

Triple oxygen isotope equilibrium between calcite and water: new constraints over 8–200 °C and their metrological implications

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High-precision measurements of carbonate oxygen-17 compositions are increasingly used for studying paleo-environments, hydrology, diagenesis, or biomineralization processes. Calibrating triple oxygen isotope equilibrium fractionations between calcite and water as a function of temperature provides a critical baseline for many applications. Here we report new observations constraining these fractionations between a suite of natural and synthetic carbonates and their parent waters, obtained using VCOF-CRDS, a new spectroscopic method providing ppm-level metrological linearity. Our observations on slow-growing natural calcites collected from Laghetto Basso and Devils Hole and those of our synthetic carbonates that closely approach $\delta^{18}\text{O}$ equilibrium are in good agreement with the latest theoretical models of calcite/water equilibrium fractionations between 8 °C and 200 °C. Data/model agreement is maximized when assuming that reference materials IAEA-603 and NBS18 have $\Delta^{17}\text{O}_{\text{VSMOW}}$ values of -0.068‰ , and -0.042‰ respectively. These estimates are consistent with some but not all of the observations reported so far by other groups. A sensitivity analysis shows that varying these parameters can strongly bias estimates of equilibrium $^{17}\theta_{\text{water}}^{\text{calcite}}$, whereas reformulating the equilibrium calibration in terms of chemically homogeneous comparisons ($\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}}$) is entirely unaffected by $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ but sensitive to the $\Delta^{17}\text{O}$ difference between IAEA-603 and NBS18. We conclude that pinning down the *relative* $\Delta^{17}\text{O}$ values of NBS18 and IAEA-603 is the most pressing short-term need for paleo-reconstructions. We also recommend systematically normalizing carbonate $\Delta^{17}\text{O}$ measurements using two carbonate reference materials with sufficiently different $\delta^{18}\text{O}$, and fully describing these normalization choices when reporting new $\Delta^{17}\text{O}$ measurements.

1 Introduction

The oxygen isotope composition of a carbonate mineral reflects that of the water from which it precipitated, modified by a combination of equilibrium and non-equilibrium processes which govern isotopic fractionations between the water, dissolved inorganic carbon and mineral phases. This primary signature may later be partially or fully overprinted by diagenetic processes. As a result, carbonate $\delta^{18}\text{O}$ archives have been one of the most versatile and widely used Earth science proxies since the dawn of stable isotope geochemistry, providing key insights into paleoclimates, past and present hydrology, diagenesis, biomineralization, ecology, and biogeochemical cycles. But this wide applicability also means that interpreting these $\delta^{18}\text{O}$ records remains challenging without bringing in additional constraints, usually from imposing key simplifying assumption and/or performing complementary geochemical measurements.

High-precision measurements of ^{17}O , the third and rarest stable isotope of oxygen, have emerged as a powerful tool for the interpretation of carbonate records. Because most ^{18}O -fractionating processes also fractionate ^{17}O in closely linked yet non-identical ways, different processes leave behind distinct “triple oxygen isotope” signatures (Sharp *et al.*, 2018). However, measuring $[^{17}\text{O}/^{16}\text{O}]$ in carbonates and CO_2 remains technically challenging, whether via isotope ratio mass spectrometry (IRMS), due to the interference between $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{13}\text{C}^{16}\text{O}$, or via emerging infrared absorption techniques with their own metrological issues. As things stand, at least four IRMS and two spectroscopic methods can achieve roughly equivalent instrumental precision for triple oxygen isotope analyses of carbonates (Passey *et al.*, 2014; Barkan *et al.*, 2015; Wostbrock *et al.*, 2020a; Perdue *et al.*, 2022; Ellis and Passey, 2023; Chaillot *et al.*, 2025). This has the advantage of helping detect method-specific artifacts, but also poses non-trivial standardization issues which hinder the comparability of results across laboratories. For example, the relative offsets between the triple oxygen signatures of the two international carbonate reference materials NBS18 and IAEA-603 reported by different groups differ significantly more than expected from nominal analytical uncertainties (Chaillot *et al.*, 2025, and references therein). As a result, two-point standardization using these reference materials is bound to yield substantially different results depending on which group’s results are used as “true” values for standardization. Such discrepancies are not limited to carbonate materials, as illustrated by the ongoing debate over the ^{17}O composition of SLAP2 relative to VSMOW (Sharp and Wostbrock, 2021; Tanaka *et al.*, 2026). These metrological issues are the most likely explanation for the conflicting values reported by various groups attempting to calibrate the fractionation laws that link the triple oxygen isotope compositions of carbonates to those

of their parent waters (Bergel *et al.*, 2020; Voarintsoa *et al.*, 2020; Wostbrock *et al.*, 2020b; Kelson *et al.*, 2022), and which provide a critical baseline for many paleo-applications.

Here we report new observations constraining triple oxygen fractionations between a suite of natural and synthetic carbonates and their parent waters. This is the first such dataset obtained using VCOF-CRDS (V-shaped Cavity Optical Feedback / Cavity Ring-Down Spectroscopy), a new optical method providing ppm-level metrological linearity (Chaillot *et al.*, 2025). These results provide new constraints on equilibrium fractionation factors over a broad temperature range (8–200 °C) to be compared with theoretical predictions, and new estimates of the triple oxygen signatures of carbonate reference materials IAEA-603 and NBS18 relative to VSMOW/SLAP. They also offer an opportunity to interrogate the choices made when converting these measurements into an actionable calibration framework. From this exercise we conclude that, among the various isotopic parameters requiring more accurate determination, pinning down the ^{17}O compositions of NBS18 and IAEA-603 *relative to each other* is the most pressing short-term need. Finally, we propose that formulating calcite-water fractionation in terms of differences in *chemically homogeneous* Δ -values (with carbonate compositions relative to carbonate reference materials, and water compositions relative to VSMOW-SLAP) is, for some applications, a more robust and immediately usable alternative to the traditional θ -value formulation.

2 Materials and Methods

2.1 Notations

We use classical notations for δ -values (e.g., $\delta^{18}\text{O}_{\text{VSMOW}}$, $\delta^{18}\text{O}_{\text{VPDB}}$) and isotopic fractionation factors. Thus $^{18}\alpha_{\text{w}}^{\text{c}}$ and $^{17}\alpha_{\text{w}}^{\text{c}}$ are the ^{18}O and ^{17}O fractionation factors between calcite (c) and water (w), and $^{17}\theta_{\text{w}}^{\text{c}} = \ln(^{17}\alpha_{\text{w}}^{\text{c}}) / \ln(^{18}\alpha_{\text{w}}^{\text{c}})$ is the corresponding triple oxygen isotope exponent. Because much of our discussion below entails comparing the triple oxygen compositions of many different materials, we use the following generalized notation for the relative compositions of materials A and B which may be any analytes, reference materials, or even general categories of materials such as carbonate (c) or water (w):

$$\Delta^{17}\text{O}_{\text{A}}^{\text{B}} = \ln\left(\frac{[^{17}\text{O}/^{16}\text{O}]_{\text{B}}}{[^{17}\text{O}/^{16}\text{O}]_{\text{A}}}\right) - \lambda \cdot \ln\left(\frac{[^{18}\text{O}/^{16}\text{O}]_{\text{B}}}{[^{18}\text{O}/^{16}\text{O}]_{\text{A}}}\right) = \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{B}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{A}} \quad (\text{Eq. 1})$$

with $\lambda = 0.528$ and:

$$\Delta^{17}\text{O}_{\text{VSMOW}} = \ln(1 + \delta^{17}\text{O}_{\text{VSMOW}}) - \lambda \cdot \ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}) \quad (\text{Eq. 2})$$

Since Miller (2002) redefined $\Delta^{17}\text{O}$ in its modern, log-linear formulation, virtually all carbonate studies have followed it, albeit under different notations. The $\Delta^{17}\text{O}$ and ^{17}O -excess notations adopted later (Barkan and Luz, 2007; Sharp *et al.*, 2018) were likely designed to avoid confusion with earlier, non-logarithmic formulations. By now, however, this risk of confusion is no longer a major concern, which is why we adopt the simplified notation of Eqs. 1-2 as a pragmatic trade-off between complexity and ambiguity.

We further extend these notations in cases where additional information is needed. When adding a qualifier to α , θ , or Δ values, *e.g.*, to denote their equilibrium values, we display this qualifier in superscript and note the two chemical phases being compared in subscript, as in $^{18}\alpha_{\text{c/w}}^{\text{eq}}$ and $\Delta^{17}\text{O}_{\text{c/w}}^{\text{eq}}$. Similarly, $\Delta^{17}\text{O}_{\text{CO}_2/\text{H}_2\text{O}}^{\text{eq}}$ characterizes triple oxygen isotope equilibrium between CO_2 and water, and $\Delta^{17}\text{O}_{\text{CO}_2/\text{CaCO}_3}^{\text{acid}}$ refers to the conversion of carbonates into CO_2 by phosphoric acid reaction.

Finally, for reasons detailed further below, we often consider the quantity $(\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}})$, which quantifies calcite/water fractionations in terms of chemically homogeneous comparisons. Hereafter, this quantity is expressed using the more compact notation $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$.

2.2 $\Delta^{17}\text{O}$ reference frames for waters and carbonates

Defining a common $\Delta^{17}\text{O}$ reference frame linking carbonates and waters is critical for mass-balance calculations involving different chemical phases, and for comparing theoretical predictions against real-world observations. Doing so requires specifying three independent quantities: one that defines the VSMOW-SLAP scale ($\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$); a second one that constrains the composition, relative to VSMOW, of one arbitrarily-chosen carbonate reference material (*e.g.*, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$); and a third one that constrains the relative compositions of two carbonate reference materials with very different $\delta^{18}\text{O}$ values (*e.g.*, $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$) in a way that is consistent with VSMOW/SLAP normalization. For a given set of two water and two carbonate materials, different formulations of the same reference scale are possible (*e.g.*, specifying $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$ instead of $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$), but these different formulations, being linear combinations of each other, are mathematically equivalent.

As described in Supplement S1, conversion from one carbonate reference frame to another (or from one water scale to another) behaves, to a very good approximation, as a shift in $\Delta^{17}\text{O}$ that scales linearly with $\ln(1 + \delta^{18}\text{O})$. For example, the fact that different groups have followed different conventions regarding $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ adds a minor but systematic complicating factor to the metrological debate about carbonate reference frames. Based on Supplement S1, the change in the $\Delta^{17}\text{O}_{\text{VSMOW}}$ value of a given sample, caused by switching

from $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = X_1$ to $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = X_2$, depends on the $\delta^{18}\text{O}_{\text{VSMOW}}$ value of that sample and is equal to:

$$\frac{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}})}{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}^{\text{SLAP}})} \cdot (X_2 - X_1) \quad (\text{Eq. 3})$$

Hereafter, whenever we compare the results obtained by different groups, we use the above equation to correct all $\Delta^{17}\text{O}_{\text{VSMOW}}$ values, including those assigned to carbonate materials, to the VSMOW-SLAP scale of Schoenemann *et al.* (2013) where $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$. This choice is not intended as an endorsement of this particular value but as a mean to focus on the other sources of inter-laboratory discrepancies. To avoid ambiguity, all such SLAP-corrected values are followed by an asterisk, so that for instance $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -48$ ppm, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -100$ ppm, and $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = +52$ ppm after Wostbrock *et al.* (2020a) are recalculated here as $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -50^*$ ppm, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -107^*$ ppm, and $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = +57^*$ ppm.

