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Dual clumped isotope thermometry of biogenic carbonates: identifying and correcting for non-equilibrium isotope effects

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The stable oxygen ($\delta^{18}O$) and clumped (Δ_{47}) isotope compositions of biogenic carbonates record Earth's surface temperature. However, the isotope compositions of some biogenic carbonates are impacted by kinetic effects, which can hinder accurate temperature reconstruction. Dual carbonate clumped isotope thermometry (i.e., simultaneous Δ_{47} and $\Delta_{\hat{A}48}$ measurements on a single carbonate) has the potential to identify kinetically driven isotopic disequilibrium in biogenic carbonate and facilitate the reconstruction of carbonate formation temperature devoid of kinetic biases[1].

We investigated the dual clumped isotopic composition of several disequilibrium calcifiers, including brachiopods, warm and cold-water corals. We confirm that corals and faster-growing brachiopod species are enriched in Δ_{47} and depleted in Δ_{48} relative to equilibrium. This pattern corresponds with recently model-predicted kinetic effects[2], specifically the mixing of an equilibrium DIC pool with kinetically derived HCO_3^- produced by hydration and hydroxylation of CO_2.

Measured offsets in the Δ_{47} and Δ_{48} of cold-water corals plot on the initial linear portion of model-predicted departure from equilibrium, where the slope of kinetically driven Δ_{47} and Δ_{48} offsets is relatively insensitive to temperature and pH change[2]. Similar patterns are observed for brachiopod calcite. Measured correlation between disequilibrium in the Δ_{47} and Δ_{48} of modern brachiopod carbonate is used to correct for non-equilibrium signatures in Eocene age brachiopods from Seymour Island, Antarctica. Derived temperatures are consistent with temperatures from Δ_{47} measurements of coeval bivalve molluscs[3], which appear to (bio-)mineralize shell carbonate in clumped isotope equilibrium. Dual clumped isotope thermometry, therefore, (re-)opens the use of brachiopod and cold-water coral carbonate as valuable archives for reconstruction of shallow and intermediate water mass temperatures on geological timescales.

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