Kinetic isotope effects during carbonate mineral formation

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The oxygen isotopic composition of natural carbonate minerals is commonly used under the assumption of equilibrium with its ambient water to determine the temperature at which the carbonates formed and the oxygen isotope composition of their parent solution [1,2]. However, oxygen and carbon isotope compositions of natural carbonates, such as corals and speleothems, often appear to be out of isotopic equilibrium [3,4]. Disequilibrium isotopic compositions arise from kinetic isotope effects (KIEs), which occur when the reaction rates of the heavy and light isotopes differ. In the inorganic carbonate system KIEs may be associated with precipitation, speciation reactions and CO_2 degassing during carbonate mineral formation. The existence of these KIEs complicates the use of carbonate repositories in the geologic record for paleoclimate and paleohydrology reconstructions. Specifying the contribution of each of the KIEs to the total observed composition remains a major outstanding challenge.

We performed a series of witherite ($BaCO_3$) laboratory precipitation experiments and measured the isotopic composition of the carbonates and the residual solutions by continuous-flow isotope-ratio mass spectrometry. Complete rapid precipitation from solutions buffered at pH values between 7.5 and 13 and temperatures between 15 and 40 °C captured the equilibrium isotopic fractionation, and agrees well with previous work [5]. Incomplete precipitation with variable yields captured isotopic distillation due to the KIEs and allowed determination of their magnitudes. Experiments at pH 13 recorded only the KIEs associated with precipitation, while experiments at lower pH recorded the combined KIEs of precipitation and inorganic carbon speciation. The full set of experiments describes the pH and temperature dependence of the KIEs in witherite formation, and could help to unlock the paleoclimatic and paleohydrological information in carbonate minerals.

[1] Urey (1947), *J Chem Soc* 562–582 [2] Epstein *et al* (1953), *Bull Geol Soc Amer* **64**, 1315–1326 [3] Wefer & Berger (1991), *Mar Geol* **100**, 207–248 [4] Hendy (1971), *Geochim cosmochim Ac* **35**, 801-824 [5] Beck *et al* (2005), *Geochim Cosmochim Ac* **69**, 3493–3503