

Preface

Mineral reactivity: from biomineralization and Earth's climate evolution, to CO₂ capture and monument conservation

Mineral reactivity is central to all geochemical processes. It controls a wide range of processes important in Earth sciences and industry, including rock weathering and soil formation, nutrient availability, biomineralization, the aqueous durability of nuclear waste materials, CO₂ capture and storage, acid mine drainage (AMD) and toxic element sequestration, and the decay and preservation of stone-based cultural heritage. Each of these processes, and its kinetics, is governed by the reactions of minerals in the presence of fluids. In the last decades, much research has been devoted to increase our understanding of the dynamic reactions involving minerals and fluids such as dissolution, growth, and mineral replacement processes. This has been approached by using mostly state-of-the-art spectroscopic and microscopic techniques, complemented by molecular simulations to confirm or predict the results of the experimental studies. In particular, the development of advanced analytical methods that allow direct observations of mineral reactions at the nanoscale while reacting in aqueous fluids have revealed new and significant aspects of the kinetics and mechanisms of reactions taking place in fundamental mineral–fluid systems. These experimental and computational studies have greatly enhanced our ability to decipher and predict the mechanisms governing mineral–fluid reactions as well as the kinetics of these processes.

In this context and realising the need for discussion between scientists active in these fields, the first Granada–Münster discussion meeting (GMDM) was born in 2013, as a result of the on-going collaborations between the Institut für Mineralogie of the University of Münster (Germany) and the University of Granada (Spain), with the aim of promoting progress on key issues in fluid–mineral interactions, through presentations and open-forum discussions. Since then, the meeting has been organized every year in Münster and Granada alternately, gaining international reputation. Presentations typically include studies on natural samples, experiments, and computer modelling. The host of the upcoming 7th GMDM will be again Granada in the autumn of 2019. Following tradition, the program will include short talks and plenty of time for discussion, as well as social events, when research can be discussed in a friendly atmosphere. Past meetings have shown that this approach is excellent for furthering new concepts as well as forming new collaborations.

This special issue contains a selection of contributions derived from the 5th GMDM on mineral reactivity. The meeting was held in Granada between November 30 and December 1, 2017. In that year, the Research Excellence Unit of the University of Granada named “Carbonates: from biomineralization and Earth's climate evolution to CO₂ capture and built heritage conservation” was established, and the 5th GMDM benefited from funding from this unit, which gave a definitive boost in the international relevance of the meeting among researchers working on different aspects of fluid–mineral interactions. Twenty-six talks were then presented during two days of conference sessions. The meeting provided an opportunity to welcome to Granada close to 50 participants from eleven different countries. In keeping with the diverse character of the meeting, presentations covered a spectrum of themes all connected by the common link of mineral reactivity. Talks dealt with experimental studies on non-classical nucleation and growth processes and mineral dissolution, simulations and computational studies of crystal and glass surfaces, solid solution–aqueous solution systems, different aspects of biomineralization, mineral hydration and carbonation, and built heritage conservation. The papers contained in this issue are a representation of this thematic diversity.

Biomineralization and biomimetic mineral formation has been one of the dominant topics of the previous GMDM meetings. In this issue, Dominguez-Gasca et al. study the chemical and structural changes occurring during demineralization of different avian bone types using optical and electron microscopy, 2D X-ray diffraction, and infrared spectroscopy. They find that both differences in crystallinity and the organic matrix composition and its structural relationship with the bone mineral are responsible for the large differences found in the solubility of cortical and medullary bones. In relation to this, Nindiyasari et al. present a biomimetic study of calcite growth in a hydrogel matrix, in which they evaluate the effect of Mg²⁺ in the mechanical parameters of different hydrogels and its relationship to the amount of gel incorporated by the growing crystals and the associated misorientations observed. Magnesium not only influences the organization of the mineral component within the aggregate but also the fabric of the occluded gel matrix. These types of biomimetic studies are

fundamental for the advancement of our understanding of natural biomineralization processes and the design of new biomimetic materials with enhanced functional properties. Finally, Avaro et al. report on a novel, simple and scalable method for the synthesis of impurity-free amorphous calcium carbonate (ACC, one of the main precursor phases for carbonate biominerals) nanoparticles, that often presents significant problems due to the instability of this phase and its rapid transformation into crystalline phases. This study is of relevance for improving the applicability of ACC in pharmaceutical and medical domains.

