A unified clumped isotope thermometer calibration (0.5–1100°C) using carbonate-based standardization

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Key Points:

- Reanalysis of previous Δ_{47} calibration samples reconciles their discrepancies.
- No statistically significant difference is observed across a wide range of temperature and sample character.
- This Δ_{47} calibration is near-identical to a suite of recent calibrations using carbonate-based standardization.

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Abstract

The potential for carbonate clumped isotope thermometry to independently constrain both the formation temperature ($T_{\Delta_{47}}$) of carbonate minerals and fluid oxygen isotope composition allows insight into long-standing questions in the Earth sciences, but remaining discrepancies between calibration schemes hamper interpretation of $T_{\Delta_{47}}$ measurements. To address discrepancies between calibrations, we designed and analyzed a sample suite (41 total samples) with broad applicability across the geosciences, with an exceptionally wide range of formation temperatures, precipitation methods, and mineralogies. We see no statistically significant offset between sample types, although comparison of calcite and dolomite remains inconclusive. When data are reduced identically, the regression defined by this study is nearly identical to that defined by four previous calibration studies that used carbonate-based standardization; we combine these data to present a composite carbonate-standardized regression equation. Agreement across a wide range of temperature and sample types demonstrates a unified, broadly applicable clumped isotope thermometer calibration.

Plain Language Summary

Carbonate clumped isotope thermometry is a geochemical tool used to determine the formation temperature of carbonate minerals. In contrast to previous carbonate thermometers, clumped isotope thermometry requires no assumptions about the isotopic composition of the fluid from which the carbonate precipitated. By measuring the clumped isotope composition (Δ_{47}) of carbonate minerals with a known formation temperature, we can construct an empirical calibration for the clumped isotope thermometer that is necessary to convert from a Δ_{47} value to formation temperature. Many previous studies have created Δ_{47} temperature calibrations, but differences between calibrations have led to large uncertainty in final Δ_{47} temperatures. This study measures a large number of samples that span a wide range of temperature (0.5–1100°C) and include many different types of carbonates. These data show that a single calibration equation can describe many sample types, and that when data are carefully standardized to a common set of carbonate materials, calibrations performed at different laboratories agree almost identically. We combine these data to present a carbonate clumped isotope thermometer calibration with broad applicability across the geosciences.

1 Introduction

Carbonate clumped isotope thermometry is a powerful geochemical tool that can determine the formation temperature of a carbonate mineral based on the temperature-dependent propensity for ^{13}C-^{18}O bond formation in the carbonate crystal lattice (Schauble et al., 2006). By reacting carbonate minerals with acid and measuring the resultant quantity of mass-47 CO_2 molecules (δ^{47}; a value primarily controlled by the abundance ^{13}C-^{18}O-^{16}O in the analyzed CO_2) and comparing it to a stochastic distribution of ^{13}C-^{18}O-^{16}O CO_2 with the same "bulk" isotopic composition ($\delta^{18}O$, $\delta^{13}C$), the excess abundance of the doubly substituted isotopologue (Δ_{47}) can be calculated (Ghosh et al., 2006; Schauble et al., 2006). Because Δ_{47} reflects an internal state of isotope distribution within the carbonate mineral phase, it can be used to calculate mineral formation temperature ($T_{\Delta_{47}}$) as well as the $\delta^{18}O$ of the precipitating fluid. This duo can be leveraged to inform long-standing questions across many geoscience disciplines, including the temperature history of the Earth's oceans, terrestrial paleotemperature, diagenetic history of carbonates, and, when coupled to chronology proxies, basin thermochronology (Finnegan et al., 2011; Snell et al., 2013; Winkelstern & Lohmann, 2016; Lloyd et al., 2017; Mangenot et al., 2018).

The calibration between Δ_{47} and carbonate mineral formation temperature is a key intermediary between measurement of CO_2 gas on a mass spectrometer and calculation of $T_{\Delta_{47}}$. Many laboratories have produced T-Δ_{47} calibrations since the initial study of Ghosh et al. (2006), spanning various temperatures, mineralogies, precipitation methods, analytical techniques, and data processing procedures (e.g., Ghosh et al., 2006; Eiler, 2007; Dennis et al., 2011; Kele et al., 2015; Kelson et al., 2017; Bonifacie et al., 2017; Bernasconi et al., 2018; Jautzy et al., 2020). While early attempts to compare empirical calibration studies across laboratories yielded large discrepancies (e.g., Ghosh et al., 2006; Dennis & Schrag, 2010), recent calibration studies have converged on statistically similar slopes for the T-Δ_{47} regression line when data is reduced consistently (Petersen et al., 2019). The convergence of these calibrations is promising, but current discrepancies between empirical calibration equations still lead to $T_{\Delta_{47}}$ differences of ∼10 °C for carbonates near Earth surface temperatures and tens of °C for higher temperature samples (Fig. 1; Petersen et al., 2019; Jautzy et al., 2020). Uncertainty from calibrations on this order compounds with analytical uncertainty and hampers interpretation of clumped isotope data.

