

Insights from oxygen and clumped isotopes and SEM imaging on equilibrium carbonate precipitation

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Laboratory precipitation experiments of CaCO_3 provide the basis for understanding precipitation mechanisms and the common calibration of both the classic oxygen isotope and the new clumped isotope thermometers; these calibrations are thought to reflect isotopic equilibrium. Such calibration studies, focus predominantly on crystals that grow deep in the bulk of the solution, often by bubbling of $\text{N}_{2(g)}$ through a saturated $\text{Ca}(\text{HCO}_3)_2$ solution, following the classic experiments of McCrea (1950). Here we compare oxygen and clumped isotopes in CaCO_3 precipitated either deep in bulk solution or at the surface of solutions that undergo passive CO_2 degassing. We discuss the temperature dependence of $\delta^{18}\text{O}$ and Δ_{47} in the context of the mineralogy and morphology of the CaCO_3 crystals. Surface precipitates are affected by enhanced disequilibrium that is associated with degassing and mineral growth under high super-saturation. They show higher $\delta^{18}\text{O}$ and lower Δ_{47} values than those of the accepted thermometer calibrations. SEM images of the CaCO_3 of both precipitation methods, show significant mineralogical and morphological differences. As expected, mineralogy generally changes from calcite to aragonite with increasing temperatures; some vaterite is observed in low temperature samples. Surface precipitates tend to form aggregates of small crystals whereas bulk solution precipitations remain as individual grains. Crystal surfaces are smoother at lower temperatures and surface precipitates, as compared to higher temperatures. In general, minerals forming in bulk solution exhibit pronounced etching of the faces, likely reflecting dissolution and reprecipitation, bringing the CaCO_3 closer to equilibrium precipitation. These morphological features are reflective of the mineral growth environment and rate, and together with the isotopic data are used to infer precipitation mechanism and equilibrium conditions.