Petrogenesis of Quaternary volcanic rocks in the Halaha River and Chaoer River area in Daxing'an Mountain range,North China

QICHENG FAN*, YONGWEI ZHAO, JIANLI SUI

Institute of Geology, China Earthquake Administration, Beijing 100029, email: fqc@ies.ac.cn

The Halaha River and Chaoer River area (HC for short), middle of the Daxing'an Mountain range, is in the north of the North-South Gravity Lineament. 28 Quaternary volcanoes, which scattered along a Quaternary NE strike fault, are found in this area. Based on studies of the volcanic field characteristics, in conjunction with geological dating by K-Ar, it is identified that the volcanism occurred in four periods: Early Pleistocene, Middle Pleistocene, Late Pleistocene and Holocene. Quaternary volcanic rocks in this area, mainly alkaline basalt, cover an area of ca. 1000 km^2. Based on studying of the geochemistry with the Quaternary volcanic rocks in HC, this paper attempts to bring mantle sources and magma genesis in this area to light. The volcanic rocks in HC is of alkali one in sodium series, dominated by alkali olivine basalts. They resemble alkali basalts in Datong, as shown by trace elements distribution patterns, and generally exhibit OIB-like characteristics. They show nearly homogeneous Sr-Nd-Pb isotopic compostition similar to the prevalent mantle. All data show that bsalts of HC have a garnet lherzolite mantle source, low degree partial melting in which at different depth result in the primitive magma. Regional extension triggered asthenospherie upwelling, which may lead to the genesis of magma and subsequent volcanism.
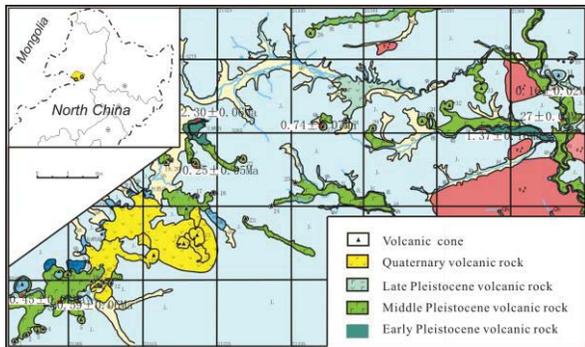
Fig.1 Quaternary volcanic rocks in Halaha River and Chaoer River area in the Great Xing'an Range, North China

$^{40}Ar/^{39}Ar$ geochronology of fluid inclusions

H.N. QIU[1]*, H.Y. WU[2], Z.H. FENG[2], J.B. YUN[2], M. WANG[1], R.G. HU[1], Y.D. JIANG[1], X.J. BAI[3], J.R. WIJBRANS[4]

[1]State Key Laboratory of Isotope Geochemistry, GIGCAS, Guangzhou, China, qiuhn@gig.ac.cn
[2]PetroChina Daqing Oilfield Company Ltd., Daqing, China, wuheyong@petrochina.com.cn
[3]Key Laboratory of Tectonics and Petroleum Resources (China University of Geosciences), Ministry of Education, Wuhan, China, xiuj.bai@gmail.com
[4]Department of Petrology, VU University Amsterdam, The Netherlands, Jan.Wijbrans@falw.vu.nl

**Theme 23: General Geochemistry Sessions
Geochronology: the role of fluids**

Our primary purpose to date fluid inclusions by $^{40}Ar/^{39}Ar$ *in vacuo* crushing was to develop a new approach to obtain ore-forming ages of hydrothermal deposits. We suceeded in dating the mineralization ages of W-Sn, Au, Cu and Pb-Zn deposits using this novel technique on quartz, siliceous breccia and sphalerite [1-4]. Our results indicate that the $^{40}Ar/^{39}Ar$ stepwise crushing technique is very useful to determine the ore-forming ages, however, some samples probably contain too low K-concentrations to be analysed.

Since 2000, we've been investigating the fluid evolution of the Dabieshan eclogites during UHP metamorphism and retrograde metamorphism by the $^{40}Ar/^{39}Ar$ progressive crushing on garnet, amphibole and quartz [5-7]. The fluid inclusions of garnet revealed the age messages of the Paleozoic UHP metamorphism, and the amphibole and quartz recorded that the retrograde metamorphism of the Dabieshan eclogites occurred from Permian to early Jurassic.

