

Ion clustering in calcium carbonate solutions and its relevance for nucleation

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Over the past decade, there has been intensive research on the mechanisms of mineral nucleation and growth, scrutinizing long-standing concepts of classical theories and bringing up new alternative pathways to the formation of crystals [1-3] which however still are heavily debated [4]. One important finding in this context was that prior to nucleation of a new phase, dissolved monomers (ions or molecules) may assemble into a stable population of so-called “prenucleation clusters”, [5] or more generally speaking solute associates that – much like simple complexes or micelles – coexist in equilibrium with the free monomers. Whether or not these clusters are relevant species for nucleation strongly depends on the chosen conditions, but in some cases it has been observed that phase separation can proceed through cluster aggregation and coalescence [2].

In the present contribution, several fundamental aspects of ion association in mineral solutions are reviewed and put into context with recent developments in the field of calcium carbonate crystallization. In particular, we focus on the thermodynamics of ion clustering in these systems and show that the solvent plays a key role in the process. Moreover, the problem of ion activity is addressed in a straightforward approach, which allows separating contributions originating from actual ion binding and sheer electrostatic effects [6]. Our analyses lead to the conclusion that for homogeneous nucleation, the concentration of *bound* constituent ions can be the critical parameter – rather than those of the *free* ones. This challenges the traditional definition of supersaturation and emphasizes the potential relevance of stable ion clusters for nucleation. Eventually, we provide evidence that effects as those described above are not exclusive to the world of calcium carbonate, but do also occur in a more or less similar manner in other mineral systems.

[1] Wallace *et al.* (2013), *Science* **341**, 885-889. [2] Gebauer *et al.* (2014), *Chem. Soc. Rev.* **43**, 2348-2371. [3] Rieger *et al.* (2014), *Angew. Chem. Int. Ed.* **53**, 12380-12396. [4] Vekilov *et al.* (2012), *Faraday Discuss.* **159**, 139-180. [5] Gebauer *et al.* (2008), *Science* **322**, 1819-1819. [6] Kellermeier *et al.* (2014), *Adv. Mater.* **26**, 752-757.