenisation of the suspensions, regardless the suspension and clay properties, can be obtained with properly designed passive mixing elements installed on the pumping line. The main results of this project are expected to provide a comprehensive understanding of clay suspension stability. It will also demonstrate the effectiveness of passive mixing elements, and the impact of raw material properties, in achieving uniform ceramic products. Understanding the complex interplay of rheological properties, particle dynamics, and mixing mechanisms is crucial for optimizing the manufacturing process and enhancing product quality in ceramic industries.

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Physicochemical Characterization and Valorization of Altered Clays from the Ankaratra Volcanic Massif in Madagascar

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Craftsmen in the Arivonimamo district of Madagascar use the numerous clay outcrops to produce baked clay bricks. The clay samples are mainly derived from the alteration of igneous and metamorphic rocks outcropping in the region. These rocks are part of a vast massif, about a hundred kilometers long between the towns of Arivonimamo and Antsirabe (i.e. Ankaratra massif). The objective of this work is to characterize the clay minerals of the Arivonimamo district, to identify avenues for development and to quantify the clay resources available on a regional scale.

The preliminary study allowed sampling alteration profiles developed on migmatized granitic rocks, migmatites and granitoid migmatites. Seventeen samples collected from 3 sites were analyzed by X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) to determine their mineralogical and chemical composition. Qualitative and quantitative estimation of the mineralogy was carried out using Eva and Topas (® Bruker) software. Laser granulometry analyses and determination of Atterberg limits provide additional information on the geotechnical properties of these deposits (i.e. proportion of clay fractions in the samples, plasticity).

The clay deposits in the study area are composed of primary minerals inherited from the substrate (10 to 43% quartz, 11 to 26% micas, 9 to 22% potassium feldspars and around 15% chlorite) and secondary minerals resulting from moderate to intense chemical alteration linked to tropical climatic conditions. The secondary minerals are mainly represented by kaolinite (30 to 81%), associated with variable proportions of iron oxides and hydroxides (1 to 19% hematite, 3 to 17% goethite) and aluminum hydroxides (4 to 36% gibbsite). The chemistry of the clay deposits shows a predominance of silica (26 to 64% SiO_2), alumina (24 to 30% Al2O3) and iron (up to 27% Fe_2O_3), in agreement with mineralogical interpretations. The oxides MgO, CaO, MnO, K_2O, and P_2O_5 are present in trace amounts (<2%). Grain size analysis revealed a high percentage of silty particles (35 to 83% of particles between 2 and 63 microns) associated with a minor clay fraction (2 to 17% of particles <2 microns). The sand fraction varies from one sample to another (1 to 63% of particles >63 microns), likely related to surface runoff. The Atterberg limits indicate a plasticity limit between 10 and 40 and a water content that varies by a factor of 2 (from 30 to 60%).

Additional sampling will be conducted to study the spatial variability of the mineralogy and grain size of the clay deposits. The objective is to estimate the extent of kaolinite-rich layers in order to compare regional Malagasy resources with kaolinite deposits exploited worldwide.

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Monitoring the quality of a kaolin mine over time: Piloni di Torniella (Tuscany, Italy)

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Italian ceramic tiles industry, a major player in the sector, suffered a deep crisis in its raw materials supply chain after the outbreak of war in Ukraine. This country, in fact, had been the main supplier, until that moment, of high plasticity ball clays. Following this disruptive event, a renewed interest in national geo-resources has raised, both for the plastic and the flux components [1, 2]. These can ensure more stable supplies, allowing at the same time to reduce costs and environmental impact connected to raw materials transport.

One of the most important kaolin mine in Italy is the Piloni di Torniella deposit (Roccastrada, Tuscany), which has been supplying raw materials to Italian tile industry since the early 2000s. In this site, a hydrothermal deposit developed due to a multi-stage alteration process, which involved the primary Roccastrada Rhyolites (2.3-2.5 Ma) [3]. However, hydrothermal fluids preferentially circulate through rock discontinuities, resulting in a marked spatial heterogeneity of the deposit. This could lead to significant fluctuations in time in the composition of the extracted material, both from a chemical and a mineralogical point of view.

This study performs a quality monitoring of the material extracted over a time mesoscale, from 2018 to 2024. Four sampling campaigns have been realized: 2018, 2021, 2023 and 2024. To evaluate variations in chemical and mineralogical compositions of the samples, a multi technique protocol has been adopted. This characterization was carried out by X-Rays Fluorescence (XRF), Loss on Ignition (LOI) determination, Fourier Transform InfraRed Spectroscopy (FTIR), polarising-light optical microscopy, X-Rays Powder Diffraction (XRPD), Scanning Electron Microscopy with Energy-Dispersive Spectrometry (SEM-EDS) and micro-Raman spectroscopy.

The characterization of the sampled material allowed to constrain the marked spatial heterogeneity of the deposit. Together with this, the mining license prescriptions have been identified as another major factor affecting raw materials quality variations in time. However, the strategy adopted by the mine holder, ie. mixing material extracted from different excavation sites within the mine, has proven effective to assure a robust compositional stability for the material supplied to ceramic industry. Moreover, a raw material quality indicator has been developed, based on LOI and chemical composition. These preliminary results can help in the planning of mining activities also in other hydrothermal kaolin deposits, characterized by the same spatial heterogeneity in kaolinization processes.

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Preliminary development of a composite Circularity Indicator applied to the Construction and Demolition Waste Sector

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The circular economy has emerged as a key strategy to promote sustainability in the construction sector, particularly in the management of Construction and Demolition Waste (C&DW). The European Union faces major challenges related to waste generation and greenhouse gas emissions, with the construction industry being one of the largest consumers of resources and producers of waste. In this context, the European Commission has launched circular economy action plans, identifying the construction sector as a strategic priority.

However, a comprehensive and widely accepted methodology for effectively monitoring circular economy processes in this sector is still lacking. Thus, in response to the need for more complete indicators, the Integrated Circularity Index for CDW (ICIRCD) is introduced, a composite indicator that seeks to provide a comprehensive assessment of circular economy performance in the construction and demolition waste sector. The methodology for its development is based on an adaptation of the OECD Handbook on Constructing Composite Indicators [3]. The methodology followed is summarised in figure 1.

Figure 1. Summary of development methodology

Effective implementation of the circular economy in the management of CDW requires a combination of technical, political and economic strategies, supported by specific indicators that reflect progress towards sustainability. The preliminary development of the Integrated Circularity Index for CDW (ICIRCD) is presented as a contribution to address the need for comprehensive indicators that consider both environmental and economic aspects in the sector. Measuring progress towards circular economy objectives demands going beyond traditional resource efficiency metrics, integrating environmental and economic dimensions to guide decision making and assess performance in the CDW sector.

The current lack of specific indicators underlines the importance of developing tools that enable comprehensive monitoring and facilitate the transition to a circular model in construction. The ICIRCD, in its preliminary formulation, seeks to simplify and combine key dimensions into a single analytical framework, incentivising sustainable practices that are also economically viable.

Acknowledgements: Grant PID2022-139100OB-100 funded by MICIU/AEI/10.13039/501100011033 and, as appropriate, by "ERDF/EU"

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Development of a strategy for obtaining lightweight artificial aggregates (LWAs) from construction and demolition waste (CDW)

Troyano-Pérez, F.J. [1], Alonso Azcárate, J.[2], Andreola, F.[3], Barbieri, L.[3], Conde Sánchez, A.[4], Cotes-Palomino, M.T.[1], López, A.B.[1], Labrincha, J.[5], Lancellotti, I.[3], Martínez-García, C.[1] Martínez Rodríguez, A. M.[4] and Cobo-Ceacero, C.J. [1]

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Construction and demolition generate enormous amounts of waste (CDW) worldwide and in Europe, accounting for a significant portion of the total waste stream. In the European Union, CDW is estimated to constitute approximately one-third of the total waste generated annually [1]. To address this challenge, it is crucial to implement circular economy strategies that transform this waste into valuable resources. A promising solution is the production of artificial lightweight aggregates from the processing and treatment of CDW. The optimisation of the production of these lightweight aggregates with tailored properties for various applications (lightweight concrete, green roofs, horticulture, gardening, etc.) can be achieved through Mixing Experiments - Design of Experiments (ME-DoE). This statistical methodology allows the identification of key process variables and their interactions to obtain products with desired characteristics [2]. The application of ME-DoE in the recovery of CDW for the production of lightweight aggregates not only reduces the amount of waste sent to landfills but also decreases the demand for natural aggregates, contributing to a more sustainable construction. A considerable number of samples of CDW from Spain, Italy and Portugal were received and characterised by X-ray diffraction to quantify, using Rietveld refinement, the crystalline phases and amorphous material present in the samples. Its particle size distribution and chemical composition (by X-ray fluorescence) were also determined. Once characterised, one of them with a neutral composition was selected as the basis for the study (CDW-B). The Design of Experiments methodology was then used to determine the effect of the contents of CDW-B, aggregate washing sludge (AWS), organic matter of residual origin (OM) and iron phase (Fe) on the development of LWAs. The incorporation of AWS is necessary to provide the initial mixture with the plasticity required for moulding and pelletising. On the other hand, OM and Fe will assure the expansion of the aggregate upon firing. The mixtures established by ME-DOE have been processed in an extruder (Nannetti), sintered in a tubular rotary laboratory kiln (Nannetti TOR-R 120) and then technologically characterized: weight loss during the preheating and firing stages (LOI_{preh} and LOI_{firing}, respectively), bloating index (BI) calculated as the percentage change in size experienced by the average of 25 samples, loose bulk density (ρ_b) (EN-1097-3), apparent density (ρ_a), oven-dry density (ρ_{rd}) and water absorption at 24 hours (WA_{24}) (EN-1097-6). Its mechanical strength (S) was also determined using a Nannetti®FM 96 press. The statistical models obtained provide a more accurate understanding, through response surface graphs and effect graphs, about the contribution of the different components of the mixtures studied, as well as the synergies that occur between them. In addition, they have made it possible to optimize the composition of the mixtures according to the characteristics sought in the LWAs for their final application. Considerable adjustments were obtained between the response given by the proposed models and the experimental values obtained for the corresponding compositions. Finally, this study will make possible to determine which CDW samples, from the ones received, are most likely to generate LWAs, depending on their composition and characteristics.

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[2] Ramos Azpeitia M et al. (2024) J Ceram Process Res 25: 5.

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Circular Engineering: effect of adding different organic wastes on the development of lightweight artificial aggregates (LWAs) from mining waste

Cobo-Ceacero, C.J.[1], Alonso Azcárate, J.[2], Conde Sánchez, A.[3], López, A.B.[1], Martínez-García, C.[1], Martínez Rodríguez, A.M.[3], Troyano-Pérez, F.J.[1] and Cotes-Palomino, M.T.[1]

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Construction and agriculture are key sectors that must evolve towards the circular economy to mitigate their environmental impact. Construction, responsible for a high percentage of emissions and waste (40% and 35% in the EU respectively [1]), needs sustainable alternatives to materials such as aggregates, whose consumption in Spain reached 143.6 Mt in 2022 and whose global demand is expected to increase by 45% by 2060 [2]. In agriculture, the circular economy seeks to recycle nutrients and reduce waste. In this context, artificial lightweight aggregates are emerging as a multifunctional material with potential in both sustainable construction (lightweight concrete, green roofs) and circular agriculture (hydroponics, gardening), offering an innovative solution for a more sustainable future by utilising waste and reducing pressure on natural resources.

This work focuses on obtaining artificial lightweight aggregates made exclusively from waste, using a protocol to establish the formulations and the subsequent analysis of the characterization results of the LWAs obtained through the Mixing Experiments - Design of Experiments (ME-DOE) methodology using the statistical software Design Expert. Six different waste materials were used. Three of mineral origin: aggregate washing sludge (AWS), granite cutting sludge (GCS) and slate cutting sludge (SCS), and three organic additives: cork dust (CD) generated in the manufacturing process of bottle stoppers, coffee grounds (CG) and olive pulp (OP), waste generated in the production of virgin olive oil. All wastes have been characterized by determining the particle size distribution by laser diffraction, the chemical composition by X-Ray Fluorescence and the thermal behaviour by simultaneous Differential Thermal Analysis-Thermogravimetric Analysis (DTA-TG) in air atmosphere. Additionally, and only for inorganic samples, dilatometric tests have been carried out and the mineralogy of the sample has been studied by X-ray diffraction both in polycrystalline powder and in oriented aggregates.

To characterize the manufactured LWAs, a number of properties have been determined. The LOI of the preheating and firing stages (LOI_{preh} and LOI_{firing}, respectively) was determined on 25 samples as the percentage change in weight before and after heating in the rotary kiln. The bloating index (BI) calculated as the percentage change in size experienced by the same samples above. The loose bulk density (ρ_b), apparent density (ρ_a), oven dry density (ρ_{rd}) and 24 h water absorption (WA_{24}) has been determined according to EN-1097-3 and EN-1097-6. The mechanical strength (S) was determined using a Nannetti®FM 96 press. Finally, all those aggregates obtained that have a ρ_b and/or ρ_{rd} lower than 1.2 and 2.0 g/cm^3 respectively, will be considered as LWAs according to the EN-13055-1. Finally, ME-DOE regression models allowed us to establish the effect of mixture composition on the technological properties of the LWAs obtained. Thus, using the model equations and setting the values of the desired final properties according to the intended application for the LWAs, we were able to determine the composition of the starting mixtures. This paves the way for obtaining the most suitable variety of LWAs depending on their use as aggregates for construction, green roofs, horticulture or gardening. Furthermore, it was found that the expansion effect of LWAs favoured by organic matter is independent of the type of organic waste used.

[1] European Commission. Building and Construction.
[2] Zhong *et al.* (2022) Nat Sustain 5: 389–392

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Manufacture of geopolymers for the sustainable recovery of construction and demolition waste (CDW)

López, Ana. B., Revelo- Rodriguez A.C., Cotes-Palomino, M.T., Martínez-García C., Jimenez-Moreno, J.M., Cobo-Ceacero C.J. and Troyano-Pérez, F.J.

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The construction sector represents almost 5.5% of the EU's GDP and employs around 25 million people in more than 5 million companies. The construction products sector has 430,000 companies in the EU, with a total turnover of 800 billion euros. Construction is a key economic and social asset for local communities in European regions and cities [1].

Buildings are responsible for around 50% of the extraction and consumption of resources and for more than 30% of the total waste produced each year in the EU; they are also responsible for 40% of the EU's energy consumption and 36% of energy-related greenhouse gas emissions [1].

Regulation (EU) 2024/3110 on Construction Products of the European Parliament and of the Council, aligned with the objectives of the Circular Economy Action Plan of the European Union, introduces specific measures to improve circularity in the construction sector, focusing on the management of construction and demolition waste (CDW). This regulation establishes requirements for construction products that seek to avoid the generation of waste by promoting practices that reduce the production of construction and demolition waste by addressing the recyclability of products at the end of their useful life. Furthermore, due to their large volume generated and their high potential for reuse and recycling, the European Commission has designated them as a priority waste stream [2].

In this sense, the recovery of construction and demolition waste (CDW) as a secondary raw material for the manufacture of geopolymers represents a key strategy within the circular economy in the construction materials sector. This paper presents the synthesis of geopolymers using selected fractions of CDW, with the aim of developing new materials with suitable properties for application in the construction field.

The CDW used has been previously characterized and subjected to a process of granulometric and chemical selection, ensuring its potential as an active precursor. The selected materials have been conditioned and mixed with an activating solution composed mainly of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3), in proportions optimized according to the nature of the waste.

The resulting mixtures were molded under controlled conditions and subjected to thermal curing at room temperature. The physical-mechanical properties of the materials obtained were evaluated, as well as their dimensional stability, porosity and mechanical resistance. Additionally, their behavior against external agents such as humidity or acid solutions was analyzed, in order to determine their viability as sustainable construction elements. The results show that the geopolymers obtained have adequate mechanical strength for non-structural applications, aligning with the principles of sustainability and reuse of resources, and demonstrating the real potential of CDW as a basis for new geopolymer products.

[1] European Commission (2020) Focus on energy efficiency in buildings. Retrieved from https://commission.europa.eu/news/focus-energy-efficiency-buildings-2020-02-17_en
[2] European Commission (2024) Reg (EU) 2024/3110 on construction products. Retrieved from https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32024R3110

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Sustainable Ceramics: Extractive Waste for Porcelain Stoneware Tiles

Fantini, R.[1], Conte, S.[2], Arletti, R.[1], Molinari, C.[2], Zanelli, C.[2], Dondi, M.[2], Bernini, M.[1] and Gualtieri, A.F.[1]

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The ceramic industry worldwide requires an increasing amount of raw materials such as clays, feldspars, and sands. Recycling extractive waste (EW) can help mitigate the environmental impact of mining and quarrying, as well as address waste management challenges. In this context, thorough characterization and laboratory analysis of the selected EW are essential, as the feasibility of recovery largely depends on the waste's chemical composition, mineral makeup, and physical properties.

This study evaluates the potential incorporation of extractive waste obtained from the washing of carbonate aggregates into porcelain stoneware bodies. Typically, these silts are used for restoration activities within the quarry itself or deposited in excavation voids or landfills for environmental restoration beyond the extraction site. Moreover, this waste was previously used in cement production at a local plant until its closure in 2009.

First, the extractive waste was thoroughly characterized in terms of its chemical, mineralogical, and thermal properties to better understand its potential role in the ceramic body. Results indicated that the waste is primarily composed of carbonates (over 70 wt.%); although the particle size is small (average grain size <30 µm), the clay mineral content is minimal. The extractive waste was incorporated as a partial substitute for the fluxing components due to its low quartz content and limited plasticity.

Laboratory-scale tests were conducted on a reference batch, two batches in which 4 and 8 wt.% of the fluxes were simply replaced with extractive waste, and two additional batches with 4 and 8 wt.% extractive waste, in which the proportions of all other raw materials were adjusted. Firing was carried out between 1150 °C and 1230 °C to monitor the evolution of technological properties, phase composition (XRPD-Rietveld), and microstructure (SEM). No critical issues were encountered during the tile production process; however, a general reduction in densification was observed in most fired samples. The addition of waste silts altered the chemical composition of the batches, highlighting the need for careful formulation in order to achieve porcelain stoneware tiles.

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Porcelain Stoneware and Sustainability: Innovation through Local Resources and Recycling

Andreola, F. [1], Conte, S. [2], Sisti, M. [3], Colombo, F. [3], Fantini, R. [3], Barbieri, L. [1], Gualtieri, A.F. [3] and Arletti, R. [3]

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Until 2022, ceramic production in Europe relied on ball clays imported from the Donetsk Basin in Ukraine. These clays exhibit unique technological properties, including excellent rheological behaviour, high plasticity, proper compaction behaviour, easy sinterability, and a light colour after firing. However, the disruption of the supply chain following the Russian invasion led to a severe shortage of these raw materials in many countries. This triggered a rush to identify alternative sources of ceramic clays, highlighting how secure access to mineral resources has become a competitive factor for tile manufacturers. The heavy reliance on a limited number of suppliers proved to be a critical risk, not only for the plastic components of ceramic batches (such as clays) but also for fluxing agents, which are currently almost entirely sourced from Turkey. The European ceramic tile industry's strong dependence on imports of both plastic and non-plastic raw materials represents a significant vulnerability in the sector's supply chain. In recent years, the ceramics sector has increasingly focused on resource efficiency and sustainability. Promoting the use of local raw materials could help reduce energy consumption associated with transportation and lower CO_2 emissions.

As part of the FAV4CER project, funded by MASE, we explored innovative approaches to improving the ceramic supply chain by testing porcelain stoneware formulations based on non-conventional raw materials. Specifically, we replaced Ukrainian ball clays with locally sourced clays for the plastic components and incorporated a percentage of recycled materials into the fluxing agents. In particular, we used Re.Wo, a frit derived from the inertization of hazardous mineral wool.

The ceramic bodies developed were fully characterized from milling to firing, evaluating the technological properties assessed at each production stage. The results were highly satisfactory. To facilitate the industrial adoption of these alternative materials, we conducted scale-up tests. Among the various formulations developed, two were successfully produced in an industrial plant. The final tiles met all the required standards for porcelain stoneware products, demonstrating the feasibility of these sustainable alternatives for large-scale production.

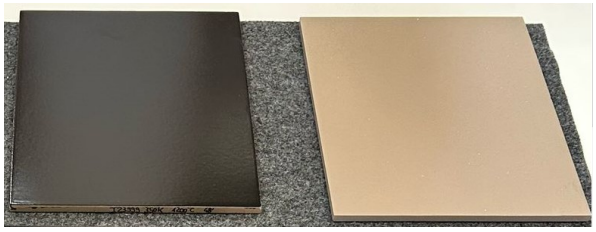

Fig. Tiles produced after the scale up tests

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Hydrothermal Synthesis of Mn- and Ni-Doped Talc and Its Effect on the Microstructure and Thermomechanical Properties of Clay-Based Stoneware

Bloise, A.[1,2], Parisi, F.[1], La Russa, M. F.[1], Godbert, N.[3,4], Aiello, I.[3,4], Giorno, E.[3,4], Croce, A.[5,6], Filicetti, S.[1], Vespasiano, G.[1], Fuoco, I.[1], Apollaro, C.[1]

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The present study investigates the hydrothermal synthesis of talc doped with Mn and Ni cations, aiming to: (i) elucidate the effects of different synthesis conditions on the resulting properties; and (ii) study the influence of both doped and undoped talc on the thermomechanical properties and microstructure of a clay-based stoneware composition. The exceptional physical properties of talc ($Mg_3Si_4O_{10}(OH)_2$), including a high melting point, hydrophobicity, and low hardness, have led to its extensive use across diverse industrial, cosmetic, and technical applications [1, 2]. Mn- and Ni-doped talc samples were synthesized at constant pressure (2 kbar) and reaction time (160 hours), under different hydrothermal conditions (temperatures of 300°C and 650°C, pH values of 5 and 7, and increasing molar ratios of dopant up to the full substitution of Mg^{2+}). Characterization techniques including Powder X-ray diffraction (PXRD), scanning and transmission electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS, TEM/EDS), differential scanning calorimetry (DSC), and micro-Raman spectroscopy (µR) were employed to analyze the starting materials and synthesized products. The study revealed a direct correlation between the amount of NiO in the initial mixture and the presence of Ni-dopant in the resulting talc, yielding a full substitution of Mg^{2+} by Ni^{2+} and the consequent formation of $Ni_3Si_4O_{10}(OH)_2$. However, in the same experimental conditions, the formation of $Mn_3Si_4O_{10}(OH)_2$ was not achieved. The incorporation of Mn or Ni into the talc structure resulted in changes in crystallinity and physical properties, as evidenced by DSC data showing variations in decomposition temperature. Furthermore, the spectroscopic analysis highlighted differences in the chemical and spectroscopic characteristics of doped talc compared to pure talc. Moreover, the study highlights that the addition of doped talc to a clay-based stoneware composition, in optimal combination with feldspar, enhances thermomechanical properties and microstructure, promoting effective vitrification at comparatively lower firing temperatures.

[1] Marzbani P et al. (2013) Ann Biol Res 4: 159–162
[2] Cornejo J et al. (2008) Clay Miner 43: 155–175

Kaolin uses in the traditional ceramic industry

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Kaolin ores are found in two types of deposits: primary and secondary. Primary deposits result from the weathering of granite-type rocks. The alteration of feldspars and micas result in the formation of kaolinite minerals (Fig. 1), which are mixed with micas, quartz, residual feldspars. A good example of this type of ore deposit is the Cornish kaolin in the UK (Fig 2.). Secondary deposits result from the sedimentation of fine particles derived from rock and soil alteration and lead to a higher content of kaolinite in the matrix compared to the primary deposit. A good example is the kaolin deposits in the Amazon River area of Brazil.

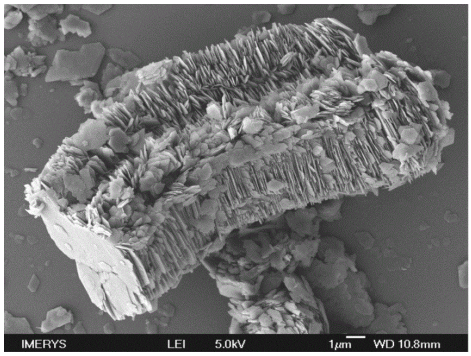

Figure 6. The beauty of kaolinite minerals (Imerys).