Due to the lack of suitable minerals for dating, the timing of hydrocarbone charging of reservoirs is one of the most difficult problems in geochronology. We recently applied the $^{40}Ar/^{39}Ar$ progressive crushing into dating the natural gas emplacement in the Songliao Basin, NE China. The igneous quartz from the Cretaceous volcanic rocks that host the gas reservoir contains abundant secondary fluid inclusions with high K contents and high methane pressures, providing an excellent closed system for $^{40}Ar/^{39}Ar$ dating. The dating results of the igneous quartz by crushing precisely constrained the gas emplacement at 42.4±0.5 Ma [8].

The crushers were improved again and again to make the crushing tubes and dropping pestles shorter and smaller in diameters. It is very important to crush the mineral grains as homogeneously as possible to obtain a good dating result. $^{40}Ar/^{39}Ar$ geochronology of fluid inclusions is very useful for us to understand various geological processes with fluids.

References:
[1] Qiu *et al.* (1989) *Chin. Sci. Bull.* **34**, 1887-1890.
[2] Qiu (1996) *Chem. Geol.* **127**, 211-222.
[3] Qiu *et al.* (2002) *Geochem. J.* **36**, 475-491.
[4] Qiu *et al.* (2007) *Earth Planet. Sci. Lett.* **256**, 224-232.
[5] Qiu *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 2354-2370.
[6] Qiu *et al.* (2008) *Earth Planet. Sci. Lett.* **268**, 501-514.
[7] Qiu *et al.* (2010) *J. Metamorph. Geol.* **28**, 477-487.
[8] Qiu *et al.* (2011) *Geology* **39**, 451-454.

Experimental study of the kinetics of CO_2-sequestration by olivines and Hawaiian picrites

LIN QIU[1]*, ZHENGRONG WANG[1], SHUN-ICHIRO KARATO[1], JAY J. AGUE[1], MICHAEL ORISTAGLIO[1], EDWARD BOLTON[1], AND DAVID BERCOVICI[1]

[1]Department of Geology and Geophysics, Yale University, New Haven, CT, USA
*presenting author: lin.qiu@yale.edu

Mafic/ultramafic rocks have been suggested as promising candidates to store anthropogenic CO_2 permanently. In this study, we employed an experimental approach to quantitatively evaluate the carbonation reaction kinetics as CO_2-rich fluids react with olivine (Fo_{90}) and high-Mg basalts (Hawaiian picrites).

Gem-quality olivine grains, olivine powders (10-20μm) and basalt powders (10-40μm) reacted with CO_2-containing solutions (e.g., 1M and 3M $NaHCO_3$ solution) in gold capsules placed in a hydrothermal autoclave over durations of 1-7 days at 200 ^{o}C and 150 bar. Dissolution experiments for these samples have also been carried out at three pH values (4.1, 6.9 and 9.3) to understand dissolution kinetics. After completion of experiments, gold capsules were checked for leaks, experimental run products were examined using SEM and electron microprobe, and the solution was analysed for alkalinity and major and trace element compositions at Yale University.

Our preliminary results show that carbonation rates of olivines and basalts are a function of the chemistry of the solution (e.g., concentration of $NaHCO_3$), the grain size, the mineralogy of the solid, and the duration of the experiments. We find that carbonation rates increase with increasing concentration of $NaHCO_3$ and decreasing grain size, but decease with time. For example, an increase of $NaHCO_3$ concentration from 1M to 3M raises the carbonation rate for olivine grain by a factor of 6, and the carbonation rate for 10- 40μm olivine powders with 1M $NaHCO_3$ solution is an order of magnitude greater than that for single olivine grains. Carbonation rates of olivine and basalts in the first day are significantly higher than that of the subsequent days and slow down after 3-days of reaction. A dissolution and precipitation model is formulated to quantitatively simulate this process.

