

## Implications of CaCO<sub>3</sub> phase heterogeneity for interpretation of the Ca isotopic fractionation factor: An *in-situ* study

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The Ca isotopic composition of calcium carbonate (CaCO<sub>3</sub>) minerals have become increasingly utilized as proxies for global weathering fluxes, changes in ocean chemistry, and climate on million-year time scales. The use of Ca isotopes as a proxy is complicated by isotopic fractionation during precipitation, the formation of polymorphs under Earth surface conditions, and the observation that isotopic effects depend on phase. While calcite is the most stable polymorph, and thus the dominant phase found in the rock record, the pathway by which the stable polymorph is achieved can vary. Additionally, proxy utility depends on fractionation factors derived from precipitation experiments.

In this study, the influence of solution chemistry on the formation of CaCO<sub>3</sub> polymorphs was investigated. Unseeded precipitation was initiated in small volume (0.1 mL) flow-through reactors, and mineral growth observed *in-situ* using optical microscopy and Raman spectroscopy. CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions were mixed in the reactor from separate reservoirs using syringe pumps to control flow rate (0.005–0.1 mL/min). Initial saturation indices (with respect to calcite) ranged from 1.5–3.0, while pH varied from 8.0–10.0. A subset of the experiments included the addition of NaCl, NH<sub>4</sub>Cl, Na<sub>2</sub>HPO<sub>4</sub>, and arginine. In nearly all experiments, both rhombic calcite and vaterite, in almond or flower morphologies, were observed. Vaterite to calcite ratios varied within reactors and were dependent on whether growth was initiated within the solution or on the reactor walls. Once present, vaterite crystals continued to increase in mass throughout an experiment and did not transition to calcite. While the addition of NH<sub>4</sub><sup>+</sup> did not affect significantly phase distribution, the presence of both Na<sub>2</sub>HPO<sub>4</sub> and arginine drastically inhibited the precipitation of vaterite while NaCl slightly promoted the precipitation of calcite.

Our results suggest that there are a variety of issues with respect to interpretation of Ca isotope data from precipitation experiments, including sampling protocol, the effects of additives, and method by which precipitation is achieved. In light of our results, we present a numerical model that quantifies the phase effect on the interpretation of Ca isotope fractionation factors.