The source of discrepancy between calibration efforts remains unclear. By reprocessing past calibration data with a consistent data reduction scheme and IUPAC parameter set (Brand et al., 2010; Daëron et al., 2016; Schauer et al., 2016), Petersen et al. (2019) reduced but did not eliminate differences between calibrations. Remaining offset in calibration schemes was attributed to one or more of the following: carbon dioxide equilibrium scale (CDES) standardization scheme (heated/equilibrated gas vs. carbonate-based standardization; number, composition, and distribution of standards), differences in the concentration, temperature, and application method of orthophosphoric acid, sample gas purification procedures, mass spectrometer methods, pressure baseline correction, and kinetic isotope effects during carbonate precipitation (Petersen et al., 2019).

The 'InterCarb' carbonate clumped isotope inter-laboratory comparison project, following the principle of equal sample/standard treatment, demonstrated that using carbonate standards (as opposed to heated/equilibrated gases) to project raw Δ_{47} values into the 'I-CDES' yields reproducibility between 25 laboratories neither greater nor smaller than predicted based on fully propagating intra-laboratory analytical uncertainties (Bernasconi et al., submitted; Daëron, submitted). Furthermore, the InterCarb study found that Δ_{47} values of measured carbonate standards are statistically indistinguishable irrespective of procedural differences between laboratories such as sample gas purification, mass spectrometer type, or sample acidification procedure. Jautzy et al. (2020) created a new calibration spanning 5–726°C using carbonate-based standardization, and found the regression equation defined by the data was statistically indistinguishable from a series of previous calibration efforts using carbonate-based standardization (Peral et al., 2018; Bernasconi et al., 2018; Breitenbach et al., 2018; Piasecki et al., 2019; Daëron et al., 2019; Meinicke et al., 2020). Together, these studies support that varying preparation and measurement procedures between laboratories produce consistent results if data are standardized using common carbonate reference materials.

Given the promising inter-laboratory consistency of the InterCarb project (Bernasconi et al., submitted), a new calibration encompassing a spectrum of carbonates relevant to geoscience researchers that is firmly anchored to the I-CDES using carbonate-based standardization is required. To ensure that this calibration is applicable across a wide range of sample material, we reanalyzed a sample suite consisting of natural and synthetic samples measured from four previously discrepant calibration efforts (Kele et al., 2015; Kluge et al., 2015; Bonifacie et al., 2017; Kelson et al., 2017) and analyzed a new suite of low-temperature lacustrine carbonates from the Dry Valleys, Antarctica and experimentally heated carbonate standards. This sample suite spans broad ranges in temperature (0.5 – 1100°C), precipitation method (active degassing, passive degassing, mixed solution, natural precipitation), mineralogy (calcite, dolomite, and minor aragonite), and initial bulk isotopic composition. In accordance with the suggestions of the InterCarb project, the latest anchor values for carbonate standards (ETH-1–4, MERCK, IAEA-C2) were used for carbonate-based standardization, measurement of each sample was replicated at least six times (mean = 9), sample to standard ratio was 1:1, IUPAC parameters were used to correct raw data, and analytical uncertainty and uncertainty associated with creation of the reference frame was propagated throughout. We compare the regression derived by data presented here to a suite of previous studies using carbonate-based standardization (recalculated with InterCarb anchor values), and combine these datasets to propose a unified and broadly applicable clumped isotope thermometer calibration.

2 Materials and Methods

2.1 Sample collection and preparation

A total of 41 carbonate samples with known precipitation temperatures from four previous calibration efforts (Kele et al., 2015; Kluge et al., 2015; Bonifacie et al., 2017; Kelson et al., 2017), a suite of Antarctic lacustrine carbonate, and a suite of experimentally heated ETH standards were (re)analyzed in this study. Sample formation temperature ranges from 0.5–1100°C. Three samples are stoichiometric dolomite, one sample is non-stoichiometric proto-dolomite, one sample is aragonite (with minor calcite) and the remainder are calcite (five with minor aragonite; one with minor goethite).

2.1.1 Natural precipitates

Six calcite samples were collected from three perenially ice-covered lakes in the Dry Valleys region of Antarctica: two samples from Lake Fryxell (see Jungblut et al., 2016), three from Lake Joyce (see Mackey et al., 2018), and one from Lake Vanda (see Mackey et al., 2017). These carbonates precipitated in association with microbial mats and are shown by previous work to have extremely low δ^{18}O values of –30 to –40‰ (Mackey et al., 2018).

Ten tufa and travertine deposits were sampled from central Italy, Hungary, Yunnan Province (China), Yellowstone (USA), and Tenerife (Spain). Detailed description of sample localities and strategy are given in Kele et al. (2015) and references therein.

2.1.2 Laboratory precipitates

Aliquots of ETH-1 (Carrara marble) and ETH-2 (synthetic carbonate) were heated to 1100°C and pressurized to 2000 bar for a period of 24 hours at the ETH Zürich Rock Deformation Laboratory. Following heating, samples were quenched to room temperature within seconds. See Text S1 in the supporting information for full methods.

Fifteen calcite samples from Kelson et al. (2017) were either precipitated with solutions of $NaHCO_3$ and $CaCl_2$ or by dissolving $CaCO_3$ in H_2O with low pH from CO_2 bubbling, and then inducing precipitation either through N_2 bubbling or passive degassing. Carbonic anhydrase was added to four samples. Temperature precision was ±0.5°C.

