EMU Notes in Mineralogy, Vol. 20 (2019), Chapter 1, 1–11

Introduction: the role of modern mineralogy in cultural heritage studies

Gilberto ARTIOLI[1] and Roberta OBERTI[2]

[1]*Department of Geosciences and CIRCe Centre, Università di Padova,*
Via Gradenigo 6, 35131 Padova, Italy
e-mail: gilberto.artioli@unipd.it
[2]*CNR-Istituto di Geoscienze e Georisorse, sede di Pavia, Via Ferrata 1, 27100 Pavia, Italy*
e-mail: oberti@crystal.unipv.it

This short introduction aims to rethink the role of modern mineralogy and highlights the diverse and important contributions that it may provide in the study of materials and processes relevant to cultural heritage. It is argued that mineralogy lies in a very special position between Earth and materials sciences and that mineralogists have a profound perception of the structural and chemical complexity of natural materials. They possess knowledge of both the ancient and recent geological and physicochemical processes which produced the raw materials used by humans, and of the analogue processes used to transform them into artefacts. It is thus highly appropriate that a volume in the EMU series acknowledges some of the recent contributions of mineralogy to the investigation of human history, art and technology.

1. Traditional *vs.* modern mineralogy

Mineralogy and crystallography are historically closely related disciplines, and unfortunately both have experienced a serious decrease in their appeal as basic formative disciplines in the most recent university curricula. Many courses have recently been cancelled or merged into general courses on geomaterials. This is not the right place to discuss such worrying trends, which are consequences of a simplistic perception of science by society and, in turn, by the recent generations of students. It is a fact, however, that mineralogy and crystallography are perceived as 'old' disciplines, with little to offer for future technologies and societal needs. During the International Year of Crystallography in 2014 (www.iycr2014.org), the International Union of Crystallography (IUCr) did revitalize the concepts and fascination of crystals and minerals for a much larger audience. The many events worldwide showed clearly that far from being a 'crystallized' technique, the basics concepts and the recent advances in crystallography are still fundamental to any investigation of the solid state and thus still have a significant impact on all aspects of human life.

DOI: 10.1180/EMU-notes.20.1

Crystallography no longer exists, in practice, as an independent discipline in most university curricula. This is unfortunate if we think that throughout most of the 20th century many laboratories of physics and chemistry actively developed crystallographic techniques and applications. The long list of Nobel prizes (www.iucr.org/people/nobel-prize) awarded to scientific achievements directly related to, or involving the use of, crystallographic methods and techniques is an impressive demonstration of the impact of crystallography. Also, a few decades ago entire Departments were dedicated to crystallography, such as the Department of Crystallography in Pittsburgh, created by George Jeffery. A few still remain, albeit devoted mostly to biological studies, such as at CSIC, Madrid, or the University of Madras, among others. The Italian CNR still has an Institute of Crystallography based in Bari, and the French CNRS has a 'Laboratoire de cristallographie et sciences des matériaux' based in Caen. However, the small amount of teaching in crystallography and diffraction left in academies is commonly disguised as 'techniques for structural investigations', 'techniques for materials science', or embedded in the basic courses of mineralogy inserted in the curricula of geosciences.

The many mutual interactions between mineralogy, crystallography and the geosciences are very interesting. A brief recapitulation may help to make clear the present and future state of the research in the field.

Crystallography has had illustrious pioneers in Vannoccio Biringuccio (*De la pirotechnia*, 1540), Kepler (*On the six-cornered snowflake*, 1611), Robert Hook (*Micrographia*, 1665) and Steno (*De solido intra solidum naturaliter contento*, 1669). This shows the constant fascination with which crystals were held in scientific minds, besides of course being valued since prehistory for their intrinsic beauty as gems and precious stones (Rapp, 2009). The developments of crystallography and mineralogy were inextricably linked. Metals and ore mining have always driven mineralogical knowledge, and after the Middle Ages the discipline started to find practical encoding (Georgius Agricola, *De re metallica*, 1556). The availability of ores and the need for metal, especially silver, in the late 15th and early 16th centuries led to the need for mineralogical expertise, strict control of mining and the establishing of state mining schools.