Figure 7. Kaolin from primary deposit: from the mine to the processing plant (Imerys, UK).

Depending on the origin of the kaolin deposits, the mineral processing is adapted to the targeted application. This paper presents an overview of the potential uses of kaolin in the traditional ceramic industry. It will illustrate it from the heavy-clay industry (roof tiles and brick), for which “red clays” are suitable, to the tableware industry, for which high whiteness and plasticity kaolin are used in the body formulation. Lastly, we will focus on the sanitaryware industry, for which the ceramic recipe is prepared in liquid form and casted into mold. It is thus needed to master the casting rate, i.e., the speed at which the particles are sedimenting and creating a wet cake, which means mastering the rheology of a high solid content suspension.

Even if traditional ceramics have a long history, there is still room to play for scientists, especially those with a background in clay mineralogy. Some old technical challenges are not solved but also new ones are arising: for example, around lightweighting while maintaining the good mechanical properties, or around valorizing some wastes, which will allow sparing kaolin for the forthcoming generations.

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Influence of red muds in the properties of alumina ceramics

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Circular Economy optimizes the use of resources and minimizes waste through reuse, recycling, and reduced material consumption, enhancing sustainability, innovation, and efficiency across industries. Spain leads the global ceramic industry in production, revenue, and technological development, consuming approximately 300,000 tons of high-purity white kaolin annually. In this study we explored the possibility of replacing part of the kaolin used in ceramic manufacturing with an alternative, low-cost material, such as red muds. 150 million tons of red muds are generated annually worldwide as by-products from the alumina extraction through the Bayer process, whose high alkalinity can be harmful to the environment [1].

Ceramics containing 100% kaolin from a kaolin deposit (Burela, NW Spain) and ceramics containing 85% of this kaolin and 15% of red muds from an alumina company (85/15) were manufactured by pressing and fired at 1000°C, 1150°C, and 1300°C under oxidizing conditions. The original kaolin contains kaolinite (51%), quartz (43%), and illite (6%), while the red mud comprises gibbsite (47%), hematite (30%), boehmite (19%), and rutile (4%). Different mineralogical transformations were observed with the increase of the temperature. At 1000°C, kaolinite and illite in pure kaolin ceramic becomes destabilized, quartz content increases and mullite and cristobalite crystallize. In contrast, at this temperature, the 85/15 ceramic still contains hematite and boehmite and has a lower mullite content than in kaolin ceramic. At 1150°C, quartz decreases and mullite increases in both ceramics, but cristobalite and hematite are more abundant in the 85/15. At 1300°C, both ceramics were mainly composed of mullite and cristobalite, but mullite formation was more advanced in the 85/15 mixture, while cristobalite content was higher in pure kaolin ceramics.

Backscattered electron images showed minimal changes at 1000°C in both ceramics, with iron-rich phases still visible in the 85/15 ceramic. At 1150°C, mullite crystals are observed in both ceramics but with higher size in the 85/15 ceramic. Finally, at 1300ºC, both ceramics exhibit a porous appearance and an advanced degree of mullite formation, specially in the 85/15 ceramic.

The mineralogical transformations that take place with the increase of the temperature affect to the physical properties of the ceramics. The density and the linear shrinkage increase with the temperature in both ceramics while the porosity decreases. It is remarkable that at 1300ºC the 85/15 ceramic present the higher density (2.50 g/cm^3) and linear shrinkage (12.56 %) values and the lower porosity (11.25 %) values due to the higher formation of mullite and vitreous phase.

Substituting 15% of kaolin with red mud is feasible for ceramic production since the 85/15 ceramic shows physical properties suitable for tiles and external cladding manufacture. Therefore, red mud can be recycled in ceramic manufacturing, which can reduce production costs and promoting sustainability within the circular economy.

[1] Rodríguez GP et al. (1999) Bol Soc Esp Ceram V 38: 220-226

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Session 14: Materials via Ordered Interstratifications

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Engineered Clays for CO_2 Capture and Biogas Separation: Influence of Layer Charge and Interlayer Cations

Fossum, J.O.[1], Breu, J.[2], Hunvik, K.W.B.[1], Loch, P.[2], Bordallo, H.N.[3], Pacakova, B.[1], Cavalcanti, L.P.[4], Kirch, A.[5], Miranda, C.R.[5]

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Smectite clay minerals, in the present context synthetic fluorohectorite, have emerged as promising materials for carbon capture and greenhouse gas separation (e.g. separation of CO_2 and CH_4 in biogas) due to their high density of compact interlayer adsorption sites, low cost, and chemical stability. Nickel-exchanged fluorohectorite exhibits a notably high CO_2 capture capacity. In situ measurements using powder X-ray diffraction, Raman spectroscopy, and inelastic neutron scattering show that both dried and hydrated nickel-exchanged fluorohectorite undergo crystalline swelling upon CO_2 exposure, driven by interactions with interlayer hydroxide complexes such as $[Ni(OH)_{0.83}(H_2O)_{1.17}]_{0.37}$.

Varying the total layer charge of Ni-fluorohectorite affects adsorption performance: lower-charge fluorohectorite clays (mimicking montmorillonite) exhibit higher CO_2 uptake and release CO_2 more readily, than higher-charge clays (mimicking vermiculite). Furthermore, exchanging different cations (e.g., Li^+, Na^+, Cs^+, Ca^{2+}, Ba^{2+}) alters the swelling behaviour and CO_2 sorption properties, underscoring the role of interlayer chemistry. These findings collectively highlight the strong potential of engineered clay minerals for CO_2 capture and biogas separation and emphasize that cation selection, layer charge, and hydration state are critical factors in optimizing their capture and separation capabilities.

[1] Hunvik K.W.B. et al. (2024) Langmuir 39, 4895
[2] Hunvik K.W.B. et al. (2021) Langmuir 37, 14491
[3] Hunvik K.W.B. et al. (2020) Journal of Physical Chemistry C 124, 26222
[4] Cavalcanti, L.P. et al. (2018) Scientific Reports 8, 11827

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Session 17: Industrial Applications of Clays

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Deep learning methods for quantitative characterization of bentonite clays via X-ray diffraction

Owen, N.D.[1], Li, R.[2], and Huang, S.[3], Fan, R.[4], Gomez-Camacho, R.[4], Roccisano, J.[4], Webster, N.A.S.[3], Self, P.G.[4], Raven, M.D.[4]

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Bentonite clays are commonly used in industrial applications such as geomembrane construction for tailings dams and landfills. While X-ray diffraction (XRD) is the standard method for essential quality control of bentonite clay products, the analysis of bentonite samples by XRD is laborious and time consuming due to the sample preparation involved. Currently, the standard method of analysis entails saturating the bentonite interlayer cation (e.g. with $CaCl_2$) to produce uniformity in the interlayer d-spacing (Figure 1a). Subsequently, fitting of the data can be applied using Rietveld XRD analysis software. The saturation step requires extensive handling of the samples, greatly slowing down the lead time of analysis and increasing associated labour costs. We propose the exploration of Deep Learning (DL) techniques to build a flexible and robust, high-throughput method for bentonite clay XRD characterisation.

Training of DL models requires a large amount of data which must contain significant variability with regards to mineral phase concentrations, and regarding bentonite clays, of the (00*l*) peak positions. The Diffraction, Mineralogy and Geochemistry team at CSIRO has collected a dataset of thousands of XRD patterns on bentonite samples collected over the last decade. This dataset is supplemented by ~1200 simulated XRD patterns (Figure 1b) via the XRD analysis software Topas v7 by Bruker AXS.

Two DL methods, via the PyTorch library for Python, are under investigation. The first is to train DL models on the real and simulated representative XRD patterns that are paired with the ground-truth mineral compositions. As an alternative, we also plan to examine the feasibility of transforming a non-treated XRD pattern to a corresponding Ca-saturated pattern. In our poster, we will report (1) our investigation into DL techniques for accurately predicting the phase concentrations, and (2) our evaluation of the above two methods using standard metrics.

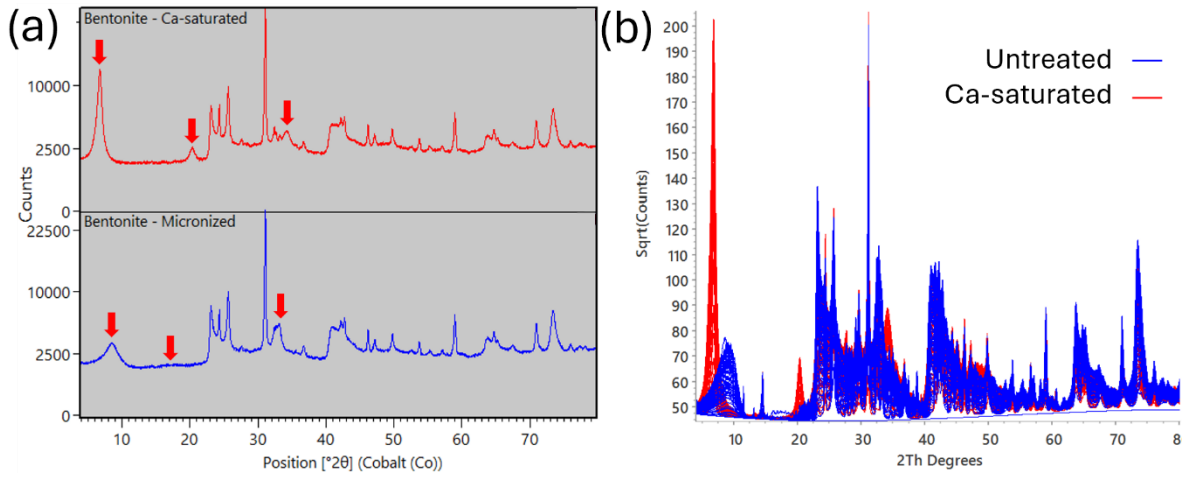

Figure 1: (a) XRD profiles showing the variability of d-spacing of the interlayer space of bentonite clays between the Ca-saturated and untreated (micronized) sample; (b) Simulated XRD data with randomised concentrations of commonly found phases in bento

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Session 18: Clay Minerals in Diagenetic and Low-Grade Studies: Implications for Resource Exploration and Sustainable Energy Development

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Clay (trans)-formation in sediment-hosted mineral systems: examples from world-class Zn and Cu districts

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Clay minerals play a critical but commonly overlooked role in the evolution of sediment-hosted mineral systems. Some of the largest sediment-hosted Zn and Cu deposits formed in mixed carbonate-siliciclastic host units undergoing several stages of diagenesis. During early diagenesis, low-temperature reactions drive the transformation of smectite to illite or chlorite, recording burial depth and basin evolution. These diagenetic clays influence fluid flow by modifying porosity, which can either trap or guide mineralizing fluids. Later, hydrothermal overprints introduce higher-temperature clay assemblages such as well-crystalline illite, kaolinite, or dickite that can be associated with metal transport or deposition. The subtle differences in clay mineral assemblages, crystallinity, and ordering, can help to distinguish diagenetic backgrounds and hydrothermal events. As such, understanding clay formation pathways is key to interpreting the timing, source, and mechanism of mineralization in complex sedimentary systems. Here, we discuss two case studies where illite has been studied in Zn and Cu mineralized systems. Both studies highlight how clay minerals can yield valuable information on mineralizing processes in sedimentary basins, thereby helping to refine genetic models.

The Teena Zn-Pb deposit is located in the Carpentaria Zn Province (Australia), where some of the largest clastic dominant (CD-type) massive sulfide Zn-Pb deposits are hosted by 1.64 Ga marine sedimentary rocks. The timing of the main stage of hydrothermal sulfide mineralization in the Teena subbasin is constrained to the midstage of burial diagenesis. To distinguish hydrothermal alteration from spatially and temporally overlapping burial diagenetic alteration, and to establish the primary controls on hydrothermal mass transfer, it is necessary to evaluate the various foot- and hanging-wall alteration assemblages that formed between early- (eogenesis) and late- (mesogenesis) stage diagenesis. Illite formed throughout diagenesis, initially at relatively low temperature (100°C) in K-rich siliciclastic rocks. In more carbonate rich rocks, illite formed at higher anchizone and epizone temperatures (<300°C), thereby highlighting differences in how carbonate and siliciclastic rocks behaved during diagenesis [1]. A small amount of smectite is preserved in mineralized samples, suggesting retrogressive alteration of preexisting illite as the hydrothermal system waned.

The Southern Permian basin in central Europe contains a number of important high-grade sediment-hosted Cu deposits. In the Kupferschiefer stratigraphic unit, Cu deposits are assumed to have formed when metal-bearing chloride-rich brines reacted with organic rich siliciclastic rocks. Transmission electron microscopy (TEM) has been used to investigate the pore-scale mineralogy of Cu mineralized mudstones from the Saale subbasin (eastern Germany). These investigations show that CuxCly(OH)z mineral phases, including $Cu_2Cl(OH)_3$ (atacamite) and, to a lesser extent, CuCl (nantokite) nanoparticles (NPs, ~ 5-20 nm), are intergrown with illite in pore spaces surrounding disseminated Cu (Fe) sulfides. The close spatial relationship between CuxCly(OH)z and pore-filling illite, including nanoparticles that are wholly enclosed by a single illite crystal, provides strong evidence that CuxCly(OH)z formation preceded and accompanied diagenetic illite precipitation [2]

[1] Magnall JM et al. (2021) Econ Geol 116, 8, 1769-1801
[2] Mohammedyasin MS et al. (accepted) Geology

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Session 20: Smectite Layer Charge and Interlayer Environment: Structure, Alteration, and Environmental and Technological Significance

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Multiscale simulation of thermal-hydraulic-mechanical-chemical (THMC) coupled processes in compacted bentonite clay

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Bentonite clay has been extensively studied as an engineered barrier material for use in geologic repositories for high-level radioactive waste. A key challenge in this application is that the barrier will be exposed to gradients in saturation, fluid chemistry, and temperature that may give rise to complex coupled phenomena, such as thermally-induced cracking. Efforts to simulate these phenomena at the scale of the engineered barrier rely largely on approaches developed for brittle poro-elastic materials, whereas compacted clay exhibits a ductile poro-viscoplastic behavior.

Here, we build upon our recent development of a computational fluid dynamics (CFD) treatment of single- and two-phase flow in compacted clay. Specifically, we implement an additional heat conservation equation that enables representation of the couplings between fluid flow, solid deformation, and heat transport in compacted bentonite at the scale of an engineered barrier. The parameterization of sub-grid-scale properties (including the heat capacity, thermal conductivity, and thermal expansion coefficient of bentonite) is guided in part by all-atom molecular dynamics (MD) simulations of smectite-water mixtures. Preliminary results are presented and compared with large-scale experimental results, and remaining challenges are identified and discussed.

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Mineralogy and geochemical processes in the Upper Eocene volcanic ash and bentonite deposits in East Central Texas, USA

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Texas Ca-bentonites represent one of the two major types (sodium- and calcium-) of commercial bentonites. They enjoy a wide range of applications in environmental, agricultural, industrial, and personal care products. The Clay Minerals Society has collected a Texas bentonite mined from the Helms deposit, Gonzales County as a Source Clay (STx-1 and STx-1b) and distributed to researchers around the world. Many characterizations have been conducted on this source clay. These characterizations would be a great asset in evaluating and explain the possible thermo-hydro-mechanical and chemical processes when Ca-bentonites are used in geological repositories for high-level nuclear waste and spent nuclear fuel as an engineered barrier system. The objective of this study was to evaluate the depositional environment of the Upper Eocene volcanic ashes and their devitrification to bentonites in East Central Texas, USA. The focus was on the mineralogy and geochemical processes in the deposits.

The Ca-bentonites in this region are mostly derived from fine sand- and silt-sized rhyolitic ashes which are rich in silica and poor in Fe and Mg. The fine particle size of the ashes indicates distant volcanic sources. Rare earth elements (REE), trace metal, paleo wind direction, and Ar-Ar dating data suggest that the volcanic ashes were most likely from the Sierra Madre Occidental Volcanic Province in Mexico or the Mogollon-Datil volcanic field in New Mexico, not from the Trans-Pecos Volcanic Province in West Texas, USA. It is believed that the ashes deposited as thin blankets on various landscapes including coastal plain valleys, floodplains, swamps, bays, shoreline, intertidal flats, and shallow marine shelf in the coastal region. Some of the thin blankets of the ash deposits were reworked by streams and redeposited into thicker tuff units in small stream courses or lakes. The ashes experienced different devitrification, which is likely controlled by the availability of Mg from the environment and the drainage condition of the deposits. Some ashes showed little sign of alterations, which are likely due to lack of interactions with sea water. In some deposits, volcanic glasses showed dissolution pits and formation of halloysite in the stretched vesicles formed during volcano eruption. Montmorillonite formed in more devitrified deposits. In thick deposits like the Helms pit, the wedge-shaped ash deposit showed full devitrification around the wedge but little sign of alteration in the interior of the wedge. When drainage was poor, zeolite clinoptilolite and opal-C formed. The nanometer-sized opal-C can function as a cementing agent in the deposits, inducing the formation of a hard bentonite. Its abundance may affect the swell/shrinkage of the bentonite for engineering barrier in the nuclear waste storage repositories. Under well drained condition, kaolinite became the dominant clay mineral in some deposits as observed in at least one case where the thin deposit (about 3 cm) was sandwiched between lignite strata, suggesting a swamp environment. REE elements migrated in the deposits with the devitrification of the volcanic glasses, enriched in the bentonites, and precipitated as separate nanometer-sized phosphate minerals monazite, xenotime and rhabdophane along with Mn oxides rancieite, todorokite, and hollandite in localized pods. In these localized pods, the REE abundances were tens of times greater than in the bentonite. Recent ground water and surface water movements had significant effects on the Fe, S, and Mn redox chemistry in the deposits, making the colors of the deposits white, blue, or red. Despite the color differences caused by the Fe oxides, the occurrence of Fe in the montmorillonite layer structure is rare among most of the bentonite samples analyzed.

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In-situ experiment Engineered Barrier 200C – Preliminary results of a mineralogical study of the bentonite barrier

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Bentonites are considered to be the most suitable sealing materials for the multibarrier system of a deep geological repository in the crystalline host rock. Current concepts assume a limit temperature limit up to 100 °C. An increase in temperature limit could led to cost savings by allowing for greater disposal capacity. The aim of the project Engineered Barrier 200C is to investigate the processes in the bentonite material in barrier at temperatures up to 200 °C using in-situ and laboratory experiments.

The in-situ experiment Engineered Barrier 200C was performed in the Josef Underground Research Laboratory, situated in granodioritic rock, in the Czech Republic. The heated experiment was in operation from November 2019 till April 2024. Pelletized bentonite extracted from Černý vrch deposit (BCV) and processed at Keramost Ltd. Obrnice Plant (Most, Czech Republic) was used as a testing material. The material was compacted around a cylindrical heater, simulating a canister with radioactive waste at a temperature of 200 °C. The BCV material is a Czech Mg-Ca bentonite, and consists mainly of montmorillonite (70 wt%), with minority of kaolinite, quartz, illite, Mg-calcite, goethite, and traces of other carbonates, including siderite and ankerite.

The experiment used an online measurement system to monitor the evolution of temperature, total pressure, pore pressure, heater power and energy consumption. Groundwater was monitored in an adjacent borehole. The system simulated the initial period in the lifetime of the repository with unfavourable dynamic conditions for bentonite when: heat is generated, pore pressure is not high enough to prevent boiling, some parts are not saturated, and dissolution/precipitation of species is possible due to water evaporation and steam generation. The aim of this mineralogical study was to determine changes that occur in the barrier using detailed modelling of X-ray diffraction patterns in the Sybilla programme [1], along with cation exchanged capacity (CEC) and silicate analysis.

The temperature close to the heater (0 mm) was around 170 °C and dropped rapidly toward the surrounding rock. Based on the cation exchanged capacity, exchangeable cation contents, average layer ratio of modelled mixed-layered minerals and chemical analysis, three zones in the barrier were distinguished. The first zone (0-60 mm) is characterized by significant change of all observed parameters. The second zone (60-180 mm) displays variation in the content of Ca- and Mg-exchangeable cations. The third zone (180 mm to rock) shows almost constant measured parameters. Although the bentonite closest to the heat source shows partially deteriorated properties, function of the most of the barrier remains unchanged.

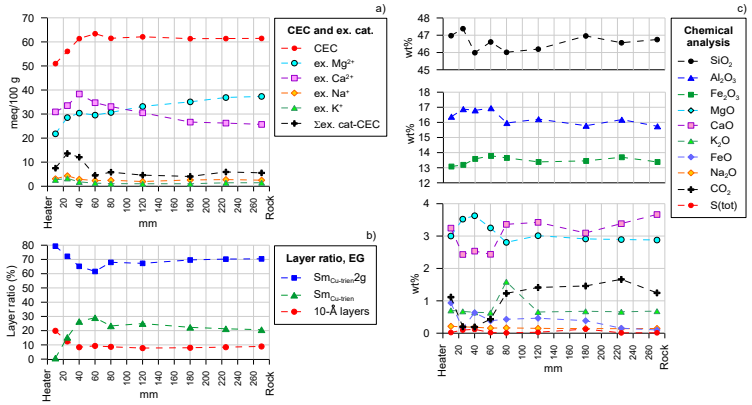

Figure 1. Mineralogical and chemical analysis of BCV bentonite, a) CEC - Cation exchange capacity and ex. cat. - exchangeable cations determined by the Cu-trien method, b) the average layer ratio of two 10-

Acknowledgements: This research was supported by the Engineered barrier 200C project (no. TK01030031) awarded by the Technology Agency of the Czech Republic.

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Behaviour of engineered safety barrier materials under deep geological repository model conditions

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The Russian Federation is currently developing a of a deep geological repository (DGR) in crystalline rocks on the periphery of the Nizhnekansky granitoid massif at the “Yeniseisky” site. As part of this concept, it is planned to use bentonite clays as a buffer material. Bentonites of the buffer layer will be affected by underground water of the massif and other barrier materials - concrete and steel. In order to justify the safety of the planned disposal site, it is necessary to obtain numerical characterizations of changes in the engineered barrier system (EBS) materials, particularly buffer clay materials [1].

A series of experiments was carried out to reveal regularities of changes in the composition, structure and properties of bentonites, as well as changes in the fine structure of smectites, under the model conditions of the DGR using model solutions of underground waters of the “Yeniseisky” site with different pH and when interacting with such materials of EBS as concrete and steel. Bentonite clays from the deposits of the 10th Khutor (Republic of Khakassia, Russian Federation) and Taganskoye (Republic of Kazakhstan) were selected for the experiments.

The results of experiments with model solutions of different pH at temperature 90 ^{o}C showed high stability of smectites up to 6 months. Under model conditions, the mineral composition changed insignificantly.

When bentonites interacted with steel, iron cations incorporation into the octahedral sheet of smectites was observed with increasing layer charge. In the smectite of bentonite of the 10th Khutor deposit Fe reduction in the octahedral sheet is observed in the experiments with model solutions and with steel, whereas its oxidation occurs in the experiment with concrete leachate [2].

At interaction of bentonite of Taganskoye deposit with steel there is a decrease of smectite fraction observed according to the data of quantitative mineral analysis and IR spectroscopy. In all conducted experiments, no synthesis of other clay minerals such as chlorite, illite and trioctahedral forms of smectite was observed, but under the same conditions the considered bentonites showed different resistance to the impact of solutions of different composition at a high temperature, which resulted in structural changes in the composition of smectite and its partial destruction.

[1] Krupskaya et al. Radioactive Waste, 2023, 2 (23), 98 - 112
[2] Morozov I. et al. Applied Science, 2022, 12, 6, 3074

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Session 21: Science and Engineering of Clays for Nuclear Waste Disposal

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Impact of a long-term thermal pulse on bentonite erosion rates in lab scale experiments: First results from samples of the LOT/ABM experiments

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[2] Forschungszentrum Jülich GmbH, IFN-2, Wilhelm-Johnen-Straße, 52428 Jülich

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Due to their advantageous properties (i.e. swelling and sorption), bentonites are used as geotechnical barrier materials in the engineered barrier system (EBS) for radioactive waste disposal in crystalline host rocks [1]. To reduce the spatial footprint of the repository, these systems are being revised for thermal optimization [2]. A key aspect is determining the maximum thermal load at the canister-bentonite and bentonite-host rock interfaces under which bentonite maintains its functionality. Thermal loading affects both swelling [3] and possibly the erosion behaviour, which could impact the long-term integrity of the barrier.