Two calcite samples from Kluge et al. (2015) were precipitated by dissolving $CaCO_3$ in H_2O and letting the solution equilibrate for 2–15 hours, filtering out undissolved carbonate, and bubbling CO_2 through the solution.

Four (proto)dolomite samples used in this study were originally described in Horita (2014) and Bonifacie et al. (2017). The 80°C sample was precipitated by mixing $MgSO_4$, $Ca(NO_3)_4H_2O$, and Na_2CO_3 in a sealed glass bottle held within 1°C of nominal temperature for 41 days. The 100, 250, and 350°C samples were made by mixing ground natural aragonite or calcite with a Ca-Mg-(Na)-Cl solution and held within 2°C of prescribed value for 6–85 days.

2.2 Mass spectrometry

2.2.1 This study

Sample Δ_{47} was measured from January 2018 to November 2020 at the MIT Carbonate Research Laboratory on a Nu Perspective dual-inlet isotope ratio mass spectrometer with a NuCarb automated sample preparation unit held at 70°C (see Mackey et al., 2020). Carbonate samples (including dolomite) weighing 400–600 µg reacted for 25 minutes in individual glass vials with 150 µl orthophosphoric acid ($\varrho = 1.93$ g/cm^3). Evolved CO_2 gas was purified cryogenically and by passive passage through a Porapak trap (1/4"

Table 1. Description of analyzed and reanalyzed samples.

Study	Mineralogy	Formation	Formation Temp. Range (°C)[a]	Samples Analyzed (this study; orig. study)
Bonifacie et al. (2017)	Dolo., proto-dolo.	Mixed solution	80–350	4; 12
Kele et al. (2015)	Calc. (minor arag.)	Tufa, travertine	5–95	12; 24
Kelson et al. (2017)	Calc. (minor arag.)	Active/passive degas, mixed sol'n	6–78	15; 56
Kluge et al. (2015)	Calc., arag.	Active degas	25–80	2; 29
This study	Calc.	Lacustrine, experimentally heated	0.5–1100	8

[a]Temperature range is only for samples reanalyzed in this study.

ID; 0.4 g 50/80 mesh Porapak Q) held at -30°C. Purified sample gas and reference gas of known composition were alternately measured on six Faraday collectors (m/z 44–49) in 3 acquisitions of 20 cycles, each with 30 second integration time (30 minute total integration time). Initial voltage was 8–20 V on the m/z 44 beam with $2e^8$ Ω resistors and depleted by approximately 50% over the course of an analysis. Sample and standard gases depleted at equivalent rates from microvolumes over the integration time.

Each run of approximately 50 individual analyses began with each of ETH-1–ETH-4 in random order, and then alternated between blocks of three unknowns and two ETH anchors. Additionally, IAEA-C1, IAEA-C2, and MERCK were respectively measured once per run. Unknown to anchor ratio was planned at 1:1 for each run, although gas preparation or mass spectrometer error occasionally modified this ratio. The reference side of the dual-inlet was refilled with reference gas every 10 to 17 analyses. In total, unknowns were measured 6–16 times over the study interval (362 total unknown analyses).

2.3 Data processing

Raw mass spectrometer data were first processed by removing cycles (i.e., single integration cycles of mass spectrometer measurement) with raw Δ_{47} values more than 5 "long-term" standard deviations (the mean of the respective cycle-level SD for ETH-1–4 over a 3-month period, 0.10‰) away from the median Δ_{47} measurement for the analysis. Analyses with more than 20 cycles (out of 60 total cycles) falling outside the 5 long-term SD threshold were removed. In total, 0.81% of cycles and 0.42% of analyses were removed. No pressure baseline correction was applied. Long-term repeatability (1SD) of Δ_{47} for all analyses (after data processing described above) is 0.036 ‰.

After cycle-level outlier removal, data were processed using the 'D47crunch' Python package (Daëron, submitted) using IUPAC ^{17}O parameters, 70°C ^{18}O acid fractionation factor of 1.00871 (Kim et al., 2007), and projected to the I-CDES with values for ETH-1–4, IAEA-C2, and MERCK from the InterCarb exercise (Bernasconi et al., submitted), which uses a 90°C acid fractionation factor of -0.088‰ from Petersen et al. (2019). Raw Δ_{47} measurements were converted to the I-CDES using a pooled regression approach that accounts for the relative mapping of all samples in δ^{47}-Δ_{47} space (Daëron, submitted). Analytical uncertainty and error associated with creation of the reference frame were fully propagated through the dataset. A full description of the data reduction procedure used in D47crunch is detailed in (Daëron, submitted). Each run (typically 50 analyses) was treated as an analytical session. IAEA-C1 was treated as an unknown and used as an internal consistency check (mean = 0.291‰, 1SE = 0.01‰). Finally, Peirce's criterion (Ross, 2003; Zaarur et al., 2013) was applied to the dataset at the analysis level; a total of six analyses were marked as outliers and removed, followed by reprocessing of the dataset.

3 Results and Discussion

Results for all analyses (re)analyzed here are summarized at the sample level in Table 2 (see Dataset S1 and S2 for full results). Accounting for uncertainty in Δ_{47} (long-term repeatability, 1SD) and formation temperature (0.5–10°C) with the regression method described in York et al. (2004), these data define a linear $1/T^2$-Δ_{47} relationship from 0.5°C–1100°C shown in Figure 1.

