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The impact of additives on crystallization of amorphous $CaCO_3$.

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The importance of amorphous calcium carbonate (ACC) as a precursor in the formation of crystalline biominerals is well established. TEM and X-ray spectroscopic studies showed conversion occurs via dehydration of initially hydrated ACC followed by its crystallization. Other studies on biominerals and materials formed in vitro found that additives, both inorganic and organic, dramatically impact ACC formation and transformation. However, investigations have largely involved bulk assays while direct observations of individual dehydration and transformation events and the impact of additives on the dynamics of those events are lacking. Here we report in situ TEM experiments on the effect of Mg, citrate and poly-acrylate on the ACC-to-crystal transformation. For citrate, PAA and low Mg content (2.5 mM), we find dissolution/re-precipitation dominates, with each additive extending the ACC lifetime and/or the timescale for dissolution, but the final crystalline polymorphs exhibit the expected morphology for the phase formed. In contrast, for [Mg] ≥ 5 mM, transformation occurs via loss of structural water seen both via an increase in electron density and changes in the Raman spectrum in the absence of a morphological change, leading to spheroidal Mg-calcite. Molecular dynamics simulations indicate Mg brings excess water into ACC and promotes atomic rearrangement. TGA data confirms the excess of water but shows dehydration is inhibited. We hypothesize that slow dehydration coupled with the ease of reorganization enables the observed isomorphic conversion. This effect may explain why Mg is a common impurity found in biominerals, as its presence would allow ACC to be more easily moulded into complex shapes and maintain those shapes while transforming into one of the crystalline polymorph.