Three samples were analysed to evaluate the effects of prolonged elevated thermal load on the erosion behaviour of bentonite: a MX-80 Wyoming-type bentonite (Block 18) from the LOT S2 experiment, and a MX-80 (Block 8) along with a FEBEX bentonite (Block 25) from the ABM 45:5 experiment, all conducted at Äspö HRL. In the LOT S2 experiment, the heater operated at a constant power of 500 W over a 20-year period, resulting in a temperature gradient ranging from approx. 95 °C at the heater-bentonite interface to 60 °C at the bentonite-host rock interface [4]. In comparison, the ABM 45:5 experiment had a higher thermal load of 1800 W, producing a temperature gradient from approximately 250 °C at the heater interface to 170 °C at the interface with the host rock [5].

Plugs (13 mm diameter, 5 mm height) were extracted from subsamples and placed in a 1 mm aperture artificial fracture within a PMMA flow cell to assess erosion rates [6]. Groundwater from the Grimsel Test Site (GTS, Switzerland), representing low-ionic-strength meteoric/glacial meltwater (0.2 mM), was used to simulate future repository scenarios with conditions potentially creating a risk for the integrity of the bentonite buffer. Swelling pressure was measured using Tekscan 5051 pressure sensors embedded in the flow cell. Gel/sol expansion of the bentonite was monitored to estimate the contact area, while effluent was collected at intervals to determine nanoparticle concentrations via Nano particle Tracking Analysis (NS 300, Malvern Panalytical), allowing mass loss and erosion rates to be calculated. Erosion rates were determined to be 0.25 ± 0.11 kg/m^2/a for raw MX-80 (runtime: 56 d) [6] and 1.72 ± 1.74 kg/m^2/a for thermally loaded MX-80 (runtime: 142 d) from the LOT experiment.

The experiments show an increase of erosion between the raw material of the same batch and the thermal loaded bentonite. Mineralogical comparison of the fraction 0.2 µm - 2 µm between raw and thermal loaded material shows no distinct alteration. However, in the fraction < 50 nm of the material there is a distinct alteration as determined via ATR-IR and XRD measurements. The higher erosion rates of thermal loaded bentonites in these short-term experiments are still below the maximum erosion rates of 6.5 kg/m^2/a for 1 mm fractures deemed safe by Posiva [7]. The most notable changes were observed in the fraction < 50 nm, which have a high impact on the erosion behavior of the bentonites despite being a small mass fraction. Based on the new results focusing on the < 50nm clay fraction, an in-depth study to provide a mechanistical understanding for the observed erosion rates appears necessary.

[1] Wersin, P. et al. (2007) Phys. Chem. Earth 32:780–788
[2] Kim, J.-S. et al. (2019) J Korean Tunn. Undergr. Space 21(5):587-609
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[4] Sandén, T. ; Nilsson, U. (2020) SKB TR-20-11
[5] Svensson, D. et al. (2023) SKB TR-23-25
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What limits the temperature at canister surface in clay-based HLRW concepts? – Discussion in an international context

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Concepts for the final disposal of radioactive waste in argillaceous formations as well as in crystalline rocks are under investigation or implementation in a number of countries. Apart from acting as main component in argillaceous host rocks, clay minerals play an important role as part of the geotechnical barriers in each of these national concepts.

Repository concepts in crystalline rocks, for example in Sweden, Finland, Czech Republic, South Korea, or Japan, are based on the Swedish KBS-3-Concept: Canisters made from different material such as cast iron or steel, in some cases coated in copper, are loaded with spent fuel or high level radioactive waste cartridges. After closure, these canisters are em-placed in vertical boreholes inside the repository. The gap between borehole wall and canister is filled up with a bentonite buffer, forming a geotechnical barrier against the release of radio-active material.

Bentonite is also used in repository concepts for argillaceous formations to backfill tunnels or boreholes, in which waste canisters are placed. In both host rock types, the geotechnical barrier composed of clay minerals is intended to fulfill different objectives, such as protecting the canisters from contact with groundwater or retaining radionuclides, which are released from the canisters. Argillaceous (geological) host rock formations consist of clay-rich rocks, serving as a geological barrier in addition to geotechnical barriers.

The performance of clay in a geotechnical or geological barrier depends on a number of factors, e.g. its mineralogical composition. Barrier functions including the performance of bentonite buffer or claystone are sensitive to environmental conditions, especially to the temperature induced by high level, heat-generating waste.

Therefore one subject of major concern in every clay based repository concept is the maximum temperature applicable at the canister surface without compromising the positive properties of the clay barrier. Although the clay based disposal concepts of different countries are of similar design, including the use of bentonite buffer as a form of geotechnical barrier [1], the always-present indicator of maximum temperature at canister surface differs between the different national designs. National concepts include different boundary conditions of on the one hand different paleo maximum temperatures of hosting clay formations [2] and on the other hand different designs including various distances of canister surfaces to the clay – host rock interfaces. This poster attempts to give a summary about different maximum temperatures in use or under discussion for disposal concepts in crystalline and argillaceous rocks and the accompanying boundary conditions.

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Session 23: Clay Mineral-Based Catalysts for Environmental Engineering and Chemical Processes

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Optimization and molecular insights into the adsorptive efficiency of Cu-Al layered double hydroxides derived from aluminum saline slags

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This study aims to optimize the adsorption process of gallic acid (GA) on Cu-Al layered double hydroxides (LDH) synthesized via a co-precipitation method at various pH levels. The procedure is based on the adsorption of organic pollutants from aqueous solutions, with evaluations carried out based on operational parameters such as pH, initial concentration, and adsorbent quantity. Two series of LDH were compared: one using aluminum extracted from saline slags and the other using a commercial aluminum salt as source of aluminum. Saline slags, a by-product of aluminum recycling, are particularly hazardous due to their high toxicity and potential for environmental contamination. Extracting aluminum from these slags and using it in the synthesis of LDH not only helps in eliminating a dangerous waste but also creates materials with beneficial environmental applications [1].

The adsorption process was optimized using response surface methodology (RSM) coupled with Box-Behnken design (BBD) to assess the effects of key operational parameters. Besides gallic acid, other organic pollutants such as diclofenac and salicylic acid were also evaluated for removal from aqueous solution. The LDH /LDO were characterized by X-ray diffraction (XRD), ATR infrared spectroscopy (ATR-IR), scanning and transmission electron microscopy (SEM/TEM), thermogravimetric analysis (TGA), and nitrogen adsorption at −196 °C. The merit data indicate that the material synthesized at pH = 9 with extracted aluminum exhibits superior adsorption capacity for gallic acid, demonstrating the highest removal rate, nearly reaching 100 %, and achieving equilibrium more quickly than other samples. This superior adsorption performance is also notable for salicylic acid and diclofenac. After four regeneration cycles, the adsorption rate of the adsorbent remains stable, indicating that CCA9 maintains a consistent and efficient adsorption performance.

This highlights the robustness of the material and its high reusability in prolonged adsorption applications. Molecular dynamics simulations (MDS) revealed that the adsorption process occurs spontaneously, driven by weak interactions: van der Waals, intermolecular, hydrogen bonding, π-interactions and short contacts [2,3].

Acknowledgements: The authors are grateful for financial support from the Spanish Ministry of Science, Innovation and Universities (MCIU/AEI/10.13039/501100011033/FEDER, UE) and the Government of Navarra (Department of Rural Development and Environment, Waste Fund 2023) through projects PID2023-146935OB-C21 and 0011–4387–2023–000001. AIB thanks Universidad Pública de Navarra for a pre-doctoral grant.

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Design of clay-based catalysts assisted by machine-learning

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Industrial processes such as biodiesel production, Volatile Organic Compounds (VOCs) removal, and chemical purification such as benzene, toluene, xylene (BTX) purification acid-activated clay-based catalysts are required as active material. Their performance is determined by pore morphology and surface activity, which are typically represented by properties such as specific surface area, pore volume, microporosity, and pH.[1]

Optimizing these catalytic properties is challenging due to the wide range of parameters involved in material processing and chemical treatment. To address this complexity, machine learning (ML) techniques have been successfully applied as a tool for optimal material design, significantly accelerating experimentation. [2] The developed algorithm allows the creation of a material design platform revealing nonlinear interactions of the clay with modifiers or active phase. The trained models were able to capture the chemistry behind the material performance and identify regions in the descriptor space where positive synergies optimized the catalytic properties. In particular, we have demonstrated the optimal catalysts design identifying process parameters of acid, acid concentration and its amount with respect to clay, temperature and time of the reaction.

As a first proof of concept, the optimized acid catalysts were synthesized and tested in oil refining revealing appreciable acid character improvement with the respect of pristine material. Specifically, it achieved 79% removal of chlorophyll-a in acid catalyzed degradation. [2]

The controlled clay acid treatment has opened new pathways for multifunctional environmental materials. In particular, it has identified the optimal condition for the synthesis of TiO_2-based nanoparticles using an acid-activated sepiolite as a growth template and carrier.

The resulting catalyst exhibited promising performance in water purification, NOx decomposition, and photocatalytic coatings.[3] We demonstrated the self-cleaning properties, as evidenced by Rhodamine B degradation rates exceeding 20% after 4 hours and surpassing 50% after 26 hours of light exposure when the catalyst was integrated into paints and mortars.[4] Furthermore, in specific mortar formulations we have observed over 50% degradation of volatile organic compounds (VOCs), highlighting their effectiveness as active decontaminating surfaces. These findings suggest the accelerated, scalable and sustainable approach to the design of versatile clay-based catalysts for environmental applications.

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[2] Lo Dico G (2021) Chem Sci 12(27):9309-9317
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[4] Acosta M F (2023) App Clay Sci 246:107189

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Advanced and sustainable piperazine functionalized clay catalyst for aldol production in water-acetone mixture

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Montmorillonite (Mt), a member of the smectite group, is a 2:1 clay mineral composed of two tetrahedral silica sheets sandwiching an octahedral alumina sheet [1-2]. It exhibits significant interactions with organic molecules, such as aminoethylpiperazine (AEP), through various mechanisms. In addition, the Mt can form chelation or coordination complexes with ions. A key feature of Mt is its swelling behaviour, wherein water molecules enter the interlayer space, facilitating the intercalation of precursors or surfactants and leading to layer expansion. Owing to its natural abundance, high surface area, and exceptional cation exchange capacity, Mt is widely used in water/air pollution treatment and organic reactions [3-5].

In this study, Mt was functionalized to develop an efficient and low-cost heterogeneous catalyst. First, it was calcined at 400°C under a nitrogen (N_2) atmosphere to enhance structural stability. Subsequently, it was functionalized with AEP in toluene at 110°C to introduce basic active sites. The resulting AEP-Mt catalyst was then applied to the aldol reaction between acetone and 4-nitrobenzaldehyde in an aqueous medium. The aldol reaction experiments carried out at temperatures of 25°C, 35°C, 45°C, and 55°C for 4 hours resulted in conversions of 9.30%, 15.5%, 31.3%, and 42.5%, respectively, with corresponding selectivities of 100%, 100%, 99%, and 98%. Kinetic studies revealed a 41 kJ/mol activation energy, indicating high catalytic efficiency. The catalyst demonstrated excellent reusability in batch experiments, retaining its activity over three cycles. In a custom-designed continuous flow system operating at room temperature (23°C), the AEP-Mt catalyst exhibited stable performance over 20 hours of time-on-stream (TOS), highlighting its potential for sustainable, large-scale applications.

This work highlights the versatility of functionalized AEP-Mt as a cost-effective and eco-friendly catalyst for aldol reactions, bridging the gap between batch and flow chemistry in green synthesis.

Keywords: montmorillonite, aminoethylpiperazine, heterogeneous catalysis, aldol reaction
Acknowledgment: This work was supported by Ghent University Global Campus (GUGC), South Korea.

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Session 25: Fundamentals of Tubular Nanoclays

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Halloysite nanotubes as stable support materials for gold/silver-nanotags

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Gold and silver nanoparticles (Au/Ag-NPs) have been employed to directly observe the adsorption sites on two morphologies of halloysite nanotubes (HNTs) and identify behaviours of each nanotag type using Transmission Electron Microscopy (TEM) and ancillary analytical techniques. The results indicate that polygonal prismatic HNTs show greater adsorption when compared to cylindrical HNTs, where NPs were detected on the external walls of the nanotubes, hypothesised as at the steps and edges of the particles, terminus of the tubes and in the hollow inner lumen.

Experiments using Au and Ag-NPs with carboxylate, phosphonic acid and methyl terminated linker molecules on polygonal prismatic HNT revealed that the Ag-NPs showed a tendency to agglomerate, making them less suitable probes for adsorption onto HNTs. With the Au-NPs the phosphonic acid and carboxylate moieties showed similar adsorption behaviour, whilst no surface adsorption was observed for the methyl terminated linkers. Thereby justifying the hypothesis that chemisorption had occurred with phosphonic acid and carboxylate terminated Au-NPs on the aluminol groups at the edge sites, steps and lumen of polygonal prismatic HNTs.

The specific anionic bonding sites have been investigated on two HNT morphologies highlighting the importance HNT morphology when HNTs are being considered as stable support materials for metal nanoparticles.

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Halloysite nanotubes dispersions in chitosan for archaeological wood conservation

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Chitosan (CHI) is among the most used biopolymers in conservation science due to its antibacterial and antioxidant properties[1,2]. On the other hand, the nanotubes of halloysites (HNT) are used as fillers due to their excellent thermal and mechanical properties besides the possibility of being used as nano-reservoir for sustained release of active agents[3].

In this work, Chitosan/Halloysite Nanotubes dispersion has been designed as a novel green protocol for the conservation of waterlogged archaeological wood. The immersion protocol of waterlogged archaeological wood was monitored for 72h and subsequently, they were dried for 24h at room temperature. Colorimetric analysis and an Optical Microscopy revealed the characteristics surface of untreated and treated archaeological wood. Chemical imaging was also applied to determine the spatial distribution of CHI/HNT dispersion on waterlogged archaeological woods. Thanks to this last analytical approach it was possible to assess that a more homogeneous distribution was possible while the concentration of nanotube was increased. However, at the same time, an increase in the aggregations of chitosan were also visible at the maximum concentration of HNT.

Meanwhile, a physico-chemical characterization was carried out on wooden samples to investigate the mechanical and thermal properties before and after treatment. A higher thermal and mechanical resistance has been shown in the samples treated with CHI/HNT dispersion compared to the untreated archaeological wood sample. Since wood is a hygroscopic material, it was important to consider water vapor absorption/desorption after CHI/HNT treatment, thus an immersion test and a water uptake measurement were performed. Finally, the aging test of archaeological wood samples led to the examination of the efficacy of CHI/HNT composites as a protective formulation for archaeological wood: lignin index of archaeological wood samples was calculated before and after they were exposed in nitric acid for 72h.

In conclusion, the proposed CHI/HNT dispersion presents a promising strategy for conserving waterlogged archaeological wood. This is attributed to the ability of chitosan to form a film with antioxidant and antibacterial properties, and the capacity of halloysite nanotubes to enhance the thermal and mechanical resistance of wood samples.

This work has been supported by grant TED2021-129299A-I00, funded by MCIN/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR and by PON "Research and Innovation" 2014-2020, Asse IV "Istruzione e ricerca per il recupero", all'Azione IV.5 "Dottorati su tematiche green". DM 1061/2021 and by the University of Palermo.

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Session 26: 1D Nanoporous Clay Materials and Their Industrial Applications

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Sepiolite-carbon based bionanocomposites: a green approach to corrosion protection

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Corrosion of metallic materials remains a significant challenge, compromising both structural integrity and economic sustainability. The chromium-based protective coatings have long been a well-established method for corrosion mitigation, but their associated toxicity has raised serious environmental and health concerns [1]. Consequently, there is an urgent need to develop safer and more sustainable alternatives. The design of bionanocomposites incorporating biopolymers and naturally occurring clays offers a promising strategy to address this issue [2].

In this context, we report the development of bionanocomposite thin films for corrosion protection of lightweight alloys. The protective coatings combine chitosan and zein biopolymers with caffeic acid and a sepiolite-carbon filler. The carbonaceous filler was obtained from the hydrothermal treatment (180 °C, 18 h) followed by pyrolysis (550 °C, 1 h, N_2) of liquid caramel impregnated into the natural phyllosilicate clay [2]. The bionanocomposite suspensions were applied onto AA2024-T3 aluminium alloy via dip-coating. A subset of these coatings received a secondary organic–inorganic hybrid layer synthesised through a sol–gel route using γ-methacryloxypropyltrimethoxysilane and tetramethyl orthosilicate. This topcoat was designed to seal microstructural porosity and extend barrier durability.

The coatings were characterised using field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric/differential scanning calorimetry (TGA/DSC). Corrosion protection was evaluated in chloride-containing media using electrochemical impedance spectroscopy (EIS). The studies revealed a two-stage degradation mechanism: an initial barrier phase dominated by the sol–gel topcoat, followed by an active corrosion inhibition response from the bionanocomposite base layer. Notably, FESEM images of tested surfaces confirmed limited degradation and high coating integrity over extended immersion times.

These studies demonstrate the potential of sepiolite-carbon based bionanocomposites as sustainable, high-performance corrosion barriers for lightweight alloys. Their formulation using natural components, solvent-friendly processing, and multifunctional performance positions them as viable candidates for applications in automotive, aerospace, and possibly biomedical sectors—where both environmental and structural demands are critical.

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Kinetics and isotherms evaluation of albumin protein adsorption on Algerian clays

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This study investigates the adsorption behavior of the protein human serum albumin (Called HSA) on three Algerian clays materials; montmorillonite (Lalithe) [1] and palygorskite in its raw state (Sif Pal) [2] and purified (Pur Pal) [2]. It systematically explores the impact of various experimental parameters; including clay mass, pH, contact time, and initial concentration on the albumin protein adsorption process. Following the adsorption step, solid samples were subject to X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) analyses. The results highlight significant variations in albumin protein adsorption capacity among the three clay types, with Lalithe consistently demonstrating the highest adsorption capacity, regardless of the amount of clay used. pH is identified as a critical parameter, with maximum adsorption occurring at a pH 7. Adsorption kinetics show an initial rapid adsorption phase followed by stabilization, and the pseudo-second-order kinetic model is the most suitable for describing this process, suggesting that chemical adsorption is the determining step. Additionally, adsorption isotherms was modeled using the Langmuir, Freundlich, and Temkin models, each exhibiting variation depending on the clay type. This work provides a fundamental contribution to our understanding of the interaction between albumin protein and clay materials, particularly regarding the influence of the physicochemical behavior of clays in solution, with potential implications in the pharmaceutical field.

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Application of tubular halloysite in low-carbon building materials: geopolymers and limestone calcined clay cement

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Halloysite, a naturally occurring aluminosilicate clay mineral with a distinctive nanotubular morphology, has emerged as a promising material for developing sustainable, low-carbon construction composites. This study shows the unique advantages of halloysite in cementitious systems through investigation of its structural characteristics, geopolymerization/hydration mechanisms, and performance in geopolymers and limestone calcined clay cement (LC^3).

The nanotubular architecture of halloysite, characterized by alternating silica and alumina layers, demonstrates good thermal stability. Controlled calcination (650-850°C) preserves this tubular morphology while dramatically enhancing the geopolymerization activity through dehydroxylation and amorphous phase formation. This calcined halloysite exhibits exceptional dissolution behavior in alkaline activation, releasing reactive silica and alumina that facilitate robust geopolymerization. The resulting halloysite-based geopolymers exhibit dense microstructures with compressive strengths exceeding 50 MPa at ambient curing conditions with desirable moisture, outperforming many conventional clay-based geopolymers.

When processed at comparable calcination temperatures, halloysite demonstrates excellent pozzolanic activity and suitability for producing limestone calcined clay cement (LC^3) with superior mechanical properties and thermal resistance. The unique tubular architecture of calcined halloysite enables simultaneous hydration pathways -both within the inner lumen and along the outer surface - when interacting with cement and limestone components. This distinctive dual-reaction mechanism significantly enhances the formation of key hydration products including calcium aluminosilicate hydrate (C-A-S-H) gel, hemicarboaluminate, and monocarboaluminate phases. Importantly, the resulting halloysite-based LC^3 exhibits remarkable thermal stability, with its high-temperature resistance showing a direct positive correlation with the incorporated halloysite content.

Notably, halloysite occurs not only as a pure mineral phase in halloysite deposits but is also a major component in ion-adsorption rare earth deposits, granite residual soils in southern China, and many solid wastes, such as construction engineering muck. This makes it a promising raw material for being used in the large-scale production of geopolymers and LC^3, particularly in regions like southern China. These findings improve the understanding of the hydration mechanisms in calcined halloysite-based geopolymers and LC^3, while demonstrating a new practical application for tubular halloysite.

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Session 27: Multiscale Computational Modeling of Clay-related Materials and their Fluid Interfaces

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Multiscale simulation of thermal-hydraulic-mechanical-chemical (THMC) coupled processes in compacted bentonite clay

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Bentonite clay has been extensively studied as an engineered barrier material for use in geologic repositories for high-level radioactive waste. A key challenge in this application is that the barrier will be exposed to gradients in saturation, fluid chemistry, and temperature that may give rise to complex coupled phenomena, such as thermally-induced cracking. Efforts to simulate these phenomena at the scale of the engineered barrier rely largely on approaches developed for brittle poro-elastic materials, whereas compacted clay exhibits a ductile poro-viscoplastic behavior.

Here, we build upon our recent development of a computational fluid dynamics (CFD) treatment of single- and two-phase flow in compacted clay. Specifically, we implement an additional heat conservation equation that enables representation of the couplings between fluid flow, solid deformation, and heat transport in compacted bentonite at the scale of an engineered barrier. The parameterization of sub-grid-scale properties (including the heat capacity, thermal conductivity, and thermal expansion coefficient of bentonite) is guided in part by all-atom molecular dynamics (MD) simulations of smectite-water mixtures. Preliminary results are presented and compared with large-scale experimental results, and remaining challenges are identified and discussed.

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A comparison study between halloysite interactions with mono-cationic and di-cationic form of irinotecan

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Halloysite (HNT) belongs to kaolinite clay minerals' group, with a spiral-shape nanotubular morphology and biocompatibility with the human body. It is widely investigated as a controlled drug delivery carrier for the loading of various bioactive molecules. Irinotecan is one of the active substances effectively loaded in halloysite nanotube [1]. It is a semi-synthetic derivative of camptothesin, a substance extracted from plants such as *Camptotheca acuminate*, and is a potent topoisomerase I inhibitor widely used for the colon cancer treatment [2,3]. When irinotecan is administered orally, the drug delivery system passes through stomach's strong acidic conditions (pH 1.2) to the almost neutral colon conditions (pH 7.4). At acidic pH conditions (pH 1.11 to 3.01), irinotecan is present in two forms; the mono-cationic form (C) and the di-cationic form (DC), while in neutral conditions the C is the dominant [4,5].

The comparison of halloysite/mono-cationic irinotecan and halloysite/di-cationic irinotecan systems is the main goal of the present study. The stability of the system and the nature and tensity of interactions prevailed in these systems were investigated by a theoretical approach and the application of classical molecular simulations methods in Materials Studio environment [6]. The results compared with experimental data of Transmission Electron Microscopy and Dynamic Light Scattering to characterize the stability of halloysite/irinotecan system under stomach and colon conditions.

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A classical forcefield for selenium oxyanions in aqueous solutions and minerals

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Selenium is one of the health-important natural occurring elements. Considered as an important micronutrient in low doses, it is becoming dangerous in higher doses [1]. Also, ^{79}Se radioactive isotopes are considered as a major dose-determining radionuclide which can affect the biosphere over geological timescale [2]. In the environmental conditions present in radioactive waste repositories selenium is more likely to occur in the form of selenite $Se(IV)O_3^{2-}$ and selenate $Se(VI)O_4^{2-}$ They are highly solvable in water and, therefore, highly mobile. Selenite and selenate ions are also stable in the cement matrix. While inner-sphere adsorption is observed for SeO_3^{2-} ions, SeO_4^{2-} ions mainly form outer sphere complexes at the interface of cement materials [3,4]. In addition, selenate could substitute sulfate ions in the AFm and AFt cement phases. Seleno-oxyanions also can retention by hydrotalcite-like compounds [5].

