The influence of pH on the oxygen isotope composition of calcite

JONATHAN D. HUNT[1]*, JAMES M. WATKINS[2], FREDERICK J. RYERSON[1] AND DONALD J. DEPAOLO[3]

[1]Lawrence Livermore National Laboratory, Livermore, CA, USA (*correspondence: hunt50@llnl.gov)
[2]University of Oregon, Eugene, OR, USA
[3]University of California Berkeley, Berkeley, CA, USA

Oxygen isotope fractionation between calcite and water is temperature-dependent and can be used as a paleo-thermometer. Although fractionation is expected from principles of equilibrium partitioning, the temperature-dependence remains uncertain because slow exchange between dissolved inorganic carbon (DIC) species and water can obscure the temperature signal. Oxygen isotopic equilibrium between water and calcite requires both equilibrium between DIC species and water, and equilibrium between DIC and the precipitated calcite. To isolate kinetic effects arising at the mineral-solution interface, isotopic equilibrium among DIC species must be maintained. Dissolving the enzyme carbonic anhydrase into the solution reduces the time of isotopic equilibration between DIC species by approximately two orders of magnitude. We conduct calcite growth experiments aimed at measuring the pH-dependence of kinetic effects during precipitation of calcite at pH 7.7-9.3 and 25°C. For each experiment, a mixture of N_2 and CO_2 is bubbled through a beaker containing ~1.3 L of solution. As the CO_2 dissolves, calcite crystals grow on the beaker walls. The pH is maintained by injecting NaOH using an autotitrator. We control the T, pH, the rate and pCO_2 of gas influx, and monitor the total alkalinity, the pCO2 outflow, and the NaOH added. A crystal growth rate of ~1.6 mmol/m^2/hr is maintained over all experiments. Results are in excellent agreement with a recently-developed ion-by-ion growth model of calcite, and provide the first constraint on the distinct kinetic fractionation factors of carbonate and bicarbonate ions.

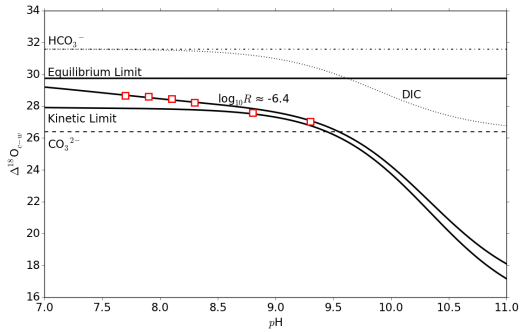

Figure 1. Measured vs. modeled pH dependence to $\Delta^{18}O_{c\text{-}w}$.