

Kinetic isotope effects during witherite (BaCO₃) formation

Z. SADE*, R. YAM, A. SHEMESH AND I. HALEVY

Weizmann Institute of Science, Rehovot 76100, Israel

(*correspondence: ziv.sade@weizmann.ac.il)

Oxygen and carbon isotope compositions of natural carbonates, such as corals and speleothems, often appear to be out of isotopic equilibrium [1,2]. Clearly, offsets from equilibrium complicate the use of carbonate repositories for paleoclimate and paleohydrology reconstructions.

Disequilibrium compositions reflect kinetic isotope effects (KIEs) during several reactions, which may be related to mineral formation: precipitation, dissolved inorganic carbon (DIC = CO_{2(aq)} + HCO₃⁻ + CO₃²⁻) speciation and CO_{2(aq)} degassing. Specifying the contribution of each of the KIEs to the total observed composition in various environments is a challenge, which bears the potential to unlock currently inaccessible paleoclimatic and paleohydrological information in natural carbonates.

To constrain the KIEs associated with carbonate mineral precipitation, we performed a series of rapid witherite (BaCO₃) precipitation experiments over a range of pH (7.5 to 13), temperature (15 to 40°C) and fractional yield of the DIC (few percent to quantitative). Our experimental protocol followed previous work [3], but involved an extended range of pH and temperature, and measurements of both carbon and oxygen isotopes.

The experiments captured the isotopic distillation due to precipitation and HCO₃⁻ dehydration reactions alone, as degassing was prevented. This allowed (*i*) determination of the magnitude and temperature dependence of the carbon and oxygen KIEs during CO₃²⁻/HCO₃⁻ precipitation, and (*ii*) investigation of the relative significance of the various KIEs during witherite formation under controlled conditions. We will discuss these findings and their implications for disequilibrium isotopic compositions in natural carbonates.

[1] Wefer & Berger (1991), *Mar Geol* **100**, 207–248. [2] HENDY (1971), *Geochim Cosmochim Acta* **35**, 801-824. [3] Kim *et al.* (2006), *Geochim Cosmochim Acta* **70**, 5790–5801.