Saxon mining officials played a huge role in the development of mineralogy and geology for about two hundred years (Laudan, 1987; Schneer, 1995). Agricola lived in the booming mining towns of Joachimstahl and Chemnitz. Roesler (*Speculum metallurgie*, 1700), Zimmerman (*Obersächsische Bergakademie*, 1740), von Oppel (*Anleitung zur Markscheidekunst*, 1749), Baumer (*Geographia et hydrographia subterranea*, 1779), von Trebra (*Erfahrungen vom Innern der Gebirge*, 1785; Fig. 1), Hoffman (*Dissertatio de Matricibus Metallorum*, 1738) were all connected extensively with mining and the mine services in the Saxony area.

Much of what we now consider geological knowledge was at that time included in disciplines defined by mineralogy and cosmogony (Fig. 2). At the end of the 18th century, Abraham Gottlob Werner (1749–1817), who is said to have originally proposed the chronological succession of rocks, defined mineralogy "*as being made up of three major subdivisions that, taken together, closely approximate the scope of*

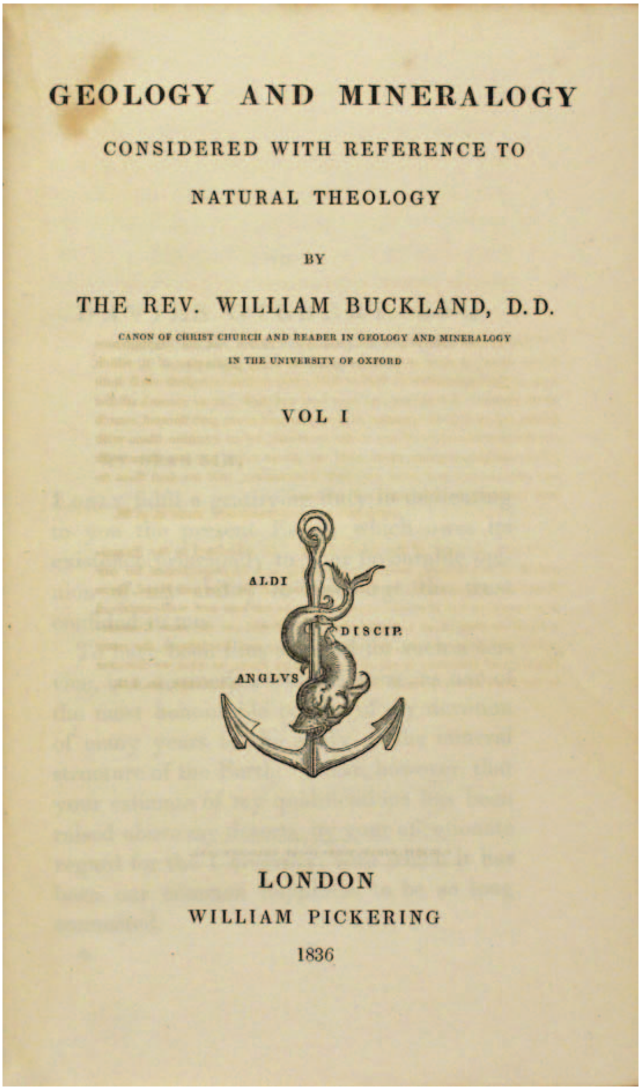
ERFAHRVNGEN
VOM
INNERN DER GEBIRGE,
nach
Beobachtungen geſammlet
und
herausgegeben
von
Friedrich Wilhelm Heinrich von Trebra,
Königl. Groſsbritt. und Churfürſtl. Braunſchweig-Lüneburgſchen Vice-Berghauptmanne, ordentlichen Mitgliede der Deutſchen Geſellſchaft zu Jena, Ehrenmitgliede der Oekonomiſchen Geſellſchaft zu Leipzig, und Ehrenmitgliede der Geſellſchaft Naturforſchender Freunde zu Berlin.

Deſſau und Leipzig,
auf Koſten der Verlagskaſſe für Gelehrte und Künſtler.
1785.

