Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.20638

# Dual carbonate clumped ($\Delta_{47}$, $\Delta_{48}$) and bulk ($\delta^{13}$C, $\delta^{18}$O) isotopes in cultured marine calcifiers provide insights into the origins of vital effects

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Biomineralization can be a highly-controlled process that is hypothesized to cause physiological signals in biomineral geochemistry (i.e., vital effects), complicating paleoenvironmental proxies. An emergent isotopic proxy for mineral formation temperatures is based on $^{13}C^{18}O^{16}O$ abundance ($\Delta_{47}$), carbonate clumped isotope thermometry, and a related active area for research relates to the origin of kinetic isotope effects on clumping. Recent work suggests that dual clumped isotope analysis (i.e., paired analysis of the $^{13}C^{18}O^{16}O$ and $^{12}C^{18}O^{18}O$ isotopologues: $\Delta_{47}$, $\Delta_{48}$) can be used to identify and correct for kinetic isotope effects. The potential power of dual clumped isotope analysis has been explored by a few theoretical studies, and a limited number of empirical studies of biominerals that focus only on one to a few taxa and utilizing field-collected specimens.

Here, we expand the number of calcifying species for which there is dual carbonate clumped ($\Delta_{47}$, $\Delta_{48}$) and conventional bulk ($\delta^{13}$C, $\delta^{18}$O) isotope data by surveying a diverse array of 12 marine calcifiers that were cultured. Aquaria conditions used a single seawater source, a single temperature (25°C), and a range of $p$CO2 (400 to 2850 ppm). Calcification responses, polymorph mineralogies, $\delta^{11}$B-estimates of calcifying fluid pH, and elemental compositions have been characterized and reported. Thus, this study presents a unique opportunity to explore broad-scale patterns of bulk and clumped carbonate isotope incorporation in a suite of ecologically and economically important marine calcifiers, where many environmental and calcification parameters have been constrained.

Our current results reveal evidence for kinetic effects in multiple taxa, with high phylogenetic signals in both the dual clumped and bulk isotope data, similar to what we have previously shown for the elemental compositions. When compared to simulations of the trajectory of $CO_2$ attaining isotopic equilibrium, these differences in kinetic isotope effects can be at least partially attributed to varied modulation of $CO_2$ hydration and hydroxylation reactions, possibly in accordance with differences in conditions at the site of calcification such as the pH of the calcifying fluid, and posit the potential for multi-isotope analyses to constrain interspecific differences underlying isotope disequilibrium in biominerals.