

Laboratory (cave-analogue) calcium isotope fractionation factors for aragonite, and their application to North African palaeohydrology

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Calcium isotope measurements in cave carbonate samples are showing significant capability as a proxy for reconstructing past rainfall amount [1,2] - an important step in developing more robust, quantitative palaeo-environmental reconstructions. To date this new proxy has focussed on calcite cave samples only. There is significant value in expanding this capability to aragonite forms of freshwater carbonates, and in improving our understanding of isotopic fractionation in aragonite sample archives.

We conducted cave-analogue experiments to derive calcium isotope fractionation factors in a controlled environment. The experimental setup closely mimics natural processes (e.g. precipitation driven by CO₂-degassing, low ionic strength solution, thin solution film) but with a tight control on growth conditions (temperature, pCO₂, drip rate, saturation index and solution chemistry), with full details in [3]. CaCO₃ was dissolved in deionized water in a 20,000 ppmV pCO₂ environment, with trace-elements (Li, Na, Mg, Co, Sr, Cd, Ba, U) at appropriate concentrations to mimic natural solutions. Mg concentrations were used to control the growth mineralogy.

We then test this new calibration of Ca isotope fractionation in aragonite speleothem carbonates on North African speleothem samples, to help constrain changes in Holocene rainfall amount in the South-of-Atlas region. This adds to the existing work of [4] that focussed on the timing and on the source of additional rainfall along the northwestern boundary of the Sahara.

[1] Owen et al., 2016. Calcium isotopes in caves as a proxy for aridity: Modern calibration and application to the 8.2 kyr event. *Earth and Planetary Science Letters*, 443, pp.129-138. [2] de Wet et al., 2021. Semiquantitative estimates of rainfall variability during the 8.2 kyr event in California using speleothem calcium isotope ratios. *Geophysical Research Letters*, 48(3), p.e2020GL089154. [3] Day, C.C. and Henderson, G.M., 2013. Controls on trace-element partitioning in cave-analogue calcite. *Geochimica et Cosmochimica Acta*, 120, pp.612-627. [4] Couper et al. (in review). North-West Saharan Holocene rainfall driven by interhemispheric temperature differences.