Figure 1. Cover of a mineralogical volume by Friedrich Wilhelm Heinrich von Trebra (1740–1819), Saxon Oberberghauptmann and a friend of Johann Wolfgang von Goethe. Author of *Erfahrungen vom Innern der Gebirge* (Essays from the interior of mountains, 1785).

modern geology: oryctognosy (the identification and classification of minerals), mineral geography (the distribution of rocks and minerals), and geognosy (the formation and history of rocks and minerals)" (Laudan, 1987, p. 21).

In addition to mining and metallurgy, in the eighteenth century the glass and porcelain industry also fostered greatly the study of mineralogy and geology in Europe. Chemical mineralogy and indeed much of inorganic chemistry were to stem from these premises.



GEOLOGY AND MINERALOGY
CONSIDERED WITH REFERENCE TO
NATURAL THEOLOGY

BY

THE REV. WILLIAM BUCKLAND, D.D.
CANON OF CHRIST CHURCH AND READER IN GEOLOGY AND MINERALOGY
IN THE UNIVERSITY OF OXFORD

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LONDON
WILLIAM PICKERING
1836

Figure 2. The cover of the work by William Buckland, in three volumes (1836).

A couple of centuries ago the standing of mineralogy was therefore quite different from the academic niche in which it tends to be confined today. This queen of the geosciences is not really abdicating from her role, however; we hope that the present situation is just another short-lived example of academic myopia. Mineralogy, and crystallography as well, are alive and kicking, and still in a position to contribute to science and society. As discussed above, mineralogy has always been linked with geology, petrology and geochemistry, but has benefited significantly from having integrated the methods and techniques of modern crystallography and advanced materials science. Not only because crystallography has deciphered the structure and the crystal-chemistry of minerals and their solid solutions, but also because it allowed understanding and modelling of the high-*T* behaviour of minerals and inorganic materials, with an impressive impact on our knowledge of both the planets and material sciences.

Arguably, this knowledge makes mineralogy ideally suited and equipped to meet the demanding challenges posed by archaeometric analysis and conservation problems (Berthoud and Cleuziou, 1981; Chiari, 2000; Maggetti, 2006; Artioli, 2010a). These are its most important assets: (1) Mineralogy (and crystallography) have strong historical and theoretical roots in fundamental physics and chemistry; hence they should not be considered to be naturalistic or phenomenological sciences. (2) Mineralogy deals with all the relevant materials: natural minerals and their transformations by man, in short the materials surrounding us in everyday life. (3) Mineralogy investigates the distribution and properties of minerals in the Earth's crust as well as their availability as resources. Geochemistry, petrology and the survey of mineral deposits stemmed from the long tradition of mineralogical investigation of ore sources. (4) Mineralogy is well acquainted with the complexity of natural systems, commonly composed of a large number of chemical elements and several crystal-chemical phases. Therefore, it is technically equipped to face the methodological and experimental challenges involved in the analysis of complex materials, and in the interpretation of the processes acting upon them (Chiari, 2000; Artioli, 2010b). (5) Modern mineralogy routinely uses the full range of crystallographic techniques to explore the solid state. In many instances it is at the forefront of the analysis of complex materials, *e.g.* at non-ambient conditions. Therefore, mineralogy is well equipped to face intricate analytical problems related to production processes, weathering and conservation.

Mineralogy and crystallography clearly have the core knowledge and expertise that are fundamental to investigating issues in the field of cultural heritage (CH).

The boundaries of cultural heritage investigations cannot be defined easily (Chiari, 2000). They are commonly related to the field of archaeology (archaeometry, archaeological sciences) and to the field of conservation (conservation science, technical art history, authentication). The two areas are currently well distinguished in academia, in professional curricula and in their theoretical and methodological traditions. However, all those disciplines are concerned with the investigation of materials produced by past human activities. From an analytical point of view, artistic and archaeological materials should be investigated using the same scientific techniques and methods, although the primary questions to be answered and the objectives of the research may be quite different. As Chiari (2000) clearly and rightly stated, the material sampled during restoration interventions could well be studied from the archaeometric point of view, and archaeometric investigations are, of course, well suited to providing the scientific basis for proper conservation approaches.