The clumped isotope geothermometer in soil and paleosol carbonate

JAY QUADE[1]*, JOHN EILER[2], MATHEIU DAERON[3], AND DAN BREECKER[4]

[1]University of Arizona, Geosciences, quadej@email.ariozna.edu (* presenting author)
[2]California Institute of Technology, Geological and Planetary Sciences, eiler@gps.caltech.edu
[3]CNRS, Science du Climat et de l'Environment, mathieu.daron@gmail.com
[4]Univerisity of Texas at Austin, Geological Sciences, breecker@jsg.utexas.edu

We studied both modern soils and buried paleosols in order to understand the relationship of temperature estimated from clumped isotopes in carbonates ($T°C_{clumped}$) to actual surface and burial temperatures. Carbonates from modern soils in a broad range of climates were sampled from Arizona, Nevada, Tibet, and India. $T°C_{clumped}$ obtained from these soils shows that soil carbonate only forms in the very warmest months of the year, largely in the afternoon, and probably in response to intense soil dewatering. The highest $T°C_{clumped}$ obtained from modern soil carbonate are <40°C On average, $T°C_{clumped}$ significantly exceeds mean annual temperature by 10-15°C due to (1) summertime bias in soil carbonate formation, and (2) sensible heating of soil. Secondary controls on $T°C_{clumped}$ are site aspect, but especially soil depth and shading.

Site mean annual temperature (MAT) across 0-30°C is highly correlated with $T°C_{clumped}$ from soils, following the equation:

$$MAT(°C) = 1.20 * T°C_{effective\ air\ T\ from\ clumped} -21.72 \qquad (r^2 = 0.92)$$
(1)

where $T°C_{effective\ air\ T\ from\ clumped}$ is the effective air temperature at the site estimated from $T°C_{clumped}$. The effective air temperature represents the air temperature required to account for the $T°C_{clumped}$ at each modern soil site. The highly correlated relationship in equation (1) permits mean annual temperature in the past to be reconstructed from $T°C_{clumped}$ in paleosol carbonate, though it should be noted that soil carbonates appear to principally reflect warm season temperatures and so the proxy might be more precisely used as a measure of warm season climate or, in combination with other mean annual temperature proxies, of seasonality.

We also measured $T°C_{clumped}$ from long sequences of deeply buried (≤5 km) paleosol carbonate in the Himalayan foreland in order to evaluate potential diagenetic resetting. We found that paleosol carbonate faithfully records soil $T°C_{clumped}$ down to 3-4 km burial depth, or ~100°C. Deeper than this and above this

Combining µSXRF, EXAFS and isotopic signature to understand the Ni cycle in impacted ultramafic soils

Cécile Quantin[1], Delphine Jouvin[1], Alexandre Gélabert[2], Emmanuelle Montarges-Pelletier[3], Yann Sivry[2], , Isabella Zelano[2], Rémy Pichon[1], Jérémie Garnier[4*], and Marc F. Benedetti[2]

[1] UMR 8148 IDES, UPS-CNRS, Orsay, France (cecile.quantin@u-psud.fr, delphine.jouvin@u-psud.fr, remy.pichon@u-psud.fr)

[2] UMR 7154, Université Paris Diderot - Sorbonne Paris Cité - IPGP , Paris , France (gelabert@ipgp.fr, sivry@ipgp.fr, zelano@ipgp.fr, benedetti@ipgp.fr)

[3] UMR 7569 LEM, CNRS-Nancy I, Nancy, France (emmanuelle.montarges@univ-lorraine.fr)

[4] Instituto de Geociências, Universidade de Brasilia, Brasilia DF, Brazil (*garnier@unb.br)

Biogeochemical cycles of metals have been deeply modified by anthropogenic activities since the industrial revolution [1]. Since the end of the 90's, the development of metal isotopic ratios analysis provides crucial information about their biogeochemical behaviour. In the case of mining or smelter activities, extracted metals can be clearly followed through their isotopic signatures [2; 3]. Only few publications [4; 5] report the use of Ni isotopes for environmental studies, in spite of its high potential for tracing anthropogenic Ni. The combination of isotopic tools with microspectroscopic techniques (µSRXF and XAS), to unravel metal local distribution and speciation, should improve our understanding of Ni behavior and predict its mobility and bioavailability.

