

Paired Δ_{47} and Δ_{48} carbonate clumped isotope data: Standard values, multi-instrument comparisons, mixing effects, and disequilibrium effects

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The clumped isotope (Δ_{47}) thermometer is a proxy that is growing in use throughout many areas of geosciences, including paleoclimate reconstructions of air and ocean temperatures, paleo-physiology, and paleoelevation. Recent work has demonstrated that isotopic disequilibrium may affect the accuracy of Δ_{47} -based reconstructions, and coupled Δ_{47} - Δ_{48} analysis may shed light on the origin of kinetic effects and increase confidence in temperature estimates from carbonate minerals (Hill et al., 2014; Tripathi et al., 2015; Fiebig et al., 2019; Bajnai et al., 2020). Due to the extremely low abundance of mass 48 CO_2 isotopologues, the development of robust standard values for Δ_{48} is critical to ensure accurate determination of unknown sample Δ_{48} values. Here we take advantage of newly developed analytical capabilities for the measurement of the primary mass 48 CO_2 isotopologue ($^{12}\text{C}^{18}\text{O}^{18}\text{O}$) and report carbonate standard values determined against equilibrated gases over a three-year interval for 8 standards (n=425), which lays the foundation for accurate determination of Δ_{47} - Δ_{48} values on an absolute reference frame using both equilibrated gas and carbonate standard-based standardization. Further, we demonstrate that the application of carbonate standardization yields reproducible Δ_{47} - Δ_{48} measurements for >12 standards on three instrument configurations using standard data collected over a five-year interval (n=4164). We report mixing experiment data and non-linear mixing model calculations for Δ_{48} and Δ_{47} vs Δ_{48} for samples with varying bulk isotope ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) values. Equilibrium and disequilibrium processes are constrained by comparing Δ_{47} - Δ_{48} data for different carbonates, including synthetic calcite, Devil's Hole cave calcite, and field-collected biogenic carbonates.