3.1 Comparison of T-Δ_{47} relationship across sample types

The published regression equations from Kele et al. (2015); Kluge et al. (2015); Kelson et al. (2017); Bonifacie et al. (2017) all fall within the 95% confidence interval of the regressions defined by this study's reanalysis of their constituent samples (supporting information Fig. S3). Natural and lab-precipitated samples fall on nearly identical regression lines (Fig. 2A); analysis of covariance (ANCOVA) fails to reject the null hypothesis that both types of samples are characterized by a single regression line at the 95% confidence level at our typical sample precision levels (1SE) of ∼10 ppm (p_{slope} = 0.41, $p_{intercept}$ = 0.19; see Table S1 in supporting information for full table of ANCOVA analyses). Natural samples display a weaker correlation coefficient (r^2 = 0.96 vs. 0.99) and larger error of the estimate, likely due to variable fluid temperatures in natural settings.

Our reanalysis of samples precipitated by Kelson et al. (2017) supports their conclusions: we observe no statistically significant Δ_{47} offset between passively and actively degassed samples (p_{slope} = 0.19, $p_{intercept}$ = 0.79) or with the addition of carbonic anhydrase (p_{slope} = 0.79, $p_{intercept}$ = 0.32; Fig. S1). Reanalysis of samples from Kele et al. (2015) and Kelson et al. (2017) confirms the results of Kele et al. (2015) in that there is no significant difference between samples precipitated at low (< 7) vs. high (> 7) pH (p_{slope} = 0.4, $p_{intercept}$ = 0.99) or intensive vs. moderate precipitation rate (p_{slope} = 0.12, $p_{intercept}$ = 0.54; Fig. S2). The low number of rapid precipitates (particularly at low temperatures) makes this claim inconclusive, but Δ_{47} values for two extremely slow-growing samples measured for this study on an Isoprime 100 dual-inlet mass spectrometer located at LCSE (methods in supporting information Text S3), respectively from Devil's Hole, NV, USA, and Laghetto Basso, Italy (see Winograd et al., 2006; Coplen, 2007; Drysdale et al., 2012; Daëron et al., 2019), are nearly identical to the expected values based on the calibration from this study (Fig. 3B). Calcite-water fractionation in ^{18}O calculated from a subset of 20 samples with fluid $\delta^{18}O$ data (Fig. S5) agrees closely with the equations of Coplen (2007) and Daëron et al. (2019). The Antarctic microbially-mediated lacustrine calcites show no discernible offset from the overall trend, but small sample numbers and limited temperature range prohibit formal analysis.

With only three stoichiometric dolomite samples, no stoichiometric dolomite samples below 100°C, and no calcite samples between 95°C and 1000°C measured for this study, we cannot rigorously compare calcite and dolomite regressions; ANCOVA variably accepts/rejects the null hypothesis depending on categorization of the single protodolomite sample. We tentatively assert that dolomite and calcite samples can be described using a single regression equation, as previously suggested by Bonifacie et al. (2017) and Petersen et al. (2019), but analysis of dolomite samples with lower (< 80°C) and higher (> 350°C) formation temperature is needed to confirm this claim. The regression through aragonitic samples (four samples < 6%; one sample = 38%; one sample = 78%) is statistically similar to the regression through all calcite samples (Fig. 2B). A single sample (Aqua Borra) with minor goethite (15%) has individual Δ_{47} analyses both much higher and lower than expected, but has a mean Δ_{47} value that closely agrees with the regression presened here.

The absence of systematic offset in T-Δ_{47} relationship corresponding to any known sample characteristic suggests that discrepancies between these exact samples from previous calibration efforts are not a product of the character of measured sample material (Wacker et al., 2014; Kele et al., 2015; Kluge et al., 2015; Kelson et al., 2017; Bonifacie et al., 2017). Furthermore, the consistency of the T-Δ_{47} relationship across a broad range of materials and temperatures (e.g., from Antarctic lacustrine microbially-mediated carbonates to laboratory-grown carbonates heated to 1100°C) indicates that a single T-Δ_{47} calibration can adequately describe a wide variety of sample types.

3.2 Comparison across calibration studies using carbonate-based standardization

Reprocessing data from the synthetic calcite calibration of Jautzy et al. (2020), as well as a suite of foraminifera-based calibration studies (Breitenbach et al., 2018; Peral et al., 2018; Meinicke et al., 2020) with updated InterCarb anchor values (Bernasconi et al., submitted) yields an almost identical regression to that calculated in this study (Fig. 3). The near-perfect agreement of these calibrations (∼0.5°C offset near 25°C; ∼2°C offset near 100°C) despite differences in sample material and measurement method points to the strength of carbonate-based standardization and the potential of a unified clumped isotope calibration.

