

Editorial

# Editorial for Special Issue “Nucleation of Minerals: Precursors, Intermediates and Their Use in Materials Chemistry”

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Nucleation is the key event in mineralization, but a general molecular understanding of phase separation mechanisms is still missing, despite more than 100 years of research in this field [1]. In the recent years, many studies have highlighted the occurrence of precursors and intermediates, which seem to challenge the assumptions underlying classical theories of nucleation and growth. This is especially true for the field of biomineralization, where bio-inspired strategies take advantage of the precursors' and intermediates' special properties for the generation of advanced materials. All of this has led to the development of “non-classical” frameworks, which, however, often lack quantitative expressions for the evaluation and prediction of phase separation, growth and ripening processes, and are under considerable debate. It is, thus, evident that there is a crucial need for research into the early stages of mineral nucleation and growth, designed for the testing, refinement and expansion of the different existing notions. This special issue of *Minerals* aimed to bring together corresponding studies from all these areas, dealing with precursors and intermediates in mineralization with the hope that it may contribute to the achievement of a better understanding of nucleation precursors and intermediates, and their target-oriented use in materials chemistry.

In his commentary, Evans [2] summarises different existing nucleation theories and discusses them from the point of view of biomineralization. The focus lies on proteins and their role in mineral precursor formation, stabilisation, and assembly into crystalline polymorphs. It is stressed that a limitation of the advancement of the understanding of protein-controlled mineralization processes [3] is, at least, partly due to variations in techniques, methodologies and the lack of standardisation in mineral assay experimentation. Evans argues that the protein community should adopt standardized nucleation assays [4,5], allowing for cross-comparisons and kinetic observations. Burgos-Cara et al. [6] use such an experimental approach for studying the effects of background ionic species on the formation and stability of  $\text{CaCO}_3$  pre-nucleation species in aqueous solutions. They find that the effective critical supersaturation in the presence of background ions with a decreasing ionic radius becomes systematically higher, and propose that the stabilisation of hydration water molecules impedes dehydration processes, which are essential steps during mineral precipitation, according to the notions of the so-called pre-nucleation cluster pathway [1].

Several papers of this *Minerals* special issue address further methodological aspects associated with research into mineral nucleation and growth. The contribution of Kröger and Verch [7] deals with studies employing liquid cell transmission electron microscopy (LCTEM). 2D finite element simulations highlight that the confinement, which occurs in typical LCTEM cells and can significantly reduce the concentration of available ions, can explain the necessity to substantially increase the supersaturation in LCTEM cells in order to induce precipitation. Zeng et al. [8] focus on another important microscopic technique for studying nucleation and self-assembly, in situ atomic force microscopy (AFM). They review the latest contributions in this field and also address the theoretical

background of AFM. Kuwahara et al. [9] use AFM for exploring the growth behaviour and kinetics of the barite (001) surface in supersaturated solutions, predicting a critical supersaturation, at which a 2D nucleation growth mechanism becomes important, significantly altering the crystal morphology. Harris and Wolf [10] focus on an experimental methodological issue, demonstrating that the desiccator size in commonly used vapor diffusion-based crystallisation assays can alter the crystallisation mechanism. This shows that a careful experimental design is required in order to identify and explore additive effects when this method is applied. Gebauer et al. [11] present a thorough investigation of a urinary stone of a guinea pig. The suggested role of amorphous calcium carbonate in pathological mineralization highlights that future studies of such stones should not be based on analytical techniques that are sensitive only to crystalline  $\text{CaCO}_3$ . Liquid [12] and amorphous mineral precursors can, in principle, be used to fill cavities, which may occur in historical artefacts or dental lesions. Gruber et al. [13] present a transparent, inexpensive, and reusable test system for the investigation of infiltration and crystallization processes by using a micro-comb test system. Ossorio et al. [14] perform synchrotron-based small- and wide-angle X-ray scattering to examine the precipitation of gypsum from solution, which occur via primary particles that aggregate and transform/re-organize towards the final precipitate, with and without the addition of  $\text{Mg}^{2+}$  and citrate. Self-assembly processes of alkaline earth carbonates in the presence of silica, on the other hand, produce a unique class of composite materials with complex morphologies, as studied by Opel et al. [15] (also see the cover page of this *Minerals* special issue). Trumpet- and coral-like structures form especially at an elevated temperature and in the presence of additional ions.

Several papers of this *Minerals* special issue deal with calcium phosphate—the most important biomineral for the human race. Pastero et al. [16] provide a review of the genetic mechanisms of apatite, paying close attention to the structural complexity of hydroxyapatite, the richness of its surfaces and their role in interactions with precursor phases regarding growth kinetics and morphology. Ibsen et al. [17] study the impact of pyrophosphate on apatite formation by synchrotron-based in situ X-ray diffraction, revealing a strong inhibition of apatite nucleation and growth. Ross et al. [18] investigate the possibility of precipitating carbonate apatite from municipal wastewater treatment plants, where a suggestive amorphous precursor transforms without changing morphology.

The transformation of aragonite into calcite by solid-state transformation is explored by Kezuka et al. [19], yielding fascinating, single-crystalline calcite needle-like particles with zigzag surface structures. Jones [20] studies the formation of jarosite–alunite solid solutions, finding a new spherical morphology of pure alunite. Notably, a distinct nucleation behaviour for jarosite and Fe-containing alunite is found, as the latter nucleates continuously rather than in a single event. Ochiai and Utsunomiya [21] investigate the crystal chemical properties of hydrous rare-earth phosphates, forming at an ambient temperature with fractions of an amorphous component with an increasing ionic radius. Finally, Bacsik et al. [22] demonstrate that amine– $\text{CO}_2$  chemistry, which is important for carbon dioxide capture, can be used to prepare amorphous calcium carbonate.

We hope that this special issue will contribute to a better understanding of nucleation and growth phenomena, and will serve as a resource and inspiration for future studies in this vibrant and topical field of research.

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