

Editorial

Editorial for Special Issue “Formation of Sulfate Minerals in Natural and Industrial Environments”

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Sulfate is abundant in the environment and, as a result, sulfate-containing minerals constitute a large and important focus of research [1–3]. These minerals play an important role in many geochemical and industrial processes, including the sulfur cycle, the construction industry (e.g., plaster of Paris), fault tectonics, acid mine drainage, and even rare biominerals [4]. Important to note are the abundant amounts of sulfate (minerals) located on the surface of Mars [5], and in meteorites [6], extending the relevance of this mineral group beyond the realm of our planet. In geological systems, sulfate minerals such as barite are also important for indicating certain sedimentation environments. In this regard, sulfate deposits can be used to evaluate the redox state of ancient oceans during early Earth time periods [7].

This Special Issue gathers a collection of studies that represent the broad spectrum of instances where different types of sulfate minerals play a key role in scientific processes. In particular, calcium sulfate phases (e.g., gypsum, bassanite, and anhydrite) are the most widespread in the considered group [3], acting as important sulfur sinks and serving as indicators of past environmental conditions on Earth and beyond. Various products relying on the crystallization of calcium sulfate minerals have been employed since antiquity, and today they are an essential part of a wide array of industrial (such as plaster, grout, mortar, and cement production) and cultural applications. Gypsum is also famous for growing into giant crystals that are many meters in length, captivating the imagination of scientists and enthusiasts alike. Importantly, these giant crystals constitute a unique “natural laboratory” for studying crystallization processes spanning many length and time scales. A detailed review on the giant crystals from Naica is presented in this volume by Carreño-Márquez and coworkers [8]. In this contribution, the authors present a description of the Naica Mine setting, where these crystals were discovered, and a state-of-the-art summary on the thermodynamic conditions favoring the crystals’ growth, and the associated kinetic aspects. In addition, they also explore the scenarios for possible deterioration. Giant crystals are a stark example of how atomic-scale mechanisms manifest themselves at macroscopic lengths. This nano-to-macro aspect, related to CaSO₄, is further explored by Reiss et al. in [9], where a thermodynamic modelling approach to calcium sulfate crystallization is explored in addition to current experimental observations. This is undertaken with an emphasis on high-salinity environments, i.e., brines, and is thus relevant for industrial and geological settings on Earth (e.g., the Dead Sea), and other planets such as Mars. Consequently, this comprehensive review synergizes the interplay of physicochemical conditions (ionic strength, brine composition, etc.), nucleation and growth mechanisms, and the resulting calcium sulfate crystal morphologies and size distributions. The nucleation and growth processes from solutions of calcium sulfate are also experimentally studied in detail in [10]. In this valuable contribution, the authors demonstrate the importance of small contamination particles (nm to microns), which drive the nucleation of gypsum,



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and whose presence is rarely, if ever, considered. This paper highlights the complexity of solution-based growth phenomena in sulfates, and clearly links to [8,9].

Calcium sulfate, as well as other sulfate minerals, are ubiquitous in anthropogenic environments in which they constitute useful resources, general waste, or disadvantageous residues such as scale. In all cases, interactions with the environment need to be investigated and often mitigated. These aspects again clearly link to the fundamental nucleation and growth processes, but also contain a socioeconomic perspective. This interplay is well illustrated by Gázquez et al. in [11]; the authors reviewed the evolution of waste management policies related to TiO_2 production, in which gypsum and several iron sulfate minerals are formed as useful byproducts. This shows how those minerals have become recyclable and are used in cement production and agriculture while complying with ever stricter environmental policies. Commercial use was developed based on the physicochemical and mineralogical characterization of precipitated sulfates. This highlights how fundamental aspects of mineral research are essential for an effective circular economy. In a similar context, Weimann et al. in [12] assessed the relevance of recycling gypsum from construction waste. The evaluation was based on data provided by the industry, and considered the transportation distance and associated carbon emissions as the major factors for determining the feasibility of recycling. The authors concluded that construction gypsum recycling is environmentally beneficial in comparison with natural and coal-fired power plant gypsum, especially in connection with land transformation and resource consumption.

Considering the environment–industry interface regarding waste management, sulfates constitute important immobilization storage materials which can prevent the proliferation of harmful substances. This is studied in [13], in which the authors model a reactive transport system associated with the immobilization of uranium by gypsum, jarosite and other sulfate minerals in mill tailings from the Cominak mine (Nigeria). The model indicated that immobilization is likely due to a high solubility uranyl-sulfate which transforms into more stable uranyl-phosphate phases. Another example of how sulfates can immobilize potentially dangerous elements is discussed by Brandt and colleagues [14]. This article considers the uptake of ^{226}Ra in (Ba,Sr) sulfate solid solutions, combining experiments with thermodynamic simulations. This study was motivated by the fact that this solid solution often occurs in natural systems. The authors discovered a complex immobilization pathway involving the dissolution of $(\text{Ba,Sr})\text{SO}_4$ and the formation of metastable phases. As such, this study links nano-scale aspects of sulfate geochemistry with their potential application for waste management. In many human activities, the formation of sulfate minerals is a common nuisance; in engineered environments they form difficult-to-remove scales, thereby decreasing efficiency and increasing operational costs. This includes desalination units, oil production, and hydrothermal systems. This is discussed by Tranter et al. [15], who assessed the scaling potential of barite (BaSO_4) in fractured–porous reservoir rocks located in the Upper Rhine Graben, using a numerical model. They observed *in silico* that fractures significantly reduced the negative impact of the scale formation. This article highlights the interactions of sulfate minerals with the geological environment at truly large length scales.