2.3 Natural calcites from Devils Hole and Laghetto Basso

Devils Hole (Nevada, USA) and Laghetto Basso (Corchia cave, Italy) are two localities widely regarded as offering the best natural conditions for achieving oxygen-isotope equilibrium between carbonate and water. At both sites, high-Mg “mammillary” calcite precipitated from barely supersaturated water at very slow rates on the order of 1 $\mu\text{m}/\text{yr}$ (Winograd *et al.*, 1992; Coplen, 2007; Piccini *et al.*, 2008; Drysdale *et al.*, 2012) but at markedly different temperatures (7.9 °C in Laghetto Basso and 33.7 °C at Devils Hole). Because of their near-equilibrium growth conditions, these two calcites have been used to constrain equilibrium values of $^{18}\alpha_w^c$ (Coplen, 2007; Daëron *et al.*, 2019) and clumped isotopes (Anderson *et al.*, 2021; Fiebig *et al.*, 2021; Daëron and Vermeesch, 2024). Devils Hole samples have also been used to constrain equilibrium triple oxygen isotope fractionation (Wostbrock *et al.*, 2020b).

We analyzed two powdered samples (DVH-2 and LGB-2) corresponding to the outer surface of a mammillary calcite slab (DHC2-8) from Devils Hole cave #2 and the top of a drill core (CD3-12) from Laghetto Basso. These samples are those previously described and analyzed in the clumped isotope studies cited above. We also analyzed modern water samples from the two sites. Water from Laghetto Basso was collected by G. Zanchetta (University of Pisa); water from Devils Hole #2 was collected by authorized Devils Hole Dive Team members (permit DEVA-2021-SCI-0031) at depths between 0.5 and 33 m. Water samples were placed in parafilm-sealed Nalgene vials and stored upside-down until analysis.

2.4 Synthetic calcites precipitated at high temperatures

Synthetic calcites were prepared in high pressure reaction cells at five different temperatures between 75 °C and 250 °C, following protocols described by Jautzy *et al.* (2020). Precipitation was achieved by mixing NaHCO₃ and CaCl₂ solutions following prolonged isotopic equilibration (24 to 144 h), using a passive degassing approach similar to that of Kim *et al.* (2007) and Dennis and Schrag (2010). Solution compositions were calculated with PHREEQC to maintain saturation indices below 2.1, with first-order precipitation rate estimates of 0.01–0.35 μmol · m⁻² · s⁻¹. Experiments were conducted in N₂-pressurized, PTFE-lined Parr reactors. After at least 24 h thermal equilibration, the CaCl₂ solution was transferred into the stirred NaHCO₃ solution through heated PTFE-lined tubing. Two 40 mL water aliquots per experiments were preserved in airtight glass vials with no head-space and stored at 4 °C until analysis. Following a minimum of 24 h of precipitation, the reactors were quickly cooled down. Precipitates were filtered, air-dried, homogenized, and stored in a desiccator until analysis.

Precipitate mineralogies were assessed based on scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Precipitates CC120, CC170, CC200, and CC250, respectively formed at 120 °C, 170 °C, 200 °C, and 250 °C, are composed almost entirely of rhombohedral crystals, each a few micrometers across (Supplementary Figure S2). Precipitate CC75, formed at 75 °C, also contains some micrometer-sized rhombohedral crystals but consists mostly of spheroidal aggregates, possibly of a non-calcite phase such as vaterite or aragonite. The FTIR absorption spectra were compared to those of pure calcite (Iceland spar, internal standard ISP-3) and pure aragonite (deep-sea coral, *Madrepora oculata*). All of the synthetic samples excepted for CC250 yield peaks consistent with our calcite standard (Supplementary Figure S3). CC250 — who, perhaps coincidentally, turned out visibly darker than the other samples — shows the the same peaks, but with broad, unidentified additional features.

2.5 Triple oxygen isotope analyses

Our analytical protocols for waters and carbonates are described in detail by Chaillot *et al.* (2025). Briefly, 150–300 μL water samples were equilibrated at 25 °C with 37–50 μmol CO₂ of known initial composition for 3+ days in flame-sealed glass ampoules before the CO₂ was cryogenically separated from water vapor, recollected and stored in flame-sealed ampoules until analysis. Carbonate samples, ~4 mg each, were reacted with 104 % orthophosphoric acid at 90 °C in a continuously stirred common acid bath. The evolved CO₂ was immediately trapped, then separated from water, air and other trace gases using cryogenic traps at –72 °C and –196 °C, before being stored in flame-sealed ampoules

until analysis. Relative abundances of $^{16}\text{O}^{12}\text{C}^{16}\text{O}$, $^{16}\text{O}^{13}\text{C}^{16}\text{O}$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ were measured using cavity ring-down spectroscopy as described by Chaillot *et al.* (2025). Raw abundance ratios were normalized by comparison with two pairs of international reference materials: VSMOW2 and SLAP2 for water-equilibrated samples, assuming that $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP2}} = 0$ (Schoenemann *et al.*, 2013); NBS18 and IAEA-603 for carbonate-derived samples, assuming that $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 26$ ppm (Chaillot *et al.*, 2025). The effects of these prior assumptions will be discussed in Sections 3.4 and 3.5.

3 Results and Discussion

3.1 Results

By choice, we only report $\Delta^{17}\text{O}$ results in terms of chemically homogeneous comparisons, because these are the metrological quantities that satisfy the principle of identical treatment of samples and standards. $\Delta^{17}\text{O}$ is thus expressed here relative to VSMOW for waters and relative to IAEA-603 for carbonates. Conversion between the two scales follows directly from Eq. 1:

$$\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{carbonate}} = \Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}} + \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} \quad (\text{Eq. 4})$$

The analytical repeatability for carbonates is 0.19 ‰ for $\delta^{18}\text{O}$ and 9 ppm for $\Delta^{17}\text{O}$ (pooled standard deviation with $N_f = 60$ degrees of freedom); repeatability for waters is 0.13 ‰ and 7 ppm, respectively ($N_f = 54$). In both cases, $\Delta^{17}\text{O}$ measurement residuals are uncorrelated with $\delta^{18}\text{O}$ residuals. All uncertainties reported hereafter correspond to 95 % confidence limits. These results are summarized in Table 1, which also reports $^{18}\alpha_w^c$ and $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ (defined in Section 2.1) for each water/calcite pair.

Samples	T °C	N _w	$\delta^{18}\text{O}_{\text{VSMOW}}^{\text{water}}$ ‰	$\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}}$ ppm	N _c	$\delta^{18}\text{O}_{\text{VPDB}}^{\text{carbonate}}$ ‰	$\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}}$ ppm	$10^3 \ln(^{18}\alpha_w^c)$	$\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ ppm
LGB	7.9	7	-7.39 ± 0.18	30.2 ± 7.3	8	-4.57 ± 0.17	12.3 ± 8.0	33.29 ± 0.25	-17.9 ± 10.9
DVH	33.7	9	-13.51 ± 0.12	32.2 ± 7.2	8	-15.79 ± 0.16	34.7 ± 7.6	28.13 ± 0.21	2.6 ± 10.5
CC75	75	3	-7.84 ± 0.18	21.1 ± 10.4	4	-20.23 ± 0.23	62.9 ± 10.6	17.88 ± 0.29	41.8 ± 14.9
CC120	120	3	-8.34 ± 0.18	20.6 ± 10.0	4	-25.39 ± 0.24	95.3 ± 11.3	13.12 ± 0.31	74.7 ± 15.1
CC170	170	2	-10.50 ± 0.21	32.7 ± 12.0	4	-30.34 ± 0.26	95.5 ± 12.3	10.20 ± 0.34	62.8 ± 17.2
CC200	200	3	-10.65 ± 0.18	34.4 ± 10.3	4	-31.92 ± 0.27	95.5 ± 12.7	8.71 ± 0.33	61.1 ± 16.3
CC250	250	9	-11.50 ± 0.11	31.1 ± 6.6	7	-35.96 ± 0.25	112.9 ± 11.8	5.41 ± 0.28	81.8 ± 13.5

Table 1 – Triple oxygen isotope compositions of the carbonates and waters analyzed here.

T is the crystallization temperature for each water/carbonate pair. N_w and N_c are the total numbers of analytical replicates for water and carbonate samples, respectively. Uncertainties are reported as 95 % confidence intervals accounting for standardization errors. As stated in Section 3.2, $\delta^{18}\text{O}_{\text{VSMOW}}$ of LGB water is the long-term average reported by Daëron *et al.* (2019), and ($\delta^{18}\text{O}_{\text{VSMOW}}$, $\Delta^{17}\text{O}_{\text{VSMOW}}$) of DVH water are the average values of 4 samples collected at different water depths (see Supplementary Figure S4).

3.2 Triple oxygen composition of our natural samples

Our $\delta^{18}\text{O}$ results for Devils Hole water and calcite are indistinguishable from those reported by Coplen (2007), Daëron *et al.* (2019), and Wostbrock *et al.* (2020b). Our $\delta^{18}\text{O}$ measurements for Laghetto Basso calcite are also very close to those of Daëron *et al.* (2019), but the $\delta^{18}\text{O}$ value of Laghetto Basso waters is 0.4 ‰ greater than the long-term average of -7.4 ‰, likely due to small seasonal variations. We thus use this seasonally biased $\delta^{18}\text{O}$ value only for the purpose of computing $\Delta^{17}\text{O}$. In Table 1 and Figure 1 we use instead the long-term average value for $\delta^{18}\text{O}_{\text{VSMOW}}^{\text{water}}$ and $^{18}\alpha_{\text{w}}^{\text{c}}$.

Water samples collected in Devils Hole Cave #2 at depths of 2, 20, 60 and 110 feet yield statistically indistinguishable $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values (Supplementary Figure S4). We thus pooled the samples from all depths to estimate the average triple oxygen isotope composition Devils Hole waters, reported as a single sample in Table 1. The resulting $\Delta^{17}\text{O}_{\text{VSMOW}}$ value, 32 ± 7 ppm, is consistent with winter precipitation values of 40 ± 15 ppm (1SD) over the Northwestern and Central USA (Aron *et al.*, 2023), and lies between previously reported values of $29^* \pm 6$ ppm (Wostbrock *et al.*, 2020b) and 45 ± 8 ppm (Affek *et al.*, 2025).

3.3 Assessing ^{18}O equilibrium attainment in our synthetic samples

As previously stated, natural calcites from Devils Hole and Laghetto Basso offer the best available constraints on low-temperature calcite/water ^{18}O equilibrium, which remains challenging to achieve in laboratory experiments. Conversely, at higher temperatures, faster isotopic exchange kinetics facilitate the attainment of isotopic equilibrium. For example, O'Neil *et al.* (1969) equilibrated various waters and carbonates at temperatures up to 700 °C, yielding $^{18}\alpha_{\text{w}}^{\text{c}}$ values that did not depend on the relative initial $\delta^{18}\text{O}$ of the reagents. Due to operational constraints, our own experiments were not repeated with different reagent compositions. However, we may still assess whether our synthetic samples approach oxygen-isotope equilibrium by comparing them to an equilibrium baseline defined by Devils Hole, Laghetto Basso, and the O'Neil *et al.* experiments from 200 °C to 700 °C. As seen in Figure 1, these baseline $^{18}\alpha_{\text{c/w}}^{\text{eq}}$ values align closely with the theoretical predictions of Guo and Zhou (2019), which we use hereafter as a general calibration of $^{18}\alpha_{\text{c/w}}^{\text{eq}}$ as a function of T.