Samples from the ultramafic massives of Barro Alto and Niquelândia (Goiás State, Brazil), constitued in ores, fly ash, slags and natural and waste impacted soils were characterized for their Ni speciation and isotopic signatures. Ni concentrations range from 0.5 to 22.9 g.kg^{-1}

Ni K-edge XAS data were collected in bulk and microbeam modes for Ni ore, pristine pyrometallurgical wastes (fly ash and slags) before and after leaching (TCLP and DTPA procedures), to evaluate Ni extractability. TCLP or DTPA leaching leads to the extraction of 0.3 to 8.1% of Ni depending on samples. XANES spectra show that Ni is octahedrally coordinated. Linear Combination Fitting of EXAFS oscillations suggests that Ni in the ore is mainly involved in Ni-phyllosilicates and less than 20% in Ni bearing goethite. The Ni speciation in wastes is dominated by olivine and ferronickel, and leaching procedures only slightly impact Ni speciation.

The relatively high temperature processes occurring during pyrometallurgy processes may be responsible of strong isotopic fractionation [2]. Hence, Ni species from slags and fly ash should be easily distinguished from natural Ni species by their different isotopic signatures. Thus, all anthropogenic materials (ores, fly ash and slags) and soils will be carefully studied for isotopic signatures, in order to trace anthropogenic Ni in this ecosystem.

[1] Rauch & Pacyna (2009) *Glob. Biogeochem. Cycles*, **23**, 1-16. [2] Sivry et al. (2008), *Chem. Geol.*, **255**, 295-304. [3] Juillot et al. (2011), *Geochim. Cosmochim. Act.*, **75**, 2295-2308., [4] Sergeev et al. (2006), *Geochim. Cosmochim. Act.*, **70**, supp., A570., [5] Sergeev et al. (2007), *Geochim. Cosmochim. Act.*, **71**, supp., A918.

Insights into biomineral growth from atomistic simulations of clusters and nanocrystals

David Quigley[1*], Matt Bano[2] and P. Mark. Rodger[2]

[1] Department of Physics, University of Warwick, Coventry. United Kingdom, d.quigley@warwick.ac.uk (* presenting author)

[2] Department of Chemistry, University of Warwick, Coventry, United Kingdom.

Introduction

The common biomineral calcium carbonate ($CaCO_3$) appears in nature as a variety of crystalline polymorphs and morphologies, exhibiting structure on a hierarchy of length scales which cannot be reproduced synthetically. Molecular simulation has a key role to play in elucidating the earliest stages of biomineral growth where length scales prohibit direct observation by experiment.

Nanoparticle simulations

Our previous free energy calculations based on metadynamics [1,2] have established that amorphous structure is energetically competitive with crystalline calcite for particles smaller than 2nm, with calcite structure increasingly preferred at sizes of 5nm and larger. This confirms experimental evidence that $CaCO_3$ growth can proceed via amorphous precursor phases.

Substantial improvements in the quality of force-fields for $CaCO_3$ [3] are enabling new questions to be addressed. Specifically water content and dehydration of the amorphous phase, and the stability of nanocrystals with aragonite or vaterite structure. The latter of these questions is a necessary step in elucidating the mechanisms of polymorph selection during nucleation and growth.

The traditional method of generating atomic representations of crystalline nanoparticles is the Wulff construction, in which a bulk crystal is cleaved such that the total surface energy is minimised. Our most recent work has demonstrated that such an approach fails for models which correctly capture the $CaCO_3$-water interfacial energetics. Surface *enthalpies* are found to be negative, with the entropic penalty of tightly-bound surface water being sufficient to generate a net interfacial free energy penalty.

We have developed an alternative Monte-Carlo method for generating nanocrystal configurations and applied this to the three $CaCO_3$ polymorphs. A discussion of magic-number effects will be presented, along with simulations comparing the energetics of these particles over a range of sizes in explicit water. Some progress toward simulating transitions between nano-crystalline polymorphs will be presented, along with challenges to calculation of transition kinetics.

