Precise comparison of clumped isotopes in synthetic carbonates and natural, slow-growing calcite

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Considerable effort has been devoted over the past decade to establish a precise, internationally standardized calibration of the carbonate clumped isotope thermometer. Despite notable improvements in the acquisition, mathematical treatment, and standardization of Δ_{47} measurements, inter-laboratory discrepancies remain larger than could be explained by instrumental precision alone. Possible causes include the use of inaccurate ^{17}O correction parameters, unrecognized sources of variability in acid reaction fractionation, and isotopic differences between carbonates synthesized using different methods. Here we precisely compare the clumped isotope compositions of synthetic carbonates produced using two different protocols (active degassing of saturated solutions vs passive degassing of non-saturated solutions) and of very slow-growing calcite from two natural sites (Devils Hole and Corchia cave) which very likely formed at or near thermodynamic equilibrium. We observe that Δ_{47} values for actively degassed samples correlate strongly with temperature (r = 0.998, N = 10), and that natural samples define a virtually identical calibration line as the actively degassed samples, with a barely resolvable Δ_{47} offset of +3.3 ppm. Δ_{47} values of passively degassed samples display a significantly lower temperature sensitivity, implying that different precipitation protocols may result in subtle but resolvable Δ_{47} differences. Based on a very conservative analysis of the uncertainties in our data (including the error from our standardization methods), the natural samples in this study define a "natural" Δ_{47} calibration whose precision ranges from 1.2 to 1.8°C (1SE) between 0 and 40°C. Strikingly, standardizing our data by comparison with equilibrated CO_2, places our calibration line 20–25 ppm below that of *Kelson et al. (2017, GCA)*. By contrast, defining our absolute Δ_{47} values relative to the ETH carbonate standards *(Meckler et al., 2014, RCMS)* noticeably improves the external reproducibility of our measurements and brings our calibration line only 1–4 ppm below that of of *Kele et al. (2015, GCA)*. Together, these observations suggest that generalized use of international carbonate standards could greatly reduce inter-laboratory discrepancies.