Two of the synthetic carbonates, formed at temperatures of 170 °C and 200 °C, have quasi-equilibrium $\delta^{18}\text{O}$ values (with offsets from $^{18}\alpha_{\text{c/w}}^{\text{eq}}$ of -0.8 ± 0.3 ‰ and -0.3 ± 0.3 ‰, respectively, for samples CC170 and CC200). The three other synthetic carbonates have lighter than equilibrium $\delta^{18}\text{O}$ values, by up to -3.1 ± 0.3 ‰. Although the physical processes involved may differ, the sign and magnitude of these offsets are comparable to

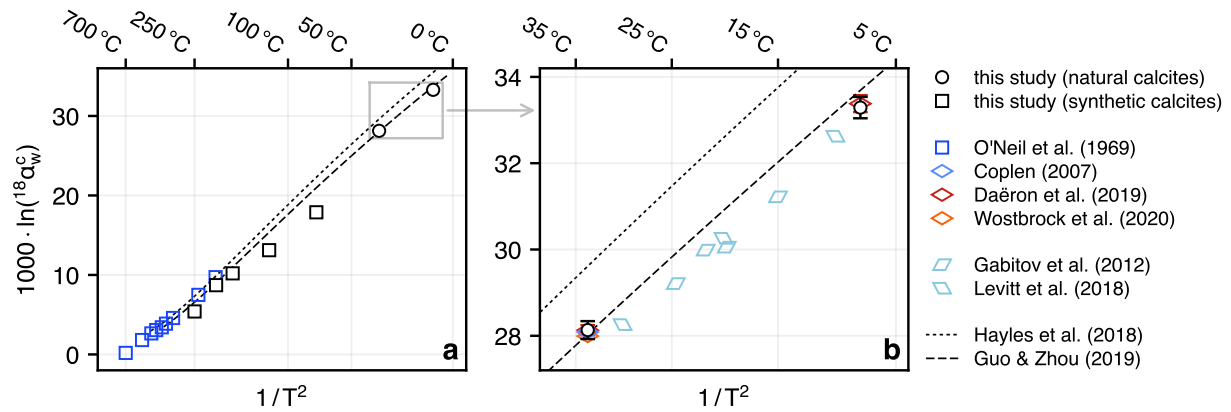


Figure 1 – ^{18}O fractionation between our calcite and water samples. Colored markers correspond to previous Devils Hole and Laghetto Basso observations reported by Coplen (2007), Daëron *et al.* (2019), and Wostbrock *et al.* (2020b); carbonates equilibrated in high-temperature experiments by O'Neil *et al.* (1969); and the slow-precipitated synthetic carbonates of Gabitov *et al.* (2012), and Levitt *et al.* (2018). Dashed lines are theoretical predictions by Hayles *et al.* (2018) and Guo and Zhou (2019). In most cases, 95 % error bars are smaller than the markers used here.

those observed in laboratory experiments and in many biogenic carbonates (e.g., Kim and O'Neil, 1997, Daëron and Gray, 2023, and references therein).

3.4 Constraining calcite/water triple oxygen isotope equilibrium

3.4.1 $\Delta^{17}\text{O}_w^c$ as a robust alternative to $^{17}\theta_w^c$

Previous studies constraining fractionation factors $^{18}\alpha_w^c$ and $^{17}\alpha_w^c$ between water (w) and calcite (c) preferentially expressed results in terms of the mass fractionation exponent $^{17}\theta = \ln(^{17}\alpha) / \ln(^{18}\alpha)$, with the implicit expectation that equilibrium values of $^{17}\theta$ vary moderately as a function of temperature, and approach 0.5305 at the high temperature limit. However, as shown by Hayles *et al.* (2016), $^{17}\theta$ may take any value when $^{18}\alpha$ approaches 1 in the high temperature limit, and, as illustrated in Section 3.5, experimental estimates of $^{17}\theta$ are likely to be disproportionately affected by small errors in the chain of isotopic parameters involved in their computation. Hayles *et al.* (2016) argued that an equally useful and more robust descriptor is the “difference in cap-deltas” defined as:

$$\begin{aligned}\Delta^{17}\text{O}_w^c &= \ln(^{17}\alpha_w^c) - \lambda \cdot \ln(^{18}\alpha_w^c) \\ &= (^{17}\theta_w^c - \lambda) \cdot \ln(^{18}\alpha_w^c)\end{aligned}\quad (\text{Eq. 5})$$

No information is lost when using this alternative formulation: for any non-zero value of $^{18}\alpha_w^c$, every value of $\Delta^{17}\text{O}_w^c$ maps to one and only one value of $^{17}\theta_w^c$. However, $\Delta^{17}\text{O}_w^c$ reliably tends to zero at high temperature and its equilibrium values are realistically bound to a natural range of $\pm 0.3 \text{ ‰}$ (Hayles *et al.*, 2016). Moreover, it can be precisely measured even at high temperature, and it is readily decomposed in terms that are either constant or derive

from water-to-water or carbonate-to-carbonate comparisons, which are metrologically less challenging than direct carbonate-to-water comparisons:

$$\underbrace{\Delta^{17}\text{O}_w^c}_{\text{physical quantity of interest}} = \underbrace{\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}}}_{\text{chemically homogeneous comparisons}} + \underbrace{\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}}_{\text{constant}} \quad (\text{Eq. 6})$$

Hereafter, we use the notation $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ as a shorthand for $(\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}})$.

3.4.2 Comparison of $\Delta^{17}\text{O}_w^c$ with theoretical predictions

Both Hayles *et al.* (2018) and Guo and Zhou (2019) derived equilibrium calcite/water triple oxygen fractionations from first-principles vibrational calculations, relying on different sets of vibrational frequencies for calcite and on similar strategies to estimate the corresponding

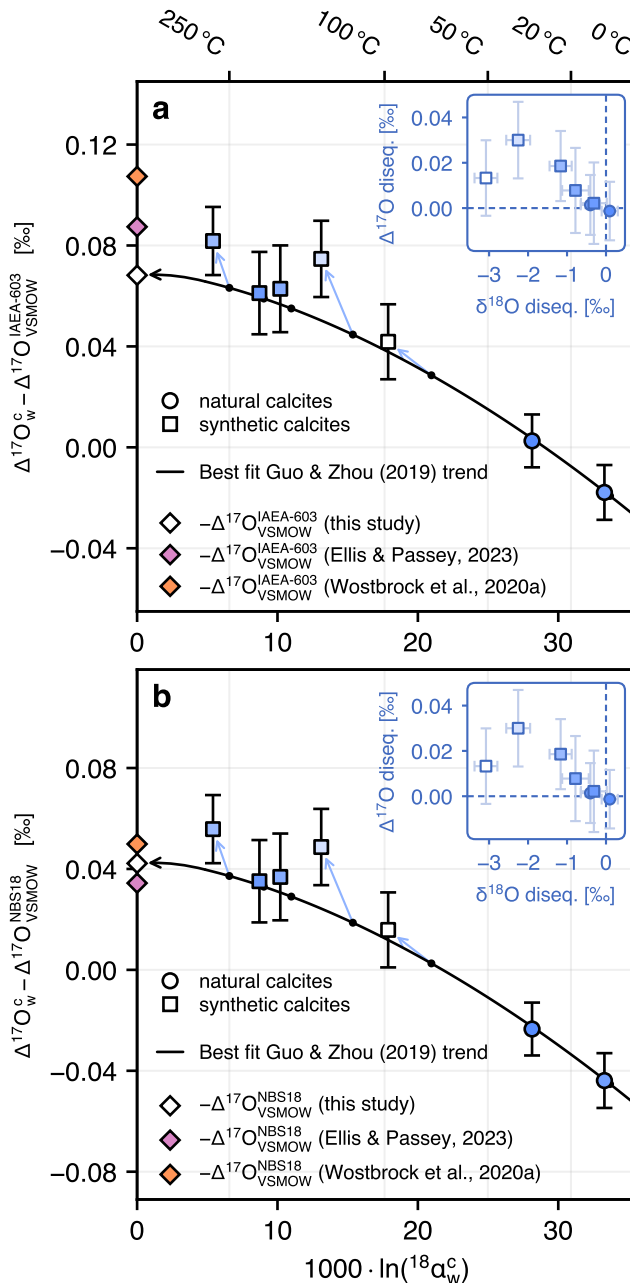


Figure 2 – Calcite/water differences in $\Delta^{17}\text{O}$.

[a] $(\Delta^{17}\text{O}_w^c - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}})$ as a function of $\ln(18\alpha_w^c)$ for the calcite/water sample pairs of Table 1. The solid black curve is the theoretical prediction of $\Delta^{17}\text{O}_{c/w}^{\text{eq}}$ (Guo and Zhou, 2019), vertically offset by the value of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ which yields the best fit to the two natural samples (white diamond marker). Predicted equilibrium compositions for our samples are shown as black circles along the theoretical curve. Blue shade of markers corresponds to the magnitude of $\delta^{18}\text{O}$ disequilibria relative to the $18\alpha_{c/w}^{\text{eq}}$ prediction of Guo and Zhou (2019), also shown in blue inset plot. Colored diamonds along the left axis correspond to previous, independent estimates of $-\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$.

[b] Same plot as in upper panel, but showing $(\Delta^{17}\text{O}_w^c - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}})$ instead of $(\Delta^{17}\text{O}_w^c - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}})$, with diamond markers corresponding to the independent estimates of $-\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$.

water values. To overcome the poorly constrained anharmonic behavior of liquid water, each study combined its own theoretical modeling of water vapor with the experimentally determined liquid/vapor $^{18}\alpha$ calibration of Horita and Wesolowski (1994). Both studies then used the liquid/vapor $^{17}\theta$ value originally computed by Hayles *et al.* (2018) to derive liquid/vapor $^{17}\alpha$.

The two models yield slightly different predictions for $^{18}\alpha_w^c$ (Figure 1), but very similar values for $\Delta^{17}O_w^c$ (-72 vs -71 ppm at 25°C ; -4.8 vs -5.0 ppm at 250°C). They predict that $\Delta^{17}O_w^c$ should increase with temperature by ~ 83 ppm over the temperature range of our samples (8 – 250°C), which is broadly consistent with our measurements. In particular, the relative $\Delta^{17}O_w^c$ values for DVH and LGB, which differ by 20 ± 13 ppm, are in good agreement with the theoretical prediction of 23 ppm.

However, a more quantitative data-model comparison requires independent knowledge of $\Delta^{17}O_{\text{VSMOW}}^{\text{IAEA-603}}$ (Eq. 6), which we address through the following approach. First, we posit that our carbonate-to-carbonate and water-to-water comparisons are metrologically accurate, and that our Devils Hole and Laghetto Basso samples (DVH and LGB) effectively achieve oxygen-isotope equilibrium. Under these assumptions, we determine the “best-fitting” value of $\Delta^{17}O_{\text{VSMOW}}^{\text{IAEA-603}}$ that optimizes, in a least-squares sense, the agreement between our measurements and the theoretical predictions. In this step, we choose to use the Guo and Zhou model because of its better fit to the $^{18}\alpha_w^c$ observations, but this choice is largely immaterial in view of the two models’ very close $\Delta^{17}O_w^c$ predictions. Finally, we assess how well the resulting predicted trend in $\Delta^{17}O_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ fits our observations for the synthetic carbonates (which were not taken into account when fitting $\Delta^{17}O_{\text{VSMOW}}^{\text{IAEA-603}}$) and how well our independent estimate of $\Delta^{17}O_{\text{VSMOW}}^{\text{IAEA-603}}$ agrees with previous, more direct measurements.