The various participants in CH studies have very different backgrounds, sometimes very specialized, so that it is often difficult to overcome cultural gaps. It is therefore mandatory that scientists, archaeologists, art historians and conservators learn how to interact efficiently when dealing with the cultural heritage (Fig. 3). Indeed, the hyper-specialization of modern academia does not favour interaction. Sometimes the language codes and semantic values of the terms used in the different disciplines are so different that a discussion itself is nearly impossible or, at best, very difficult.

Pollard and Bray (2007) recall the general perception of scientists, who often feel that it is easier to teach the fundamentals of archaeology to a student in physics or chemistry (or mineralogy, may we add), in order to bring him or her to a sufficient level of understanding of the problems to be confronted at the experimental level, than to teach physics and chemistry to an archaeologist. Of course we can quote alternative experiences, where excellent archaeology students started to follow with great success scientific courses in order to reach a deep understanding of the materials investigated, whereas science-based students never quite grasped the anthropological, archaeological or social consequences of their scientific data. Nonetheless, the lesson to be kept in mind is that cultural heritage is a truly interdisciplinary field. Patience, willingness to listen to other people's points of view, and the flexibility to change long-trusted assumptions and protocols are crucial for a fruitful collaboration.

Scientific hyper-specialization has often been welcomed as the sign of increased competence and a sound way to progress. However, the amount of information required by each specific discipline is so vast, that it can hardly be grasped competently by single researchers. Nowadays, computers, databases and networking can greatly facilitate knowledge acquisition, retrieval and exchange. Unfortunately, disciplines perceived as devoted to natural sciences and classification are going out of fashion because some may think that their knowledge, if needed, can be retrieved easily from databases.

This is not the right way to go. What we need in CH studies is an appropriate training in critical investigation and a deep understanding of how to relate the data observed to the problems at hand. The real problem facing cultural heritage is not 'mineralogy or not mineralogy' .... The real problem is to find a person who: (1) is able to deal with natural and man-made materials; (2) is well trained in terms of characterization

Figure 3. Appropriate positive and intense interaction between all players involved in the analysis and management of cultural heritage is mandatory.

techniques; (3) knows the basics of statistics and mathematical treatment of data; and (4) is able to translate complex problems into analytical strategies and to interpret the experimental observations correctly in order to reconstruct the whole picture.

All scientific disciplines can contribute to solving cultural heritage issues, provided that the problems and questions are well posed. The real problem is to avoid the syndrome of the "friendly scientist" (Chiari, 2000), who thinks that he or she can solve any problem by using the fistful of techniques he or she has mastered (*i.e.* the "scientist without parachute", according to the metaphor of Pollard and Bray, 2007). In public lectures, we often quote the honest archaeologist handing a piece of pottery to a mineralogist and petrologist friend (then getting XRD-XRF-OM data back), or to a chemist friend (getting FTIR-Raman data back) or to a physicist friend (getting TEM-XPS data back). Of course each friend will use the techniques with which he is best acquainted, those that are readily available in his laboratory, or the cheapest/easiest ones to apply. If the "friendly scientist" is not an expert in the problem under investigation, the answer will be trivial irrespective of the technique adopted and in most cases it will offer poor information (Fig. 4).

In order to solve a complex problem properly, the competent scientist should be able to select the most appropriate techniques, optimize sampling, methodologies, and measurement protocols according to the material and the questions being asked, and interpret the results rigorously and stringently. To fulfil these conditions, the 'modern mineralogist' should be acquainted with mineralogy and the traditional experimental techniques, such as X-ray diffraction and optical microscopy. However, he/she should also extend his/her mineralogical background to industrial products and synthetic

