

## **A non-classical view of the modulation of mineral precipitation by organic additives**

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Questions persist on the mechanisms of crystallization of sparingly soluble minerals such as calcium carbonate, calcium oxalate or barium sulphate. Compared to  $\text{CaCO}_3$ , the mechanisms of nucleation and growth in the  $\text{CaC}_2\text{O}_4\text{-H}_2\text{O}$  or  $\text{BaSO}_4\text{-H}_2\text{O}$  systems have received less attention. These phases are important due to their relevance as biominerals and/or unwanted mineral deposits in technological applications. Growing evidence suggests that sparingly soluble salts form by non-classical nucleation and growth pathways, where pre-nucleation ion associates and amorphous (solid or liquid) precursor phase(s) play a critical role (e.g. Rodríguez-Navarro et al. (2015), Ruiz-Agudo et al. (2015)). Indeed the identification of pre-nucleation species in these systems and their strong interactions with organic compounds (Verch et al. 2011) raises the possibility that the control of organics on biomineralization may begin even earlier than previously thought. A sound knowledge of the physical mechanisms by which acidic macromolecules affect nucleation and early growth may offer general insights concerning the molecular control of biomineralization, as well as being critical for improving strategies to control unwanted mineral deposition or for the synthesis of biomimetic materials.

Here we present investigations on the initial stages of the precipitation of these relevant minerals in organic-free solutions to identify the precipitation pathway and to look for any potential precursor phase(s) to the final, crystalline polymorph. As well, we explore the effects that several acidic organic compounds have on the different precipitation stages identified. We find that organic additives such as citric acid, polyacrylic acid or a commercial copolymer of maleic acid/allyl sulfonic acid with phosphonate groups can be active at modifying pre-nucleation stages (destabilizing of pre-nucleation species or hampering the aggregation and growth of pre-nucleation associates) and subsequently strongly inhibit the nucleation of solid phases. These effects are linked to the influence of these molecules on polymorph selection. As well, these additives can affect non-classical growth by oriented assembly of nanoparticles.

### **REFERENCES**

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