There are many experimental studies on selenium oxyanions in the aqueous phases and at the minerals interface [6,7]. At same time, computational studies are limited, as there are no well-established classical forcefields developed for these molecules and mostly *ab initio* methods were previously applied to these molecules [8,9]. In this study we have developed a classical forcefield for SeO_4^{2-}, SeO_3^{2-} oxyanions, compatible with the ClayFF potential [10]. This potential will allow to better study selenium mobility in aqueous solutions, as well as better understand its interaction with clay-like sorbents at the nano-scale. The initial approximation for the force constants and charges were taken from double-hybrid density functional theory calculations with an implicit solvent. The initial values were used in classical molecular dynamics calculations for further optimization, based on an algorithm described by Williams and Carbone [11]. The solvation energy estimation and Se—O bonds length were chosen to fit the force field parameters.

We calculate structural, transport, and relaxation properties of oxyanions dissolved in aqueous solution. Results show that the number of hydrogen bonds in the first solvation sphere is higher for SeO_3^{2-}. Our potential combined with ClayFF force field gives good agreement of SeO_4-ettringite, SeO_4-AFm and $CaSeO_4 \cdot 2H_2O$ structural parameters with *ab initio* molecular dynamics calculations and experiments. The deviation in the calculated lattice parameters from the reference data is less than 5%. The discrepancy of the average interatomic distance between our potential and *ab initio* calculations ranges from 2 to 4%.

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ClayCode: A software tool for modelling realistic clay systems

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Clay minerals exhibit a wide range of properties and uses. Clay-based materials have found applications as barriers for waste disposal, pollution sequestration agents, pharmaceutical excipients and their presence in the environment determines soil properties, fertility and accumulation of contaminants.

Their physicochemical behaviour is closely linked to their molecular assembly, and slight perturbations in clay structure can significantly impact their performance. Molecular modelling techniques provide atomic-level insights that can guide experimental approaches and elucidate the mechanisms behind observed phenomena. However, models used in molecular dynamics simulations often oversimplify the clay structure, sacrificing the accuracy and representability of computational predictions.

We present ClayCode [1], a Python software designed to facilitate the modelling of clay systems that closely match their experimental counterparts. As an output, the user obtains a realistic clay model, assigned with ClayFF force field parameters [2] and input files for simulations with the GROMACS engine [3].

The significance of employing realistic clay models in molecular modelling studies is demonstrated in a benchmarking study on competitive barium and sodium adsorption, which is relevant to nuclear waste disposal. We find that a commonly used simplified Wyoming montmorillonite model features noticeably different adsorption patterns from a realistic model built with ClayCode. A further comparison of sodium and barium adsorption behaviour onto realistic Wyoming montmorillonite, Georgia kaolinite, and Montana illite models highlights how structural differences dictate adsorption behaviour.

This work demonstrates the importance of realistic clay models in molecular simulations. By automating the construction of clay models, ClayCode enables more accurate predictions through molecular simulations, leading to a better understanding of clay structures and properties.

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Physical adsorption of OH- ions at mineral-water interface

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Charging of mineral-water interface plays a central role in many natural, lab and engineering processes. Chemical adsorption of proton and hydroxide ions is the most common process that causes interface charging.

By using first principles simulation, we recently identified a new interface charging phenomenon that is caused by physical adsorption of hydroxide ion rather than chemical bonding. Taking corundum-(0001) as the model surface, FPMD simulations showed that the negative interfacial charges are not from surface OH groups or surface-bound water molecules. Instead, we found that the special interfacial structure effectively trapped the OH- ions through physical adsorption, that led to negative charges on the interface. This adsorption mechanism should also apply to other types of minerals. To deepen understanding of this novel adsorption phenomenon, we investigated more mineral interfaces e.g., kaolinite, gibbsite and brucite. Based on the simulations, more microscopic information will be provided. We will discuss the geochemical and environmental implication of this novel interface-charging mechanism.

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Various concentrations of atorvastatin intercalated into Mg-Al layered double hydroxides

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Layered double hydroxides (LDHs) are promising materials for hosting pharmaceutical compounds due to their tunable layered structure and high biocompatibility. This study explores the intercalation of atorvastatin, a poorly water-soluble anionic drug, into a magnesium–aluminium LDH host using a restacking approach. In this method, atorvastatin dissolved in ethanol was added to an aqueous dispersion of LDH nanosheets prepared via direct coprecipitation of magnesium and aluminium nitrates in an excess of aqueous ammonia solution under a nitrogen atmosphere. Despite the large molecular size of atorvastatin, products with varying drug loadings—from 75.8 wt% to lower concentrations—were successfully synthesized.

Powder X-ray diffraction confirmed successful intercalation through a significant increase in the d_{oo3} basal spacing—from 0.876 nm to 3.808 nm for atorvastatin. Computational modelling using force field methods provided atomistic insights into the arrangement of interlayer components via energy minimization [1]. The simulations revealed that weak electrostatic interactions between the LDH layers and the carboxyl groups of atorvastatin play a key role in stabilizing the structure.

Despite variations in drug content, the LDH basal spacing remained relatively constant, suggesting a self-regulating mechanism in the intercalated structures. The study employed systematic conformational analysis, molecular dynamics simulations, and X-ray diffraction pattern predictions to match experimental results. This combined computational approach reveals how atorvastatin concentration and molecular arrangement influence the structural stabilization of drug-intercalated LDHs, paving the way for more efficient drug delivery systems based on layered inorganic carriers.

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Session 28: Nanoelectronic and Nanophotonic Applications

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Memory Effects in Ultrathin $MoSe_2$/Clinochlore Devices

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Layered materials (LMs) have garnered considerable attention since the obtention of monolayers (1Ls) of graphite, so-called graphene [1]. Among the LMs, there are the Transition Metal Dichalcogenides (TMDs), which belong to the semiconductors category [2]. 1Ls of these materials can be obtained via exfoliation processes onto flat dielectric surfaces, and, for better quality, great effort is made to find alternative insulators for the commonly used hexagonal boron nitride (hBN). Promising as substrate for 1L-TMDs, a naturally occurring material called clinochlore, a member of the phyllosilicate's family, presents an atomically flat surface, large bandgap, and different impurities [3]. How these impurities affect the 1L-TMDs is not completely known so far, especially the charge transfer between the material surface and the 1L-TMDs, a crucial parameter for the performance of multifunctional devices. In this work, a gated-device (capacitor-like structure) containing an encapsulated hBN/1L-$MoSe_2$ onto a clinochlore flake was studied by photoluminescence (PL) spectroscopy (1.88 eV excitation) at cryogenic temperatures. The excitonic emissions (exciton and trion) showed an optical hysteretic behavior (in the PL energy and integrated intensity) when exposed to an external electric field, induced by external bias (V up to +/- 10V). The hysteresis is reproductible in time, stable, and highly modulated by external parameters (i.e., V sweep rate, V range, laser power…) and can be comparable with the behavior of generic memory devices. We will then discuss that this phenomenon can be explained by charge dynamics in the LMs, opening new paths for optical memory effect-based devices [4].

Acknowledgements to FAPESP (2014/07375-2 and 2015/13771-0), CNPq and CAPES for the support in the execution of this project.

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Nitrogen-doped graphene in the interlayers of a nanolayered silicate *for sustainable upscaled energy applications*

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A major current issue is how to make battery components in the most sustainable way while simultaneously preserving the circularity of the material and processing. Here, we demonstrate how we can use toxic dye pollutants in water for the fabrication of graphene battery anodes at significantly lower cost than current approaches. In this context, we demonstrate the efficient production of nitrogen-doped graphene from toxic dyes, which is desirable for electronics applications. We show how this is achieved by the intercalation of a cationic nitrogen-containing dye, safranin, in the interlayer 2D nanospace of a layered silicate, followed by 750°C pyrolithic synthesis of single graphene nanosheets in the interlayer nanospace. Compared with bulk protocols, the synthesis of graphene at such low temperatures significantly reduces the energy cost in carbon industry applications.

Detailed characterization allows us to describe this system and propose a plausible mechanism for the formation of isolated graphene islands in silicate interlayers, alongside carbon nanotube biproducts growing on the edges of silicate nanosheets. An initial electrochemical test of an anode made from this material revealed a lower performance than that of standard graphitic anodes. However, it can be expected that further optimization can improve this significantly.

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Session 29: Properties and Applications of Novel Smart Clay, LDH and Clay-related Nanomaterials

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Aspect Ratio Control of Layered Double Hydroxide Nanosheets and Their Application for High Oxygen Barrier Coating in Flexible Food Packaging

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We report a method to rationally control the aspect ratio of layered double hydroxide for use as a barrier coating for food packaging films. The reconstruction of a Mg_2Al-layered double oxide (LDO) in concentrated aqueous glycine solutions produces dispersions of Mg_2Al-LDH nanosheets. The nanosheet thickness decreases and diameter increases with increasing reconstruction time from 16 to 96 h. We observe a limiting nanosheet aspect ratio of ca. 336 ± 170. These Mg_2Al-LDH nanosheets can be dispersed in PVA to give a water-based dispersion that can be used to coat flexible polymeric films. Oxygen transmission rate (OTR) of a PET film decreases when the thickness of the dried coated layer increases, an OTR of <0.005 $mL \cdot m^{-2} \cdot day^{-1}$ is observed for a coating with thickness of 1175 ± 101 nm.

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Durable radially polarized tubular nanoreactors for catalysis

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The escalating global energy demand and the imperative to diminish fossil fuel reliance for mitigating climate change have accelerated the search for innovative clean energy collection technologies. One promising approach is the generation of valuable molecules (such as dihydrogen and methane) by harnessing solar energy through photocatalysis. Recent research has focused on semiconductors with hollow nanostructures as potential co-photocatalysts due to their attractive attributes, including high and accessible specific surface areas, and enhanced charge separation capabilities.

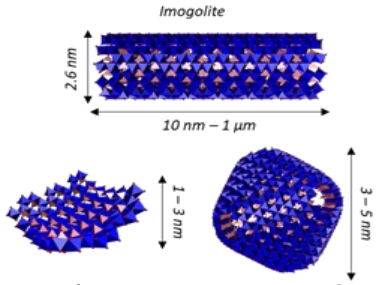

Figure 8: ImoLS

We will present in this poster potentially interesting co-photocatalysts from the imogolite family (ImoLS, or imogolite-like structures). Imogolites are clay-based materials characterized by a hollow nanocylinder morphology with the composition of $(HO)_3Al_2O_3Si(OH)$. Notably, this geometry induces a permanent wall polarization that spatially separates the valence and conduction bands on the inner and outer surfaces of the tube, respectively [1]. As a result, the separation of photo-induced charges is significantly enhanced, enabling oxidation reactions within the cavity and reduction reactions on the external surface [2]. These features render imogolite a promising candidate for use as a nanoreactor in photocatalysis. However, its substantial band gap energy value (greater than 5.5 eV) prevents its application based on photons from the visible light spectrum.

Imogolites systems can also be derived into other morphologies (Figure 2) retaining the same local structure: nanospheres (called allophanes) and nanotiles (called proto-imogolites). The inner wall of these samples can also be modified with methyl groups, making it hydrophobic [3, 4]. However, to this date, only the band diagrams of the nanotubes were proposed [1]. The objective of the present work is to address this gap by presenting the construction of band diagrams for the various polymorphs of the imogolite family, regardless of whether their internal cavity is hydrophilic or hydrophobic.

Moreover, the reactivity brought by the structure can be modulated through functionalization. Thus, substituting aluminum with iron reduces the band gap energy value of imogolites, allowing the sample to be excited by photons from the visible spectrum [5]. Additionally, grafting gold nanoparticles on the outer wall of the material has been shown to affect the reactivity of imogolite (Figure 2) [6]. We are currently exploring similar synthesis strategies with the different polymorphs from the ImoLS family.

The poster will highlight the main characteristics of the various morphologies of the ImoLS family and examine how these differences influence wall polarization and H_2 production under illumination.

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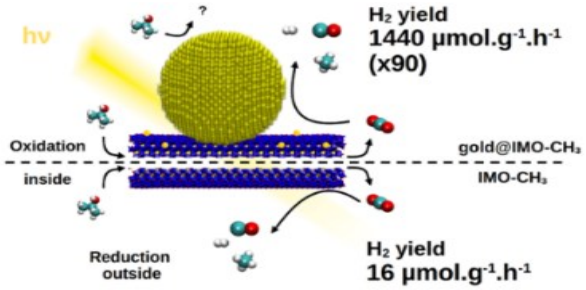

Figure 9: Gold nanoparticles grafting: increase of H_2 production [6]

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Tuning the interlayer space of Li-Al LDHs as adsorbents with application in the direct lithium extraction (DLE) technology

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Since the invention of the first lithium-based battery by Stanley Whittingham in 70s and its later adoption, the demand for lithium has significantly increased [1]. The largest deposits of lithium, accounting for 59% of the total global reserves, are found in continental brines [2]. In order to extract lithium from brines, mainly the water evaporation method is used which requires large land areas. To overcome this a direct lithium extraction (DLE) technology was developed [3]. Its principle is to pass lithium-containing brine through an adsorbent selective for lithium ions. Then, the extracted lithium is recovered from an adsorbent and further processed. For the DLE different types of adsorbents are used and tested including Li/Al layered double hydroxides (LDHs). Current research shows that further studies are needed regarding the development of Li/Al LDHs selectivity and stability.

Thus, the aim of this study was to investigate the impact of interlayer modification of LDHs on the efficiency and selectivity of lithium recovery from brines. The tuning of the interlayer space of Li/Al LDHs with anions, such as: NO^{3-}, SO_4^{2-} and PO_4^{3-} can potentially prevent de-lithiation and improve long-term stability of materials. The Li/Al-LDHs were synthesized using the coprecipitation method at room temperature. For that, the solutions of lithium and aluminum nitrates were added dropwise (5 mL/min) to a beaker initially containing distilled water. Different Li/Al molar ratios were tested (1:3, 1:2, 1:1, 1:2, 1:3) as well as the pH effect (5-9) on the materials' quality was investigated. The final precipitates were aged for 30 min, then centrifuged at 4500 rpm (5 min), washed twice with distilled water and dried at 60°C for 24 h. The XRD patterns of LDHs obtained at pH_{eq} 5-9 revealed basal spacing values in the 9.5-7.5 Å range with lower d values observed at high pH_{eq}. Additionally the high pH favoured the formation of bayerite admixture. Thus, further syntheses were conducted at pH_{eq} 5-6. Based on XRD analysis the LDHs with various molar ratios did not show clear differences in basal spacing. In all cases the presence of gibbsite was detected. The selected materials were further modified by anion exchange and tested for Li adsorption/desorption. The presentation will outline the effect of LDHs interlayer modification on the materials' affinity towards lithium recovery.

This project was supported funded by the National Science Centre, Poland under the OPUS call in the Weave programme No. 2023/51/I/ST11/00368. The authors also greatly acknowledge the Fund for Scientific Research – Flanders for financial support FWO-WEAVE G000425N.

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Synthesis and Characterization of BODIPY with different *meso* groups for the study of hybrid materials

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Boron-dipyrromethene dyes (BODIPYs) are characterized by their photostability, tunable fluorescence, and structural versatility, making them excellent candidates for applications as hybrid materials.[1][2] This study focuses on the synthesis and characterization of a series of BODIPY derivatives, including cationic and neutral substances, to investigate their interactions with saponite (Sap), a layered silicate with promising potential in materials science. The cationic BODIPYs were designed to exploit electrostatic interactions with the negatively charged surface of Sap, while the neutral compounds with different polarity served as a control to investigate non-electrostatic binding mechanisms. The BODIPY compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, UV-Vis spectroscopy and fluorescence spectroscopy to determine their structural and photophysical properties.

Based on preliminary experiments, two BODIPY compounds were selected from a variety of different BODIPY molecules synthesized, one cationic, the other neutral, and studied in the systems with Sap to determine how charge affects their binding and photophysical behavior. Depending on the BODIPY type, both fluorescence quenching and surface fixation-induced emission were observed. Unexpected insights into their photoactivity and interaction modes pave the way for new functional hybrid materials with implications for sensing, catalysis, and optoelectronics.

Acknowledgements: The work was supported by the Slovak Research and Development Agency under contract No. APVV-22-0150 and APVV-21-0302.

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Efficiency Enhancement of Circularly Polarized Luminescence from a Binaphthyl Compound via Interlayer Confinement in Clay

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Circularly polarized luminescence (CPL) materials are of interest for applications in photonic devices such as 3D displays and LEDs. To meet practical demands, such materials should be in the form of low-scattering thin films. Hybrid films combining clay minerals and organic compounds have been reported to exhibit reduced light scattering and enhanced photoluminescence efficiency due to restricted molecular motion. In this study, we investigated the CPL properties of hybrid films composed of a chiral binaphthyl derivative ((R)- or (S)-CBNC – Fig. 1) and Sumecton SA (SSA), as layered clay mineral.

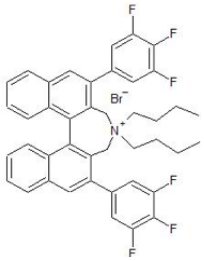

Figure 10. Chemical structure of CBNC

SSA–CBNC hybrid films were synthesized according to a previously reported method [1], with the CBNC content corresponding to 5% and 10% of the cation exchange capacity (CEC).

Fluorescence spectra and CPL spectra of SSA–CBNC hybrid films are shown in Fig. 2. The fluorescence peak of CBNC red-shifted from 365 nm in aqueous solution to 377 nm in the hybrid film, reflecting expansion of π -conjugated system upon intercalation. The quantum yield improved from approximately 0.01 in the solid state to around 0.06 in the hybrid film, though still lower than in aqueous solution (~0.13).

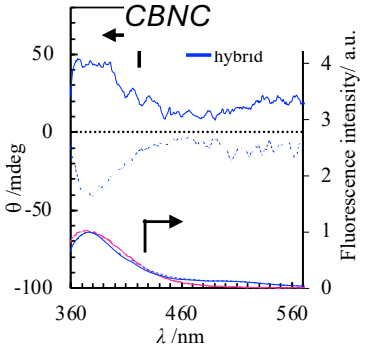

Figure 2. Fluorescence (right vertical axis) and CPL spectra (left vertical axis) of aqueous solutions of (R) or (S) CBNC (red line) and (R) or (S) CBNC-SSA hybrid films (blue line). The solid

The CPL spectra were observed in the almost same wavelength region as fluorescence emission, confirming that CPL originated from the CBNC molecules. The CPL spectra of the SSA-(R)CBNC and SSA-(S)CBNC hybrid films exhibited positive and negative ellipticity, respectively, analogous to that of the aqueous CBNC solution. The *g* values of each sample were summarized in Table 1. The enhancement of the g value of CBNC upon hybridization with SSA was observed. It is known that the g values of binaphthyl compounds are correlated with the dihedral angle of the excited state of binaphthyl [3]. In the hybrid film, the binaphthyl moiety presumed to adopt a more planer conformation due to confinement within the interlayer space of SSA. Thus, the enhancement of the g value of CBNC might be attributed to the narrowing of the dihedral angle of CBNC in excited states resulting from hybridization with SSA.

Table 1. g values of aqueous solutions of CBNC and SSA-CBNC

	g value
(R)CBNC aq	2.0×10^{-5} [1]
(S)CBNC aq	2.0×10^{-5} [1]
5%CEC (*R*)CBNC-SSA hybrid	3.3×10^{-3}
5%CEC (*S*)CBNC-SSA hybrid	2.9×10^{-3}

Acknowledgment: CPL measurements were conducted using CPL-200 (JASCO) at N-BARD, Hiroshima University.

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Unlocking Fluorescence Enhancement in Benzothiazole-based Dyes in Hybrid Silicate Dispersions

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Layered silicates in combination with organic dyes represent a promising group of photoactive materials with tunable optical properties. The enhancement of luminescence in these systems is primarily attributed to the immobilization of dye molecules on the two-dimensional surface of the silicate, with the phenomenon of Surface-Fixation Induced Emission (S-FIE) playing a key role. This effect restricts the rotational motion—a major cause of fluorescence quenching of free dye molecules in solutions— and leads to improved emission efficiency [1]. Hybrid materials exhibiting the S-FIE phenomenon are emerging as a promising alternative to aggregation-induced emission (AIE) materials, which have attracted much scientific attention in recent years. Compared to AIE materials, they are cost-effective, and offer better sustainability and the possibility of sample preparation in the solid state [2].

In this study, we developed hybrid dispersions by combining cationic benzothiazole derivatives with synthetic saponite (Sap), a layered silicate from the smectite group, selected for its low surface charge and small particle size, which are favourable for S-FIE-based enhancements [3]. We investigated five benzothiazole derivatives with different spatial arrangements of the triarylamine subunit, ranging from freely rotatable to fully rigid, to assess their influence on the S-FIE phenomenon and overall photophysical properties. The hybrid dispersions were synthesized with different dye/saponite ratios and characterized using spectroscopic techniques, including UV-Vis absorption spectroscopy, fluorescence spectroscopy, quantum yield determination, and fluorescence lifetime measurement.

Our findings reveal that the photophysical properties of these hybrid systems are primarily influenced by the spatial structure of the dye molecules and the composition of the hybrid dispersions. The most pronounced luminescence enhancements were observed for dyes with freely rotatable triarylamine and carbazole substituents, achieving quantum yields of about 10%. In contrast, benzothiazole derivatives with planar structure tended to form molecular aggregates, leading to fluorescence quenching. Furthermore, we developed a model based on energy transfer and molecular distances at the surface to explain the observed fluorescence trends, which are generally applicable to S-FIE systems. These materials hold significant potential for next-generation applications in optoelectronics, bioimaging, and photomedicine [4].

Acknowledgement: The work was supported by Doktogrant APP0623.

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Synthesis of transition metal-doped Li-Al layered double hydroxides and their application for selective lithium extraction from brines

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The demand for lithium has risen substantially in the last decades. Therefore, there is a need to optimize extraction methods, to meet the needs of rapidly developing world. Direct lithium extraction technology (DLE) is one of the most promising unconventional method in this field [1]. The DLE is based on the use of lithium selective adsorbents. It combines some key features such as wide application in various brine sources, effective and simple operational processess and high selectivity for lithium. The DLE has potential to largely reduce land usage, which is one of the biggest drawbacks of conventional extraction methods. One group of efficient adsorbents used in the DLE includes Li/Al layered double hydroxides (LDHs). However current research indicated the need for their further improvement in particular in terms of stability and adsorption capacity towards lithium. Therefore, our study focuses on the influence of the LDHs doping with selected transition metals on the efficiency and selectivity of lithium recovery from brines.

The syntheses were carried out by coprecipitation method at room temperature by using $LiNO_3$ and $Al(NO_3)_3 \times 9H_2O$ as substrates. The Li/Al solution was added dropwise (5 mL/min) to a beaker containing distilled water. The Li to Al ratio was set to 1:2 and the pH during syntheses was maintained at 5-6 with 3 M NaOH solution. The doping by Zn(II) was performed by including $Zn(NO_3)_2 \times 6H_2O$ in the aqueous metal-containing solution. It was assumed that Zn(II) will substitute the structural Al(III) and its content was set to 5, 10 and 20% in relation to Al(III). The final precipitates were aged for 30 min, then the materials were centrifuged, water washed and dried at 60°C.

The XRD analysis confirmed the formation of LDH in all cases with basal spacing reflection equal to ~9.1 Å. The XRD patterns showed that the Zn(II) addition hampered formation of Al-rich phases: gibbsite and bayerite. The XRD peaks of these minerals were clearly visible for the Li/Al LDHs formed in identical experimental conditions. For the Li/Zn-Al LDHs the position of the non-basal reflections, which represents the mean cation-cation distance in the brucite-like layer, shifted after doping. This indicated Zn(II) incorporation within the LDH structure. The selected materials were tested in lithium adsorption experiments with varying Li concentration both in distilled water and simulated brine. The presentation will outline the Zn(II) doping effect on the lithium adsorption efficiency and the materials' stability in the applied experimental conditions.

This project was supported funded by the National Science Centre, Poland under the OPUS call in the Weave programme No. 2023/51/I/ST11/00368. The authors also greatly acknowledge the Fund for Scientific Research – Flanders for financial support FWO-WEAVE G000425N.