The results of this exercise are shown in Figure 2a. We find that data/model agreement is maximized when $\Delta^{17}O_{\text{VSMOW}}^{\text{IAEA-603}} = -68.2 \pm 7.5$ ppm. Taking this estimate at face value for now, we extend the resulting best-fit equilibrium curve to higher temperatures and test whether it is consistent with our synthetic samples. We find that CC170 and CC200, the two synthetic samples with oxygen-18 compositions closest to equilibrium, also have $\Delta^{17}O_w^c$ values statistically indistinguishable from equilibrium, while the other synthetic samples plot further away from both of their respective $^{18}\alpha_w^c$ and $\Delta^{17}O_w^c$ equilibrium values. As shown in the inset plot of Figure 2a, isotopic disequilibria in these two dimensions are correlated, a pattern compatible with a shared kinetic process driving isotopic fractionation.

Even without a quantitative understanding of these disequilibrium observations, the close agreement of CC170 and CC200 with the best-fit equilibrium trend going through DVH and LGB supports the interpretation of this curve as an accurate approximation for

$\Delta^{17}\text{O}_{\text{c/w}}^{\text{eq}}$ as a function of T. The theoretical predictions of Hayles *et al.* (2018) were formulated as fifth- and seventh-order polynomial functions of inverse temperature, and those of Guo and Zhou (2019) as temperature-tabulated values. The following simplified polynomial expression may be used as a more practical approximation, which remains consistent within ± 0.2 ppm with the best-fit equilibrium curve shown in Figure 2a.

$$\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}} [\text{‰}] = 0.020 + 61.6 / T - 20400 / T^2 \quad (\text{Eq. 7})$$

3.4.3 Resulting new estimates of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$

Our best-fitting value $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -68.2 \pm 7.5$ ppm, differs substantially from previous estimates of $-107^* \pm 14$ ppm and $-87^* \pm 10$ ppm (Wostbrock *et al.*, 2020a; Ellis and Passey, 2023, respectively). Conceptually, the choice of IAEA-603 as a reference point for expressing carbonate-to-carbonate relative measurements of $\Delta^{17}\text{O}$, as done in Table 1, is somewhat arbitrary. We may repeat the same fitting exercise as above, this time using NBS18 as a reference point and plotting $(\Delta^{17}\text{O}_{\text{NBS18}}^{\text{carbonate}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{water}})$ as a function of T (Figure 2b). In that case, we obtain a best-fit estimate of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -42.2 \pm 7.5$ ppm, which lies halfway between those reported by Wostbrock *et al.* (2020a) and Ellis and Passey (2023), respectively $-50^* \pm 18$ ppm and $-34^* \pm 10$ ppm.

3.4.4 Testing alternative $\Delta^{17}\text{O}$ -normalization scales

The contrast between our NBS18 value, which agrees with previous estimates, and our IAEA-603 value, which does not, is a consequence of the well-documented disparity between laboratories regarding the relative $\Delta^{17}\text{O}$ of these two materials (Chaillot *et al.*, 2025, and references therein). Because we standardize our carbonate measurements relative to IAEA-603, we do not require any knowledge of the true $\Delta^{17}\text{O}_{\text{VSMOW}}$ values of the two carbonate standards, but we still need to make some assumption regarding $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$. Here we used $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 26$ ppm, following Chaillot *et al.* (2025), which agrees within uncertainties with the 31 ppm reported by Barkan *et al.* (2019), but not with the 57^* ppm and 53^* ppm reported by Wostbrock *et al.* and Ellis and Passey, respectively. To assess how our interpretations might change when using a greater value, we fully reprocessed our data assuming $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 57^*$ ppm.

This choice can be evaluated against a general theoretical expectation: at sufficiently high temperature, $^{18}\alpha_{\text{w}}^{\text{c}}$ and $^{17}\alpha_{\text{w}}^{\text{c}}$ both approach 1. Carbonates will thus tend to have oxygen isotope compositions that closely approach those of their parent water. A hypothetical carbonate formed from VSMOW at an infinitely high temperature would thus have $\Delta^{17}\text{O}_{\text{VSMOW}} = 0$, and its $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{carbonate}}$ value would directly constrain the unknown quantity $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$. The suite of our samples never reach $^{18}\alpha_{\text{w}}^{\text{c}} = 1$, obviously, but they are never-

theless expected to collectively verify the physical prediction that $\Delta^{17}\text{O}_w^c$ should approach, but barely (if at all) exceed, zero at high temperatures (Hayles *et al.*, 2018):

$$\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}} \xrightarrow{T \rightarrow \infty} -\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} \quad (\text{Eq. 8})$$

Reprocessing with $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 57^*$ ppm causes the final $\Delta^{17}\text{O}_{\text{IAEA-603}}$ values of our carbonate samples to increase by an amount that varies linearly with $\ln(1 + \delta^{18}\text{O})$. Because our samples decrease in $\delta^{18}\text{O}$ as their formation temperature increases, the overall effect is that $\Delta^{17}\text{O}_w^c$ varies more steeply with T (Supplementary Figure S5). As a result, synthetic samples CC170 and CC200, which were previously in good agreement with the extrapolated theoretical trend passing through DVH and LGB, now plot 37 ± 20 ppm above the best-fit equilibrium curve. This pushes synthetic sample CC250 even higher, exceeding the various estimates of $-\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ (white, orange and magenta diamonds in Figure S5) by 40 ± 14 ppm. Taken at face value, these observations would imply that samples formed above 170 °C have large, strictly positive $\Delta^{17}\text{O}_w^c$, which is at odds with our physical expectations.

Considering (a) the fact that the general trend of Eq. 8 appears to hold true when we normalize data to $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 26$ ppm (Figure 2), but not for 57* ppm (Figure S5), and (b) the finding that $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 26$ ppm yields relative $\Delta^{17}\text{O}_w^c$ values for the samples in oxygen-18 quasi-equilibrium (DVH, LGB, CC170, and CC200) very close to the concordant theoretical predictions of Hayles *et al.* (2018) and Guo and Zhou (2019), we provisionally stand by our initial choice of $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}} = 26$ ppm.

3.4.5 Self-consistent metrological framework linking water and carbonate $\Delta^{17}\text{O}$

The new results reported here, the earlier observations of Chaillot *et al.* (2025), and the theoretical predictions of Hayles *et al.* (2018) and Guo and Zhou (2019) can all be unified within a self-consistent framework, provided the following values are assigned:

$$\begin{cases} \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0 \\ \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -0.068 \text{ ‰} \\ \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -0.042 \text{ ‰} \end{cases} \quad (\text{Eq. 9})$$

This combination is not the only acceptable one. For example, the internal consistency between the theoretical models and our data is nearly unaffected by an alternative choice of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ (cf Section 3.5 below). However, based on the computations described in Supplement S1, any change in $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ would require the following adjustments:

$$\begin{cases} \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -0.068 \text{ ‰} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} / 2.03 \\ \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -0.042 \text{ ‰} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} / 7.96 \end{cases} \quad (\text{Eq. 10})$$

On the other hand, as discussed above, our estimates of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$ are jointly constrained by the projection of our $\Delta^{17}\text{O}_{\text{w}}^{\text{c}}$ measurements for LGB, DVH, CC170, and CC120 along the theoretical equilibrium trend (Figure 2). In Figure 3 we compare our findings to those of three other groups (Barkan *et al.*, 2019; Wostbrock *et al.*, 2020a; Ellis and Passey, 2023). The values originally reported by Wostbrock *et al.* and by Ellis and Passey were SLAP-corrected to $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ as described in Section 2.1, causing only modest changes of 2–7 ppm. The Barkan *et al.* results were originally reported for CO_2 obtained by acid reaction at 25 °C, and were normalized to VSMOW-SLAP based on an experimental determination of equilibrium $\Delta^{17}\text{O}_{\text{H}_2\text{O}}^{\text{CO}_2}$ at 25 °C (Barkan and Luz, 2012). Using instead the theoretical $\Delta^{17}\text{O}_{\text{H}_2\text{O}}^{\text{CO}_2}$ proposed by Guo and Zhou (2019) would increase $\Delta^{17}\text{O}_{\text{VSMOW}}$ for both reference materials by 67 ppm, and correcting the resulting numbers for the acid fractionation effects computed by Liu and Cao (2026) would increase both $\Delta^{17}\text{O}_{\text{VSMOW}}$ values by ≈ 50 ppm, making Barkan *et al.*'s results statistically indistinguishable from ours. As seen in Figure 3 and Table 2, under these assumptions the four groups obtain mutually consistent values for NBS18, but substantial discrepancies persist regarding IAEA-603.

$\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-NBS18}}$	$\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$	Study
-45 ± 10 ppm	-76 ± 12 ppm	Barkan <i>et al.</i> (2019)
$-50^* \pm 18$ ppm	$-107^* \pm 14$ ppm	Wostbrock <i>et al.</i> (2020a)
$-34^* \pm 10$ ppm	$-87^* \pm 10$ ppm	Ellis and Passey (2023)
-42 ± 8 ppm	-68 ± 8 ppm	this study

Table 2 – Recomputed estimates of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$ shown in Figure 3, with 95 % confidence limits based on currently known sources of uncertainties. The original results of Barkan *et al.* (2019) were recomputed as detailed in Section 3.4.5. The original results of Wostbrock *et al.* (2020a) and Ellis and Passey (2023) were corrected to $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ as described in Section 2.2.

3.4.6 Comparison with previous calibration studies

Observations relevant to calcite/water triple oxygen isotope fractionation were previously reported by Passey *et al.* (2014), Bergel *et al.* (2020), Voarintsoa *et al.* (2020), Wostbrock *et al.* (2020b), Sha *et al.* (2020), Kelson *et al.* (2022), Huth *et al.* (2022), Affek *et al.* (2023), and Roy *et al.* (2025). These measurements were performed on various types of natural and synthetic carbonates, using different techniques, and normalized to different isotopic scales. All three of these factors likely contribute to any apparent disagreements between groups, but isolating their respective effects remains challenging.

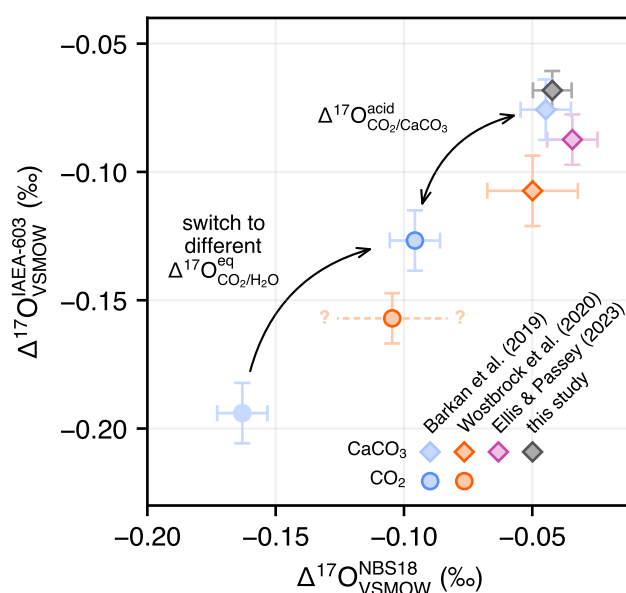


Figure 3 – $\Delta^{17}\text{O}$ characterization of NBS18 and IAEA-603 by different groups

Our own results are from Section 3.4.3. The original results of Wostbrock *et al.* (2020a) and Ellis and Passey (2023) were corrected to $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ as described in Section 2.2. The Barkan *et al.* (2019) results were originally normalized to VSMOW-SLAP assuming $\Delta^{17}\text{O}_{\text{CO}_2/\text{H}_2\text{O}}^{\text{eq}} = -205$ ppm after Barkan and Luz (2012). Assuming instead that $\Delta^{17}\text{O}_{\text{CO}_2/\text{H}_2\text{O}}^{\text{eq}} = -138$ ppm after Guo and Zhou (2019) shifts both $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18-CO}_2}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603-CO}_2}$ by +67 ppm. The final Barkan *et al.* (2019) results for carbonates are then derived from the experimental determination of $\alpha_{\text{CO}_2/\text{CaCO}_3}^{18} = 1.01025$, $\alpha_{\text{CO}_2/\text{CaCO}_3}^{17} = 0.5230$ (Wostbrock *et al.*, 2020a), yielding $\Delta^{17}\text{O}_{\text{CO}_2/\text{CaCO}_3}^{\text{acid}} = -51$ ppm, consistent with the theoretical predictions of Liu and Cao (2026).

