Direct observation of $CaCO_3$ formation pathways

MICHAEL H. NIELSEN[1,2] AND JAMES J. DE YOREO[3]*

[1]University of California, Berkeley, Berkeley, CA 94720, USA
[2]Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA (mhnielsen@lbl.gov)
[3]Pacific Northwest National Laboratory, Richland, WA 99352, (*correspondence: james.deyoreo@pnnl.gov)

There exist many long-standing questions surrounding nucleation from solutions due to a lack of experimental approaches suitable for probing this seminal event in mineral formation. While electron and x-ray based techniques have allowed observations at length-scales appropriate for the initial stages of nucleation, these techniques have traditionally required the sample to be held under vacuum and therefore have only provided isolated slices in time of the formation process. In situ experimental approaches, while allowing the evolution to be followed over time, have either lacked the appropriate time resolution (scanned probe microscopy) or spatial resolution (optical microscopy and spectroscopy).

Within the past decade developments in transmission electron microscopy (TEM) have produced platforms allowing observation of fluid environments. Using fluid cell TEM, we observe direct formation of amorphous calcium carbonte (ACC). Furthermore, we observe the direct formation of the three predominant crystalline phases of calcium carbonate: calcite, vaterite, and aragonite. The direct formation of the crystalline phases is observed under conditions in which ACC readily forms. These observations provide direct evidence that multiple phases of calcium carbonate can form directly without the intermediate stage of ACC. For all phases measured, we find radial/edge growth rates following nucleation are linear with respect to time.

Beyond these direct formation pathways, we additionally observe transformation from ACC to aragonite and vaterite, but, significantly, not to calcite. In these observations, ACC transforms directly to the crystalline phases, rather than undergoing a process of dissolution and reprecipitation. These formation pathways are confirmed by collecting diffraction information of the various phases of calcium carbonate.

Finally we observe two different dissolution behaviors for ACC. Some ACC particles disappear like liquid droplets, while others exhibit the pitting and rough edges common for solid particles. This suggests that ACC may be a term that either encompasses a few discrete structures, as proposed in some literature, or describes a spectrum of structures encompassing the amorphous solidifaction from a dense liquid precursor.