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Ionic Conductivity of Ion Defect Introduced Layered Double Hydroxide and its Mechanism

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Layered double hydroxide (LDH) is known as a hydroxide ion conductor. In order to realize high ionic conductivity, ionic conductors need to have defects in the crystal that allow ion migration within the crystal. Therefore, it is believed that ion transfer by the so-called vehicle mechanism does not occur in the LDH structure. In the present study, we attempted to improve the conductivity of LDH by introducing hydroxide ion defects into MgAl-based LDH, which exhibits hydroxide ion conductivity, and discussed the conductive mechanism based on these results. LDH is known as a layered compound with anions inserted between the layers to compensate for the positive charge, and is characterized by the free exchange of anions between the layers. By taking advantage of this structural feature, we introduced defects into LDH. The hydroxide ion defect was introduced by inserting hydrogen carbonate ions into the interlayer of LDH, and some hydroxyl groups were decomposed by acid-base reactions. We tried to introduce hydroxide ion defects into LDH by heat treatment at 150 to 200°C to desorb protons from LDH after ion exchange to bicarbonate ions. The 003 diffraction peak in the XRD diffraction pattern was shifted to the low-angle side by the heat treatment. This is thought to be due to the introduction of hydroxide ion defects in the host layer. The positive charge in the host layer increased due to the desorption of hydroxide ions, and the interlayer space expanded due to increased repulsion between the host layers. Fig. 1 shows Arrhenius plots of the conductivity of samples containing carbonate ions as interlayer ions in the initial state after heat treatment at 150 and 200˚C. In the system with carbonate ions, the conductivity decreases significantly with heating, and in the sample annealed at 200˚C, the conductivity drops to the detection limit, indicating that the ionic conductivity is almost lost. On the other hand, in the hydrogen carbonate ion system, no significant change in conductivity was observed, only a change in slope. This suggests that in the bicarbonate ion system, a new ionic conductivity mechanism was activated by the introduction of ion deficiencies.

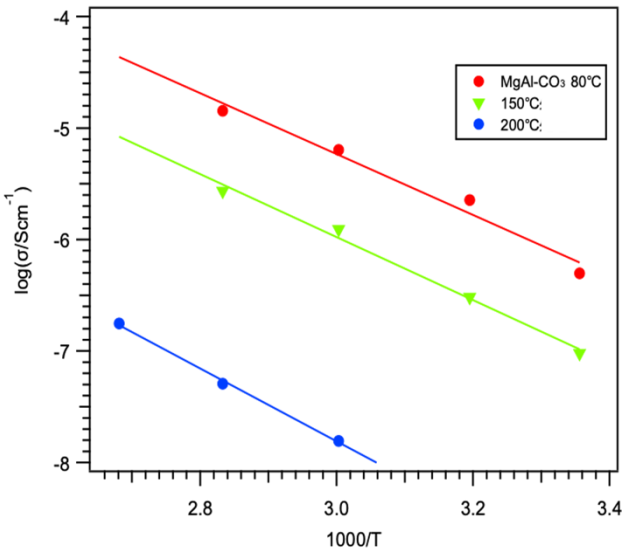

Figure 1 Arrhenius plots of Mg-Al LDH with CO_3^{2-} heat treated at various temperatures.

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Analysis of the abrasive and micro-impact wear of hydrotalcite-like coatings on zinc alloy

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Thin coatings or top layers are usually applied to improve resistance to tribological, chemical, corrosive or thermal wear, creating hard anti-wear coatings and/or tight barriers against the effects of harmful environments. Therefore, the adhesion and wear resistance of the coating or layer is crucial to control the durability of the element that is exposed to wear in contact with the counterpart solid or the environment. Geology-inspired synthetic clay minerals provide novel opportunities to design layered solids with tuned properties and extended applications. The intelligent design of new structures made possible by an in-depth understanding of the essential mechanisms of clay formation (e.g. anionic layered double hydroxides, LDH) together with advanced technologies results in innovative routes of synthetic clay production. This is particularly important when layer hydroxides, which belong to the family of versatile 2D nanomaterials, are formed in-situ on the surface of a metallic solid phase. In this study, we focus on the development of a series of ZnAl-NO_3 LDH coatings with the formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2][An^-]_{x/n}\cdot mH_2O$ (where M^{2+} and M^{3+} are respectively two- and three-positive cations) by their in situ formation on the surface of Zn alloy using the substrate alloy as an internal source of Zn cations. To obtain the series of ZnAl-NO_3/CO_3/LDH naturally adherent coatings on the surface of Zn alloys, the pH and temperature of mother liquor containing $Al(NO_3)_3 \cdot 9\ H_2O$ were under control. The effect of the roughness of the pretreated Zn steel surfaces ensured by alloy substrate polishing with 1000 and 4000 grit on the formation and growth of LDH structure on the surface of the alloy was investigated. SEM analysis showed formation of a dense LDH layer on the Zn alloy surface with higher packing for films obtained on surfaces with greater roughness (1000 grit). Increasing the crystallization time enhanced this effect. EDS point analysis performed in the micro-areas of the studied samples confirmed the presence of Zn and Al in the formed LDH layer. Consequently, the amount of Al increases with progressive synthesis time. XRD method supported by FTIR technique confirmed the crystallization of the hydrotalcite-like layer on the Zn alloy surface in the function of exposure time to the solution containing Al^{3+} ions.

Wear resistance investigations of the coatings were conducted in several stages. In the first step, the hardness and elastic modulus were determined using the nano-indentation technique with the Berkovich indenter at a load of 2 mN. The measurement results indicate low hardness and elastic modulus of the coatings. Scratch tests carried out using the spherical Rockwell diamond indenter showed good adhesion of the coatings to the substrate. Wear resistance of coatings under dry sliding friction conditions was also tested. Knowledge of the intensity of abrasive wear allows for estimating the service life of the coated elements. The coatings with the highest resistance to frictional wear were subjected to micro-impacts. The tests consisted of low-cycle impact on the coating surface with a 0.5 mm radius of Al_2O_3 ball at a constant load and frequency. The wear caused by friction was mainly abrasive but was initiated by coating cracks and local micro-chipping. The wear products present in the friction contact accelerated the abrasion process. As a result of micro-impact interaction, craters were formed in the samples, and the wear was caused by cracking and chipping of coating fragments. Analysis of the abrasive and micro-impact wear mechanisms was carried out using a light microscope and SEM-EDS.

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Session 30: Clays in Geotechnics – Problems and Applications

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An appraisal on the characteristics of organically modified clays for applications as engineered barriers

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Clays are used for long for the control of the migration of pollutants and for the protection of environment as engineered barriers. It is established beyond doubt that the effective performance of any clay as a barrier material is largely controlled by its swelling behaviour apart from their sorption efficiency (1). Natural clays are used widely for waste containment applications due to the significant reduction in the contaminant migration owing to the low hydraulic conductivity and high sorption capacity attached to the clays(2,3&4). Clay's inherent negative charge is an added advantage. As rule of thumb, clays are hydrophilic in general. However, the previous studies have proved that the hydrophobic organic contaminants are not sorbed to the clay surface (5) and the use of conventional clay in engineered barrier system is limited when it comes to the question of disposing leachates containing organic contaminants. Different approaches can be adopted to modify clay for enhancing the sorption capacity of clays towards organic contaminants.

Ion exchange with alkyl ammonium ions is a well-known and the preferential method to modify clays for enhancing organic sorption of clays (6). When surfaces of the clay materials are modified by introducing long or short chain organic compounds, they are referred as organically modified clays or organo clays. The modified surfaces in organo clays can act as a sorption sink for toxic metals, metalloids and hydrophobic organic compounds.

As the effectiveness of organic modification and sorption depends on several factors, there is a need to understand the mechanism of organic modification particularly with respect to bentonites available in given region. Hence a study has been carried out on the effectiveness of modification of bentonites of Indian origin with different modifiers. It is necessary to understand the effect of organic modification on the geotechnical characteristics as it is likely to cause concern about the hydraulic performance and stability of barrier systems when amended with organo clays (7).

The study presents the effect of modification, role of type of clay and type of modifiers on the characteristics of organo clays by comparing the physico chemical characteristics of different modified and unmodified clays. It is revealed that irrespective of the type of clay modified or the modifier used all the organo clays tend to become hydrophobic, and the surface area of the clays was found to decrease. The effect of incorporating unmodified bentonite with organically modified clay on the index properties of bentonite has also been studied. The results suggested that the effect of organo clay addition to bentonite was always to reduce its plasticity and free swell in water. However, in pore fluids of lower dielectric an increase in the plasticity and free swell was observed with increasing organo clay content in the mixture. This owes to the fact that organo clays can interact strongly with organic fluids, changing its fabric arrangement (8). Swelling ability of the unmodified clays was not completely suppressed even in the presence of low polar miscible organic liquids as they were molded at water contents corresponding to the optimum moisture content (OMC). The order of the swelling for the unmodified bentonites was in the order of the polarity of the pore fluids used, while the order is reversed upon organic modification of clays. Both organic modification and addition of organo clay to bentonite resulted in the suppression of the swelling of clays in water irrespective of the type of modifier or the extent of organic modification.

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Experimental method for testing thixotropic properties of clays

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Thixotropy is an ability of soils to change from the solid to a liquid state when exposure to vibrations or mechanical disturbances. Disruption of the thixotropic soil structure can alter pore pressure, which may affect their plasticity index and, in severe cases, lead to liquefaction. Thixotropic properties apply to soils that are composed of grains smaller than 0,002 mm.

The study presents a innovative method for testing thixotropic properties of soils using a prototype device designed for measuring penetration of the sharpened weight directly after exposure the soil sample to vibrations, which provides the means to determine the consistency of the sample in question.

For purpose of this study a range of samples were collected from areas with documented occurrences of thixotropic soils located in southern-east part of Poland. For the sake of comparison both more and less cohesive soils were retrieved. To characterize the collected soil samples, a series of laboratory tests were conducted in accordance with ISO 17892.

This approach, which focuses on soil behaviour under varying conditions, provides valuable insights into the response of specific soil types – especially those with thixotropic properties – to mechanical disturbances. Moreover, executed tests allowed for documentation of the thixotropic strengthening phenomenon.

The research was financed by the AGH University of Krakow, Excellence Initiative–Research University (Project No. 12588).

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Strength and Liquidity Index Correlation in Transitional Oil Sands Tailings

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Some tailings deposits encountered in oil sands mine sites today fall into the sandy-fine category, characterized by fines content and sand-fines ratio ranging from 25% to 50% and 1 to 3, respectively. These include some soft centrifuged tailings and thickened tailings deposits; more can be expected from coarse sand and centrifuged fluid fine tailing mixtures resulting from the emerging co-mingling deposition approach. Tailings in this category may be too fine to behave as cohesionless or too sandy to behave as cohesive, depending on the amount and properties of fines included.

For decades now, undrained shear strength (S_u) has been predicted by using cohesive soils' index properties, mainly the liquidity index. Different S_u-I_L correlation functions for soils with different values of I_L were developed from experimental tests by Wroth and Wood [1], Leroueil et al [2] and Locat and Demers [3]. Su-IL correlation approaches are relatively easy and inexpensive, yet reasonably reliable for estimating S_u compared to counterpart laboratory S_u measurement methods.

Due to the limited research on the properties of transitional oil sands tailings, this study aims to create synthetic mixtures of fine tailings and sand sourced from oil sands mining operations and determine the suitability of these correlation functions in these materials. Mixtures will contain varying fines content (<44 µm), ranging from 25% to 50%, to determine their Atterberg limits and correlation with shear strength. Atterberg limits will be measured with compliance to modified ASTM D4318 – 17, the air-dried sample preparation procedure will be used and both bitumen and sand (>425µm) particles will not be removed from the sample before testing. Vane Shear tests will be done on these samples to measure their strength values for comparison to values obtained from I_L and to determine the suitability of these correlation functions.

Preliminary findings have shown these sandy-fines tailings to be in a low-plasticity soil zone, with a good correlation between shear strength values estimated by Leroueil et al. [2] and Locat and Demers [3], especially for strength values below 20 kPa.

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The role of vermiculite in the geotechnical behaviour of Plioquaternary clayey soils from the Zagreb Podsljeme hilly area

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Due to the specific geomorphological and geological structure, as well as frequent instances of inadequate construction, the Zagreb Podsljeme hilly area faces numerous engineering-geological challenges. One of the most significant issues in this region is slope instability, with numerous landslides posing a threat to residents and their properties. Many of these landslides are associated with fine-grained Plioquaternary (PLQ) soils, predominantly composed of low-plasticity and high-plasticity clays. These soils exhibit significant variability in both physical and geomechanical properties, and changes in mineral composition, particularly in the clay minerals, have also been observed. The aim of this study was to conduct a detailed analysis of the mineral composition of these soils, with a focus on expandable clay minerals, and statistically examine their influence on the soils' physical properties.

A total of 39 fine-grained PLQ soil samples, collected from boreholes at three different locations within the Podsljeme zone of Zagreb, were analysed for mineral composition (bulk and clay minerals), Atterberg limits (liquid limit – WL, plastic limit – WP, and plasticity index – IP), cation exchange capacity (CEC), and specific surface area (SSA). The identified clay minerals include vermiculite (Vr), smectite (Sm), kaolinite (Kln), illite and muscovite (Ilt/Ms), with trace amounts of chlorite (Ch). Vermiculite was found in all PLQ samples and has varying effects on the soils' physical properties depending on soil type. In PLQ-CH soils, vermiculite is the primary mineral that affects the soil's plasticity, with a correlation between water content and vermiculite (Vr-WP correlation, $r = 0.55$). This is due to cation exchange occurring at the edges and interlayer spaces of vermiculite particles, supported by correlations between vermiculite and CEC ($r = 0.56$) and CEC and WP ($r = 0.76$). In PLQ-CL soils, vermiculite does not correlate with WP or CEC, but shows negative correlations with WL ($r = –0.65$), SSA ($r = –0.43$), and IP ($r = –0.67$). This suggests that in soils with more vermiculite, larger crystallites reduce SSA and WL. This relationship may result from the transformation of chlorite or biotite into vermiculite, followed by further weathering into smectite or kaolinite.

This research was conducted as a part of the internal research project „ZG-LAB“ at the Croatian Geological Survey, funded by the National Recovery and Resilience Plan 2021–2026 of the European Union – NextGenerationEU, and monitored by the Ministry of Science and Education of the Republic of Croatia

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Experimental Study on Biogenic $CaCO_3$ for Sustainable Stabilisation of Dredged Fine Sediments

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In the context of sustainable geotechnical engineering, this study explores the potential of biogenic calcium carbonate ($CaCO_3$) derived from mussel shells as an eco-efficient alternative to quarried limestone in the mechanical stabilisation of fine dredged sediments. These sediments, rich in clay minerals and produced in large volumes by port dredging operations, pose significant management challenges. However, they also present opportunities to produce new construction materials. The innovative approach presented here utilizes the specific reactivity of biogenic $CaCO_3$ to actively participate in chemical reactions within the system sediments-water-binder.

In order to validate the efficacy of biogenic calcium carbonate from shells, a series of laboratory tests were conducted on dredged sediment mixtures stabilised with Portland cement and mussel shell powder compared to the same sediment mixtures stabilised with cement and quarry limestone (i.e., geogenic calcium carbonate). Both sources of calcium carbonate were admixed as partial replacement of cement with two replacement ratios (¼ and ½ of the total binder content) and two particle sizes (coarse and fine) evaluated. The experimental programme involved testing the short-term (7-day) performance of the mixtures through mechanical and chemical tests, followed by a 28-day multidisciplinary, multiscale characterisation of the sediment mixtures with mussel shell powder to investigate the role of the shell in the stabilised matrix. The results obtained appear to confirm that biogenic $CaCO_3$, which is mainly composed of calcite and aragonite, has a high specific surface area that favours the formation of nucleation sites for hydration products, in particular calcium silicate hydrate (C-S-H) [1], [2]. These nucleation sites have been shown to enhance the kinetics of the early stages of cement hydration, especially in the presence of clay minerals, resulting in improved cementing and mechanical performance. In addition, ion exchange and surface interactions between the biogenic carbonate and the clay matrix contribute to denser microstructures and more efficient utilisation of the binder [3]. The present study proposes a circular strategy for low-carbon soil improvement through the coupling of sediment valorisation with the reuse of industrial shell waste, with direct implications for both sustainability and resource efficiency in geotechnical applications.

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Clay materials identified within construction and demolition waste

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The application of construction and demolition wastes (CDW) largely depends on its properties, which vary based on the material's origin and the treatment it undergoes at the processing plant. By carefully considering and controlling these factors, it is possible to produce more homogeneous CDW. In addition to particle size, cation exchange capacity and specific surface area, the mineralogical composition of the CDW plays a critical role in determining its chemical reactivity for various applications. Given the importance of incorporating such waste into circular economy practices, a thorough understanding of its composition is essential.

In this study, two types of CDW were analyzed, both collected from areas characterized by tertiary clayey-sand arkoses. These materials originate from regions rich in phyllosilicates, which are of interest due to their potential applications. One sample corresponds to a mixed demolition material (02), while the other comes from trenching activities (Z060). Granulometric analysis revealed that both materials are fine-grained, with D50 values of approximately 2 mm for Z060 and between 0.5–1 mm for 02. Based on the granulometric data, the sorption capacity of the finest fraction (< 0.063 mm) was assessed using cation exchange capacity (CEC) and specific surface area (SSA) measurements. The CEC values were 20.0 ± 1.9 cmol(+)/kg for Z060 and 15.8 ± 1.1 cmol(+)/kg for 02. Corresponding SSA values were 18.8 ± 2.3 m^2/g for Z060 and 14.2 ± 0.3 m^2/g for 02. These results are slightly higher than those of natural aggregates such as fine sand (FS) and normal sand (NS), which show CEC values of 0.9 ± 0.6 cmol(+)/kg and 3.3 ± 0.2 cmol(+)/kg, and SSA values of 4.5 m^2/g and 0.67 m^2/g, respectively. Previous X-ray diffraction (XRD) analyses of the < 0.063 mm fractions indicated that approximately 50% of the material consists of clay minerals, with around 10% being smectites.

We characterized the mineral content to evaluate the added value these CDW materials may offer for future applications and to determine whether interaction with cementitious materials has caused any alterations. For this purpose, the <2 µm fraction was analyzed as oriented aggregates using a Bruker D8 Discover diffractometer. In material Z060, the presence of smectite, illite, kaolinite, and traces of chlorite was identified. In material 02, in addition to these phyllosilicates, calcite was also detected. These findings are consistent with the ~50% clay mineral content previously observed in the <0.063 mm fraction. Analysis of the specific surface area (SSA) of the <2 µm fraction yielded values of 46.3 ± 0.1 m^2/g for Z060 and 51.3 ± 0.1 m^2/g for 02. The measured CEC and SSA values align with those expected for the identified clay mineral types, as supported by the material properties and standard references [1].

The composition determined for CDW makes possible to study added value applications related to adsorption properties of materials or even to be used in ceramic process [2]. Future work will study the presence of amorphs in the powdered sample of the < 2 µm fraction.

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Session 31: Advances in Calcined Clays as Supplementary Cementitious Materials in Blended Cements

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Calcined Clay interaction with superplasticizers: adsorption behaviour and ion release kinetics

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Around 8% of the global CO_2 emissions originate from the cement production [1]. However, this high CO_2 footprint can be significantly reduced by replacing parts of the Ordinary Portland Cement (OPC) with calcined clays (CCs), e.g. ~30% CO_2-reduction in the form of 'limestone calcined clays (LC^3)' [2].

In this work, four CCs were investigated and compared regarding their ion release (Si, K, Al and Ca), superplasticizer (SP) adsorption kinetics and surface charge (zeta potential): a) CC_{ref} (from Liapor) [3]; b) Ca/Mg-montmorillonite (Calcigel), c) Na-montmorillonite (Volclay) and d) Illite (Arginotec). The optimum calcination temperatures were 850 °C for all clays except 900 °C for the Illite. Kinetic experiments were done in water/binder (w/b) ratios of 50:1 (for zeta potential 1000:1 to exclude precipitation), whereas the 'water' here was saturated $Ca(OH)_2$ solution (22 mM, pH 12.5–13.1) to provide a Ca source for the hydration process. CC-SP interactions were studied using SPs 'VP 2018/13.1' and 'VP 2018/14.1' (Master Builders Solutions, Germany), both based on polycarboxylate ether (PCE) at four concentrations (0.1, 0.2, 0.8 and 1.0 wt.% (PCE) [4]. Supernatants < 0.22 µm were measured via inductively coupled plasma – optical emission spectrometry (ICP-OES) to gain ion release kinetic information as well as via liquid chromatography coupled to an organic carbon detector (LC-OCD) to investigate SP-CC adsorption kinetics including the study of polymer fractionation processes.

Ion release results revealed that the addition of SP increases Si ion release for all CCs with increasing SP concentration. This was found for Al and K only for some CCs and not at all for Ca ion release. Generally, CCs showed significant differences in ion release, and CC-dependent rapid precipitates were formed after ≤ 5 min reaction time, especially for Ca, and Al but not for K and Si. This suggests the formation of Ca-Si phases within the first minutes. Adsorption kinetic results suggested a quick (≤ 5 min) adsorption process of SP onto CCs with preferred polymer (larger masses) adsorption, compared to the residual monomer (smaller masses). Additionally, after SP-CC contact a polymer fractionation to smaller masses was found for all CCs. In any case, the SP-CC adsorption potential and kinetics were different between clays (from high/fast to low/slow SP adsorption): Na-Mont. > CC_{ref}, Ca/Mg-Mont. > Illite. Finally, zeta potentials only showed electrostatically repulsion (≥ 20 mV) for the case of Illite and Na-Mont. without SP addition. After adding SP, zeta potentials were ~0 $\pm$ 5 mV for all CCs independently of the SP concentration suggesting the possibility of particle agglomeration. For all systems and parameters, only minor differences were observed between the SPs investigated.

Overall, this study provides a methodology approach to better understand the SP-CC interaction behaviour in suspension in terms of ion release and adsorption kinetics as well as electrostatic stability. A next step is the coupling to the rheological properties of CC-mixtures in contrast to pure OPC.

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The role of accessory minerals in the activation of natural bentonites

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Activated clays can be used as Supplementary Cementitious Materials (SCMs) to replace clinker in Portland cement, a key strategy to produce low-carbon cements and to decrease the carbon footprint of this industry [1]. Consequently, current research focuses on optimizing clay activation, especially for kaolinitic clays, recognized as the most reactive clay group after thermal treatment [2]. However, the influence of different mineral phases on clays' reactivity remains not fully understood, with this property often attributed primarily to the clay mineral content. This knowledge gap is even more pronounced for non-kaolinitic clays, or common clays, which are less studied due to the attribution of a lower reactivity, despite their great availability worldwide and potential use in cementitious systems [3]. Therefore, this research aims to analyse the effects of four calcination temperatures on natural smectite-rich clays with varying compositions, in order to assess the chemical and physical modifications and to define the role of accessory minerals in calcined clays' final properties.

Four natural bentonitic clays from the same region were ground and calcined using a laboratory furnace at 600, 700, 800 and 900°C. The samples were submitted to X-ray diffraction (XRD), BET and BJH tests in order to assess mineralogical composition and phase modification during activation, specific surface area and pore distribution of the particles. The degree of dehydroxylation through each calcination temperature was determined by thermogravimetric analysis (TGA). Additionally, ^{27}Al and ^{29}Si MAS-NMR spectroscopy was conducted in order to monitor changes in the aluminium and silicon environments throughout activation. Finally, the calcined samples were submitted to the R^3 isothermal calorimetry test to assess their reactivity in a cement-like environment.

The results reveal distinct modifications in clays' properties, linked not only to calcination temperature, but also to clays' mineral composition. Qualitative and quantitative XRD analysis indicated various smectite contents and the presence of different accessory minerals in each clay sample, even though they originate from the same region. A significant influence of accessory minerals was observed regarding clays' reactivity, especially between the calcination temperatures of 700 and 800°C.

This work highlights the critical role of accessory minerals in governing the final properties of calcined clays. It was possible to conclude that clays' reactivity is not only ruled by the clay mineral content, but also by the composition and transformations of accessory minerals during calcination. Therefore, this study provides valuable insights into the role of accessory minerals and their influence on the behaviour of calcined clays. These findings contribute to a better understanding of the optimization of common clays for cementitious applications, advancing knowledge on the role of accessory minerals in clay activation mechanisms and their impact on reactivity.