Mineral–fluid interactions are also critical in the control of key environmental problems, such as nuclear waste disposal, AMD, including mining-induced toxic element mobilization or CO₂ capture and storage. In this issue, Cruz-Hernandez et al. evaluate the effect of As(V) on the kinetics of schwertmannite (a poorly crystalline Fe oxyhydroxysulfate) precipitation and its transformation into goethite. This precipitate is commonly found in riverbeds affected by AMD, one of the main causes of water pollution worldwide. Its formation exerts an important control on the mobility of As and other toxic elements in waters contaminated by AMD due to the high capacity of schwertmannite to sequester As and other toxic elements. Schwertmannite precipitation is inhibited by As, and it is shown how its transformation into goethite results in sulfate release and, over longer times, also As. The contribution by Curti et al. focuses on the modelling of Ra-bearing baryte precipitation within a porous medium similar to altered nuclear waste glass. Baryte plays a critical role in the safety assessment of planned disposal sites for nuclear waste, as Ba and Ra released from nuclear wastes have the potential to react with sulphate-rich pore water resulting in the formation of Ra-bearing baryte. The precipitation of this phase is thus fundamental for the mobility of this radioactive element. However, the nucleation of baryte has a complex kinetic behaviour, and even highly supersaturated solutions may remain metastable. The proposed model allows exploring the influence of baryte nucleation/precipitation kinetics on Ra partitioning between aqueous solutions and the precipitated baryte. The gained quantitative knowledge on the kinetics of baryte nucleation is essential to predict radionuclide release into the environment in nuclear waste repository systems. Cánovas et al. report on the influence of mineralogy and grain size of sulphide mine wastes from the Iberian Pyrite Belt. Processes that result in increased rock surface area are expected to enhance mineral reactivity and the associated release of toxic elements. These authors conclude that, although grain size is a major control of metal release from sulphide mine wastes, the key factor is the partitioning of highly soluble secondary minerals among the different grain size fractions. Finally, using ab initio calculations, Zhang et al. present a modelling study on the structure, energetics, dynamics and kinetics of Mg²⁺ (de)hydration, a fundamental controlling process in the nucleation and subsequent growth of Mg-carbonates. Magnesite, one of these Mg-carbonates, is a potential product of mineral carbonation strategies for capture and storage of atmospheric CO₂ of anthropogenic origin. Kinetic factors limit its formation under ambient conditions, and thus research on characterization and optimization of the fundamental aspects of magnesite precipitation is needed to increase the efficiency of mineral carbonation processes.

The study of the reactivity of minerals forming the materials present in the structure of historical buildings allows for the design of new methods for the protection and conservation of the historical-artistic heritage. In this respect, Ruiz-Agudo et al. present an experimental study of the replacement of gypsum by baryte in contact with aqueous solutions using both single crystals and polycrystalline porous materials. This process is of relevance for the design of treatments for the conservation of gypsum sculptures and plasterwork, as the formation of baryte layers on gypsum substrates can substantially increase their resistance against water and humidity while preserving the surface features of the original mineral substrate. These authors provide evidence suggesting that this process occurs via a fluid-mediated interface-coupled dissolution–precipitation mechanism, resulting in the formation of pseudomorphs. Moreover, it is found that the structure of the parent gypsum exerts a certain degree of crystallographic control on the precipitated BaSO₄ layer. In the final article of the series, Saenz et al. study the effects of additives (fly-ash, household glass and spent beer grain) on the chemical, mineralogical, textural and physical characteristics of fired bricks and the raw clay mixture. All additives seem to alter brick porosity and compactness, although bricks made with added glass were found to be the most compact and mechanically resistant, while those made with spent beer grain were the most porous and fragile. This study shows that waste materials can be used for the preparation of new bricks that may find applications both in new construction and as replacement material in the conservation of the built heritage.

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Contributions (alphabetical)

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