Effect of citric acid on amorphous calcium carbonate (ACC) structure, stability and crystallisation

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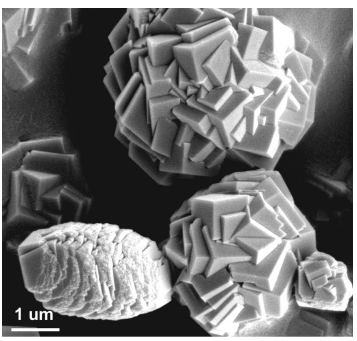
The formation of calcium carbonates ($CaCO_3$) in natural environments frequently occurs in the presence of organic molecules. These are known to strongly modify crystal structure, morphology and properties, often leading to more resilient and stronger crystals. Detailed understanding of how organic molecules modify $CaCO_3$ growth kinetics and mechanism is therefore a field of great interest.

The initial steps of $CaCO_3$ crystallization can occur via the formation of amorphous calcium carbonate (ACC). Here, we investigated the role of citric acid (CIT) in ACC crystallisation using in-situ synchrotron-based pair distribution function (PDF) analyses combined with time-resolved UV-Vis spectrophotometry, X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and electron microscopy. The initial ratio of CIT to $CaCO_3$ had a profound effect on the hydration, formation kinetics, and stability of ACC. At 0% CIT, ACC crystallised rapidly (< 2 min at 25 °C) to vaterite and then calcite through dissolution / reprecipitation. With increasing CIT (10-50%), ACC lifetime steadily increased (~30 min at 50% CIT), as did the water content and sorbed CIT of the ACC nanoparticles. In contrast to the pure system, ACC with sorbed CIT crystallised directly to calcite, with no vaterite intermediate. *In situ* PDF results confirmed the short range ordering for ACC (<15 Å) and showed slight variations between the pure system and ACC with CIT. We argue that CIT strongly binds to Ca, forming solution complexes and thereby decreases ACC saturation levels. This leads to the formation of more hydrous ACC, which eventually crystallises spherulitically to calcite (Figure).



Calcite grown in the presence of 10 % CIT