This clumped isotope calibration covers the broadest range of temperatures, includes diverse carbonates, replicates measurements several times, and uses a low unknown:anchor ratio to firmly tie unknown measurements to the I-CDES. However, this calibration has an unequal distribution of samples in $1/T^2$ space, is anchored at the coldest temperatures by unusual carbonates, and does not contain marine carbonates, which are of particular interest to the clumped isotope community. To address these weaknesses, we combine data from this study with four other carbonate-standardized calibrations (Breitenbach et al., 2018; Peral et al., 2018; Meinicke et al., 2020; Jautzy et al., 2020) to present a composite $1/T^2$-Δ_{47} regression that has smaller temperature gaps, is anchored at low temperatures by a variety of samples, and extends the calibration to biogenic marine carbonates:

$$\Delta_{47(I-CDES90^{\circ}C)} = 0.0390 \pm 0.0004 \times \frac{10^6}{T^2} + 0.153 \pm 0.004 \ (r^2 = 0.97) \qquad (1)$$

Along with excellent agreement between laboratories using carbonate-based standardization, this dataset and the community-developed InterCarb anchor values (Bernasconi et al., submitted) narrow the discrepancy between calibrations using carbonate anchor values and heated/equilibrated gases, most notably Petersen et al. (2019). Specifically, calibrations of Jautzy et al. (2020) and Petersen et al. (2019) differed by 5°C near 25°C and 20°C near 100°C; the composite calibration regression shown in Equation 1 differs from Petersen et al. (2019) by 3°C near 25°C and by 7°C near 100°C (Fig. 1A).

3.3 Non-linearity of $1/T^2$-Δ_{47} relationship for high-temperature precipitates

At high temperatures, theory predicts a non-linear $1/T^2$-Δ_{47} relationship (e.g., Guo et al., 2009; Hill et al., 2014), which is supported by recent empirical calibrations (e.g., Müller et al., 2019; Jautzy et al., 2020). A third-order polynomial regression through our data falls within the 95% CL of our linear fit over the entire temperature range (Fig. 3A) and does not improve the goodness of fit ($r^2 = 0.97$ for both); we observe no evidence that a non-linear fit better describes high-temperature data.

4 Conclusions

When measured in a consistent analytical setting with carbonate-based standardization, no systematic offset is observed between samples precipitated across a broad spectrum of conditions that were previously determined to have disparate Δ_{47} values. Among sample types measured here, we find no evidence that the particular character of sample material (e.g., mineralogy, addition of carbonic anhydrase, pH, precipitation rate, biological mediation) influences the Δ_{47} calibration, although our tentative claim of calcite and dolomite agreement remains inconclusive.

Furthermore, when anchor values from the InterCarb exercise (Bernasconi et al., submitted) are used to correct all data with data reduction best practices (Petersen et

Table 2. Final corrected $\delta^{13}C_{VPDB}$ (‰), $\delta^{18}O_{VSMOW}$ (‰), and $\Delta_{47(CDES90^{\circ}C)}$ (‰) results.

Sample name	Author	Mineralogy	Method	T(°C)	N	$\delta^{13}C$	$\delta^{18}O$	Δ_{47}	SE	95% CL
IPGP_100-A3	Bonifacie	Dolomite	Lab	102.3	9	-46.3	-17.4	0.425	0.015	0.029
IPGP_250-A5	Bonifacie	Dolomite	Lab	252.1	9	-52.8	-28.0	0.272	0.025	0.049
IPGP_350-A9	Bonifacie	Dolomite	Lab	351.4	10	-55.6	-32.0	0.229	0.018	0.035
IPGP_80-1	Bonifacie	Proto-dolo.	Lab	80.2	10	-6.9	-16.2	0.494	0.012	0.024
ETH-1-1100-SAM	This study	Calcite	Lab	1100	10	2.0	-2.0	0.177	0.018	0.036
ETH-2-1100-SAM	This study	Calcite	Lab	1100	10	-10.1	-18.4	0.190	0.017	0.034
HT_25C	Kluge	Calcite	Lab	25	9	2.1	-6.2	0.609	0.013	0.026
HT_80C	Kluge	Aragonite	Lab	80	9	1.1	-15.4	0.486	0.013	0.025
AQUA_BORRA	Kele	Calcite	Natural	36.1	11	1.7	-8.4	0.576	0.012	0.023
BUK_4	Kele	Calcite	Natural	54.9	9	2.2	-15.0	0.539	0.013	0.025
CANARIAN	Kele	Calcite	Natural	33.8	8	0.1	-10.2	0.583	0.014	0.027
CANNATOPA	Kele	Calcite	Natural	11	8	-4.1	-5.4	0.627	0.014	0.027
IGAL	Kele	Calcite	Natural	75	10	0.6	-13.5	0.474	0.012	0.024
LAPIGNA	Kele	Calcite	Natural	12.5	9	-11.4	-5.5	0.620	0.013	0.026
NG_2	Kele	Calcite	Natural	60.4	9	3.6	-24.6	0.504	0.013	0.025
P5_SUMMER	Kele	Calcite	Natural	12	9	5.4	-14.3	0.632	0.013	0.026
P5_WINTER	Kele	Calcite	Natural	5	10	5.1	-12.7	0.635	0.013	0.026
SARTEANO	Kele	Calcite	Natural	20.7	9	0.4	-7.3	0.593	0.013	0.025
SZAL-2	Kele	Calcite	Natural	11	9	-10.3	-8.2	0.653	0.013	0.026
TURA	Kele	Calcite	Natural	95	9	3.7	-23.2	0.408	0.013	0.025
LF2012-9_7-A	This study	Calcite	Natural	2.5	4	2.6	-27.2	0.662	0.023	0.045
LF2012-D1-A	This study	Calcite	Natural	2.5	4	3.4	-27.1	0.656	0.023	0.044
LJ2010-12A-Z1A	This study	Calcite	Natural	0.5	13	7.7	-39.4	0.667	0.014	0.028
LJ2010-12A-Z2A	This study	Calcite	Natural	0.5	6	8.1	-38.1	0.671	0.020	0.039
LJ2010-5B-A	This study	Calcite	Natural	0.5	11	8.1	-37.6	0.674	0.014	0.027
LV26NOV10-2A	This study	Calcite	Natural	4	6	11.2	-29.0	0.651	0.018	0.035
UWCP14_20C_9	Kelson	Calcite	Lab	23	8	-21.1	-10.8	0.603	0.014	0.028
UWCP14_20C_CA_11	Kelson	Calcite	Lab	23	10	-14.1	-10.9	0.614	0.013	0.025
UWCP14_21C_1	Kelson	Calcite	Lab	22	8	-18.6	-11.1	0.609	0.014	0.028
UWCP14_4C_3	Kelson	Calcite	Lab	6	8	-21.3	-6.6	0.648	0.014	0.028
UWCP14_4C_4	Kelson	Calcite	Lab	6	9	-23.4	-6.7	0.657	0.013	0.026
UWCP14_50C_2	Kelson	Calcite	Lab	51	9	-18.4	-16.4	0.533	0.013	0.026
UWCP14_50C_7	Kelson	Calcite	Lab	54	9	-0.2	-17.4	0.517	0.013	0.025
UWCP14_50C_CA_11	Kelson	Calcite	Lab	50	9	-18.5	-15.9	0.526	0.014	0.027
UWCP14_60C_2	Kelson	Calcite	Lab	66	9	-12.5	-18.2	0.489	0.013	0.026
UWCP14_70C_4	Kelson	Calcite	Lab	72	8	-17.7	-18.8	0.488	0.014	0.028
UWCP14_70C_CA_4	Kelson	Calcite	Lab	71	9	-0.2	-19.6	0.491	0.013	0.025
UWCP14_80C_2	Kelson	Calcite	Lab	78	9	-6.9	-20.9	0.482	0.013	0.025
UWCP14_8C_2	Kelson	Calcite	Lab	9	9	-15.1	-7.7	0.632	0.013	0.026
UWCP14_8C_6	Kelson	Calcite	Lab	9	9	0.4	-8.8	0.647	0.013	0.026
UWCP14_8C_CA_4	Kelson	Calcite	Lab	9	8	-17.4	-8.1	0.647	0.014	0.028

