

Experimental evaluation of water-mediated clumped isotope resetting in abiotic and biotic calcite

ZEYANG SUN¹, SAUL PEREZ-BELTRAN¹, WILLIAM F. DEFLIESE², SARBAJIT BANERJEE¹ AND ETHAN L. GROSSMAN¹

¹Texas A&M University

²The University of Queensland

Presenting Author: zeyang.sun@tamu.edu

Carbonate clumped isotope compositions (Δ_{47}) can be reset at elevated temperatures either through solid-state carbonate ^{13}C – ^{18}O bond reordering and carbonate-structural water interaction (reordering), or through oxygen exchange with fluid inclusions and organic-associated water (resetting). Recent first-principles simulations and heating experiments indicate internal water can facilitate the reordering/resetting of carbonate clumped isotopes [1, 2, 3, 4]. The abundance and form of internal water in biogenic carbonate is essential to the preservation of primary carbonate clumped isotope signatures and paleoclimate reconstructions. However, the relationship between apparent clumped isotope resetting kinetics and internal water is still not well understood. Here, we compare the carbonate clumped isotope resetting kinetics for four calcitic materials with different internal water contents: optical calcite, speleothem calcite, a fossil brachiopod shell (mid-Carboniferous), and a modern brachiopod shell (North Sea). Samples were heated at 375, 423, and 470 °C for up to 5760 minutes. A high-temperature elemental analyzer (TC/EA)-isotope ratio mass spectrometer (IRMS) system and a Fourier Transform Infrared Spectroscopy (FTIR) are employed to measure the abundance of internal water for original and heated materials to examine the corresponding dehydration progress. Our preliminary results show that 1) fluid inclusion-rich speleothem calcite shows faster clumped isotope resetting kinetics than the dry optical calcite; 2) the Δ_{47} of the modern brachiopod resets faster than the fossil brachiopod, presumably due to high abundance of internal water and organic matter; 3) all samples show an initial decrease in the $\delta^{18}\text{O}$ except the dry optical calcite. Thus, in both the abiotic and biotic calcite, resetting is faster in the water-rich calcite. Based on measured water contents and isotopic compositions, we propose mechanisms to explain the kinetic link between thermally induced dehydration, changes in carbonate $\delta^{18}\text{O}$, and Δ_{47} resetting.

References

- [1] Staudigel, P. *et al.*, *Geochem. Geophys. Geosystems* **24**, (2023).
- [2] Looser, N. *et al.*, *Geochim. Cosmochim. Acta* (2023).
- [3] Perez-Beltran, S. *et al.*, *Sci. Adv.* **9**, eadf1701 (2023).
- [4] Sun, Z. *et al.*, *Earth Planet. Sci. Lett.* **624**, 118467 (2023).