Biomolecule control on $CaCO_3$ mineralisation

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Biomolecules produced by organisms are well known to affect the nucleation, growth and aggregation of $CaCO_3$ minerals. In this process, the biomolecules often get incorporated within the precipitating $CaCO_3$ phase, leading to more stable and resilient mineral structures and textures. Such biomineralisation processes have been studied for several decades, but the mechanisms by which the organic molecules control $CaCO_3$ crystallisation rates, polymorph selection and stability are still not fully understood. In particular, little is known about their impact on the initial stages of $CaCO_3$ formation, which is often preceeded by a metastable amorphous precursor phase (ACC).

This study focusses on the role of biomolecules in the mineralisation processes of $CaCO_3$ from the ACC precursor. Synchrotron radiation pair distribution function (PDF) was combined with time-resolved UV-Vis spectrophotometry, X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and electron microscropy to quantify changes in the ACC atomic scale structure, composition and stability as a function of biomolecule type (i.e., amino acids, carboxylic acid and polysacharides) and concentration in solution. Also, ACC crystallisation was monitored to assess the impact of the organic molecules on polymorph selection, transformation rate, morphology and size. The addition of an organic acid, such as citric acid, considerably prolongs ACC lifetime, increases its thermal stability and promotes the formation of calcite with spherulitic crystal shapes different from the pure system [1]. In contrast, single unit amino acids (e.g., aspartic acid, glutamic acid and glycine) promote the formation of vaterite but have less effect on ACC stability, composition and structure, despite being detected on the ACC surface [2].

[1] Tobler et al. (2015) *Adv. Funct. Mat.* **25**, 3081-3090 [2] Tobler et al. (2014) *Proc. Earth Planet. Sci.* **10**, 143.