al., 2019; Daëron, submitted), the $1/T^2$-Δ_{47} regression defined by data presented here is nearly identical (0.5°C offset at 25°C; 2°C offset at 100°C) to the regression defined by a suite of recent calibration studies (Peral et al., 2018; Breitenbach et al., 2018; Meinicke et al., 2020; Jautzy et al., 2020) and closely approximates the composite calibration of Petersen et al. (2019). Equation 1 spans the broadest range of temperatures measured in a consistent analytical setting and, when corrected with carbonate anchor values from the InterCarb exercise (Bernasconi et al., submitted) or heated/equilibrated gases, may be applied across a wide range of natural and laboratory-grown carbonate material.

Acknowledgments

Regression equations from previous publications are included in cited papers. Sample and replicate level data are included in this manuscript in the supporting information and will be archived in the EarthChem database using a data template specifically designed for carbonate clumped isotope data (Petersen et al., 2019) pending acceptance of this manuscript. N.T. Anderson acknowledges the support of the J.H. and E.V. Wade Fellowship and the mTerra Catalyst Fund. Members of the Bergmann Lab (Marjorie Cantine, Athena Eyster, Sam Goldberg, and Julia Wilcots) provided helpful feedback an early drafts. K. Bergmann acknowledges support from the Packard Foundation, NASA Exobiology Grant 80NSSC19K0464 and the MIT Wade Fund.

