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Calcite precipitation from saline solutions: How dissolved NaCl affects DIC speciation, DIC isotopic equilibration, and $\delta^{18}O$ in calcite

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We report results from experiments where inorganic calcite is grown from aqueous solution in the presence of the enzyme carbonic anhydrase (CA). The CA promotes isotopic equilibrium between dissolved inorganic carbon (DIC) species and H_2O in the bulk solution, enabling us to probe the mass dependence of ion attachment and detachment rates at the mineral surface. Our previous work showed that kinetic isotope effects (KIE) vary systematically with growth rate and pH at a given temperature. Here, we investigate how other dissolved ions influence oxygen isotope fractionation between carbonate minerals and their host solution.

Experiments were carried out at constant temperature (25°C), constant pH (8.3), and salinities ranging from 5 to 85 g/kg. During calcite growth, the degree of supersaturation ($\Omega=[Ca^{2+}][CO_3^{2-}]/K_{sp}$) is typically around 5±2 during crystallization. An increase in salinity is expected to: (a) shift DIC speciation to higher CO_3^{2-}/HCO_3^- ratios at a given pH, (b) decrease the solubility product K_{sp} and therefore change the $[Ca^{2+}]/[CO_3^{2-}]$ ratio at which calcite precipitates, and (c) interfere with ion attachment and detachment kinetics near the crystal surface. All three factors should affect the $\delta^{18}O$ of crystals grown under far-from-equilibrium conditions.

We find that oxygen isotope fractionation between calcite and water varies systematically with salinity (S), spanning a 3‰ range between freshwater (5 g/kg) and saline water (45 g/kg). Saltier solutions result in calcite that is isotopically lighter. The isotopic fractionations vary by about 1‰ between $S = 45$ and 85 g/kg. The strong dependence of oxygen isotope fractionation on salinity is either due to surface reaction controlled kinetics or a not fully equilibrated DIC pool. We are currently undertaking CA assays to assess whether dissolved NaCl inhibits the activity of the enzyme CA. The results from calcite precipitation experiments and CA assays will be use to discuss vital effects in biogenic carbonates as well as paleoclimate reconstructions based upon carbonates precipitated from different environments.