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Hydration Mechanisms and Phase Assemblage Of Very-Low Clinker Cement Blends Comprising Non-Kaolinitic Calcined Clays

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Reducing emissions from cement production is difficult because it relies on carbon-based raw materials and high-temperature processes. To achieve substantial emission reductions, it is essential to adopt innovative green technologies. Supplementary Cementitious Materials (SCMs) are promising, especially in the short term. However, the regional availability of traditional SCMs, such as fly ash, slags, and metakaolin, is limited and won't meet future global demand. Therefore, new SCMs are urgently needed. Kaolinitic clays are a promising clay resource for SCMs. Conversely, non-kaolinitic clays have been less studied due to their lower reactivity and performance. In this work we investigate the use of a waste product from port activities in Antwerp, Belgium, as an alternative SCM in very low clinker cements. The dredged port sediments, primarily composed of 2:1 clays such as montmorillonite and illite, were pretreated using a flash-calcination process. These materials are abundant enough to meet the local demands of cement, while exhibiting fairly good levels of reactivity when the fine-grained clay minerals are activated upon calcination.

Six different cement blends were studied with a fixed water-to-binder ratio of 0.5 and compared to a regular cement (CEM I) and a cement blend with limestone as references. The first analysed blend contained 70% cement (C) and 30% clay (Q). Additionally, two ternary blends were made with limestone, an LC^3 like blend with 55% C, 30% Q, and 15% limestone (LL), and the other one with 70% C, 20% Q and 10% LL. Then two ternary blends with blastfurnace slag (GGBFS) were prepared, one with 45% C, 20% Q, 35% GGBFS (S), and the other one with 20% C, 30% Q, 50% S. Finally a quaternary blend containing 20% C, 30% Q, 30% S, 20% LL was also investigated. The hydration kinetics of the eight cement pastes were assessed by isothermal calorimetry measurements, for seven days, following standardized procedures. The blends were also cured under constant temperature in water bath of 20°C, and submitted to X-ray diffraction (XRD) and thermogravimetry (TG) measurements at the ages of 1, 2, 7, 28, and 90 days. Mortar bars were prepared from selected blends, according to EN 196-1, for compressive strength testing and analysed up to 90 days of curing.

Quantitative XRD and TGA measurements revealed that an early increase in ettringite content is a key mechanism for enhancing performance. In the LC^3-like system, for example, portlandite forms rapidly up to seven days and then stabilizes. Ettringite levels remain stable up to 28 days, while alite is largely consumed by the second day. Moreover, monocarbonate levels are significantly high at 28 days. The presence of limestone is believed to suppress the formation of strätlingite, as more aluminium is consumed to form monocarbonate, thus retaining ettringite. Furthermore, compressive strength results showed values as high as 48 MPa at 28 days for a 45% clinker replacement level. Ultimately, to investigate porosity refinement, microstructural analysis was performed using scanning electron microscopy (SEM) and micro-intrusion porosimetry.

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Sedimentation as a low-cost alternative to laser diffraction for particle size measurement of calcined clays – limitations and opportunities

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Calcined clays are an increasingly important cementitious constituent given the abundance of clays at the global scale. The particle size distribution of calcined clays influences workability and reactivity, and is an important parameter in industrial processing and quality control. Laser diffraction is the most widely used technique to measure the particle size distribution of calcined clays; it is fast and relatively simple to carry out, but the instrument cost is high. Sedimentation is a technique widely used in soil science and geotechnics [1]; it is a very low-cost technique which could be complementary to particle size distribution as a quality control measure.

This study measured the extent of agreement in particle size distribution descriptors between laser diffraction and sedimentation; and evaluated the potential for sedimentation to be used as a low-cost alternative to laser diffraction. Laser diffraction measurements were carried out using ultrasonic agitation in a dilute sodium hexametaphosphate solution to achieve dispersion typical sample preparation procedures and typical analysis parameters for calcined clays; sedimentation measurements were carried out according to ISO 17892-4:2016 [2]. 15 calcined clays were tested, from a range of locations. The extent of agreement between the two techniques for the particle size distribution curves varied extensively between different clays. Compared to the values obtained by laser diffraction, sedimentation systematically gave volume fractions that were larger for the sand range (>63 µm), smaller for the silt range (2-63 µm) and smaller for the clay range (<2 µm) (ISO 14688-1:2017 definitions [3]). Inferred d_{50} values from sedimentation curves exhibited a far wider spread than d_{50} values from laser diffraction.

Sedimentation has too many constraints to be a direct alternative for measuring the full particle size distribution of calcined clays; however, it has potential as a simple quality control method, if measurement time is adjusted to correspond to a desired particle size threshold.

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Part 1: Identification and description

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Session 32: Sustainable and eco-friendly clay-based materials

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Experimental Design-Based Optimization of Clay Bricks from Rissani for Enhanced Mechanical and Thermal Performance

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As global energy demand continues to rise, the construction sector, being one of the most energy-consuming industries, increasingly requires materials that offer both lightweight properties and high thermal efficiency. In this study, a multi-objective optimization approach was employed to determine the optimal solutions for producing fired clay bricks with high strength and low thermal conductivity. Porous bricks were created using organic waste additives to explore the relationship between compressive strength and thermal performance. The experimental work followed a 3-factor, 3-level Box-Behnken design, with key variables including the pore-forming additive ratio (0–5% by weight of wheat straw), firing temperature (25–900 °C), and liquid-to-solid ratio (17–21%). Standard analysis methods were used to assess the physical, mechanical, and thermal properties of the fired bricks. Predictive models were developed for compressive strength and thermal conductivity, with the objectives being to minimize thermal conductivity while maximizing compressive strength. The results showed that firing temperature (X1) positively influenced compressive strength, while the wheat straw ratio (X2) negatively affected it. For thermal conductivity, X1 had a reducing effect, aligning with the goal of minimizing thermal conductivity, while X2 demonstrated its effectiveness as a pore-forming agent

Keywords: Fired clay bricks; Box-Behnken Design; compressive strength; thermal conductivity; Pore-forming agent

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From fired clay bricks to an accessible eco-material in the Sudano-Sahelian zone of Cameroon: what local appropriation for sustainable development?

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Access to housing remains a challenge in sub-Saharan countries, and the findings made in the mid-1960s are still relevant today. Nerfin [1] emphasized that "*the housing situation in most African countries is characterized, in both quality and quantity, by an absolute insufficiency explained by both demographic and socio-economic factors*". According to Walley [2], three billion people in developing countries will need housing by 2030. The housing issue deserves particular attention because housing is the "*mediator of universal well-being (shelter)*" [3]. The housing shortage is a fact in Cameroon, despite the precarious, substandard, and vulnerable housing that shelters many households in both urban and rural areas. According to figures from the Ministry of Housing and Urban Development (MINHDU), the urban housing deficit is estimated at 2.5 million units in 2024 with an estimated annual need of 200,000 units [4]. To meet this pressing demand, several local techniques for producing building materials are being used. Some are questionable from a sustainability point of view, such as fired bricks, the production and use of which are increasingly widespread in northern Cameroon. Uncontrolled logging and the degradation of the ecosystem through the proliferation of clayey quarries without mitigation measures are, among other practices, in conflict with the environment because they promote desertification and make living beings in these environments vulnerable. Faced with these realities, how can changes be brought about with lowest social, economic and environmental cost? In other words, what are the levers and modalities for the sustainable appropriation of new eco-responsible materials, alternatives to clay bricks, by local populations?

This contribution from the social sciences responds to the call for interdisciplinary collaboration highlighted in this session. It will help shed light on the innovation appropriation process illustrated by the Research and Development Project (PRD) on the valorisation of local resources, implemented in Cameroon with funding from the Academy of Research and Higher Education (ARES). It is within this project that our doctoral research is taking place, focusing on the social, economic, and environmental issues of fired clay brick construction in the Sudano-Sahelian region of Cameroon. The data used and processed to develop this contribution come from a corpus of interviews (21) and ethnographic observations conducted in Yagoua and Pitoa in the Far North and North regions of Cameroon.

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Potential reuse of Steel Slag and Phosphogypsum in Bentonite-Lime Composites

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The increasing need for sustainable materials in construction has prompted research into the valorization of industrial by-products such as steel slag and phosphogypsum (PG) as alternative materials in building applications. The aim of this study is to investigate the sustainable use of steel slag (SS) in bentonite-lime-phosphogypsum (BLPG) composites, focusing on their mineralogical, mechanical, and environmental properties. X-ray diffraction (XRD) analysis of mortars Ss0-Ss20 (0 to 20 wt.% SS) after 28 days of hydration revealed mineral phases such as C-S-H and ettringite. The addition of SS improved the compressive strength up to 2.03 MPa at 8 wt.% SS. However, higher SS contents (20 wt.%) led to a decrease in the compressive strength by 28%, likely due to dilution effects or the formation of voids.

Scanning Electron Microscopy (SEM) analysis provides further insight into the microstructural evolution. The SEM image of Ss2 (2 wt.% SS) revealed a layered smectite structure with altered external surfaces, alongside the formation of C-(A)-S-H gel and ettringite. For Ss8 (8 wt.% SS), a higher presence of C-(A)-S-H gel and ettringite filling the spaces between clay particles was observed which aligns with the compressive strength results. However, at 16 wt.% SS (Ss16), the SEM image showed high alteration of the smectite surface and high porosity, with less C-(A)-S-H gel and ettringite formation, leading to a decrease in compressive strength.

Thermal transport properties, including thermal conductivity (λ) and diffusivity (α) were also measured. With the addition of 2 wt.% SS (Ss2), λ dropped to 0.422 W m^{-1} K^{-1}, corresponding to a 1.78% increase in thermal resistance regarding Ss0. At 16 wt.% SS, λ reached 0.394 W m^{-1} K^{-1}, showing an 8.34% gain in thermal resistance. However, moving from the Ss0 mixture (0 wt.% SS) to the Ss16 mixture (16 wt.% SS), the diffusivity decreases from 0.268 to 0.244. Likewise, thermal diffusivity (α) increased with the addition of steel slag.

This research highlights the potential of steel slag as a sustainable additive in BLPG composites, improving both mechanical and thermal properties while promoting the circular economy through the use of industrial waste in eco-friendly building materials.

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Porosity in sustainable bricks: merging tradition with environmental innovation

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The pathway to a more sustainable future is paved with the efficient utilisation of resources, the optimisation of waste management, and the creation of value. The increased incorporation of secondary and renewable resources is anticipated to play a pivotal role in advancing the sustainable use of building materials. While it is broadly acknowledged that recycled minerals alone may not fully satisfy global material demands by 2050, there is consensus that enhanced recycling efforts can significantly contribute to meeting these needs, supporting a low-carbon transition and mitigating disruptions to natural ecosystems.

Recently, we have successfully obtained bricks by replacing 10, 30 and 50 wt% of an industrial illitic clay with hydrothermally treated sewage sludge from the FREEDOM HT plant (LIFE19 ENV/IT/000165, https://life-freedom-project.eu/), installed at the wastewater treatment plant in Cassano d'Adda, Italy. The present study focuses on the physical properties, in particular the porosity, and possible applications of such bricks aiming at meeting the challenges of sustainability and environmental responsibility.

The ceramics show a significant decrease in bulk density with increasing biosolid content. Such density values are very promising for future applications. However, results obtained with the N_2 gas pycnometer and Hg intrusion porosimetry show observable differences in the real density of the material, which is quite high compared to the apparent density, and increases with increasing the amount of cake in the samples. The increase in the real density could be explained by a higher degree of sintering of the material, which can be explained by the presence of ceramic bridges consisting of calcium iron phosphate derived from the biosolid. Micro computed tomography coupled with 3D image analysis was performed in order to better assess the porosity and pore systems in the synthetised bricks.

From a technical standpoint, the incorporation of hydrothermally treated sludge in brick production enhances porosity and reduces the thermal conductivity of the bricks, improving their thermal insulation and energy efficiency. The resulting bricks can be applied in various contexts, such as construction and insulation, contributing to more sustainable and environmentally friendly building practices.

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Clay minerals in earthen binders for Earth Additive Manufacturing (EAM) applications

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With recent developments in the construction sector exploring more environmentally friendly solutions, clay-rich sub-soil, commonly referred to as “earth”, is currently being re-evaluated as a building material [1]. As traditional earth-building techniques are being adapted to modern setups, additive manufacturing shows great potential for combining modern digital automated techniques with highly recyclable and sustainable earthen materials [2]. Earth Additive Manufacturing (EAM) techniques require high reproducibility for both equipment and material. Failure to account for key material parameters leads to time-consuming trial-and-error approaches, which over time can also strain or damage the robotic equipment used in EAM. An often-overlooked parameter is mineralogy, as inconsistencies or a complete lack of mineralogical data can be observed across studies, and established standards of earthen construction [3]. The present study introduces a systematic investigation of the clay mineral components of earthen binders and its effect on emerging EAM techniques.

The heterogeneity of clay-rich materials around Germany is first assessed through the collection of samples with a sufficient range of spread in composition. Commercial clay products with high purity are chosen to simulate the isolated clay mineral component of earthen material systems. Non-swelling clay minerals, kaolinite (K) and illite (I), were targeted for the present study and their ratio (K/I) is varied within a range of 0.33 – 3. The first stage focuses on investigating the material on a microstructure scale. This includes a full quantitative mineralogical and chemical characterization using X-Ray Powder Diffraction (XRD) and Inductively Coupled Plasma Mass Spectroscopy (ICP-OES). Further microstructure characterization is carried out with Specific Surface Area (SSA) measurements using the Brunauer-Emmett-Teller (BET) method, surface charge determination with Zeta Potential (ZP), grain size distributions collected with Laser Diffraction (LD) and Scanning Electron Microscopy (SEM) used for imaging.

For the second stage, the microstructure is linked to geotechnical and mechanical parameters focusing on how the materials interact with water and perform in EAM processes. Two types of mixtures are prepared: simplified "mortar" (clay and sand) to isolate the role of clay minerals, and more complex "concrete” (clay, sand, fibres, and/or gravel) that simulates realistic earthen building materials. The mortar mix highlights the contribution of the clay fraction in the binder, while the concrete mix allows for direct testing under EAM conditions. Fresh-state properties such as workability (consistency) and buildability (layer stacking and bonding) are evaluated. Finally, hardened-state properties, including shrinkage, compressive strength, and flexural strength, are measured to connect the clay mineral composition to overall mechanical binder performance.

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Addition of stevensite to a magnesium potassium phosphate cement formulation with application for 3D printing

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Magnesium potassium phosphate cements (MKPC) are considered a type of chemically bonded ceramic with very interesting properties such as high early strength and chemical stability. In contrast to conventional cement and ceramic formulations, MKPCs set quickly at ambient temperature, opening up novel uses for cutting-edge techniques like 3D printing in the construction industry.

Basically, MKPCs form as a result of the acid-base reaction between KH_2PO_4 and MgO in presence of water, being K-struvite the main reaction product. A chemical retarder is usually added to delay the hardening rate and a filler material, with none or minimum chemical interaction with the binder, is also added to increase the fluidity of the fresh cement paste, decrease the initial heat of the exothermic hydration reaction and improve the mechanical strength of the resulting ceramic product. The filler helps to reduce the porosity but, at long term, does not prevent the formation of micro-cracks due to slow partial dissolution of K-struvite under wet environments. Man et al. [1] demonstrated that the addition of 10-15 % of bentonite clay to a magnesium phosphate cement greatly improved the density and resistance to water permeability in both, air and water environments.

In the present work, the addition of stevensite, a 2:1 trioctahedral smectite with the octahedral sheet rich in Mg, to MKPC is evaluated with the objective to improve key characteristics considered in extrusion-based 3D printing, enhancing the consistency of the fresh paste with an adequate setting and improving the long-term durability of the printed material.

The MKPC formulation contains low grade MgO and KH_2PO_4 in a Mg/P molar ratio equal to 4, boric acid used as retarder in a retarder/binder ratio = 1 wt.% and volcanic ash (VA) used as filler in a VA/binder ratio within the range 0.5 to 0.25. The decreasing VA/binder ratio is compensated by additions of stevensite maintaining the filler/binder ratio constant at 0.5. The binder is considered the sum of MgO and KH_2PO_4 in the mixture.

Addition of the stevensite decreases the mechanical strength at short time (1-3 days) but a stevensite/binder ratio up to 0.15 largely decreases the final setting time without varying significantly the initial setting, thus shortening the hardening of the printed material and providing greater resistance for printed extruded layers over layers. As foreseen, some expansion is observed at short term when stevensite is added, attributed to smectite hydration, although remains in any case <4 %.

The durability of samples and mineralogical stability under dry and wet conditions at long term will be further investigated. Nevertheless, the initial outcomes with small stevensite additions are encouraging since the plasticity of the fresh pastes, an essential characteristic sought for 3D printing, is significantly enhanced, not achieved by modifying other parameters in the formulation.

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Compressed lime-stabilized clay from Benoue valley (North, Cameroon) for sustainable construction: Evolution of their properties

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This study investigates the properties of lime-stabilized blocks of clay materials from the Benoue valley (North, Cameroun) for their potential uses in sustainable construction. The clay materials named DG, PB and TA were lime-treated at 10, 15 and 20% and cured for 28 and 1095 days (3 years), then subjected to several analyses such as mineralogical (XRD, FTIR, TG/DSC), physical (water absorption, bulk density, open porosity) and mechanical (compressive strength).

The bulk density and water absorption decrease with increase in stabilizer rate and curing time. The open porosity slightly increases (for two samples PB and TA). Compressive strength values ranged between 1.5 MPa to 3.1 MPa at 28 days curing time were obtained for lime-stabilized specimens from 10% and above, DG and TA specimens for all stabilizer rate (10, 15 and 20%) satisfying the minimum value of 2 MPa prescribed by Cameroonian compressed earth blocs standards, unlike for specimens PB stabilized blocks, who 15 and 20% less than 2 MPa. At 1095 days (3 years), the compressive strengths of all stabilized samples increase significantly, reaching values of 20 MPa. Thus, depending on the mineralogical composition (clay mineral content) of each clay sample, we note different trends in terms of compressive strength: DG specimens have compressive strengths value ($10.0 \leq Rc \leq 12.1$) MPa; PB specimens ($10.1 \leq Rc \leq 20.0$) MPa and TA specimens ($15.7 \leq Rc \leq 20.7$) MPa. Particularly, at 1095 days, TA lime-stabilized specimens have a lower value of water absorption ($16.1 \leq Wabs \leq 16.9$).

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Promoting green compressed earth bricks towards net zero emissions commitment of Vietnam

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The project "Promoting green compressed earth bricks towards net zero emissions commitment of Vietnam," supported by the Académie de Recherche et d'Enseignement Supérieur (ARES), represents a vital step in aligning local housing development with Vietnam COP26 net-zero carbon emissions pledge by 2050. The initiative successfully promoted sustainable, non-fired building materials—particularly compressed earth bricks—as an eco-friendly alternative to traditional fired bricks, whose production significantly contributes to greenhouse gas emissions. In a country where annual brick demand is enormous [1], and rural housing needs are critical, the project provided a multi-faceted response integrating environmental, technical, and social goals [2].

Through extensive field surveys in northern mountainous provinces such as Cao Bang, Hoa Binh, and Nghe An, the project evaluated current housing conditions and local soil resources. Research teams developed innovative soil mixtures incorporating local raw earth, cement, and natural additives to produce durable compressed bricks with compressive strengths exceeding 3.5 MPa. The development of interlocking brick forms and low-tech production equipment—both manual and motorized presses—enabled local communities to participate in decentralized, low-energy brick production using accessible resources.

Architectural designs were tailored to local climatic conditions, cultural practices, and natural ventilation and insulation needs, resulting in energy-efficient, culturally sensitive housing models. These models not only met structural stability standards but also incorporated rainwater collection and passive solar strategies, advancing green building practices in underserved regions.

The project also addressed policy alignment, leveraging government programs that support ethnic minority housing. By integrating local materials, labor, and know-how transfer with technical innovation, the project provided a scalable and replicable model for sustainable rural housing development. Workshops and collaborative fieldwork involving academic institutions (Phenikaa University, Hanoi University of Civil Engineering), Belgian partners (Université de Liège), NGOs, and local communities fostered capacity building and knowledge transfer.

Key outcomes include validated prototypes for eco-houses, documented performance assessments of materials and structures, protocols for manufacturing non-fired bricks from manually operated presses, and presses powered by gasoline or diesel engines and community engagement in sustainable construction. The project exemplifies successful South-North cooperation, bridging environmental goals with socio-economic development, and lays the groundwork for future expansion across rural regions of Vietnam, supporting long-term resilience and carbon neutrality goals.

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[2] Lavie Arsène Mango-Itulamya and Nathalie Fagel (2022)

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High strength eco-cement from alkali-activated gravel wash mud and quartzite dust

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Gravel wash mud (GWM) is a widely available industrial by-product from sand and gravel mining. A total deposition quantity of 50 million tonnes per year is estimated in Central Europe [1]. GWM is commonly accumulated in decanting basins which are responsible for territory losses and may cause surface water pollution. The deposited material frequently is abundant with clay minerals, which would allow usage in ceramics or as supplementary cementitious material in Portland cement industry. However, one of the main obstacles preventing industrial use of GWM is heterogenous mineralogical composition. Without clay minerals also high quantities of fine quartz particles may be present. For instance, we have determined the quartz content of 10 different GWMs originating from Germany, Luxembourg, France and Belgium which may vary from 34 % to 74 %.

In this study a kaolinitic GWM (Kaolinite 42%, Illite 23%, Quartz 34% and Feldspar 1%) was used as aluminosilicate source in eco-cement formulations. The GWM originates from Eifel in the SW Germany with estimated annual production of 10 000 tons.

To explore the impact of fine quartz particles, quartzite dust (Quartz 83%, Illite/Muscovite 17%) was added in the alkali-activated cement formulations. The quartzite dust is collected in filters during quartzite mining in the quarry of the company Gebr. Arweiler GmbH & Co. KG, SW Germany. The estimated annual production is 25 000 tons. Ten different GWM and Quartzite dust cement formulations were prepared. In the formulations quantity of the GWM deceases gradually from 100 wt.% to 10 wt.%. The percentage of quartzite dust increases from 0 – 90 wt.% in 10% steps respectively. Mixture of the GWM and quartzite dust was grout and calcined by 750°C. Thereafter calcined material was activated with NaOH solution, mixed with laboratory cement mixer and cast in prismatic moulds. Samples were cured at 65°C for 28 days, keeping specimens wrapped in a plastic foil.

The results of compressive strength testing after 28 days indicate the highest compressive strength equal 72.6 MPa for sample with only 10 wt.% of GWM and 90 wt.% quartzite dust activated by 10 mol/L activating solution, whereas pure GWM cement has the lowest strength equal 26.5 MPa.

Obviously, quartzite dust acts as an effective filler in the cement formulation with GWM, densification of cement structure due to high quartz content also may result into compressive strength increase.

Consequently alkali-activated cements with very high content of fine quartzite dust particles can be made moreover it attains the highest compressive strength. Another advantage related with the quartz content is low liquid demand because quartz particles absorb significantly less activating solution. This is also a significant cost reducing factor. For instance, a cement from 100 wt.% calcined GWM demands 0.4 ml NaOH solution on 1 g cement whereas mixture with 10 wt.% of GWM demands almost twice less - 0.22 ml solution for 1 g cement, at the same time, dramatical increase of compressive strength from 26.5 to 72.6 MPa was observed. Whereas the main environmental benefit of calcined GWM as binder in cement production are zero CO_2 Emissions from material itself during calcination process and lower energy demand for calcination as required for the ordinary Portland cement clinker.

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Physico-mechanical and mineralogical properties of lime-treated clay materials from Northern Cameroon (Pitoa and Gaschiga)

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This study aims to investigate the physical, mechanical and mineralogical properties of lime-stabilized blocks of clayey materials in North Cameroon, in the localities of Pitoa and Gaschiga. The clay samples were lime-stabilized at 0, 2, 4, 6, 8, 10 and 12% and cured for 7, 14, and 28 days, then subjected to physical, mechanical and mineralogical analyses.

