

Stable and clumped isotope behaviour over the aragonite-calcite transition: implications for sample prep and proxy interpretation

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At the earth's surface, aragonite is thermodynamically unstable and will readily convert to calcite; this can be accelerated by heating and mechanical stress. In experiments where aragonite is directly heated, we have shown that the alteration of the mineral structure shows a linear correlation between changes in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the carbonate. Experiments conducted in sealed vessels showed that the isotopes did not change when heated in a vacuum, and showed a different relationship when exposed to isotopically labeled CO_2 , this indicates that the change in mineralogy facilitates isotopic exchange with atmospheric CO_2 . Using different gasses, we are able to calculate the isotopic enrichment ($\alpha_{\text{gas-carbonate}}$) of this process. $\delta^{13}\text{C}$ displays correlation ($r^2 = .99$) between phases however $\delta^{18}\text{O}$ displays weaker correlation ($r^2 = .63$), likely due to the release of water during heating.

Clumped isotopes (Δ_{47}) behave very differently from $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during this transition. Even in a vacuum Δ_{47} will change independently from, and invariably at a faster rate than the mineral transition. At temperatures relevant to the mineral transition ($>300^\circ\text{C}$) Δ_{47} rapidly equilibrates to the higher temperature, likely due to solid-state diffusion. This process has been described in other carbonate minerals (Passey and Henkes 2012, Stolper and Eiler 2015) however the Δ_{47} of aragonite appears to be much more sensitive to heating than of Calcite, Dolomite or Apatite. At temperatures less than 300°C , the mineral transition is minimal, however Δ_{47} will continue to alter at temperatures below 175°C .

The heat and stress from drilling samples is sufficient to partially convert aragonite to calcite, previous work has shown a relationship between $\delta^{18}\text{O}$ and mineralogy under these conditions (Waite and Swart 2015). The effect of this alteration on the $\delta^{18}\text{O}$ proxy will typically result in a small change, usually less than .5‰ (approximately $+2^\circ\text{C}$). We evaluated the behavior of this transition on the Δ_{47} of sclerosponge and coral skeletons. Using a dental drill and an automated micromill we sub-sampled skeletal material using different drill settings. Under some conditions, we were able to convert over 20% of the skeletal material to calcite. The extent of this conversion varied depending on drill RPM and raster speed. The Δ_{47} decreased with the mineralogy, decreasing by .05‰ (approximately $+10^\circ\text{C}$) accompanying a 20% conversion. The existence of a linear relationship between the Δ_{47} and mineral change indicates that the heat produced by the drill is highly localized, completely altering small portions and leaving others unaltered. We therefore recommend that future studies sampling aragonite archives pay close attention to minimizing the mineral shift. Δ_{47} can be corrected if the mineral transition can be quantified (e.g. using XRD) using the empirical correction equation: $\Delta_{47(\text{corrected})} = \Delta_{47(\text{measured})} + .28\text{‰} \times f_{\text{calcite}}$.

Passey, B. H. & G. A. Henkes (2012) Carbonate clumped isotope bond reordering and geospeedometry. *Earth and Planetary Science Letters*, 351-352, 223-236.

Stolper, D. A. & J. M. Eiler (2015) The kinetics of solid-state isotope-exchange reactions for clumped isotopes: A study of inorganic calcites and apatites from natural and experimental samples. *American Journal of Science*, 315, 363-411.

Waite, A. J. & P. K. Swart (2015) The inversion of aragonite to calcite during the sampling of skeletal archives: Implications for proxy interpretation. *Rapid Communications in Mass Spectrometry*, 29, 955-964.