

New Insights into the Early Stages of Calcium Sulfate Formation

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In recent years, the picture of the emergence of a solid crystalline phase from a supersaturated solution of ions has changed substantially and is still being heavily debated. There is increasing evidence that stable solute clusters play a pivotal role at the very onset of phase separation (i.e. nucleation) and that subsequently, a series of intermediate stages – varying in terms of structure and degree of hydration – can occur before a stable crystalline material is obtained [1]. These may include dense (solvent-rich) liquid phases resulting from binodal or spinodal demixing [2], more or less hydrated amorphous nanoparticles, as well as metastable crystalline polymorphs [3]. While most of the above-mentioned studies have focused on prominent biominerals like calcium carbonates or phosphates [1], less is known about other important mineral systems, as for instance calcium sulfate, a major scale-forming compound and widely used building material, which moreover is abundant in geological environments. Indeed, it has been suggested that growth of gypsum (the stable polymorph) is preceded by the precipitation of nanocrystalline bassanite (an actually metastable phase) [4] and/or certain amorphous precursor species [5]. However, details of the nucleation process itself have remained largely unexplored.

In the present work, we have addressed this issue by performing titration-based crystallization assays that allow for tracing solution speciation in situ and in real time prior to, during and after nucleation [6]. The resulting data shed light on ion association equilibria in the liquid phase and indicate the presence of solute clusters, which are independently detected by means of high-resolution techniques like analytical ultracentrifugation. Using cryo-transmission electron microscopy, we are furthermore able to identify the key steps in the homogeneous nucleation of CaSO₄ as well as the early stages of phase transformation and growth, all the way from dissolved ions and clusters to micron-sized gypsum crystals. The developed methodology can also be applied to quantitatively assess the influence of selected additives and/or external conditions on the distinct precursor and intermediate species along the proposed pathway, thus providing a potentially valuable tool to test and optimize crystallization modifiers, as well as to rationalize the formation of calcium sulfate sediments in natural settings.

[1] Gebauer *et al* (2014), *Chem. Soc. Rev.*, DOI: 10.1039/C3CS60451A. [2] Wallace *et al* (2013), *Science* **341**, 885-889 [3] Rodriguez-Blanco *et al* (2011), *Nanoscale* **3**, 265-271 [4] Van Driessche *et al* (2012), *Science* **336**, 69-72 [5] Wang *et al* (2012), *Chem. Commun.* **48**, 504-505 [6] Kellermeier *et al* (2014), *Adv. Mater.* **26**, 752-757