

The Mg-dependent solubility and local structure(s) of Amorphous Calcium Carbonate (ACC)

SEBASTIAN MERGELSBERG¹, JAMES DE YOREO², F. MARC MICHEL¹, J. DONALD RIMSTIDT¹, PATRICIA DOVE¹

¹Department of Geosciences, Virginia Polytechnic Institute & State University, Blacksburg, VA 24061, USA

²Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA.

Recent advances show multistep pathways to mineralization are widespread in biological and geological settings (De Yoreo et al., 2015; *Science*). These findings highlight the importance of understanding roles of amorphous intermediates in determining the composition of final crystalline products. For example, final chemical signatures may be recording the properties of intermediate amorphous phase(s). Thus, it is critical to understand the structure and physical properties of ACC and establish the mechanistic basis for the transformation to carbonate minerals.

This experimental study quantified the chemical and structural properties of ACC and its evolution in situ. We first synthesized under controlled chemical conditions using a flow-through reactor developed by our group (Blue et al., 2017; *GCA*). The experimental design varied Mg concentration and total alkalinity at an environmentally relevant pH. Composition and structure of the corresponding amorphous products were characterized using Thermogravimetric Analysis (TGA), *in situ* high energy x-ray scattering, and pair distribution function (PDF) analyses. ACC solubility was determined at specific time points from both super- and under-saturated conditions.

The measurements demonstrate at least two types of ACC are produced by tuning Mg concentration and alkalinity. Each phase exhibits a different short-range order with distinct structural properties. TGA independently confirms separate composition ranges for each structure. We also find temporal evolution of ACC structure and morphology after precipitation is dependent on solution chemistry. The solubility measurements independently confirm enthalpies of solution reported by Radha et al., (2012, *GCA*) that quantify the dependence on Mg content. The analysis also supports the idea that anhydrous, Mg-rich ACC is more stable. The findings hold promise for reconciling discrepancies in the structure, composition, and thermodynamical landscape of ACC and the transformation to final crystalline polymorphs.