

Fluid inclusions and dual-clumped isotopes: is it checks and balances all the way down?

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From its inception, clumped isotope geochemistry promised a means to calculate the $\delta^{18}\text{O}$ value of water from which a carbonate mineral formed. Parallel lines of inquiry have made a similar promise for fluid inclusion measurements, as they may sample the fluids from which minerals formed. Nevertheless, natural materials often yield discrepant values for primary fluids from these two methods¹. Experiments in which biogenic minerals are heated in a dry environment have shown that internal water-mineral equilibration can occur, this happens in such a way that these two recorders of temperature/fluid composition may give discrepant values². These alteration processes are problematic for deep-time paleoclimate reconstruction, as they do not necessarily alter mineralogy or microstructure, and are thus difficult to identify in unknown samples^{3,4}. Dual-clumped isotopes have the potential to better constrain the dynamics of this alteration process, in addition to the kinetics associated with initial mineral precipitation.

The approach we are implementing, involving coupled fluid inclusion and dual-clumped measurements, will better constrain our understanding of these processes and has the promise to identify the extent to which samples have undergone thermal alteration. This workflow is intended to increase confidence deep-time climate records, as it can independently screen for diagenetic processes.

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2. Nooitgedacht, C. W., van der Lubbe, H. J. L., Ziegler, M. & Staudigel, P. T. Internal Water Facilitates Thermal Resetting of Clumped Isotopes in Biogenic Aragonite. *Geochemistry, Geophysics, Geosystems* **22**, 1–13 (2021).
3. Staudigel, P. T. & Swart, P. K. Isotopic behavior during the aragonite-calcite transition: Implications for sample preparation and proxy interpretation. *Chemical Geology* **442**, (2016).
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