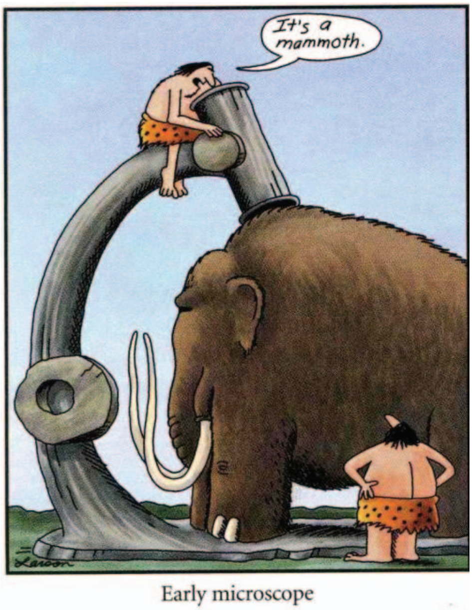

Figure 4. Poor technical choice is bound to provide a trivial answer (from Gary Larson's *Far Side*, retrieved from www.pinterest.ca/pin/321585229621926143/).

systems, including phase transformations and the physical properties of manufactured materials (Rapp, 2009). Many of these topics are commonly treated in the area of applied mineralogy or applied petrology. An updated knowledge of modern physical and chemical techniques for the investigation of matter (microscopy, imaging, spectroscopy) is also fundamental to improve the characterization of CH materials (Janssens and Van Grieken, 2004). Thefore, the solid crystallographic and crystal-chemical backgrounds of mineralogists are commonly an advantage. Knowledge of advanced techniques should include the proficient use of large-scale facilities, such as those providing brilliant electromagnetic radiation (synchrotrons, free-electron lasers) and neutron beams (nuclear reactors, spallation sources) (Kockelmann *et al.*, 2006; Creagh and Bradley, 2007; Bertrand *et al.*, 2012; Mannes *et al.*, 2015). These are commonly treated in courses of solid-state physics and analytical chemistry. Finally, a solid background in data treatment and statistics is also crucial nowadays.

The conscientious mineralogist approaching this field must also be aware of the fact that the material to be investigated is only the interface between scientific analysis and a more general approach to cultural heritage problems. To avoid producing trivial answers (as in Fig. 4), the material investigated needs to be inserted into a "big picture" (Chiari, 2000) and used to answer well defined questions. The work which follows must be conducted with continuous and intense confrontation with the humanistic collaborators, and must produce reciprocal understanding and mutual improvements. To sum up, a multidisciplinary investigation ought to share: (a) common targets, (b) common language, and (c) reciprocal respect and intellectual equilibrium.

There is a constantly increasing attendance of scientists at archaeological and conservation workshops and conferences, but unfortunately we cannot say the same for the attendance of archaeologists and conservators at scientific meetings. Even the attendences at International Symposia of Archaeometry (www.ims.demokritos.gr/ISA/), which ought to be natural fora for innovative applications and fruitful discussions between archaeologists and scientists, are weighted heavily towards scientists.

2. The materials of cultural heritage

The ultimate aim of the scientific investigation of CH artefacts is to relate them to human life and history. Most people visiting an archaeological museum or an art exhibition enjoy a more complete experience if the object is not only valued for its aesthetic appeal, but is also immersed in its context, so that its origin, practical use and anthropological/social meaning can be appreciated readily.

We can consider this process as the insertion of a given artefact into the time-line of its thermodynamic evolution (*e.g.* fig. 1 in Artioli and Angelini, 2011).

Any change in the physical state of the material, starting from production of the specimen from the raw geological/mineralogical sources through manufacturing, diffusion through trade and use, and ending with the deployment in the archaeological record. Even the archaeological excavation itself causes sudden changes to the thermodynamic equilibrium of the material. Chemical-physical reactions are therefore triggered in an attempt to bring the material back to the ground state. Conservation treatments cannot stop these thermodynamically driven processes, they can hope only to slow down their kinetics and extend the lifetime of the object.

Any information provided by scientific investigation will increase our knowledge of the object. Also, scholar competence will be expanded, the general context of production, use and distribution of the material/object will be better defined, and as a consequence public awareness and acceptance will be expanded as well.

In CH studies, various participants often have a very different perception of the materials. Most scientists generally have a good perception of the physicochemical aspects of the material at the atomic and molecular scale (nano- and micro-scale). Some also have a correct vision of the structure and texture of the material at the meso-scale. Some others only have a macroscopic perception of the material. The choice of the spatial scale of investigation is a critical point in understanding the object as a whole. Bear in mind that the various analytical techniques operate at very different space-time-energy scales. Appropriate analytical strategies should follow.