All recomputed carbonate $\Delta^{17}\text{O}$ values are listed in Table 2.

In a similar spirit to Huth *et al.* (2022), we attempted to renormalize previous data to the reference frame of Eq. 9. Our aim here is assessing inter-laboratory consistency, as opposed to claiming that Eq. 9 is necessarily the “best” choice. We do so using the linear approximation for conversion between $\Delta^{17}\text{O}$ normalization scales described in Supplement S1. Instead of tracking the full chain of calculations (including triple oxygen isotope fractionations associated with acid reactions, $\text{H}_2\text{O}/\text{CO}_2$ equilibration, or O_2/CO_2 exchange), this approach only requires some knowledge of the $\Delta^{17}\text{O}$ values reported for IAEA-603 and NBS18 in the different studies, or in studies reported at the time by the same group and using the same analytical methods.

Table 3 summarizes the reference frame information available for each of the reprocessed studies. We do not include the speleothem observations of Sha *et al.* (2020) and Affek *et al.* (2023) because of the large, well-documented oxygen-18 disequilibria affecting most speleothems. In cases where $\Delta^{17}\text{O}$ values of IAEA-603 and/or NBS18 were not reported, we tentatively estimate them based on $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS19}}$, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS19-CO}_2}$ and/or $\Delta^{17}\text{O}_{\text{NBS19}}^{\text{NBS18}}$.

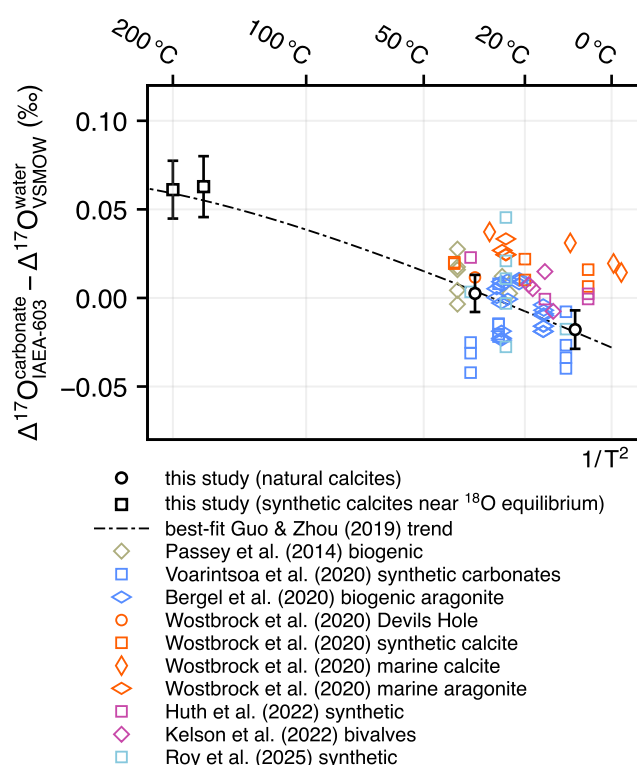


Figure 4 – Compiled observations constraining $\Delta^{17}\text{O}_{\text{carb/IAEA-603 water/VSMOW}}$ as a function of T. Systematic two-point normalization of water and carbonate analyses using reference materials of the same chemical nature should allow robust comparison of measurements performed on different analytes (CO_2 vs O_2), even using very different analytical techniques. Here, previously reported results from various groups were converted to the metrological framework of Eq. 9 based on the information summarized in Table 3 and the linear conversion formula of Supplement S1. This exercise is primarily limited by the fact that not all studies report $\Delta^{17}\text{O}$ measurements of two carbonate and two water reference materials analyzed in the same period as the unknown samples.

values from the same group/technique, filling any missing constraints using our own measurements of $\Delta^{17}\text{O}_{\text{IAEA-603 NBS19}}$ and $\Delta^{17}\text{O}_{\text{NBS18 NBS19}}$ (Chaillot *et al.*, 2025).

As shown in Figure 4, after conversion to the metrological framework of Eq. 9 the previous calibration data still display substantial scatter around our best-fit equilibrium curve (Eq. 7). This reprocessing attempt is encouraging but we readily acknowledge the limitations of our approach, which remains ultimately limited by the lack of reported normalization data. This exercise can however be seen as a snapshot of things as they stand today, and further motivate ongoing efforts to anchor carbonate $\Delta^{17}\text{O}$ measurements to a two-point reference frame. We recommend that future studies explicitly and systematically report $\Delta^{17}\text{O}$ values for both IAEA-603 and NBS18, measured around the same time and using the same method as their carbonate samples. It may eventually be preferable to replace these two primary reference materials with local standards, but doing so at this stage would add to the chain of uncertainties we are already faced with.

Passey <i>et al.</i> (2014) Huth <i>et al.</i> (2022) Kelson <i>et al.</i> (2022) $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -100 \text{ ppm}$	Notes: Original carbonate data were reprocessed by Huth <i>et al.</i> (2022), applying a single-point normalization based on the $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ value of Wostbrock <i>et al.</i> (2020a). Lacking coeval measurements of NBS18 from the same group reprocessed in the same way, here we tentatively assign $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -66 \text{ ppm}$ in this reprocessed “Huth <i>et al.</i>” reference frame based on the following decomposition: $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = \Delta^{17}\text{O}_{\text{NBS19}}^{\text{NBS18}} + \Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS19}} + \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ with $\Delta^{17}\text{O}_{\text{NBS19}}^{\text{NBS18}} = +37 \text{ ppm}$ after Passey <i>et al.</i> (2014) and $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS19}} = -3 \text{ ppm}$ after Chaillot <i>et al.</i> (2025). We use this decomposition instead of the $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ value derived from Ellis and Passey (2023) because the method they used to convert carbonates into O_2 is not the same as that used in the 2014–2022 studies listed here.
Wostbrock <i>et al.</i> (2020b) $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = -15 \text{ ppm}$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -100 \text{ ppm}$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -048 \text{ ppm}$	Notes: All three values are from Wostbrock <i>et al.</i> (2020a).
Voarintsoa <i>et al.</i> (2020) Bergel <i>et al.</i> (2020) $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603-CO}_2} = -194 \text{ ppm}$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18-CO}_2} = -163 \text{ ppm}$	Notes: Original carbonate data were expressed as $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{CO}_2}$ measured after acid reaction at 25 °C. $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603-CO}_2}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18-CO}_2}$ are from Barkan <i>et al.</i> (2019).
Roy <i>et al.</i> (2025) $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$ $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS19-CO}_2} = -199 \text{ ppm}$	Notes: Original carbonate data were expressed as $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{CO}_2}$ measured after acid reaction at 25 °C. Lacking coeval measurements of IAEA-603 and NBS18 from the same group, we tentatively assign $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -196 \text{ ppm}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -170 \text{ ppm}$ based on the following decompositions: $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = \Delta^{17}\text{O}_{\text{NBS19}}^{\text{IAEA-603}} + \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS19}}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = \Delta^{17}\text{O}_{\text{NBS19}}^{\text{NBS18}} + \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS19}}$ with $\Delta^{17}\text{O}_{\text{NBS19}}^{\text{IAEA-603}} = +3 \text{ ppm}$ and $\Delta^{17}\text{O}_{\text{NBS19}}^{\text{NBS18}} = +29 \text{ ppm}$ after Chaillot <i>et al.</i> (2025).

Table 3 – Summary of the original reference frame parameters reported in the calibration studies compiled in Figure 4, with notes providing context and describing how we estimate corresponding $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$ values consistent with these reference frames.

3.5 Sensitivity of different formulations to the choice of a calcite/ water reference frame

The reprocessing exercises of Sections 3.4.4 and 3.4.6 highlight that any calibration dataset is sensitive to the choice of a normalization scale. In order to investigate the resulting systematic biases, we reprocessed our calcite/water calibration dataset using different reference frame assumptions, systematically varying $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$, and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}}$. For simplicity, the reprocessed dataset comprises only our two natural sample pairs (DVH and LGB) and the two synthetic sample pairs achieving $^{18}\alpha_w^c$ within <1 ‰ of equilibrium (CC170 and CC200).

The results of this exercise are shown in Figure 5. In the top panel (Fig. 5a), we compute $^{17}\theta_w^c$ for the four sample pairs. As expected from the previous sections, our “baseline” reference frame (in gray) yields a good fit with the theoretical $^{17}\theta_{c/w}^{\text{eq}}$ predictions of Hayles *et al.* (2018) and Guo and Zhou (2019) (dashed lines in Figure 5a). We also find that a

different choice of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ (in blue) does not substantially shift $^{17}\theta_w^c$, because the waters considered here are much closer in composition to VSMOW than to SLAP. By contrast, and despite our synthetic samples having much larger error bars, increasing $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ by 24 ppm (in yellow) yields $^{17}\theta_w^c$ values at high temperature that are statistically irreconcilable with those obtained assuming our baseline reference frame. The same is true, but for all temperatures and in the other direction, when decreasing $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ by 32 ppm (in red). It would clearly be possible to design a combination of $(\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}, \Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}})$ values that would yield similar $^{17}\theta_w^c$ values as those obtained using our baseline reference frame. However, as discussed in Section 3.4.4, increasing both $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$ and $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ in this way eventually causes our observations to diverge from first-order physical predictions.