Although the mineralogy of sulfates has been extensively studied, not all phases are known or understood in detail, and therefore further research efforts are still required. This is especially true for conditions related to human activities and so-called anthropogenic minerals [16]. Complex mixtures of anhydrous sulfates can crystallize, for instance, in coal-burning heaps such as those found in Silesia, Poland. Such hostile environments are poorly understood and, to a certain extent, resemble volcanic conditions. However, some of the formed compounds do not have purely geological equivalents. Interestingly, such sulfates form without any presence of water; however, one may assume that, as the heaps cool down, the interactions at the water–solid interface could lead to new and potentially complex processes.

In summary, the present collection of articles gives a comprehensive overview of the wide range of natural and engineered processes in which sulfate minerals play a decisive role. Given the abundance of sulfate minerals on Earth and beyond, understanding the formation and interaction of these minerals with their surroundings is of utmost importance to better comprehend the past, present, and future evolution of our environment. As such, this Special Issue has contributed to advancements in the field.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Brimblecombe, P. 10.14—The Global Sulfur Cycle. In *Treatise on Geochemistry*, 2nd ed.; Holland, H.D., Turekian, K.K., Eds.; Elsevier: Oxford, UK, 2014; pp. 559–591, ISBN 978-0-08-098300-4.
2. Patrick, R.A.D. C.N. Alpers, J.L. Jambor and D.K. Nordstrom (Eds) Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance. Washington, D.C. (Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 40). 2000, Xiv + 608 pp. Price \$32. ISBN 0 939950 52 9. *Mineral. Mag.* **2001**, *65*, 817–818. [[CrossRef](#)]
3. Van Driessche, A.E.S.; Stawski, T.M.; Kellermeier, M. Calcium Sulfate Precipitation Pathways in Natural and Engineered Environments. *Chem. Geol.* **2019**, *530*, 119274. [[CrossRef](#)]
4. Bosselmann, F.; Epple, M. Sulfate-Containing Biominerals. *Met. Ions Life Sci.* **2008**, *4*, 207–217.
5. King, P.L.; McLennan, S.M. Sulfur on Mars. *Elements* **2010**, *6*, 107–112. [[CrossRef](#)]
6. McSween, H.Y. On the Nature and Origin of Isolated Olivine Grains in Carbonaceous Chondrites. *Geochim. Cosmochim. Acta* **1977**, *41*, 411–418. [[CrossRef](#)]
7. Huston, D.L.; Logan, G.A. Barite, BIFs and bugs: Evidence for the evolution of the Earth's early hydrosphere. *Earth Planet. Sci. Lett.* **2004**, *220*, 41–55. [[CrossRef](#)]
8. Carreño-Márquez, I.J.A.; Castillo-Sandoval, I.; Pérez-Cázares, B.E.; Fuentes-Cobas, L.E.; Esparza-Ponce, H.E.; Menéndez-Méndez, E.; Fuentes-Montero, M.E.; Montero-Cabrera, M.E. Evolution of the Astonishing Naica Giant Crystals in Chihuahua, Mexico. *Minerals* **2021**, *11*, 292. [[CrossRef](#)]
9. Reiss, A.G.; Gavrieli, I.; Rosenberg, Y.O.; Reznik, I.J.; Lutge, A.; Emmanuel, S.; Ganor, J. Gypsum Precipitation under Saline Conditions: Thermodynamics, Kinetics, Morphology, and Size Distribution. *Minerals* **2021**, *11*, 141. [[CrossRef](#)]
10. Oshchepkov, M.; Popov, K.; Kovalenko, A.; Redchuk, A.; Dikareva, J.; Pochitalkina, I. Initial Stages of Gypsum Nucleation: The Role of "Nano/Microdust". *Minerals* **2020**, *10*, 1083. [[CrossRef](#)]
11. Gázquez, M.J.; Contreras, M.; Pérez-Moreno, S.M.; Guerrero, J.L.; Casas-Ruiz, M.; Bolívar, J.P. A Review of the Commercial Uses of Sulphate Minerals from the Titanium Dioxide Pigment Industry: The Case of Huelva (Spain). *Minerals* **2021**, *11*, 575. [[CrossRef](#)]
12. Weimann, K.; Adam, C.; Buchert, M.; Sutter, J. Environmental Evaluation of Gypsum Plasterboard Recycling. *Minerals* **2021**, *11*, 101. [[CrossRef](#)]
13. Seigneur, N.; De Windt, L.; Déjeant, A.; Lagneau, V.; Descostes, M. Long-Term Evolution of Uranium Mobility within Sulfated Mill Tailings in Arid Regions: A Reactive Transport Study. *Minerals* **2021**, *11*, 1201. [[CrossRef](#)]
14. Brandt, F.; Klinkenberg, M.; Poonosamy, J.; Bosbach, D. Recrystallization and Uptake of ²²⁶Ra into Ba-Rich (Ba,Sr)SO₄ Solid Solutions. *Minerals* **2020**, *10*, 812. [[CrossRef](#)]
15. Tranter, M.; De Lucia, M.; Kühn, M. Barite Scaling Potential Modelled for Fractured-Porous Geothermal Reservoirs. *Minerals* **2021**, *11*, 1198. [[CrossRef](#)]
16. Parafiniuk, J.; Siuda, R. High Temperature Sulfate Minerals Forming on the Burning Coal Dumps from Upper Silesia, Poland. *Minerals* **2021**, *11*, 228. [[CrossRef](#)]