The apparent porosity, linear shrinkage and water absorption decrease with increase in stabilizer rate and curing time. Compressive strength values above 2 MPa at 28 days curing time were obtained for lime-stabilized specimens from 2% and above, satisfying the minimum value of 2 MPa prescribed by Cameroonian compressed earth blocs standards, unlike for those of unstabilized blocks (0% lime), all less than 2 MPa. A general increase in mechanical strength is observed with increase in stabilizer rate and curing time.

Powder X-Ray diffractograms of stabilized non-fired bricks reveal the occurrence of new mineral phases (i.e. calcite, portlandite, stratlingite, ettringite, ankerite, calcium sulfoaluminate (CSA), calcium silicate hydrate and vaterite. These results are confirmed by Fourier Transform Infrared Spectroscopy (FTIR), as evidenced by the appearance of new vibration bands at 2929 cm^{-1}, 2848 cm^{-1} and 1425 cm^{-1}, which are related to the C-O bond characteristic of carbonate (calcite) formation.

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Session 33: Mechanical and Mechano-chemical Activation of Clays

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Impact of metakaolin characteristics on properties of alkali-activated materials

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Ordinary Portland Cement (OPC) is extensively used in the construction industry. However, its production consumes substantial amounts of limestone [1] and generates significant greenhouse gas emissions, accounting for approximately 5-8% of global CO_2 emissions [2]. A potential alternative to OPC lies in the synthesis of novel alkali-activated materials (AAM), particularly those based on phyllosilicates (typically kaolin/metakaolin). These clays serve as key sources of silicon and aluminum, promoting the neoformation of secondary crystalline or pseudo-amorphous phases, thereby enhancing physico-chemical and functional properties. Metakaolin (MK) is widely referenced in the literature as a commonly used precursor for alkali activation processes [3]. However, many MK industrial grade exists, differing in terms of mineralogy and physicochemical properties, processing methods, and thus reactivity. Among the reagents used in alkaline activation, carbonate-based reagents have demonstrated filler effects and additional nucleation, which can enhance the properties of geomaterials [4]. The objectives of this study are to (i) evaluate the properties of geomaterials (mechanical strength, kinetics reaction, and newly solid phases) within a system of activators composed of Ca-Na-CO_3-OH, and (ii) assess the influence of the type of MK on these properties.

Several pre-characterized MK (chemical composition, mineralogy, reactivity) are incorporated into two formulations, with Na/Ca molar ratios of 0.5, 1, and 1.5, in order to observe their influence on the properties of the resulting AAM. The samples are cured for 3, 6, and 18 days. AAM are subsequently characterized using various structural methods such as X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM-EDS), and ^{27}Al and ^{29}Si nuclear magnetic resonance (MAS-NMR) as well as functional tests such as compressive strength.

These analyses revealed the formation of distinct mineral phases over time, depending on the Na/Ca molar ratio and the type of MK, including carbonate phases such as gaylussite, pirssonite, and calcite. Simultaneously, the dissolution of MK leads to the development of silicate phases, notably C-(Na)-S-H. The nature and proportion of these mineral phases significantly influence the functional properties of the resulting materials, particularly their mechanical performance, with average compressive strengths increasing by up to a factor of sixteen depending on the formulation selected.

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Session 35: The Role of Clays in Human Health and Biomedical Sciences

A Novel Nanomaterial Based on Halloysite and Laccase: A Sustainable Approach for Dyes Degradation

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The increasing contamination of water resources by synthetic dyes, especially azo dyes, necessitates the development of efficient and sustainable methods for their removal.[1] Mineral clays, and in particular halloysite, have gained considerable attention as promising nanomaterials for environmental applications due to their unique structural properties, such as available, low cost, and biocompatibility.[2] Halloysite nanotubes, due to their chemical composition and the possibility of performing covalent modifications on their external surface, represent an interesting platform for the immobilization of enzymes, such as laccase, capable of degrading various types of pollutants.[3,4]

In this study, a novel nanomaterial based on halloysite nanotubes (HNTs) was synthesized, and laccase, was covalently immobilized onto the external surface of HNTs. The resulting nanomaterial was characterized by various techniques, including FT-IR spectroscopy, TGA, DLS and ζ-Potential. The morphology of nanomaterial was characterized with scanning electron microscopy (SEM), and High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM), confirming the successful immobilization of laccase. The biocatalytic potential of the nanosystem was evaluated for the degradation of an azo dye, methyl orange, in aqueous solutions. The results demonstrated that the laccase-halloysite nanomaterial exhibited remarkable stability and high efficiency in dye degradation, with the process showing promising reusability over multiple cycles. This approach offers a promising strategy for the bioremediation of wastewater containing azo dyes, combining the advantages of enzyme catalysis and the reusability of nanomaterials.

Acknowledgements: This work was supported by National Recovery and Resilience Plan (NRRP), funded by the European Union– Next Generation EU-DD 1409 Progetti di Rilevante Interesse Nazionale (PRIN) 2022 PNRR published on 14-09-2022 by the italian MUR, Missione 4 (Istruzione e Ricerca) Component 2, Investment 1.1. Project Title: Small Molecule Anticancer Ligands Library from mediterranean plants (SMALL)–CUPB53D23025910001.–Code P2022YJZ5F and by "SiciliAn MicronanOTecH Research And Innovation CEnter "SAMOTHRACE" (MUR, PNRR-M4C2,ECS_00000022), spoke 3-Universitàdegli Studi di Palermo "S2-COMMs-Micro and Nanotechnologies for Smart & Sustainable Communities",spoke 1, WP2-Environment, Task "Application of new materials for the real-time control of contaminants of emerging concern in water.

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Photosensitizer-Loaded Nanocomposite Hydrogels with Functional Photoactive Surfaces for Photodynamic Applications

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Photodynamic inactivation (PDI) is emerging as a promising antibiotic-free antimicrobial strategy with the added benefit of accelerating wound healing. A key factor in its effectiveness is the controlled generation of reactive oxygen species (ROS) by photosensitisers (PSs). Hydrogels have proven to be effective carriers for PSs in antimicrobial PDI. However, despite the growing interest, PS-loaded hydrogels face several limitations, such as shallow light penetration, potential damage to surrounding tissues due to uncontrolled PS and ROS release, and poor solubility, stability, and bioactivity of many photosensitisers under physiological conditions [1]. Additionally, the uniform dispersion of PS molecules in hydrogels remains challenging during fabrication. Smectites are low-cost and eco-friendly inorganic hosts for PS molecules to improve their fluorescence and photoactivity, enhance dye stability and reduce photodegradation [2]. In this study, organoclays of synthetic saponite (Sap) are used as the carrier for the PS, phloxine B (PhB). Thin films of the PhB-loaded organoclays with a thickness of a few µm were prepared via vacuum filtration. The hydrogel precursor solution, composed of dissolved poly(vinyl alcohol) (PVA) and glycerol as a crosslinker, was poured onto the prepared film to penetrate inside and swell the organoclay layer partially. The *in situ* crosslinking led to the formation of a hydrogel. A thin nanocomposite film on the surface of the hydrogel was formed from the phase of penetration of the hydrogel precursor molecules into the thin organoclay layer during the crosslinking process [3], [4]. Instead of bulk incorporation, this strategy offers greater control over PS content. It allows a high concentration of the active substance on the surface, which is absent in the hydrogel bulk. Absorption and luminescence spectroscopy in the visible region showed an inverse relationship between PhB loading and fluorescence intensity, indicating concentration quenching and molecular aggregation. X-ray diffraction reveals the structural changes upon the intercalation of PhB molecules and nanocomposite formation. Infrared spectroscopy indicates that hydrogen bonding dominates the interaction between organoclay and hydrogel. The novel method of surface-modified hydrogels represents a facile fabrication route that enables precise control over PS loading and distribution, potentially improving the therapeutic efficacy and clinical applicability of hydrogel-based PDI systems.

Acknowledgement: This work is supported by Doktogrant project No: APP0572 from the Slovak Academy of Sciences.

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Photosensitizer-Loaded Nanocomposite Hydrogels with Functional Photoactive Surfaces for Photodynamic Applications

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Photodynamic inactivation (PDI) is emerging as a promising antibiotic-free antimicrobial strategy with the added benefit of accelerating wound healing. A key factor in its effectiveness is the controlled generation of reactive oxygen species (ROS) by photosensitisers (PSs). Hydrogels have proven to be effective carriers for PSs in antimicrobial PDI. However, despite the growing interest, PS-loaded hydrogels face several limitations, such as shallow light penetration, potential damage to surrounding tissues due to uncontrolled PS and ROS release, and poor solubility, stability, and bioactivity of many photosensitisers under physiological conditions [1]. Additionally, the uniform dispersion of PS molecules in hydrogels remains challenging during fabrication. Smectites are low-cost and eco-friendly inorganic hosts for PS molecules to improve their fluorescence and photoactivity, enhance dye stability and reduce photodegradation [2]. In this study, organoclays of synthetic saponite (Sap) are used as the carrier for the PS, phloxine B (PhB). Thin films of the PhB-loaded organoclays with a thickness of a few µm were prepared via vacuum filtration. The hydrogel precursor solution, composed of dissolved poly(vinyl alcohol) (PVA) and glycerol as a crosslinker, was poured onto the prepared film to penetrate inside and swell the organoclay layer partially. The *in situ* crosslinking led to the formation of a hydrogel. A thin nanocomposite film on the surface of the hydrogel was formed from the phase of penetration of the hydrogel precursor molecules into the thin organoclay layer during the crosslinking process [3], [4]. Instead of bulk incorporation, this strategy offers greater control over PS content. It allows a high concentration of the active substance on the surface, which is absent in the hydrogel bulk. Absorption and luminescence spectroscopy in the visible region showed an inverse relationship between PhB loading and fluorescence intensity, indicating concentration quenching and molecular aggregation. X-ray diffraction reveals the structural changes upon the intercalation of PhB molecules and nanocomposite formation. Infrared spectroscopy indicates that hydrogen bonding dominates the interaction between organoclay and hydrogel. The novel method of surface-modified hydrogels represents a facile fabrication route that enables precise control over PS loading and distribution, potentially improving the therapeutic efficacy and clinical applicability of hydrogel-based PDI systems.

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Application of Ukrainian Kaolins for the Development of Novel Hemostatic Agents

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Clay minerals based on kaolin possess a wide range of practical applications including the food, construction, cosmetic, pharmaceutical, paper, and ceramic industries, owing to their adsorption, thermal, and plastic properties [1]. In the medical field, kaolins are predominantly used as sorbents and carriers. However, the potential of thermally treated kaolins (metakaolins) remains insufficiently explored, particularly regarding their unique hemostatic properties. Meanwhile, mineral materials are already widely used for such purposes in both military and civilian medicine [2, 3]. Recent studies have demonstrated that metakaolin can initiate blood coagulation through multiple simultaneous mechanisms—by activating the contact phase (via factor XII and the kallikrein-kinin system) and through the “availability reaction” of tissue factor (factor VII), leading to the formation of prothrombinase and subsequent fibrin clot formation [4]. These unique properties open up new opportunities for developing novel kaolin-based hemostatic agents.

This paper explores the potential for creating new, highly effective hemostatic and therapeutic composites incorporating metakaolins. The proposed composition, "Coagulox_N", combines mineral materials, plant extracts, and synthetic metal nanoparticles (Ag + Au) to deliver a multifunctional therapeutic effect, including hemostatic, anti-inflammatory, wound-healing, and antibacterial properties. Specifically, Juglans regia L. extract provides anti-inflammatory and wound-healing action; Aerosil A-300 ensures sorptive and structure-forming properties; and mix of Ag and Au nanoparticles exhibit antibacterial activity, including against antibiotic-resistant strains. Metakaolin, in turn, acts as the key hemostatic component [5]. Due to the synergistic action of its ingredients, this composition may be effectively used for treating both common wounds and injuries in patients with hemophilia or diabetes, as well as in military medicine for wound.

The composition was developed using thermally treated kaolin (metakaolin) from the Glukhovetsky deposit (Ukraine). Experimental studies have shown that the optimal temperature for achieving the hemostatic effect ranges from 600 to 800 °C. The report details the specifics of primary kaolin preparation for medical applications. Interestingly, even a small amount of metakaolin in the composition provides a significant hemostatic effect (only 2-7 wt. %). This highlights the promising potential of metakaolin in the biomedical field, especially in military and civilian medicine, and indicates significant prospects for further detailed research in this direction.

The authors acknowledge financial support from the National Research Foundation of Ukraine, Project No. 2023.04/0041: "Development of an innovative medicinal product "Coagulox_N" with antimicrobial, hemostatic, and wound-healing properties", under Contract No. 20/0041.

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Interactions of cyclic peptides with montmorillonite surface for a natural drug delivery system

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Cyclic peptides are a versatile class of molecules produced either naturally by terrestrial and marine organisms, such as bacteria, fungi, and plants, or synthetically. Their diverse biosynthetic pathways—especially the non-ribosomal ones—yield structures with rigid conformations that confer exceptional chemical and conformational stability, making them less prone to enzymatic degradation. These attributes, along with high selectivity, potency, and favorable bioavailability, make cyclic peptides promising alternatives to conventional drugs. Their potential applications span from detoxification and heavy metal sequestration to a range of biological activities including antimicrobial, immunosuppressive, cytotoxic, anti-inflammatory, and antimalarial effects. Although oral administration of cyclic peptide-based drugs is attractive for its non-invasiveness, reduced production costs, and lower infection risks, the peptides' susceptibility to degradation by gastric enzymes presents a significant challenge, often necessitating parenteral routes. To overcome this limitation, research has focused on designing smaller cyclic peptides capable of interacting with shallow protein surfaces and employing controlled delivery systems that utilize natural clay minerals such as phyllosilicates. These minerals have unique physicochemical properties—owing to their high structural disorder and fine particle size—that can protect peptide drugs from unwanted degradation while enabling gradual drug release. However, the small size of these mineral crystals combined with the flexibility of peptides complicates the precise identification and characterization of their interactions, which is crucial for optimizing controlled drug release systems. In this context, molecular modeling emerges as an invaluable tool for investigating organic–inorganic interfaces at the atomic level to identify specific binding sites and elucidate interaction mechanisms. In this work, the structure of a cyclic octapeptide, Ribifolin, is studied in a molecular modeling approach. The crystal structure has been reproduced, validating the theoretical approach. The adsorption of this peptide into the confined interlayer space and in the external surface of montmorillonite has been calculated and compared. These computational studies predict the absorption and desorption of this peptide from montmorillonite indicating that this composite peptide-montmorillonite can be a good drug delivery system.

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Session 36: Clay Materials in Healthcare Technologies

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Monitoring the cellular internalization of Eu^{3+}-Laponite using combined Raman imaging and fluorescence microscopy

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Laponite has emerged as a promising nanoplatform for applications in drug delivery, tissue engineering, and nanoscale bioimaging. Laponite is a synthetic nanoclay that holds high potential for biomedical applications due to its precisely controlled chemical composition. Characterized by disc-shaped particles and a remarkable aspect ratio, Laponite particles typically measure around 25 nm in diameter and 0.92 nm in thickness [1]. A comprehensive understanding of how this synthetic clay interacts with biological systems under physiological conditions is essential for accurately assessing its therapeutic potential and possible toxicological effects.

Moreover, the design of novel materials incorporating lanthanide ions into diverse host matrices offers significant promise for sensing applications, particularly in the development of fluorescent probes for biomedical use. Among them, the trivalent europium ion (Eu^{3+}) stands out due to its strong red luminescence, which is observed not only in crystalline environments but also when coordinated with organic ligands. Eu^{3+} ions are especially appealing because of their narrow emission bands, low toxicity, good biocompatibility, and excellent photostability. For instance, fluoroapatite nanorods doped with europium have been proposed as potential agents for cell imaging and targeted drug delivery in cancer therapy [2].

In this study, we present a methodology that integrates luminescence and confocal Raman microscopy to simultaneously monitor the nanosystem and detect its cargo, utilizing Eu^{3+} as a fluorescent probe. For this purpose, Eu-doped Laponite was employed as a proof of concept to track the uptake and internalization of Laponite nanoparticles in the J774 macrophage cell line. Raman spectroscopy is a powerful tool for cellular imaging, capable of providing detailed information about the chemical composition and properties of biological materials. Furthermore, combining Raman spectroscopy with confocal microscopy enables precise localization of nanoparticles within the cell by mapping their distinct Raman spectral fingerprint [3]. The simultaneous acquisition of the Raman signal from both the nanoparticle and the cell, along with the Eu^{3+} luminescence at the same location, enables the separate identification of the nanoparticle and Eu^{3+} ions within the cell. In this system, Eu^{3+} ions act as a surrogate for the cargo, which could be substituted with a fluorescent drug, while Laponite functions as the drug delivery platform.

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Sessions 39+42: Role of Minerals and Mineral weathering in Carbon Sequestration and Other Ecosystem Services of Soils

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Changes in Clay Mineral Composition in Pit-Mound Profiles Resulting from Tree Uprooting in the Žofín Forest, Czech Republic

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Tree uprooting is a major biogeomorphic disturbance in many forest soils, significantly impacting carbon (C) content. Research shows [1] that naturally disturbed clayey soils may accumulate more carbon over centuries compared to undisturbed soils. However, in waterlogged soils, uprooting can lead to carbon loss due to drainage and respiration. Such disturbances can either increase soil aeration, moving carbon closer to the surface and potentially depleting it, or transfer carbon deeper into the soil, enhancing storage. They also indirectly affect soil through changes in morphology, structure, hydrology, and biodiversity. An important factor influencing carbon storage is, among others, the mineralogical composition of soils, especially clay minerals and Fe-(oxy)hydroxides.

This study aims to understand the relationship between disturbance regimes in old-growth forests and soil microbiology, mineralogy, and chemistry, focusing particularly on carbon storage across soil depths. The research was conducted at the Žofín site, a temperate, humid primavel forest with moderate podzolization on acidic Entic Podzols. Dominated by broadleaf Fagus sylvatica, the site receives an average annual rainfall of 900 mm and maintains a mean temperature of 4.3°C. The elevation ranges between 730 and 837 m, with a gentle slope of 8° [2].

The study identified and modelled various minerals in the clay fraction of three soil profiles: pit, mound, and control. Using Sybilla software, vermiculite, kaolinite, illite (mica), chlorite and interstratifications such as R1 illite (0.50)-vermiculite and illite-rich illite-smectite-chlorite were modelled. It was found that iron is significantly present in the octahedral layer of TOT. In deeper soil horizons (100-130 cm), there is an increase in kaolinite and illitic layers (especially the content of interstratifications), while the surface horizons (0-10 cm) show an increase in smectitic and illitic layers, with a decrease in vermiculitic layers content compared to other depths. Plagioclase and Fe-mica („biotite“) weathering towards the subsurface (15 cm) leads to the formation of vermiculite and illite-vermiculite. Vermiculite transformes in surface horizons forming smectite. The control profile showed a lower amount of kaolinite and steeper trend of decreasing vermiculitic layers and increasing illitic layers content with increasing depth except 0-10 cm horizon compared to the pit and mound profiles. Higher vermiculitic layers content was detected in the mid-depths (15-50 cm) in the pit profile than the mound.

Acknowledgements: The work is funded by the Czech National Grant Agency (GAČR) within project 24-11119S named „A global model of treethrow forms and the role of tree mortality in carbon storage“.

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Quantifying N_2 and H_2O isotherm-based mineral surface area and cation exchange capacity: Revisiting basic properties related to mineral reactivity

Blattmann, T.M.[1,2], Galili, N.N.[1], Yoshimura, T.[2], Usman, M.O.[1], Eglinton, T.I.[1] and Plötze, M.[3]

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Cation exchange capacity (CEC) and mineral surface area (MSA) of clay minerals are key for quantifying the reactivity of clays in the environment and therefore for understanding their impact on global biogeochemical cycles. Despite over a century of research on mineral reactivities, quantifying these mineral properties remains far from straightforward [1]. We demonstrate a method for the determination of CEC using an ammonium-based method delivering highly reproducible CEC quantities for a range of cation-exchanged clay minerals. While clay minerals homoionized with calcium largely showed a clear dominance of exchangeable calcium, sodium-exchanged forms revealed that other cations (especially calcium) still dominate exchangeable sites, contrary to evidence from X-ray diffraction and to expectations from what could be regarded as a rigorous cation exchange procedure. Additionally, we present a comparison of water- and nitrogen-based MSA, both using the BET theory, for a variety of minerals and mineral matrices relevant for earth, environmental and clay science. These systematic investigations aim to help understand CEC and MSA as measures of mineral reactivity relevant for binding, protecting and ultimately sequestering organic matter (OM) in sedimentary environments. Fundamental questions remain regarding how MSA is modified as sediments traverse across the land-ocean interface, subjecting them to ion exchange reactions and gradients in ambient water chemistry. Furthermore, it is unclear how OM is associated with and is released from different mineral surfaces, particularly the interlayer surfaces of expanding phyllosilicates. These processes are crucial for understanding molecular-scale binding processes in nature. Together, these basic questions motivate further investigations of MSA and CEC, which remain of fundamental importance for understanding the reactivity of complex environmental mineral matrices.

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Impact of Clay on Soil Organic Carbon in Response to Agricultural Management in Central Kansas

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Phyllosilicates play a key role in the long-term potential carbon storage in soils. Investigating the relationship between total clay, soil organic carbon (SOC), and aggregates can help to better identify and implement management for soils when looking to maximize carbon and agricultural output. Soil physical and chemical dynamics are directly impacted through land management through means like aggregation and microbial activity. These processes are critical to the soil carbon cycle which must be considered to develop sustainably intensified agricultural systems. Aggregates help to insulate stored carbon from becoming labile, and increased tillage breaks aggregates and leads to decomposition of organic matter. Clay-sized particles and organic matter largely contribute to aggregate formation and stabilization, and adaptable management considering clay and other inherent soil properties can help to make site-specific management decisions that can have a greater impact than a blanket recommendation across diverse land areas.

Soils were collected from 150 farmer-owned fields in Kansas, and analyses included particle size analysis, SOC and SIC determination, as well as water stable aggregation. Management ranges from native grassland, replanted grassland, long-term conservation-oriented cropping, and intensively tilled monocropped. We expect to see that soils with higher clay content have the ability to produce a larger number of stable aggregates when management intensity promotes formation. We also expect to see different distributions of carbon between sites with annual crops and perennial cover due to different rooting systems and depth. More information on soil capability to store carbon under different conditions is extremely important in developing expectations of future carbon sequestration and current land management planning.

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Redox-Driven Interactions of Fe^{2+} with Imogolite Nanotubes in the Presence of Ca^{2+} and As(III) under Anoxic and Oxic Conditions

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Iron (Fe) plays a vital role in geochemical and environmental processes through surface redox reactions facilitated by clay minerals. This study investigates the catalytic role of imogolite (Imo), a natural aluminosilicate with a nanotubular structure, in the surface oxidation of Fe^{2+} under varying redox conditions (oxygenated and anoxic) and in the presence of divalent electrolytes (Ca^{2+}) and arsenic (As(III)) as a contaminant. The objective is to elucidate the redox behavior of Fe and its impact on the formation of new mineralogical phases, taking into account the influence of dissolved O_2 and the colloidal physicochemical environment.

The results indicate that Imo has a high density of Brønsted acid sites (0.2278 $\mu mol \cdot mg^{-1}$) compared to Lewis sites (0.1227 $\mu mol \cdot mg^{-1}$). This suggests that silanol (≡Si–OH) and aluminol (≡Al–OH) bonds play a crucial role in interacting with dissolved ions. FT-IR analysis demonstrated that the structure of Imo remained largely unchanged, although a shift in the band at 1088 cm^{-1} was observed. This band corresponds to the stretching of Si-O bonds in the tetrahedral network of Imo. Consequently, this shift may indicate changes in the angles or bond lengths of the Si-O-H or Si-O-Al groups, pointing to local structural modifications. Raman spectroscopy revealed the formation of Fe oxyhydroxides, such as lepidocrocite or akaganeite (noted at 328 cm^{-1}), under oxic conditions, as well as the presence of gypsum (Gyp) in both redox states (with a characteristic band at 1009 cm^{-1}). Additionally, the vibrational band at 1025 cm^{-1} has been identified by other researchers as a characteristic fingerprint for Fe-O-Si vibrational modes, which suggests the diffusion of Fe through the nanotubes to the internal ≡Si–OH groups.

Transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) analyses revealed differences in the morphology of aggregates in Imo and Ca^{2+} suspensions depending on redox conditions, with larger structures observed under oxic conditions compared to anoxic conditions. Finally, X-ray photoelectron spectroscopy (XPS) results confirmed the coexistence of Fe^{2+} and Fe^{3+} in the Imo/Ca^{2+} suspension solids under anoxic conditions, indicating incomplete oxidation of Fe.

These findings suggest that Imo can catalyze the oxidation of Fe^{2+}. Even under anoxic conditions (with O_2 levels below 1 $mg \cdot L^{-1}$), specific active sites on Imo's surface can facilitate electron transfer from Fe^{2+} to other surface or internal electron acceptors. For instance, structural defects such as vacancies in the tetrahedral or octahedral positions can function as electron acceptors, promoting the partial oxidation of Fe^{2+} adsorbed on the surface.

Overall, this study underscores the significance of divalent cations and the mineral substrate in the redox transformations of Fe^{2+}. It enhances our understanding of Fe behavior in natural systems and its potential implications for the immobilization of pollutants, particularly arsenic. Additionally, it provides a foundation for designing clay-based environmental remediation strategies.

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Modeling cohesive fine-grained sediment erosion using a computational fluid dynamics framework

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Erosion of fine-grained cohesive sediments, such as clays and muds, has significant environmental impacts due to their ability to sorb pollutants, impact ecological habitats, and influence large-scale geomorphic processes. Although fine-grained cohesive sediments constitute a significant portion of all sediments and play important roles in sediment transport, our ability to accurately predict the movement of these sediments remains limited due to associated complex hydraulic-chemical-mechanical couplings. This work improves our mechanistic understanding of clayey sediments through capturing these couplings and examining their influence on erosion by utilizing the Darcy-Brinkman-Biot framework, a recently developed computational fluid dynamics framework. We simulate erosion of an unconsolidated Na-smectite sediment bed with modelled rheology parameters and critical erosion thresholds validated through rheological and flume experiment comparison. Lastly, parametric studies of sediment parameters are performed to examine key sediment (permeability, sediment grain density, porosity, rheology) sensitivities to erosion.

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Long-Term Agricultural Inputs and Clay Mineral Weathering, Plus Potential Evidence of Shallow Mixed-Layer Silicates

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After over a century of cultivating continuous wheat, they are still able to harvest grains from the zero-input check plot in the Magruder Plots of Oklahoma State University [1]. The inherent fertility of these soils is amazing, and how these soils have changed over time can provide valuable insight into anthropogenic impacts on the rich cultivated soils of the central United States and potentially inform farmers on future nutrient management decisions. In 1947, these plots were moved to their current location, relocating the top 40.6 cm of soil 1.6 km west of their original location [2]. The six plots contain a a zero-input check, manure applied quadrennially (270 kg ha^{-1} N), annual NPK fertilization, NPK plus lime (maintaining pH > 5.5), annual nitrogen and phosphorus applications, and annual phosphorus-only application. To assess the mineralogical changes within the Magruder plots, we sampled the soil down to 90 cm and analysed surface and subsurface clays in the profile. We expected to see greater kaolinite fractions and increased iron oxides, especially in high fertilizer input plots due to increased weathering from soil acidification in surface samples. Clay fractions were analysed using the Jackson method and x-ray diffraction (XRD). Patterns were assessed using Profex and MacDiff software. Non-crystalline iron content was determined using Na-CBD extraction. Samples were also analysed for total carbon, total nitrogen, pH, and cation exchange capacity (base saturation).

Results from XRD patterns indicate a lithic discontinuity between the surface and subsurface layers, potentially due to the relocation in 1947. Surface samples contained mica, kaolinite, and quartz, while subsurface samples contained significant amounts of smectite and increased amounts of kaolinite. The zero-input check plot had lower iron quantities than other treatments, and iron increased with increasing inputs. The addition of lime appears to have lower iron levels than the NPK treatment without. Increased soil acidification may be linked to these increased levels of non-crystalline iron quantities. Additionally, results are pending on the kaolinite quantification. On a separate, interesting note, XRD patterns indicate the presence of mixed-layer chlorite-smectite and/or smectite-illite in the deep samples. Further analyses will include assessment of the mixed-layer clay percentages, as well as XRD and ICP data from a bedrock sample to determine the source of these relatively shallow mixed-layer minerals.

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Mapping organic carbon species in soils with contrasting clay minerals

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Understanding organo-mineral interactions at micro-spatial scales is critical to determine the processes that help in the preservation of organic carbon (OC) in soils. The lack of suitable analytical techniques often hinders analysis of OC in association with minerals within intact soil microaggregates. In this study, we examined soil microaggregates (53–250 µm) from four soils with contrasting dominant clay minerals — Acrisol (illite, kaolinite, goethite), Cambisol (kaolinite, illite, hydroxy interlayered vermiculite), Ferralsol (kaolinite, goethite, hematite), and Vertisol (smectite, kaolinite). The soils were collected from surface (0–10 cm) and subsurface (40–50 cm) layers from agricultural regions of New South Wales, Australia. The OC concentration in the surface and subsurface layers varied across soils, with respective values of 2.87%, 0.49% in Acrisol, 3.13%, 1.14% in Cambisol, 4.34%, 2.88% in Ferralsol, and 0.81%, 0.70% in Vertisol. Microaggregates were separated by drying sieving and thin sections (~300 nm) were prepared using an ultramicrotome. Sections were scanned with a Bruker Hyperion 2000 infrared microscope coupled to a Vertex 80V spectrophotometer at the infrared microspectroscopy beamline of the Australian Synchrotron. This technique allows us to examine the organo-mineral interactions at a spatial resolution of 8-10 µm. Peak areas for aliphatic C–H (2826–3000 cm^{-1}), aromatic C=C (1480–1550 cm^{-1}), oxygen-containing groups C=O (1550–1760 cm^{-1}), and mineral –OH (3550–3750 cm^{-1}) were integrated. Across all soils, stronger correlations were observed between mineral –OH and C–H (mean r^2 = 0.61) and C=O (mean r^2 = 0.50) groups of OC, compared to aromatic C=C (mean r^2 = 0.09) of OC, which suggest a selective binding of aliphatic C species to soil minerals. The relationships were stronger (mean r^2 =0.51) in the Vertisol, Ferralsol and Cambisol than Acrisol (mean r^2=0.13). The co-localisation of different organic carbon (OC) functional groups with mineral –OH groups indicates chemical interactions between mineral surfaces and OC, suggesting that adsorption is a key mechanism for OC stabilisation in the selected soils. This study provides valuable insights into the role of chemical adsorption for C stabilisation within microaggregates in diverse agricultural soils.

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Potential of Clays from the Nahuelbuta Mountain Range in Chile for Agricultural Crop Applications

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Introduction. Clay minerals are among the most diverse materials known to humankind. In soil management for agricultural production, both the texture, referring to particle size distribution, and the amount of clay present are of critical importance. In this context, clay is considered a non-metallic resource in Chile. Although it is abundant, it does not receive the same prominence as copper or other metals. Therefore, this study investigated the behaviour of Chilean clay samples in relation to selected parameters of agricultural crop performance.

Methodology. The research involved the analysis of 16 samples collected from the Nahuelbuta Mountain Range using X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques, to identify the mineral composition of the clays. In the second part of the study, a greenhouse experiment was conducted to assess the effect of different types of clay on the early development of *Lactuca sativa* L. (lettuce). For this purpose, experimental units were prepared using pots filled with a soil substrate mixed in equal volume (1:1) with each of the 16 clay types evaluated, with three replicates per treatment. Lettuce seedlings were then transplanted into each pot and maintained under controlled conditions for a period of one month. At the end of the trial, parameters related to plant development were assessed, including plant height and foliar pigment content (chlorophyll, flavonoids and anthocyanins), to determine the differential impact of each clay type on the species' physiological response.

Results. The clay samples were characterised by the presence of quartz, iron minerals, kaolinite, montmorillonite, feldspars and other minor minerals. In the greenhouse trial, it was observed that certain types of clay had a significantly positive effect on the early growth of lettuce, while others had little or no impact, or may have even limited development. Regarding physiological parameters such as chlorophyll production, some clays appeared to promote greater synthesis or retention of chlorophyll in lettuce leaves, potentially reflecting an improved physiological or nutritional status in comparison with other formulations. In addition, some clays induced higher flavonoid accumulation in lettuce, possibly as an adaptive response to the physicochemical properties of the amended substrate. Finally, it was found that certain clays favoured greater anthocyanin accumulation, which may be linked to antioxidant mechanisms induced by the specific physicochemical properties of these mineral amendments.

Discussion and Conclusion. The use of clay materials has been shown to significantly improve soil quality, and as a result, there is a growing number of applications in agriculture. The Nahuelbuta Mountain Range in Chile contains clay deposits that are rich in minerals and other elements, offering potential for use in sustainable agricultural development.

This research was funded by FONDEF Project ID24I10350.

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Session 40: Clays in Mining

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Portable VNIR-SWIR spectroradiometry for material classification in clay mineral deposit exploitation works

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The identification of clay minerals is relatively straightforward in the context of industrial minerals; however, quantifying these minerals remains a challenge at all scales. During the exploitation of a clay deposit containing special clays (kaolin, bentonite, and sepiolite-palygorskite), a key challenge is assessing material quality, as the concentration of economically valuable minerals can vary significantly throughout the deposit. In many cases, companies classify the extracted materials based on a limited number of samples and conduct conventional mineralogical analyses, such as X-ray diffraction (XRD), chemical assays, or other methods. These procedures require time and, in some cases, the use of chemical reagents. An alternative approach is the use of portable VNIR-SWIR spectroradiometry, which enables rapid data acquisition directly from the quarry face, providing extensive information in a very short time.

This study presents two examples of the application of portable VNIR-SWIR spectroradiometry for the semi-quantification and classification of clays based on their mineralogical composition. In the first case, kaolinite and smectite occur together in highly variable proportions, ranging from kaolinite-rich to smectite-rich materials. The company exploits this variability by classifying and marketing five distinct industrial products, each with different properties according to their kaolinite/smectite ratios. For this deposit, using a large set of samples with mineralogy previously determined by X-ray diffraction (XRD) and corresponding spectral data, two regression equations were developed to estimate the contents of kaolinite and smectite. In the second example, the focus is on estimating palygorskite content relative to carbonates (calcite and dolomite) and other impurities. In both cases, data derived from second-derivative of the spectra, selected through statistical analysis, are used. Notably, the spectral data employed are not affected by the relative humidity of the materials, allowing the method to be applied regardless of weather conditions.

The main advantage of using portable VNIR-SWIR spectroradiometry during exploitation works is the speed and efficiency of data acquisition: a spectrum can be collected in seconds, and tens or even hundreds of spectra can be processed within minutes by an operator without requiring a high level of specialization.

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Sessions 38+43: Chemical reactions with clay minerals: implication for environmental challenges and remediation strategies

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Adsorption of short-chain perfluoroalkyl acids (PFAAs) on montmorillonite clay using density functional theory

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The growth of industry has led to extensive water pollution issues accompanied by per- and polyfluoroalkyl substances (PFASs), and in particular perfluoroalkyl acids (PFAAs), in the environment from the historical widespread implementation of these substances in consumer and industrial products. As a result of their resistance to degradation and possible toxicity, PFAAs pose new and exciting challenges to environmental and human health. Of the various approaches to treatment, adsorption, principally using clay minerals, has emerged as a successful, environmentally friendly, and low-cost method of PFAAs removal. [1]. Natural and modified clays have demonstrated superior effectiveness in removing PFAA contaminants compared to conventional adsorbents like activated carbon and ion exchange resins [2].

This study investigates the adsorption mechanisms of short-chain perfluoroalkyl acids (PFAAs) on montmorillonite (Mt), with the goal to analyze of adsorption energies and evaluating the stability of the resulting systems. The Density Functional Theory (DFT) method implemented in the Vienna *Ab Initio* Simulation Package (VASP) [3] is employed to explore the interactions within the proposed models. Structural optimizations are performed using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional to account for exchange-correlation effects. A comparative analysis is conducted for three systems: montmorillonite with perfluorobutyric acid (Mt–PFBA), perfluoropentanoic acid (Mt–PFPA), and perfluorohexanoic acid (Mt–PFHA).

The findings confirmed the stability of hybrid systems of Mt clay with all studied PFAAs and highlighted differences in structural stability attributed to variations in chain length. These results reinforce the potential of using natural clays as efficient adsorbents for the removal of short-chain PFAAs from contaminated water sources.

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Adsorption performance of Eu(III) on natural clays and high-charge synthetic micas: Isotherm and kinetic studies comparison

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Clay minerals are widely extended as ideal adsorption materials, due its swelling behaviour, high specific surface area and high cation exchange capacity (CEC). Common uses for natural clays, as bentonites, are related to environmental remediation, heavy metals depollution and high-level radioactive waste management. Bentonites are composed mainly by montmorillonite, a T-O-T layer phyllosilicate. Lately, a novel family of synthetic T-O-T (T: tetrahedral; O: octahedral) layer fluorosilicates referred as high-charge micas (Na-n-micas), has been proposed as alternative barrier material because its exceptional adsorption properties, with theorical CEC values up to four times higher than bentonites and its great selectivity for radioactive divalent and trivalent cations [1].

Trivalent europium (Eu(III)) has been previously assessed as stable lanthanide isotope in isotherm models for various clay absorbents [2,3]. Mechanisms of sorption of europium in clay surface and interlayer space are crucial for understanding the incorporation and immobilization of radioactive cations, preventing migrations to aquatic environments and host-rock in deep geological repositories (DGR). Differences of sorption mechanisms are expected between natural clays and synthetic micas, according grade of substitution in octahedral sheet (O) and resulting net layer charge.

The purpose of this research is to study the adsorption mechanism of europium (III) from aqueous suspensions by montmorillonite clay and synthetic Na-n-micas. Kinetics adsorption analysis were conducted were several initial concentrations of europium nitrate (10 – 180 mg/L) in aqueous solution. X-ray diffraction patterns for recovered clays indicates that MMT reaches a complete exchange of Ca by Eu(III) interlayer, according basal reflection of (001) plane on Figure 1. Na-2-mica showed a partial exchange cation by intercalation of Eu/Na cations, while Na-4-mica sorption are primarily by surface adsorption. At equilibrium, percent of removed Eu(III) indicates that MMT are capable to retain up to 87%, while Na-n-micas reach a value of 66,1% and 91,5% retention for n = 2 and 4, respectively.

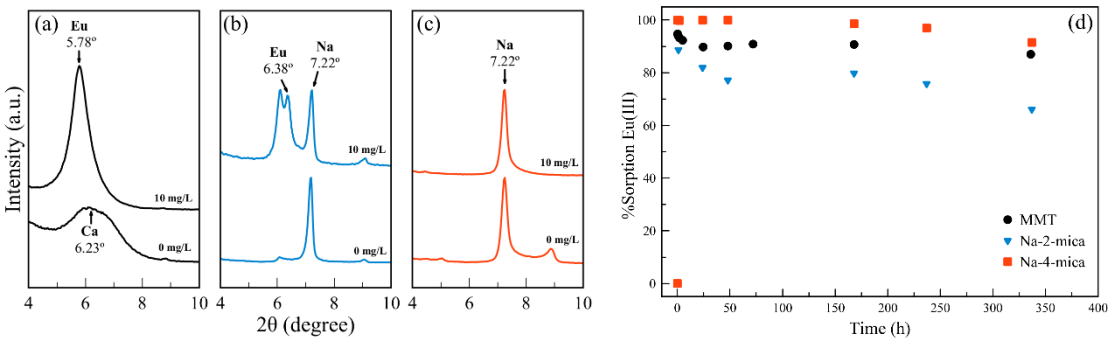

Figure 1. XRD patterns of MMT (a), Na-2-mica (b) and Na-4-mica (c) for initial and after equilibrium. Removed percentage of Eu in clay and synthetic micas (d) in for aqueous solution C_0 = 10 mg/L Eu(III).

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Session 44: Synthesis and Applications of Modified Clays in Environmental Remediation

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Monitoring drug adsorption by smectite composites

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The increasing of the pollution of wastewater with organic micropollutants negatively affect not only the environment, but directly also the health of human and animals. As one of the relatively new alarming pollutant has recently been marked drugs such as analgesics, antibiotics, antidepressants, etc. Potentially cheap adsorbents for the adsorption of such pollutants seem to be the composite materials based on clay minerals which represent a significant development trend of new materials with predefined and required properties. The aim of this work was to prepare novel sorbents based on smectite matrix and organic compounds. The series of hectorite composites prepared by chemical modification were tested for removal of selected types of drugs. Smectite samples in organically modified form demonstrated sufficient sorption ability of drugs from aqueous solutions in the order analgesics > antibiotics > antiepileptics > bronchodilators. An important part of the monitoring of the drug adsorption was the use of molecular modelling to obtain information about the distribution of the drug on the sorbent during the absorption process. It follows from the results, that prepared composites possessed an adequate sorption ability with respect to the relatively low concentrations of drugs and their metabolites in wastewaters. These novel materials have a high potential for environmental applications not only for the removal of drugs from wastewater or natural streams but also for building barriers during waste disposal.

Acknowledgements: This research was supported by the ESF in „Advanced Materials for Energy and Environmental Technologies“ project, reg. nr. CZ.02.01.01/00/23_021/0008592 within the Programme Johannes Amos Comenius.“ and also by Mobility programme of the Czech Academy of Sciences and the Polish Academy of Sciences, Mobility Project, no. PAN-24-22.

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Adsorption of Cs-137 and Co-60 by metabentonite and metakaolin-based geopolymer composites

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In this study, metabentonite (MB) and metakaolin-based geopolymer composites (GPs) were prepared by calcination at 700, 800 °C and activated with 10 and 20 wt.% NaOH. The prepared GPs were characterized by FTIR, PXRD and SEM. A scintillation gammaspectrometry was used to determine the activity of applied artificial radionuclides ^{60}Co and/or ^{137}Cs in the collected solution samples and in GPs. XRD and FTIR spectroscopy confirmed in MK-based GPs that the amount of zeolite increased simultaneously with the concentration of alkaline activator, whereby zeolite A and zeolite P were determined as the predominant phases. At higher concentrations of NaOH in MB-based GPs, the presence of zeolitic phases of faujasite and gobbinsite was confirmed. SEM analysis showed that with increasing concentration of alkaline activator, cuboidal formations were observed in both cases, indicating the formation of zeolitic phases. All prepared GPs (weight ratio GP : solution = 1 : 1,000 to 1 : 10,000) exhibited significant Co and Cs binding efficiencies ranging around 90% of the total Co and Cs in solution containing 100 µmol/dm^3 of both metals. From the comparison of the adsorption efficiency or adsorption capacity of the individual prepared GPs, it was found that there are no significant differences between GPs prepared on the basis of MK and MB in their ability to bind Co and Cs from their two-component solutions radiolabelled with ^{60}Co and ^{137}Cs. However, for a better understanding of the adsorption of ^{137}Cs a sample of geopolymer composites calcined at 800 °C and an alkaline activator concentration of 10 wt% (GP10_MB800) was selected. In this case, we observed that the Cs adsorption efficiency increased linearly with increasing applied amount of GP (0.5 to 4.0 g/dm^3) in a solution of 1,000 mg/dm^3 CsCl radioactively labelled with ^{137}CsCl. On the contrary, the specific adsorption of Cs expressed in mg/g decreased exponentially in this comparison. To evaluate the effect of exposure time on Cs adsorption, we observed Cs adsorption kinetics that exhibited the typical pattern observed in adsorption processes and corresponding to rapid metal ion binding processes upon reaching a concentration equilibrium of $[Cs]_{adsorbent}$: $[Cs]_{solution}$. Furthermore, we observed that the Cs adsorption efficiency decreased linearly with increasing Cs concentration in solution. Conversely, the specific Cs adsorption (mg/g) increased nonlinearly, suggesting a gradual saturation or saturating of the applied GP with Cs ions. From the description of the Cs adsorption data using the nonlinear forms of the adsorption isotherms according to Langmuir and Freundlich, we found that the Langmuir model (R^2 = 0.973) described our data slightly better than the Freundlich model (R^2 = 0.960). Moreover, the Langmuir model allowed us to predict the maximum achievable adsorption capacity Q_{max} for GP10_MB800 and the binding of Cs^+ ions ,which reached the value Q_{max} = 116±10 mg/g. All these findings show that the developed geopolymer composites based on MB and MK are very suitable for the remediation of the environment associated with artificial radionuclide contamination.

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Multifunctional smectite composites

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The worldwide effort to reduce harmful pollutants into the environment leads to invent of advanced materials with highly specific properties that outperform existing materials and enable more innovative product designs. Smectites as a non-toxic natural raw material with a considerable surface area, excellent adsorption properties and thermal/mechanical stability represent promising materials for obtaining environmentally friendly catalysts and sorbents. A series of inorganic smectite composites were prepared by incorporating manganese dioxide particles into a clay matrix of selected clay minerals. This contribution describes the detailed physico-chemical characterization of the synthesized materials by powder X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetry differential thermal analysis, energy-dispersive X-ray spectroscopy, BET surface area analysis and contact angle measurement, together with verification of their sorption and catalytic properties. Adsorption experiments aimed at micropollutants in the aqueous environment, specifically antileptics, were carried out in a batch mode with different initial concentration of lamotrigine and primidone solutions. Removal of both antiepileptics from aqueous solutions showed efficiency up to 90%. Oxidative combustion tests also showed the catalytic activity of smectite composites, which confirmed that they can be a suitable alternative to effective and affordable catalysts for toxic volatile organic compounds (VOCs). The acquired knowledge can contribute to innovative solutions to current problems associated with environmental protection.

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Session 47: Interactions of Iron-rich Clays and Iron Oxides with Organics and Heavy Metals: Implications for Iron/Carbon/Metal Cycling

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Structural Fe promotes allophane reactivity towards model organic compounds

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Short-range ordered aluminosilicates (SROAS) play a key role in stabilizing soil organic carbon (OC). Allophane minerals are porous, amorphous aluminosilicates with Al/Si molar ratio between 1 and 2, mainly formed from volcanic ash weathering. They have a hollow nanospherical structure with octahedral Al in the external- and tetrahedral Si in the internal-walls of the spherules. Owing to their high surface area and depending on the Al/Si ratio, allophanes show a strong affinity for organic molecules and they are thought to play a crucial role in organic C accrual in soil [1]. In Fe rich environments, Fe can substitute for Al or formed surface clusters during allophane precipitation [2]. While previous studies investigated the adsorption capacity of synthetic and natural allophanes towards dissolved organic matter and synthetic organic acids, little is known about how Fe incorporated in allophane structure impacts the mineral surface reactivity.

In this work, we synthesized allophane minerals with (Al+Fe)/Si molar ratio of 2 and Fe/Al ratio of 0, 0.05 and 0.1. The nanoparticle structure was characterized by XRD, Fe K-edge XAS and Electron Microscopy, the ζ potential was determined and the specific surface area was calculated with BET method. Sorption isotherms were performed with citric, glucuronic, vanillic acids and phenylalanine, as model molecules present in natural dissolved organic carbon. The mineral/solution ratio was fixed at 5 g L^{-1}, the organic molecule concentrations varied from 0.1 to 0.5 mM and pH values were adjusted at 5 and 6.5. After 24 h interaction, the suspensions were filtered at 0.22 µm and the concentration of organic substrates was measured by High-Performance-Liquid-Chromatography.

The preliminary results show that phenylalanine is not retained by allophane in any of the studied conditions. Adsorption of vanillic acid is mainly pH dependent and up to 50 % is adsorbed at pH 5, suggesting the saturation of the adsorbent surface. Conversely, up to 93 % of citric acid is adsorbed by Fe-free allophane, increasing to 100 % in presence of Fe, regardless of pH value. Both the lower pH and the Fe presence seem to promote the glucuronic acid adsorption, which increases from about 30 to 50 % at pH 6.5 and 5, respectively, in Fe-free allophane, and from 50 to 75 % at pH 6.5 and 5, respectively, in presence of Fe. This study highlights the role of Fe as a driver of soil C dynamics. While allophane type minerals are known to adsorb OC, our results show that, depending on the organic substrate structure, the presence of structural-Fe may enhance the SROAS organic C stabilization capacity.

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[2] Baker L. L. and Strawn D. G. (2012) 39: 675–684