

## **The control of organic matrices on nucleation and growth of $\text{CaCO}_3$**

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Formation of carbonates, iron oxides, and other minerals often occurs in the context of macromolecular matrices. Insoluble matrices present functional surfaces believed to exert control over the nucleation phase, while soluble species impact growth morphology, as well as the kinetics of solute and impurity incorporation into the growing crystal. Recent chemical analyses, microscopy studies, and computer simulations suggest mineral formation starts with pre-nucleation clusters and proceeds by particle-mediated growth processes involving amorphous or liquid-like precursors, eventually forming a mesocrystal. Here we use results from in situ TEM, AFM and optical studies of  $\text{CaCO}_3$  nucleation and growth in the presence of insoluble and soluble organic matrices to critically evaluate the mechanisms underlying these processes, as well as the role played by the organics.

Using alkane thiol self-assembled monolayers (SAMs) to explore the effect of insoluble organic surfaces on nucleation, we find that calcite nucleation is described well in purely classical terms through a reduction in the nucleation barrier due to decreased interfacial free energy, which scales linearly with SAM-crystal binding free energy, as expected classically. The results provide a mechanistic basis for the conventional wisdom that good binders are good nucleators.

Introduction of a polyionic macromolecule, which acts as a surrogate for highly acidic proteins and complexes calcium, leads to formation of a globule phase. The first mineral appears within these globules and is amorphous calcium carbonate (ACC). Once ACC is replaced by calcite crystals, the macromolecules interact with the atomic steps on the growing surface of the crystals. As with simple acidic amino acids and peptides, this leads to step pinning, stabilization of new step directions, and extreme roughening of the surface. The resulting crystals have the outward appearance of mesocrystals, but form through completely classical mechanisms. These results provide a mechanistic picture of nucleation and growth in the context of organic matrices.