

Editorial

# Editorial for Special Issue “Mineral Surface Reactions at the Nanoscale”

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**Abstract:** Reactions at mineral surfaces are central to all geochemical processes. As minerals comprise the rocks of the Earth, the processes occurring at the mineral–aqueous fluid interface control the evolution of the rocks and, hence, the structure of the crust of the Earth during such processes at metamorphism, metasomatism, and weathering. In recent years, focus has been concentrated on mineral surface reactions made possible through the development of advanced analytical techniques, such as atomic force microscopy (AFM), advanced electron microscopies (SEM and TEM), phase shift interferometry, confocal Raman spectroscopy, advanced synchrotron-based applications, complemented by molecular simulations, to confirm or predict the results of experimental studies. In particular, the development of analytical methods that allow direct observations of mineral–fluid reactions at the nanoscale 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 enabled new and exciting possibilities to elucidate the mechanisms that govern mineral–fluid reactions, as well as the kinetics of these processes, and, hence, to enhance our ability to predict potential mineral behavior. In this Special Issue “Mineral Surface Reactions at the Nanoscale”, we present 12 contributions that highlight the role and importance of mineral surfaces in varying fields of research.

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When a mineral comes into contact with an aqueous solution, the mineral is out of equilibrium and so will start to dissolve. As a mineral surface has a complex energy landscape of steps and kinks, mineral dissolution is now known to be a process dominated by a spectrum of dissolution rates over a continuously changing surface. In their article, “Temporal Evolution of Calcite Surface Dissolution Kinetics”, Bibi et al. [1] quantify the kinetics of dissolution on a calcite surface using vertical scanning interferometry that allows 3D imaging of a changing mineral surface during the reaction, resulting in a temporal evolution of a calcite surface and presenting insights into the role of various surface components during dissolution.

If an aqueous solution is supersaturated with respect to a mineral phase, that phase may precipitate, that is, a mineral grows from a supersaturated solution. Crystal growth has been studied continuously for well over a century, but it is only in recent times that the classical mechanisms of crystal growth have been questioned and new concepts developed of non-classical nucleation, that challenge existing concepts of mineral growth [2]. In the article, “How can Additives Control the Early Stages of Mineralization”, Denis Gebauer [3] presents an overview, as well as new observations, on the interaction of additive molecules and potential mineral precursor species at the mineral–fluid interface.

Historically, mineral dissolution and growth thermodynamics and kinetics have been investigated separately. However, there is increasing evidence that in the Earth, dissolution is often accompanied by the growth of a new phase [4]. The feedback mechanisms involved in this coupled dissolution–precipitation scenario present interesting and important information for the understanding of Earth processes, as well as enabling conditions to be determined for the control of crystal growth

through replacement reactions, to enable potential environmental remediation strategies, as well as the design of preferential crystal growth. Several articles focus on the coupling of dissolution and precipitation at the mineral–fluid interface. Toxic elements may be sequestered into a more stable phase through this coupled process. Hövelmann et al. [5] describe AFM experiments where potentially polluting heavy metal ions, released from industrial processes, are precipitated in a new phase on a brucite  $\text{Mg}(\text{OH})_2$  surface. Direct in situ observations allow the elucidation of the reaction mechanism. Such experimental research can be complemented by molecular dynamics simulations, as described in the article by Garcia et al. [6], “Water Structure, Dynamics and Ion Adsorption at the Aqueous {010} Brushite Surface”. A computational approach to the understanding of mineral–surface reactions can also predict and confirm experimental observations.

Di Lorenzo et al. [7] present a mineral carbonation process as a potential mechanism for  $\text{CO}_2$  sequestration in their article “The Carbonation of Wollastonite: A Model Reaction to Test Natural and Biomimetic Catalysts for Enhanced  $\text{CO}_2$  Sequestration”. With ever-increasing amounts of  $\text{CO}_2$  in the atmosphere, as a result of anthropogenic activities, it is essential to explore possible sequestration methods, and the formation of stable carbonate minerals is one potential solution. Other contributions also explore coupled reactions at the mineral–fluid interface in terms of potential element sequestration or immobilization of pollutants, such as phosphate by Wang et al. [8] or rare earth elements by Fei et al. [9].

The identification of mineral surface processes is further explored by Silva-Quñones et al. [10] using polarization microscopy and X-ray photoelectron spectroscopy (XPS). The effective and efficient extraction of metals from ores requires knowledge of the changes occurring at mineral surfaces during ore processing. It is only by understanding mineral surface reactions that industrial processes can be more energy efficient as well as effective for successful ore treatment. In this case, advanced analytical techniques are employed. King and Geisler [11] in “Tracing Mineral Reactions using Confocal Raman Spectroscopy” present a review of the increasing use of Raman spectroscopy together with isotope tracing to identify phases at the mineral–fluid interface during coupled reactions.

Detailed micro-structural evidence is presented by Greiner et al. [12] to introduce biomineral reactivity during the fluid-mediated replacement of biological aragonite (in bivalve, coral, and cuttlebone skeletons) to apatite (the mineral of bone material). This is a pseudomorphic replacement as a result of a tight interface-coupled dissolution–precipitation process. The authors emphasize the formation of porosity during the replacement process, allowing for the infiltration of fluid within the parent aragonite. The development of porosity has been recognized as an essential feature of an interface-coupled dissolution–precipitation process [13].

