

Reanalyzing carbonate clumped isotope calibration materials using robust carbonate standardization

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Abstract:

The ability of carbonate clumped isotope thermometry to independently constrain both the fluid oxygen isotope composition ($\delta^{18}\text{O}_w$) and formation temperature ($T_{\Delta 47}$) of carbonate minerals allows for new insights into a range of long-standing questions in the Earth sciences. Recent empirical calibrations of the clumped isotope thermometer have shown increasing agreement, but remaining discrepancies between calibration schemes produced at different laboratories amplify uncertainty of final Δ_{47} temperatures. It is unclear whether these discrepancies arise from the various procedural differences of each laboratory (e.g., standardization scheme, reference frame stability, mass spectrometer type) or from the characteristics of specific sample materials (e.g., temperature range, precipitation method, mineralogy) used to empirically derive the calibration equation. To address the latter as a potential source of calibration discrepancy, we re-analyze a total of 40 samples selected from four previous empirical calibration studies as well as a suite of low-temperature lacustrine carbonates from the Dry Valleys region of Antarctica and two high-temperature calcite samples. This sample suite spans a wide range of formation temperature (0.5 °C–1100 °C), precipitation method (natural, various laboratory methods), and mineralogy (calcite, dolomite). Each sample was analyzed at least eight times and corrected to the absolute reference frame using IUPAC parameters and carbonate-based standardization (using ETH-1–4, MERCK, and IAEA-C2 values from the InterCarb project) with a 1:1 sample:standard ratio. All Δ_{47} measurements from this diverse sample suite fall within error of a single Δ_{47} -T regression equation, and regressions derived from different precipitation methods or mineralogies are statistically indistinguishable at the 95 % confidence level. The consistency of the Δ_{47} -T relationship across a wide array of sample material measured in a fixed analytical setting suggests that the character of samples is not a likely source of discrepancy between past calibration schemes. Our data (359 unknown analyses) define the following regression equation for calcite and dolomite samples from 0.5 °C–1100 °C (projected to 25 °C reaction temperature):

$$\Delta_{47} = 0.0388 \pm 0.0006 \cdot (10^6/T^2) + 0.244 \pm 0.0067 \quad (r^2 = 0.99).$$