Pre-nucleation clusters

Improved atomistic models have also allowed larger scale simulations to probe the earliest stages of ion aggregation, suggesting an explanation for the formation of stable pre-nucleation clusters [4]. This talk will present recent attempts to capture this phenomenon in simple lattice models of nucleation and growth.

[1] Quigley & Rodger (2008) *J. Chem. Phys.* **128**, 221101. [2] Quigley *et al* (2011) *J. Chem. Phys.* **134**, 044703. [3] Raiteri *et al* (2010) *J. Phys. Chem. C.* **114**, 5997-6010. [4] Demichelis *et al* (2011) Nature Comms. **2**, 590.

Nucleosynthetic anomalies of Ni and other transition metals in chondrites and possible carrier phases

QUITTÉ G. [1*] AND POITRASSON F. [2]

[1]CNRS UMR 5276, ENS de Lyon, Université Lyon 1, Lyon, France,
Ghylaine.Quitte@ens-lyon.fr (* presenting author)
[2]GET, CNRS - UPS – IRD, Toulouse, France.

Introduction

The numerous nucleosynthetic anomalies found in refractory inclusions, presolar grains and particular phases carried by chondrites suggest that the matter constituting the solar system results from a mixing between different sources. Over the last few years, Ni isotope heterogeneities – among other elements – have been reported in various meteorites. Many samples including ureilite silicates, CAIs, CB metal nodules fall on a mixing line between an s-process and a e-process components [e.g. 1-2] ; altogether it is clear that meteorites come from at least 3 isotopically distinct Ni reservoirs [2-3]. However, the carrier phases of these nucleosynthetic anomalies have not been fully identified yet.

Leachates of carbonaceous chondrites

Focused studies of specific components or stepwise dissolution of carbonaceous chondrites are powerful tools to characterize the fine-scale isotope heterogeneities of the solar system, even if leaching procedures may induce some mixing between the various nucleosynthetic components. Acid leachates of carbonaceous chondrites already display anomalies for a variety of elements [e.g. 4-5]. A stepwise dissolution procedure similar to those previously used in other studies has been applied to facilitate the comparison of the isotopic results. Nickel is a suitable element to resolve the different nucleosynthetic components as ^{61}Ni is overproduced by s-process (AGB stars) when excesses of ^{62}Ni and ^{64}Ni witness nucleosynthesis in a neutron-rich environment (e.g. supernova explosion). Powdered whole rock samples of Allende, Murchison, and Orgueil were sequentially digested with reagents of increasing acid strength. Nickel is not isotopically uniform among the various host phases. Murchison and Orgueil show similar patterns, with widespread deficits in neutron-rich Ni isotopes. Allende is quite different: most leachates are slightly enriched in those isotopes. In Orgueil, the ^{62}Ni-deficit increases with increasing acid strength, which is consistent with the s-process component being carried by acid-resistant SiC presolar grains. Besides, most of the Ni is dissolved by concentrated acetic acid and nitric acid confirming that metal is a major carrier phase. As ^{58}Fe is the most neutron-rich Fe isotope, a correlation is expected with the neutron-rich Ni isotopes: hint towards negative $\varepsilon(^{58}Fe/^{54}Fe)$ values indeed exists in Orgueil fractions [6]. Isotope measurements of Cu and Zn in the same leachates are in progress with the aim of combining data for several elements from the "iron peak group". Correlations, if any, will potentially bring stronger and more precise constraints on the astrophysical setting where the nuclides have been produced, and help better identify the carrier phases of the isotope anomalies.

[1] Quitté G. et al. (2007) *ApJ* **655**, 678-684. [2] Quitté G. et al. (2010) *ApJ* **720**, 1215-1224. [3] Regelous M. et al. (2008) *EPSL* **272**, 330-338. [4] Rotaru M. et al. (1992) *Nature* **358**, 465-470. [5] Schönbächler M. et al. (2005) *GCA* **69**, 5113-5122. [6] Poitrasson F. and Freydier R. (2006) *MAPS* **41**, A141.