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Addressing kinetic model limitations through combined clumped and triple oxygen isotopes measurements in cold-water aragonitic corals

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Recent advances in theoretical modeling, such as the IsoDIC model [1], have provided valuable insights into how kinetic isotope effects (KIEs) in the CO_2-H_2O-DIC system influence the isotopic composition of dissolved inorganic carbon (DIC) and, by extension, carbonate minerals. Initial observations of dual-clumped isotopes (Δ_{47}, Δ_{48}) in cold-water corals (CWCs) support this model, suggesting that kinetic fractionation and mixing effects following addition of metabolic CO2 to the DIC are key drivers of oxygen and carbon isotopic disequilibrium in CWCs. This finding has opened the door to quantitative estimates of calcification temperatures in CWCs using dual-clumped isotopes. The model also predicts that the same mechanisms should produce a strong positive correlation between $\Delta'^{17}O$ and $\delta^{18}O$, a prediction recently challenged by the first combined $\Delta'^{17}O$ and $\delta^{18}O$ observations in CWCs [2]. Here, we present results from the first characterization of isotopic disequilibrium in modern CWCs in all five isotopic dimensions ($\delta^{13}C$, $\delta^{18}O$, Δ_{47}, Δ_{48}, and $\Delta'^{17}O$), allowing a comprehensive test of the predictions of the IsoDIC model. We leveraged recent advancements in spectroscopic techniques (VCOF-CRDS) to measure $\Delta'^{17}O$ in CO_2 released during carbonate acid digestion. The amplitudes and θ exponent of $\Delta'^{17}O$ disequilibrium in corals were estimated using a newly established $\Delta\Delta'^{17}O$ equilibrium curve, constrained by VCOF-CRDS analyses of natural and synthetic calcites. Our dual-clumped isotope data align well with previous studies, reinforcing IsoDIC predictions of Δ_{47} - Δ_{48} disequilibrium trends (**Figure 1**). However, the observed θ value in CWCs deviates considerably from both theoretical expectations and recently published values for the same species [2]. These new experimental data highlight two key challenges: (1) our current understanding of isotopic disequilibrium in CWCs remains incomplete, requiring the development of more comprehensive models, and (2) addressing standardization issues of oxygen-17 measurements in carbonates is essential to guarantee consistent and comparable results across laboratories, thereby enhancing the reliability of this emerging proxy.

[1] Guo. W. (2020). "Kinetic clumped isotope fractionation in the DIC-H_2O-CO_2 system: Patterns, controls, and implications." *Geochimica et Cosmochimica Acta,* 268, 230-257.

[2] Bajnai, D., et al. (2024). "Correcting for vital effects in coral carbonate using triple oxygen isotopes." *Geochemical Perspectives Letters,* 31,38-43.