In Figure 5b, we plot the same reprocessed data showing $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ (or, equivalently, $\Delta^{17}\text{O}_w^c - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$) as a function of $\ln(^{18}\alpha_w^c)$. Once again, the change in $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ (yellow) strongly shifts the apparent $\Delta^{17}\text{O}_w^c$ for the synthetic sample pairs, while that in

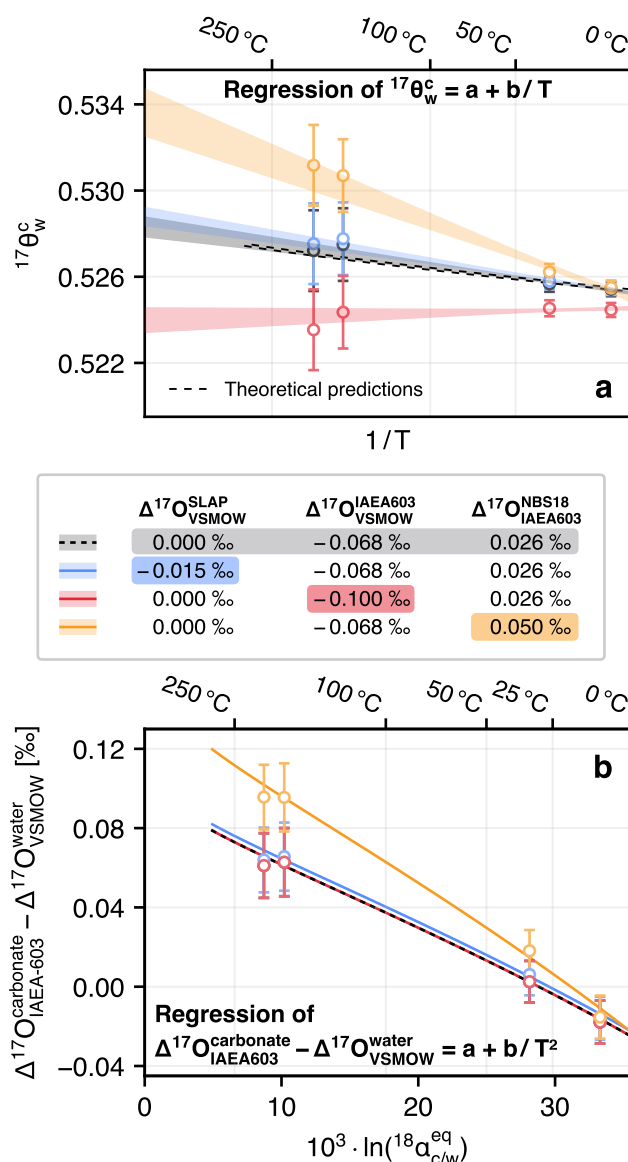


Figure 5 – Testing the sensitivity of our calibration observations to the choice of a carbonate/water reference frame

Only the sample pairs approaching oxygen-18 equilibrium (LGB, DVH, CC170, CC200) are plotted here.

[a] $^{17}\theta_w^c$ as a function of $1/T$, making different reference frame assumptions: in gray, with primary reference materials defined as in Eq. 9; in blue, red, and yellow, using different definitions for SLAP relative to VSMOW, IAEA-603 relative to VSMOW, and NBS18 relative to IAEA-603, respectively. Shaded colored regions correspond to 95 % confidence bands for regressions of $^{17}\theta_w^c$ as an affine function of $1/T$.

[b] $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ as a function of $\ln(^{18}\alpha_w^c)$, making the same reference frame assumptions. By contrast with $^{17}\theta_w^c$, $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ remains entirely insensitive to the choice of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$. For this suite of observations, the primary factor influencing the calibration is the value assigned to $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$.

$\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ has minimal effects. However, this representation is entirely insensitive to the value of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$, which cancels out by design when calculating $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$.

The effect of a change in $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ appears to correlate with temperature in this particular example, but this is not necessarily so. Our synthetic samples are strongly affected by $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ not because they formed at high temperatures per se, but because they have very low carbonate $\delta^{18}\text{O}$. Hypothetical natural carbonates formed at low temperature from waters with very low $\delta^{18}\text{O}$ would be just as strongly affected. Conversely, carbonates formed at high temperature from isotopically enriched waters, resulting in $\delta^{18}\text{O}$ close to that of IAEA-603, would remain mostly unaffected by $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$.

From this exercise we draw two conclusions. First, for the purpose of reconstructing $\Delta^{17}\text{O}$ of past waters from the triple oxygen composition of carbonate archives, formulating a calcite/water calibration in terms of $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$ makes reconstructions entirely immune to errors caused by any inaccuracies in $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}}$. Quite clearly, however, $^{17}\theta_{\text{w}}^{\text{c}}$ -formulated calibrations remain necessary for mass-balance and theoretical models. Secondly, the accuracy of future paleo-hydrological reconstructions depends critically on resolving the apparent contradictions in the estimates of $\Delta^{17}\text{O}_{\text{IAEA-603}}^{\text{NBS18}}$ reported so far. Errors in this quantity are likely to introduce substantial biases when comparing samples with different $\delta^{18}\text{O}$ compositions, such as marine vs continental carbonates.

4 Conclusion and recommendations

The challenges of unifying oxygen-isotope metrological scales for carbonates and waters are all but new. The early carbonate oxygen-18 calibrations of Epstein *et al.* (1953), Craig (1965) or Shackleton (1974) were, by necessity, defined as a function of the “isotopic difference between carbon dioxide extracted from the carbonate and carbon dioxide equilibrated with the water, both under specified conditions” (Shackleton, 1974). Only later, after the modern VPDB and VSMOW scales were formally anchored to each other (Coplen *et al.*, 1983), did it become practical to express empirical calibrations in terms of $^{18}\alpha_{\text{w}}^{\text{c}}$, and to use these $^{18}\alpha_{\text{w}}^{\text{c}}$ laws for paleo-reconstructions. Regarding triple oxygen isotope metrology, we are at a similar stage as our predecessors were in the 1970’s. It is not that we lack the proper reference materials, but we have not yet fully reconciled the experimental results of groups using different methods to constrain the $\Delta^{17}\text{O}$ values (relative to VSMOW or to each other) of our primary reference materials. As illustrated here, the choices of carbonate/water reference frame definition directly affect our calculations of $^{17}\theta_{\text{w}}^{\text{c}}$ and/or $\Delta^{17}\text{O}_{\text{w}}^{\text{c}}$.

Until we collectively resolve these issues, it is worth considering the potential benefits of formulating carbonate/water calibrations also in terms of $\Delta^{17}\text{O}_{\text{water/VSMOW}}^{\text{carb/IAEA-603}}$, not as a long-

term replacement for $^{17}\theta_w^c$ or $\Delta^{17}O_w^c$ but as a pragmatic, short-term method to minimize the impact of certain sources of uncertainty (e.g., on $\Delta^{17}O_{VSMOW}^{IAEA-603}$, as seen in Figure 5). We also recommend that carbonate triple oxygen isotope measurements be systematically normalized relative to two carbonate reference materials with sufficiently different $\delta^{18}O$ values (e.g., as described in Supplement S2), and that normalization choices (which standards, and which assigned values) always be reported alongside the measurements. Much like the definition of the VPDB scale, which improved carbonate $\delta^{18}O$ metrology without severing its link to VSMOW, normalizing in this way adheres to the principle of identical treatment of samples and standards and should improve comparability across laboratories, while keeping all triple oxygen isotope data traceable to the VSMOW-SLAP scale.

The observations reported here support the argument that the latest theoretical models of triple oxygen isotope calcite/water equilibrium accurately predict the variation of $\Delta^{17}O_w^c$ between 8 °C and 200 °C as long as the quantity $\Delta^{17}O_{IAEA-603}^{NBS18}$ is close to 26 ppm. They also provide new, tentative estimates of $\Delta^{17}O_{VSMOW}^{IAEA-603}$ and $\Delta^{17}O_{VSMOW}^{NBS18}$, which are consistent with some if not most of the previously reported evidence. In view of these results, we conclude that among the three quantities defining a common VSMOW/SLAP/IAEA-603/NBS18 reference frame, the accuracy of our paleo-reconstructions depends critically on pinning down the true value of $\Delta^{17}O_{IAEA-603}^{NBS18}$. Lacking that information, we risk introducing systematic biases when applying triple oxygen isotope frameworks to carbonates and waters from realms with different $\delta^{18}O$ compositions, such as marine vs continental, hyperarid, periglacial and/or high-latitude settings.

Data, code, and outputs availability

The full dataset and codebase used here are freely available under MIT license at Zenodo, with the following DOI: [10.5281/zenodo.23366165](https://doi.org/10.5281/zenodo.23366165). The repository will also be mirrored at <https://github.com/mdaeron/D170calib-paper> for convenience and issue tracking.

Author contributions

Conceptualization: MD; Resources: MD, JC, JJJ, SK; Funding acquisition: MD, SK; Methodology: MD, TC, JC, MP, JJJ, BRF, SK; Analytical work: MD, TC, JC, MP, SK; Precipitation experiments: JJJ, BRF; Investigation: MD, TC, JC, MP, JJJ, BRF, SK; Supervision: MD, JC, JJJ, SK; Data curation: MD, TC, JC, SK; Writing: MD (original draft), TC, JC, MP, JJJ, BRF, SK.

Competing interests

The authors declare no competing interests.

Use of AI tools

So-called AI tools were used only for language editing (alternative phrasing). The authors take full responsibility for all content.

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Supplemental Material for Triple oxygen isotope equilibrium between calcite and water: new constraints over 8–200 °C and their metrological implications

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S1 – Conversion between $\Delta^{17}\text{O}$ -normalization scales

Here we consider the case of $\Delta^{17}\text{O}$ values normalized by comparison with two reference materials (e.g., VSMOW2 and SLAP2, or IAEA-603 and NBS18) whose nominal $\Delta^{17}\text{O}$ values are uniquely defined in a given normalization scale. For example, two such normalization scales are defined respectively by $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP2}} = 0$ (Schoenemann *et al.*, 2013) and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP2}} = -0.011 \text{ ‰}$ (Sharp and Wostbrock, 2021). For carbonates, one example of such a scale is that proposed by Wostbrock *et al.* (2020) and defined by $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{IAEA-603}} = -0.100 \text{ ‰}$ and $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{NBS18}} = -0.048 \text{ ‰}$.

In this study we use the following linear approximation: **the change in $\Delta^{17}\text{O}$ when converting between two normalization scales is approximated as a affine function of $\ln(1 + \delta^{18}\text{O})$** . This is mathematically expressed, noting the scales ① and ②, as:

$$\begin{aligned} & \Delta^{17}\text{O}_{\text{VSMOW}}^{②} - \Delta^{17}\text{O}_{\text{VSMOW}}^{①} = \\ & x \cdot [\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{R1}②} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{R1}①}] + (1 - x) \cdot [\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{R2}②} - \Delta^{17}\text{O}_{\text{VSMOW}}^{\text{R2}①}] \end{aligned} \quad (\text{Eq. 11})$$

with

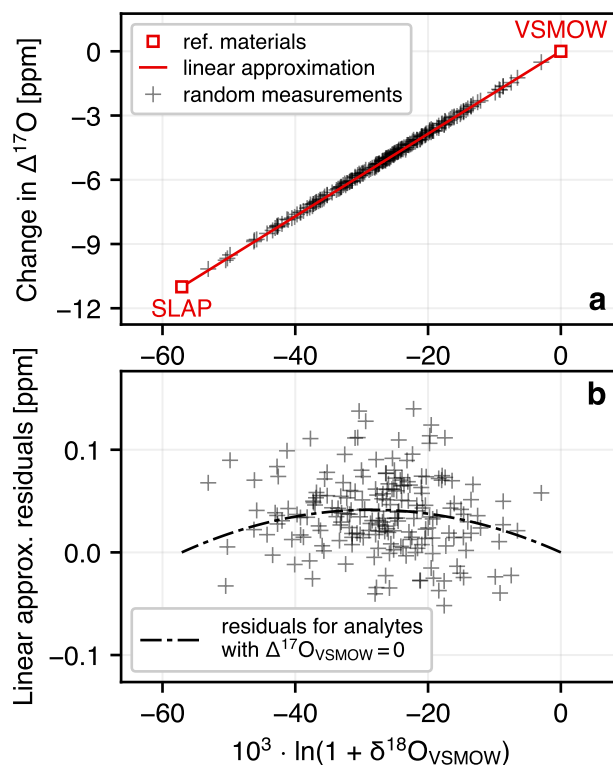
$$x = \frac{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}) - \ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}^{\text{R2}})}{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}^{\text{R1}}) - \ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}^{\text{R2}})} \quad (\text{Eq. 12})$$

In the case of the VSMOW-SLAP scale, this simplifies to:

$$\Delta^{17}\text{O}_{\text{VSMOW}}^{②} - \Delta^{17}\text{O}_{\text{VSMOW}}^{①} = \frac{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}})}{\ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}^{\text{SLAP}})} \cdot [\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} - \Delta^{17}\text{O}_{\text{VSMOW}}^{①}] \quad (\text{Eq. 13})$$

To test the accuracy of this linear approximation, we start by arbitrarily assuming that the Schoenemann *et al.* scale is exactly true ($\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$). We then generate a large number of simulated measurements with random ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$) values in this scale, then reprocess them by applying two-point normalization to their ($\delta^{17}\text{O}$, $\delta^{18}\text{O}$) values (Paul *et al.*, 2007) using a different scale (here, we used $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = -0.011$ ‰ after Sharp and Wostbrock).

