

Nucleation of Portlandite

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Numerous recent studies have shown that the formation of minerals can be far more complex than envisaged by classical models of nucleation and growth.^[1,2] In particular, the early stages of mineralization often involve multiple precursor species that successively transform into one another to finally yield the well-known crystalline bulk state. This was shown explicitly for prominent minerals like calcium carbonate, where stable pre-nucleation clusters, liquid-like phases, amorphous nanoparticles, metastable crystalline polymorphs and other intermediates have been observed during crystallization.^[3-4]

In this context, we have studied the formation of portlandite (Ca(OH)₂) crystals from aqueous solutions, a process of considerable significance to industrial applications (e.g. in the area of construction materials). To that end, we have developed a titration-based assay in which the two relevant ions are added simultaneously, leading to a slow increase of supersaturation at constant stoichiometry until nucleation occurs. This procedure allows detailed analyses of both pre- and early post-nucleation phenomena, which were complemented by various other characterization techniques, including (cryo-)transmission electron microscopy (TEM) and in-situ small-angle X-ray scattering (SAXS). Our results show that the crystallization of portlandite starts by association of ions into clusters, which at some point coalesce to nucleate well-defined amorphous nanoparticles in an essentially barrier-free manner. Subsequently, these particles aggregate into networks, from which hexagonal Ca(OH)₂ crystals grow upon continued ripening. Further studies in the presence of soluble polymers highlight how typical crystallization additives can interfere with the identified “non-classical” mechanisms of portlandite formation at various stages.

[1] De Yoreo *et al.* (2015), *Science* 349, 6247. [2] Stawski *et al.* (2016), *Nat. Comm.* 7, 11177. [3] Gebauer *et al.* (2014), *Chem. Rev.* 43, 2348. [4] Rieger *et al.* (2014), *Angew. Chem. Int. Ed.* 53, 12380. [5] Gebauer *et al.* (2008) *Adv. Mater.* 21, 435.