It is not appropriate to recall here all the issues involved in the investigation of CH materials. In many cases the parameters controlling the type and mode of the experimental investigations to be designed are critically linked to the following choices:

- Whether the measurements can be carried out in specialized laboratories (Laboratory work), either by sampling the object or by moving it to the laboratory, or the measurements are to be carried out in the field (Field work, *in situ* measurements), *e.g.* during archaeological excavations or when non-movable objects such as large architectural components or precious museum items are to be analysed.
- The qualitative *vs.* the quantitative character of the results. Very often the non-invasive character of the investigation as well as the limited time/funding available for the analysis imply that the quantitative information obtained is limited.
- The quantity of sample that can be extracted for the analysis may vary from none to a substantial amount. This imposes severe constraints on the techniques that can be adopted for the investigation. The quantity of sample investigated often determines whether or not the results are representative.

Nowadays, the rapid development of portable instrumentation for diffraction, spectroscopy and imaging has created enormous expectations in the CH community. Many curators, museum managers, archaeologists and even some scientists are increasingly convinced that a sufficient amount of information can be obtained quickly with reasonably cheap instruments, operated by specialists or even by non-specialists. This is of course true in many fields, where portable instruments can indeed provide appropriate data. However, it is important (albeit difficult) to convey the concept that measurements can be done on the same material/object in many different ways but with very different precision and accuracy. For example, measuring the chemical composition of a given material in the field with a portable X-ray fluorescence spectrometer (pXRF), or using the same instrument in the laboratory, or using conceptually different probes (such as mass spectrometry or optical emission spectroscopy) is expected to provide different results. As scientists, we should be aware of this issue but this is a concept not always shared by all counterparts. As an example, recently the authors made a proposal for micro-sampling metal objects for lead isotope analysis and provenance investigations which was rejected by the (in)competent authorities, because their view was that the analysis should be done by non-invasive pXRF analysis. Should we write in each proposal that XRF cannot measure isotopic ratios because of the physical nature of the signal?

To sum up, the study of CH materials is strongly interdisciplinary, and must be carried out by competent people in a complex network of collaboration. Indeed the scientific investigation of cultural heritage is a very privileged area where different disciplines may interact efficiently and evolve jointly. Because mineralogists broadly have the correct time-space-energy perception of materials, they ought to be given a relevant role in the team.

The chapters collected in the present volume, of necessity, show only a selection of examples of the mineralogical applications to CH. Natural minerals and rocks (silica, obsidian, lithics, gems, pigments) used by man in antiquity for different purposes are described, as well as their transformation products to provide fundamental man-made materials (glass, mortars, metals, ceramics).

A recent comprehensive survey (López Varela, 2018) encompasses a wider variety of other important mineral materials, such as those produced by normal or pathological bio-mineralization (Mann, 2001). Iron oxides produced by bacterial activity, amber resulting from the diagenesis of plant resins, carbonates bio-synthesized by corals and shells are all examples of biologically produced materials that have been employed by humans in the past for tools and decorations, or transformed into usable compounds, though they are not fully reviewed in the present volume.

Apatite-related minerals (Harlov and Rakovan, 2015) present in bones and teeth of vertebrates are especially important because of their implication for medicine, forensic science, anthropology, palaeontology and archaeology (White and Folkens, 2005). The mineralogical investigation of the mechanisms of hydroxylapatite crystallization and the detailed understanding of the transformations occurring after the death of the organism (Hedges, 2002; Kendall *et al.*, 2018) represent yet another example of the relevant contribution of mineralogy to modern CH. Recent advances in the mineralogical characterization of modern and fossil bones include the spectroscopic assessment of the microstructural evolution of carbonated hydroxylapatite during diagenesis, burial and cremation (Keenan, 2016; Dal Sasso *et al.*, 2018a,b; Mamede *et al.*, 2018). Notwithstanding our efforts, these studies could not be included in the present volume.

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