Supplementary Figure S1 shows the resulting changes in $\Delta^{17}\text{O}$ values. Based on these results, we conclude that the $\Delta^{17}\text{O}$ residuals relative to our linear approximation are on the order of ± 0.1 ppm, well below current instrumental precision limits. These residuals were found to scale 1:1 with the postulated change in $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$, so that changes in the nominal value of $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}}$ in excess of 0.1 ‰ would be required for the residuals to reach ~ 1 ppm.



Supplementary Figure S1 – Testing the accuracy of our linear conversion between $\Delta^{17}\text{O}$ normalization scales.

[a] Change in $\Delta^{17}\text{O}$ when switching from the Schoenemann *et al.* (2013) scale ($\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = 0$) to the scale proposed by Sharp and Wostbrock (2021, $\Delta^{17}\text{O}_{\text{VSMOW}}^{\text{SLAP}} = -0.011$ ‰). Gray crosses correspond to 200 simulated measurements with random $\delta^{18}\text{O}_{\text{VSMOW}}$ spanning the full $\delta^{18}\text{O}$ range between VSMOW and SLAP, and $\Delta^{17}\text{O}$ spanning 0 ± 0.1 ‰ (1σ). [b] $\Delta^{17}\text{O}$ residuals of the linear approximation (red line in [a]). Residuals for analytes with $\Delta^{17}\text{O} = 0$ would follow the dashed line. Non-zero $\Delta^{17}\text{O}$ values introduce additional scatter still well below the current instrumental precision limits.

S2 – Formal and numerical propagation of the uncertainties associated with two-point normalization of $\Delta^{17}\text{O}$

Consider a suite of three carbonate triple oxygen isotope measurements with “raw”, uncorrected ($\delta^{18}\text{O}_{\text{VSMOW}}$, $\Delta^{17}\text{O}_{\text{VSMOW}}$) values noted ($\# \delta^{18}\text{O}_i$, $\# \Delta^{17}\text{O}_i$) with $i \in \{1, 2, 3\}$. These uncorrected compositions can be those of the carbonates themselves (after fluorination or high temperature conversion) or those of CO_2 produced by their acid digestion. The analytical uncertainties associated with $\# \delta^{18}\text{O}_i$ and $\# \Delta^{17}\text{O}_i$ are noted $\# \sigma_{\delta_i}$ and $\# \sigma_{\Delta_i}$, respectively. As is well established, standard deviations estimated from a small number of replicates are

themselves highly imprecise. Analytical uncertainties such as $^{\#}\sigma_{\delta_i}$ and $^{\#}\sigma_{\Delta_i}$ are therefore best estimated from the pooled standard deviation of all measurements performed under comparable conditions, assuming common variance ($\overline{\sigma_{\delta}}$ or $\overline{\sigma_{\Delta}}$) across those measurements. In that case, with N_i being the number of replicate analyses for i :

$$^{\#}\sigma_{\delta_i} = \overline{\sigma_{\delta}} / \sqrt{N_i} \quad \text{and} \quad ^{\#}\sigma_{\Delta_i} = \overline{\sigma_{\Delta}} / \sqrt{N_i} \quad (\text{Eq. 14})$$

Assuming that these measurements are normalized using two reference materials x and y with nominal ($\delta^{18}\text{O}_{\text{VSMOW}}$, $\Delta^{17}\text{O}_{\text{VSMOW}}$) compositions noted ($^{\blacksquare}\delta^{18}\text{O}_j$, $^{\blacksquare}\Delta^{17}\text{O}_j$) with $j \in \{x, y\}$, and raw measured values equal to ($^{\#}\delta^{18}\text{O}_j$, $^{\#}\Delta^{17}\text{O}_j$) with respective standard errors of ($^{\#}\sigma_{\delta_j}$, $^{\#}\sigma_{\Delta_j}$), the normalized oxygen-18 compositions of the three unknown samples, noted $^{\square}\delta^{18}\text{O}_i$, then follow:

$$\begin{aligned} ^{\square}\delta^{18}\text{O}_i &= a \cdot ^{\#}\delta^{18}\text{O}_i + b \\ a &= (^{\blacksquare}\delta^{18}\text{O}_y - ^{\blacksquare}\delta^{18}\text{O}_x) / (^{\#}\delta^{18}\text{O}_y - ^{\#}\delta^{18}\text{O}_x) \\ b &= (^{\#}\delta^{18}\text{O}_y ^{\blacksquare}\delta^{18}\text{O}_x - ^{\blacksquare}\delta^{18}\text{O}_y ^{\#}\delta^{18}\text{O}_x) / (^{\#}\delta^{18}\text{O}_y - ^{\#}\delta^{18}\text{O}_x) \end{aligned} \quad (\text{Eq. 15})$$

The joint uncertainties on a , b , and $^{\square}\delta^{18}\text{O}_i$ are derived through first-order error propagation laws and expressed by the following variance-covariance matrices:

$$\begin{pmatrix} \sigma_a^2 & \text{cov}(a, b) \\ \text{cov}(a, b) & \sigma_b^2 \end{pmatrix} = \mathbf{J} \cdot \mathbf{C} \cdot \mathbf{J}^T \quad \text{with} \quad \mathbf{J} = \begin{pmatrix} \frac{\partial a}{\partial ^{\#}\delta^{18}\text{O}_x} & \frac{\partial a}{\partial ^{\#}\delta^{18}\text{O}_y} \\ \frac{\partial b}{\partial ^{\#}\delta^{18}\text{O}_x} & \frac{\partial b}{\partial ^{\#}\delta^{18}\text{O}_y} \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} ^{\#}\sigma_{\delta_x}^2 & 0 \\ 0 & ^{\#}\sigma_{\delta_y}^2 \end{pmatrix} \quad (\text{Eq. 16})$$

$$\sigma^2 \begin{pmatrix} ^{\square}\delta^{18}\text{O}_1 \\ ^{\square}\delta^{18}\text{O}_2 \\ ^{\square}\delta^{18}\text{O}_3 \end{pmatrix} = \mathbf{J} \cdot \mathbf{C} \cdot \mathbf{J}^T \quad \text{with} \quad \mathbf{J} = \begin{pmatrix} ^{\#}\delta^{18}\text{O}_1 & 1 & a & 0 & 0 \\ ^{\#}\delta^{18}\text{O}_2 & 1 & 0 & a & 0 \\ ^{\#}\delta^{18}\text{O}_3 & 1 & 0 & 0 & a \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} \sigma_a^2 & \text{cov}(a, b) & 0 & 0 & 0 \\ \text{cov}(a, b) & \sigma_b^2 & 0 & 0 & 0 \\ 0 & 0 & ^{\#}\sigma_{\delta_1}^2 & 0 & 0 \\ 0 & 0 & 0 & ^{\#}\sigma_{\delta_2}^2 & 0 \\ 0 & 0 & 0 & 0 & ^{\#}\sigma_{\delta_3}^2 \end{pmatrix} \quad (\text{Eq. 17})$$

Normalizing $\delta^{17}\text{O}$ measurements first requires computing $^{\#}\delta^{17}\text{O}_i$, $^{\#}\delta^{17}\text{O}_j$ and $^{\blacksquare}\delta^{17}\text{O}_j$ values:

$$\begin{aligned} ^{\#}\delta^{17}\text{O}_i &= \exp(^{\#}\Delta^{17}\text{O}_i) \cdot (1 + ^{\#}\delta^{18}\text{O}_i)^{\lambda} - 1 \\ ^{\#}\delta^{17}\text{O}_j &= \exp(^{\#}\Delta^{17}\text{O}_j) \cdot (1 + ^{\#}\delta^{18}\text{O}_j)^{\lambda} - 1 \\ ^{\blacksquare}\delta^{17}\text{O}_j &= \exp(^{\blacksquare}\Delta^{17}\text{O}_j) \cdot (1 + ^{\blacksquare}\delta^{18}\text{O}_j)^{\lambda} - 1 \end{aligned} \quad (\text{Eq. 18})$$

The affine transformation for $\delta^{17}\text{O}$ is then similar to that of Eq. 15:

$$\begin{aligned}\delta^{17}\text{O}_i &= c \cdot \delta^{17}\text{O}_x + d \\ c &= (\delta^{17}\text{O}_y - \delta^{17}\text{O}_x) / (\delta^{17}\text{O}_y - \delta^{17}\text{O}_x) \\ d &= (\delta^{17}\text{O}_y \delta^{17}\text{O}_x - \delta^{17}\text{O}_y \delta^{17}\text{O}_x) / (\delta^{17}\text{O}_y - \delta^{17}\text{O}_x)\end{aligned}\quad (\text{Eq. 19})$$

The joint uncertainties on $(\delta^{18}\text{O}_i, \delta^{17}\text{O}_i)$, which are required to compute those on $(\Delta^{17}\text{O}_i)$, are derived through first-order error propagation laws and expressed as the following (6×6) variance-covariance matrix:

$$\sigma^2 \begin{pmatrix} \delta^{18}\text{O}_1 \\ \delta^{18}\text{O}_2 \\ \delta^{18}\text{O}_3 \\ \delta^{17}\text{O}_1 \\ \delta^{17}\text{O}_2 \\ \delta^{17}\text{O}_3 \end{pmatrix} = \mathbf{J} \cdot \mathbf{C} \cdot \mathbf{J}^T \quad (\text{Eq. 20})$$

where $\mathbf{J}$ is the Jacobian matrix of $(\delta^{18}\text{O}_1, \delta^{18}\text{O}_2, \delta^{18}\text{O}_3, \delta^{17}\text{O}_1, \delta^{17}\text{O}_2, \delta^{17}\text{O}_3)$ with respect to $(a, b, c, d, \delta^{18}\text{O}_1, \delta^{18}\text{O}_2, \delta^{18}\text{O}_3, \delta^{17}\text{O}_1, \delta^{17}\text{O}_2, \delta^{17}\text{O}_3)$, and $\mathbf{C}$ is the variance-covariance matrix of $(a, b, c, d, \delta^{18}\text{O}_1, \delta^{18}\text{O}_2, \delta^{18}\text{O}_3, \delta^{17}\text{O}_1, \delta^{17}\text{O}_2, \delta^{17}\text{O}_3)$.