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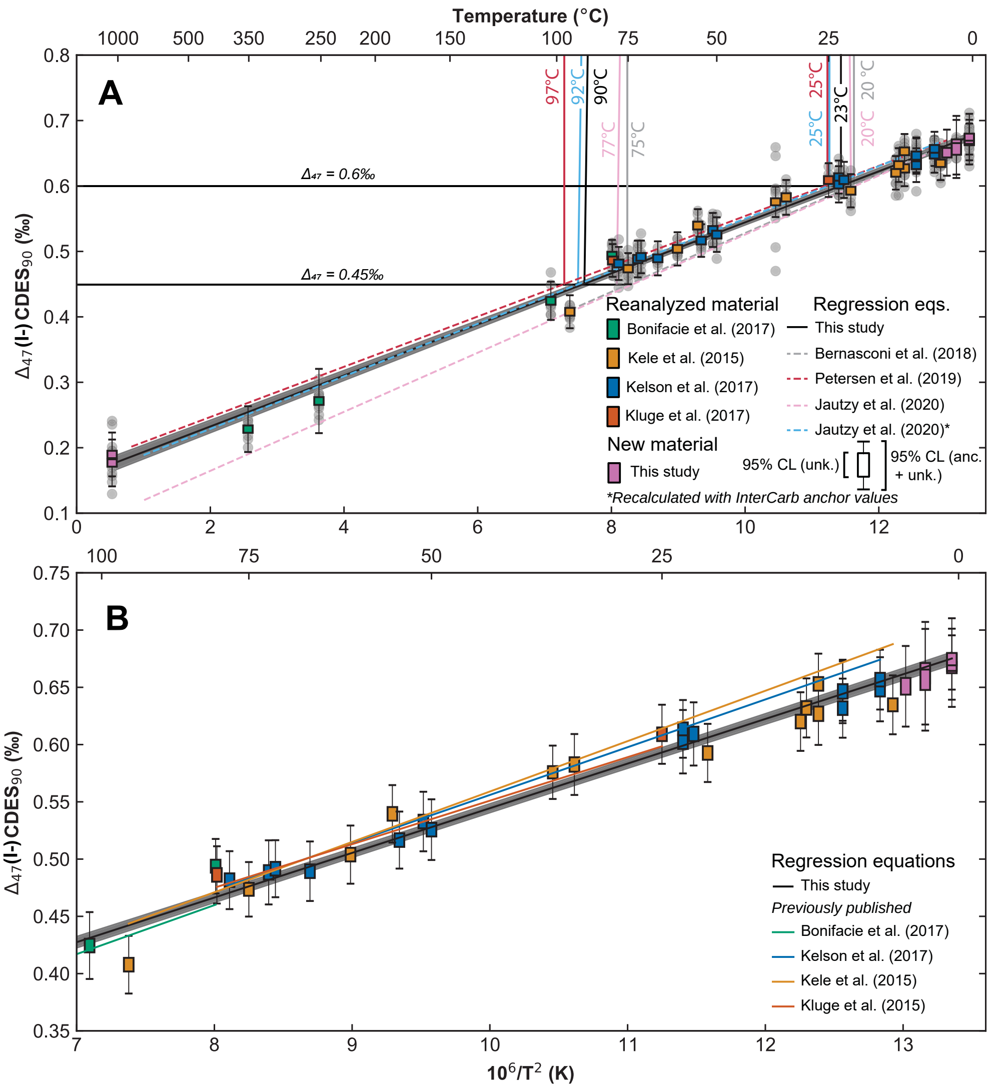

Figure 1. A. Linear $1/T^2$-Δ_{47} regression and 95% confidence interval (York et al., 2004) for samples (re)analyzed in this study shown with recently published calibrations. Solid vertical lines show approximate formation temperature for each calibration when $\Delta_{47} = 0.45$‰ and $\Delta_{47} = 0.6$‰ . Error bars correspond to 95% confidence limits accounting for error from unknown and anchor analyses; boxes correspond to 95% CL not accounting for normalization errors. The regression from this study is nearly identical to the regression from Jautzy et al. (2020) when all Δ_{47} values are calculated with 'InterCarb' (Bernasconi et al., submitted) anchor values. B. T-Δ_{47} relationship for samples 0–100°C including regressions from studies with material reanalyzed for this study (Bonifacie et al. (2017), Eq. 1; Kele et al. (2015), Eq. 1; Kelson et al. (2017) Eq. 1; Kluge et al. (2015), Table 1, 'This study, linear fit'; all converted to 90°C acid temperature using AFF values from Petersen et al., 2019).

