



Closing in on the oxygen isotopic fractionation factor between calcite and water using natural carbonates

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The oxygen isotopic fractionation between water and calcite is the cornerstone for estimating the formation temperature of calcite [1, 2, 3]. The oxygen isotope thermometer is one of the most valuable tools in geothermometry, palaeoclimatology and palaeoceanography. Despite 60 years of laboratory experiments and search for carbonate material precipitating at (near-)equilibrium [4, 5], establishing the temperature-dependent calcite-water fractionation factor has proven challenging. Here we address this problem with coupled traditional and clumped isotope measurements from an unconventional carbonate archive – subaqueously-precipitated carbonates (SPC) which form in cave pools and drip sites, as well as natural hot springs. SPC include cave pearls, cave pool rim carbonates, hot spring pisoids, and carbonate geodes. Their common feature is subaqueous formation from supersaturated waters with an unlimited pool of calcium bicarbonate and very slow CO₂-degassing, which promote (near-)equilibrium conditions. Here, we expand on earlier work that used SPC as calibration material for clumped isotope thermometry [6] by measuring $\delta^{18}\text{O}$ of 20 (sub-)modern SPC samples from caves and hot springs with known temperatures (0.8°C and 76°C) with calcite or aragonite mineralogies, together with their host water. Our results enable determination of the fractionation factor between carbonate and water for a wide temperature range. Additionally, clumped isotope measurements confirmed isotopic equilibrium for both, $\delta^{18}\text{O}$ and Δ_{47} of the analysed SPCs, supporting the equilibrium equations of Coplen [4] and Watkins et al. [7]. SPC grown at thermodynamic equilibrium provide potential standard materials for temperature calibration of clumped isotopes.

References

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