

# An in situ view of $\text{CaCO}_3$ nucleation

J. J. DE YOREO<sup>1\*</sup>, M. H. NIELSEN<sup>2</sup>, P. J. M. SMEETS<sup>3</sup> AND  
N. A. J. M. SOMMERDIJK<sup>3</sup>

<sup>1</sup>Pacific Northwest National Laboratory, Richland, WA 99352,  
USA (\*correspondence james.deyoreo@pnnl.gov)

<sup>2</sup>Department of Materials Science and Engineering, Univ. of  
California, Berkeley, 94720 USA (mhnielsen@lbl.gov)

<sup>3</sup>Laboratory of Materials and Interface Chemistry, Eindhoven  
Univ. of Technology, 5600 MB Eindhoven, Netherlands  
(P.J.M.Smeets@tue.nl, N.Sommerdijk@tue.nl)

Nucleation is the seminal event in growth of minerals from solution. Recent chemical analyses, ex situ microscopies, and computational studies argue for multi-step nucleation pathways involving cluster aggregation or liquid-liquid separation. Moreover, the role of macromolecular matrices in controlling nucleation, which is a common feature in biomineralizing systems, is unclear. Here we use fluid cell TEM to investigate calcium carbonate nucleation in both pure solutions and in the presence of organic matrices.

During nucleation in pure solutions, we observe direct formation of amorphous calcium carbonate (ACC), as well as the three predominant crystalline phases: calcite, vaterite, and aragonite, even under conditions in which ACC readily forms. In addition to direct formation pathways, we observe transformation from ACC to aragonite and vaterite, but, significantly, not to calcite. ACC transforms directly to the crystalline phases starting on or just beneath the surface, rather than via dissolution and reprecipitation, through distinct nucleation events followed by consumption of the parent ACC particle. These formation pathways are confirmed by collecting diffraction information of the various phases of calcium carbonate. For all phases measured, radial/edge growth rates following nucleation are constant, showing growth is limited by reaction kinetics.

Introduction of the charged polymer polystyrene sulfonate (PSS), which acts as a surrogate for highly polysaccharides and acidic proteins, leads to formation of 10–20 nm diameter Ca-PSS globules through counter ion condensation. Titration calorimetry shows that more than 50% of the Ca ions are sequestered into these globules. Under conditions for which vaterite appears randomly throughout the cell in the absence of PSS, the first mineral to appear in its presence is ACC, which forms only within these globules. Analysis of growth rates shows that the supersaturation relative to ACC at the time of nucleation is about twice as high as that relative to vaterite when it nucleates without PSS. Hence PSS stabilizes ACC formation, but is still an inhibitor of its nucleation. These results provide a mechanistic picture of  $\text{CaCO}_3$  nucleation and growth.