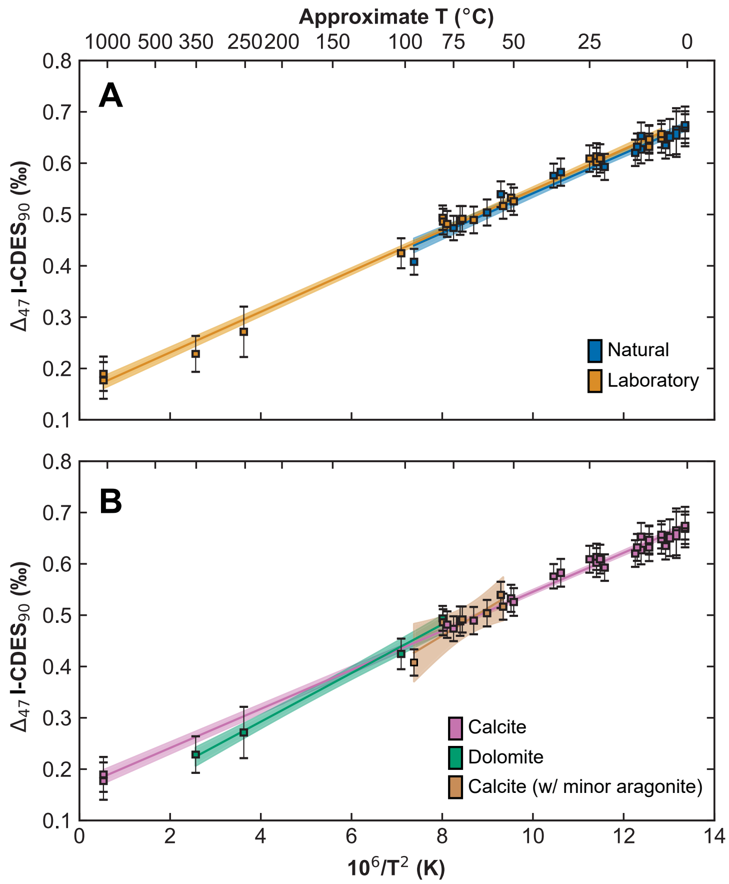

Figure 2. A. $1/T^2$-Δ_{47} comparison of natural and laboratory precipitated sample material. Error bars correspond to 95% confidence limits accounting for error from both unknown and anchor analyses; boxes correspond to 95% CL not accounting for normalization errors. Natural samples have larger uncertainty of the estimate and a poorer fit, likely due to natural variability in formation temperature and a smaller temperature range. B. Comparison of calcite, (proto)dolomite, and aragonite sample material. The regression lines between calcite and dolomite diverge but 95% confidence intervals overlap; divergence of regression equations may be related to the small temperature range of dolomite (relative to calcite) measured in this study and the small number of dolomite samples.

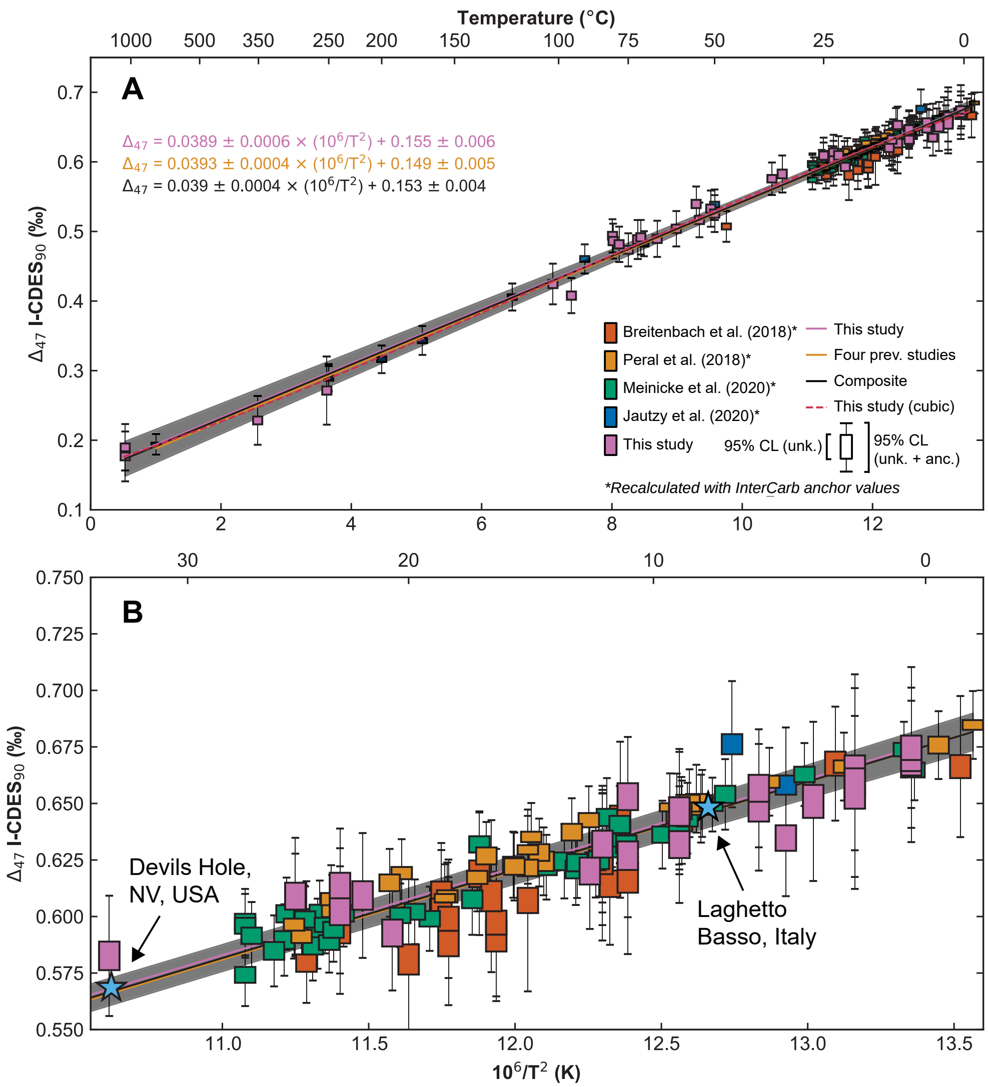

Figure 3. A. All Δ_{47} results from this study shown with data from four recent studies using carbonate-based standardization using laboratory precipitates (Jautzy et al., 2020) and foraminifera (Breitenbach et al., 2018; Peral et al., 2018; Meinicke et al., 2020), recalculated here with InterCarb anchor values (Bernasconi et al., submitted). Error bars correspond to 95% confidence limits accounting for error from both unknown and anchor analyses; boxes correspond to 95% CL not accounting for normalization errors. Regressions through this study (cubic and linear), previous data, and the composite dataset are nearly identical. B. Inset of A from 0–30°C. Slow-growing calcites respectively from Devils Hole, NV, USA, and Laghetto Basso, Italy, measured on an IsoPrime100 at LCSE (see supporting information Text S3) fall directly on the plotted regression lines.