In the end, the joint uncertainties on $(\Delta^{17}\text{O}_i)$ are computed as:

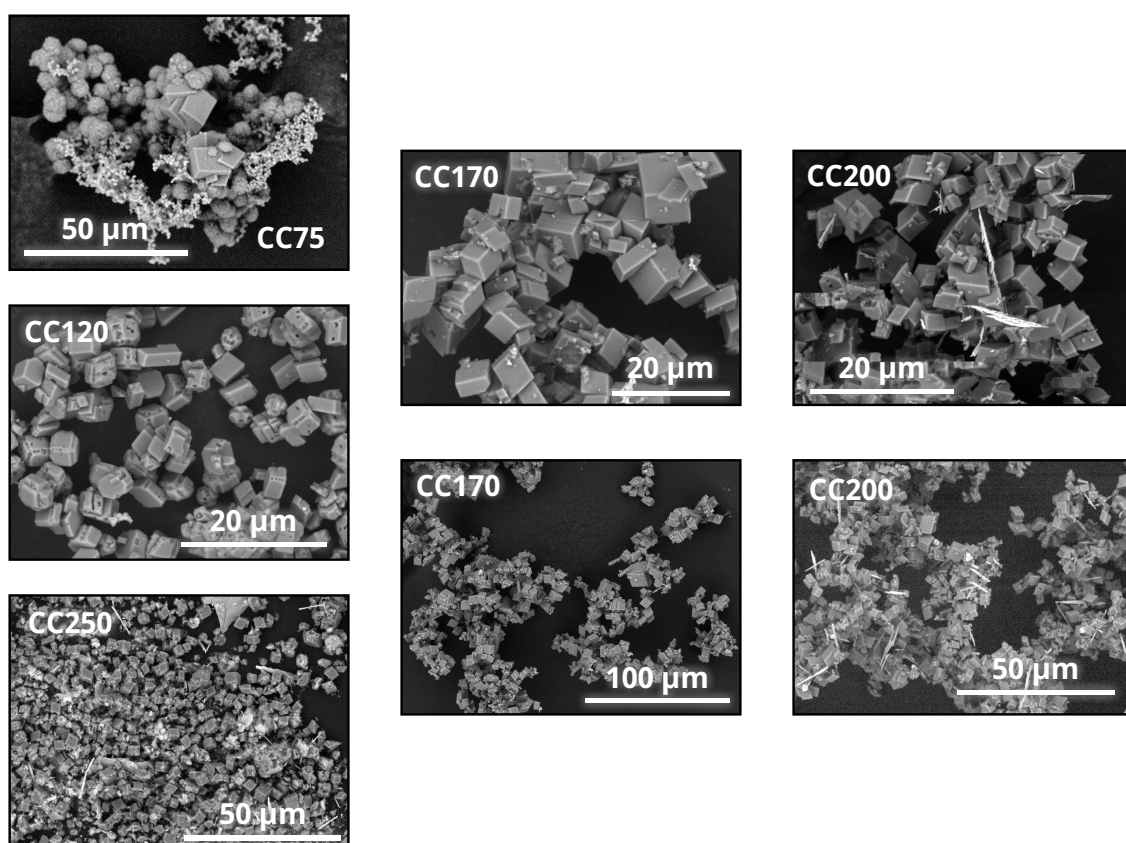
$$\sigma^2 \begin{pmatrix} \Delta^{17}\text{O}_1 \\ \Delta^{17}\text{O}_2 \\ \Delta^{17}\text{O}_3 \end{pmatrix} = \mathbf{K} \cdot \mathbf{V} \cdot \mathbf{K}^T \quad (\text{Eq. 21})$$

where $\mathbf{V}$ is the variance-covariance matrix computed in Eq. 20 and $\mathbf{K}$ is the Jacobian matrix of $(\Delta^{17}\text{O}_1, \Delta^{17}\text{O}_2, \Delta^{17}\text{O}_3)$ with respect to $(\delta^{18}\text{O}_1, \delta^{18}\text{O}_2, \delta^{18}\text{O}_3, \delta^{17}\text{O}_1, \delta^{17}\text{O}_2, \delta^{17}\text{O}_3)$:

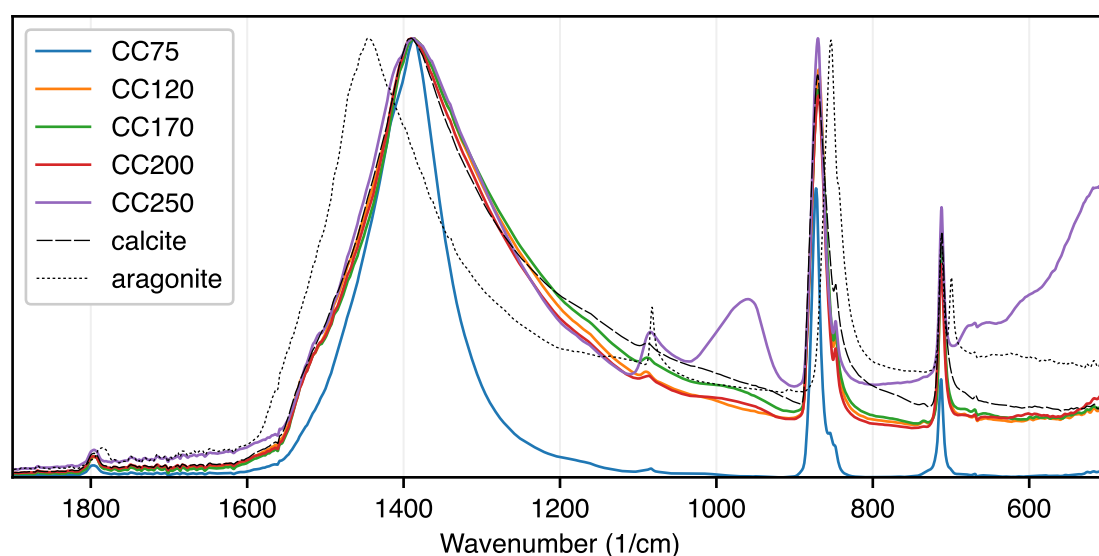
$$\mathbf{K}^T = \begin{pmatrix} \lambda / (1 + \delta^{18}\text{O}_1) & 0 & 0 \\ 0 & \lambda / (1 + \delta^{18}\text{O}_2) & 0 \\ 0 & 0 & \lambda / (1 + \delta^{18}\text{O}_3) \\ 1 / (1 + \delta^{17}\text{O}_1) & 0 & 0 \\ 0 & 1 / (1 + \delta^{17}\text{O}_2) & 0 \\ 0 & 0 & 1 / (1 + \delta^{17}\text{O}_3) \end{pmatrix} \quad (\text{Eq. 22})$$

The laborious calculations described above can be greatly simplified by using software libraries which implicitly track covariant uncertainties across an arbitrary number of variables¹. The Python package **D170scaling** implements all of the above calculations in this way (Daëron, 2026). It is MIT-licensed and freely available from the Python Package Index (<https://pypi.org>).

¹ for example: *Uncertainties: a Python package for calculations with uncertainties* (E. O. Lebigot.) <https://pythonhosted.org/uncertainties>

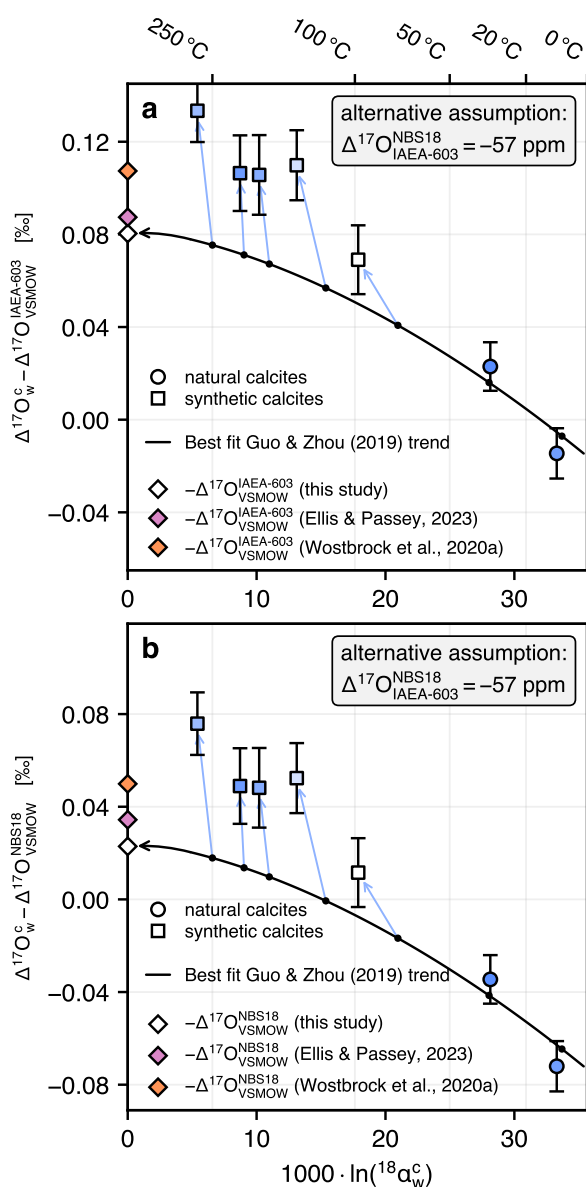
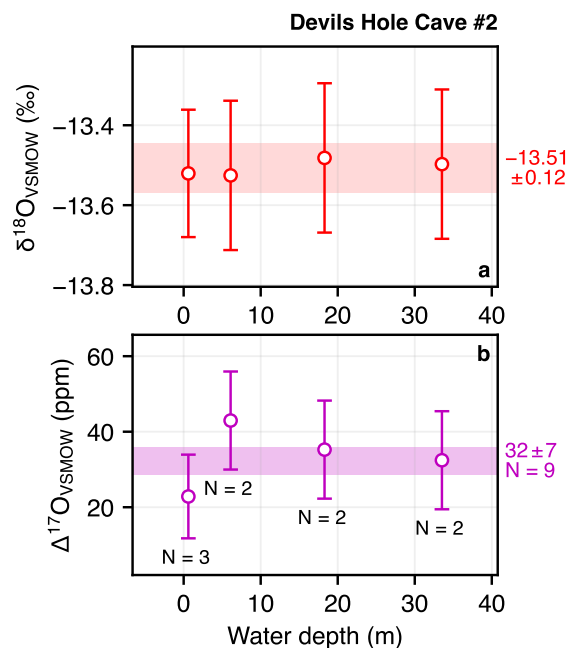


Supplementary Figure S2 – SEM images of synthetic CaCO_3 samples



Supplementary Figure S3 – FTIR absorption spectra of synthetic CaCO_3 samples

Supplementary Figure S4 – Devils Hole water profile Triple oxygen isotope compositions of water sampled at various depths in Devils Hole Cave #2 in September 2022 by authorized Devils Hole Dive Team members (permit DEVA-2021-SCI-0031). N-values in the lower panel correspond to the number of analytical replicates for each depth. Based on their respective root mean squared deviations of 0.25 and 1.59, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values are homogeneous (at 95 % confidence level) among the four samples.



Supplementary Figure S5 – Reprocessing of our data assuming $\Delta^{17}\text{O}_{\text{NBS18/IAEA-603}} > 26 \text{ ppm}$

The two plots are the exact counterparts of those in Figure 2, apart for a different choice of $\Delta^{17}\text{O}_{\text{NBS18/IAEA-603}} = 57^* \text{ ppm}$ after Wostbrock *et al.* (2020). The white diamonds on the left axes shown here correspond to the values of $\Delta^{17}\text{O}_{\text{IAEA-603}}$ (panel [a]) and $\Delta^{17}\text{O}_{\text{NBS18}}$ (panel [b]) that yield the best fit to the Laghetto Basso and Devils Hole observations ($-80 \pm 8 \text{ ppm}$ and $-23 \pm 8 \text{ ppm}$, respectively). Note that this alternative choice of $\Delta^{17}\text{O}_{\text{NBS18/IAEA-603}}$ results in a worse fit between the observations reported here and the theoretical predictions.

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