Albite is a common rock-forming mineral. During metasomatic processes, such as weathering, albite is replaced by other Na-bearing minerals. In natural and experimental samples, the replacement of albite by Na-rich secondary phases, such as sodalite and nepheline, has been investigated by Drüppel and Wirth [14]. Their observations indicate that the replacement is formed by an interface-coupled dissolution–reprecipitation mechanism. Their results also add to the understanding of element mobility, including trace element mobilization, and; therefore, indicate important implications for the interpretation of mineral reactivity in the presence of a fluid phase.

The final contribution by Zhao and Pring [15] presents an overview of the replacement of gold-(silver) telluride minerals that form a significant part of important gold-containing deposits across the world. Under hydrothermal conditions, gold-silver alloys replace the telluride minerals. Experiments highlight the replacement process and detailed textural analysis of the product phases allows for an interpretation of the reaction mechanism.

All the contributions in this special issue of *Minerals* are connected by mineral surface reactions at the nanoscale and as such indicate the importance of detailed and careful analysis of mineral surfaces before, during, and after reactions in aqueous fluids. The knowledge gained from interpretations of mineral surface reactivity spans a wide range of important Earth processes as well as potential

environmental remediation. The mechanism highlighted in these contributions, whereby one mineral phase is replaced by another more stable phase, is interface-coupled dissolution–precipitation.

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## References

1. Bibi, I.; Arvidson, R.S.; Fischer, C.; Luttge, A. Temporal evolution of calcite surface dissolution kinetics. *Minerals* **2018**, *8*, 256. [[CrossRef](#)]
2. Gebauer, D.; Kellermeier, M.; Gale, J.D.; Bergström, L.; Cölfen, H. Pre-nucleation clusters as solute precursors in crystallization. *Chem. Soc. Rev.* **2014**, *43*, 2348. [[CrossRef](#)] [[PubMed](#)]
3. Gebauer, D. How can additives control the early stages of mineralization. *Minerals* **2018**, *8*, 179. [[CrossRef](#)]
4. Ruiz-Agudo, E.; Putnis, C.V.; Putnis, A. Coupled dissolution and precipitation at mineral-fluid interfaces. *Chem. Geol.* **2014**, *383*, 132–146. [[CrossRef](#)]
5. Hövelmann, J.; Putnis, C.V.; Benning, L.G. Metal sequestration through coupled dissolution-precipitation at the brucite-water interface. *Minerals* **2018**, *8*, 346. [[CrossRef](#)]
6. Garcia, N.A.; Raiteri, P.; Vlieg, E.; Gale, J.G. Water structure, dynamics and ion adsorption at the aqueous {010} brushite surface. *Minerals* **2018**, *8*, 334. [[CrossRef](#)]
7. Di Lorenzo, F.; Ruiz-Agudo, C.; Ibañez-Velasco, A.; Gil-Sian Millán, R.; Navarro, J.A.R.; Ruiz-Agudo, E.; Rodríguez-Navarro, C. The carbonation of wollastonite: A model reaction to test natural and biomimetic catalysts for enhanced CO<sub>2</sub> sequestration. *Minerals* **2018**, *8*, 209. [[CrossRef](#)]
8. Wang, L.; Putnis, C.V.; Hövelmann, J.; Putnis, A. Interfacial precipitation of phosphate on hematite and goethite. *Minerals* **2018**, *8*, 207. [[CrossRef](#)]
9. Fei, Y.; Hua, J.; Liu, C.; Li, F.; Zhu, Z.; Xiao, T.; Chen, M.; Gao, T.; Wei, Z.; Hao, L. Aqueous Fe(II)-induced phase transformation of ferrihydrite coupled adsorption/immobilization of rare earth elements. *Minerals* **2018**, *8*, 357. [[CrossRef](#)]
10. Silva-Quiñones, D.; He, C.; Jacome-Collazos, M.; Benndorf, C.; Teplyakov, A.V.; Rodríguez-Reyes, J.C.F. Identification of surface processes in individual minerals of a complex ore through the analysis of polished sections using polarization microscopy and X-ray photoelectron spectroscopy (XPS). *Minerals* **2018**, *8*, 427. [[CrossRef](#)]
11. King, H.E.; Geisler, T. Tracing mineral reactions using confocal Raman spectroscopy. *Minerals* **2018**, *8*, 158. [[CrossRef](#)]
12. Greiner, M.; Fernández-Díaz, L.; Griesshaber, E.; Zenkert, M.N.; Yin, X.; Ziegler, A.; Veintemillas-Verdaguer, S.; Schmahl, W.W. Biomineral reactivity: The kinetics of the replacement reaction of biological aragonite to apatite. *Minerals* **2018**, *8*, 315. [[CrossRef](#)]
13. Putnis, A.; Putnis, C.V. The mechanism of reequilibration of solids in the presence of a fluid phase. *J. Solid State Chem.* **2007**, *180*, 1783–1786. [[CrossRef](#)]
14. Drüppel, K.; Wirth, R. Metasomatic replacement of albite in nature and experiments. *Minerals* **2018**, *8*, 214. [[CrossRef](#)]
15. Zhao, J.; Pring, A. Mineral transformations in gold-(silver) tellurides in the presence of fluids: Nature and experiment. *Minerals* **2019**, *9*, 167. [[CrossRef](#)]

