

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

Noah Anderson¹, J R Kelson², S Kele³, M Daëron⁴, M Bonifacie⁵, J Horita⁶, T J Mackey⁷,
C M John⁸, T Kluge⁹, P Petschnig¹⁰, A B Jost¹, K W Huntington¹¹, S M Bernasconi¹²,
and K D Bergmann¹

¹Massachusetts Institute of Technology

²University of Michigan

³Research Center for Astronomy and Earth Sciences

⁴Université Paris-Saclay

⁵Université Paris Diderot

⁶Texas Tech University

⁷University of New Mexico

⁸Imperial College

⁹Karlsruhe Institute of Technology

¹⁰ETH Zürich, Institute of Geochemistry and Petrology

¹¹University of Washington

¹²ETH Zurich

November 23, 2022

Abstract

The potential for carbonate clumped isotope thermometry to independently constrain both the formation temperature ($T_{[?]47}$) 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 $T_{[?]47}$ 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.

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

N.T. Anderson^{1*}, J.R. Kelson², S. Kele³, M. Daëron⁴, M. Bonifacie⁵, J. Horita⁶, T.J. Mackey⁷, C.M. John⁸, T. Kluge⁹, P. Petschnig¹¹, A.B. Jost¹, K.W. Huntington¹⁰, S.M. Bernasconi¹¹, K.D. Bergmann¹

¹Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, 02135

²Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109

³Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, 1112 Budapest, Hungary

⁴Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Orme des Merisiers, F-91191, Gif-sur-Yvette Cedex, France

⁵Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France

⁶Department of Geosciences, Texas Tech University, Lubbock, TX, 79409

⁷Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, 87131

⁸Department of Earth Science and Engineering, Imperial College, Prince Consort Rd, London SW7 2AZ

⁹Institute of Applied Geosciences, Karlsruhe Institute of Technology, Adenauerring 20b, 76131 Karlsruhe, Germany

¹⁰Department of Earth and Space Sciences and Quaternary Research Center, University of Washington, Seattle, WA, USA

¹¹Geological Institute, ETH Zürich, CH-8092 Zürich, Switzerland

Key Points:

- Reanalysis of sample material from previous Δ_{47} calibration studies reconciles their discrepancies.
- No statistically significant difference is observed across a wide range of temperature and sample character.

*77 Massachusetts Ave., Cambridge, MA 02139

Corresponding author: N.T. Anderson, nanderso@mit.edu

- This Δ_{47} calibration is near-identical to a suite of recent calibrations using carbonate-based standardization.

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 ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$), 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 $\delta^{18}\text{O}$ 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; Mangelot 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 $\sim 10^\circ\text{C}$ for carbonates near Earth surface temperatures and tens of $^\circ\text{C}$ 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.

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 perennially 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 $\delta^{18}\text{O}$ 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 NaHCO₃ and CaCl₂ or by dissolving CaCO₃ in H₂O with low pH from CO₂ bubbling, and then inducing precipitation either through N₂ bubbling or passive degassing. Carbonic anhydrase was added to four samples. Temperature precision was $\pm 0.5^\circ\text{C}$.

Two calcite samples from Kluge et al. (2015) were precipitated by dissolving CaCO₃ in H₂O and letting the solution equilibrate for 2–15 hours, filtering out undissolved carbonate, and bubbling CO₂ 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 MgSO₄, Ca(NO₃)₄H₂O, and Na₂CO₃ 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 ($\rho = 1.93 \text{ g/cm}^3$). Evolved CO₂ 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	Samples
			Temp.	Analyzed
			Range (°C) ^a	(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

^aTemperature 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 $2e^8 \Omega$ 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 anal-

ysis. 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, ^{18}O acid fractionation factor from 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 $\delta^{47}\text{-}\Delta_{47}$ space. 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 of supporting information for sample metadata and full analysis-level data). Accounting for uncertainty in Δ_{47} (long-term repeatability, 1SD) and formation temperature (0.5–10°C) using the regression method described in York et al. (2004), these data define a linear $1/T^2\text{-}\Delta_{47}$ 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 hypoth-

esis 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). Based on reanalysis of samples from Kele et al. (2015); Kelson et al. (2017) we confirm 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). However, the low number of rapid precipitates (particularly at low temperatures) makes this claim inconclusive. In support of minimal offset based on precipitation rate, 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). 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 ($< 80^\circ\text{C}$) and higher ($> 350^\circ\text{C}$) 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 presented 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 ($\sim 0.5^\circ\text{C}$ offset near 25°C ; $\sim 2^\circ\text{C}$ 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:

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

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 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 on early drafts. K. Bergmann acknowledges support from the Packard Foundation, NASA Exobiology Grant 80NSSC19K0464 and the MIT Wade Fund.

References

- Bernasconi, S. M., Daëron, M., Bergmann, K. D., Bonifacie, M., Meckler, A. N., Affek, H. P., . . . Ziegler, M. (submitted). InterCarb: A community effort to improve inter-laboratory standardization of the carbonate clumped isotope thermometer using carbonate standards. *Geochemistry, Geophysics, Geosystems*. doi: DOI:10.1002/essoar.10504430.2
- Bernasconi, S. M., Müller, I. A., Bergmann, K. D., Breitenbach, S. F., Fernandez, A., Hodell, D. A., . . . Ziegler, M. (2018). Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems*, 19(9), 2895–2914. doi: 10.1029/2017GC007385
- Bonifacie, M., Calmels, D., Eiler, J. M., Horita, J., Chaduteau, C., Vasconcelos, C., . . . Bourrand, J. J. (2017). Calibration of the dolomite clumped isotope thermometer from 25 to 350 °C, and implications for a universal calibration for all (Ca, Mg, Fe)CO₃ carbonates. *Geochimica et Cosmochimica Acta*, 200, 255–279. Retrieved from <http://dx.doi.org/10.1016/j.gca.2016.11.028>

Table 2. Sample information and final $\delta^{13}\text{C}_{VPDB}$ (‰), $\delta^{18}\text{O}_{VSMOW}$ (‰), and $\Delta_{47(CDES90^\circ\text{C})}$ (‰) results.

Sample name	Author	Mineralogy	Precip.	T(°C)	N	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Δ_{47}	SE	95% CL
IPGP_100-A3	Bonifacie	Dolomite	Lab	102.3	9	-46.3	12.9	0.515	0.018	0.035
IPGP_250-A5	Bonifacie	Dolomite	Lab	252.1	9	-52.8	2.0	0.367	0.03	0.058
IPGP_350-A9	Bonifacie	Dolomite	Lab	351.4	10	-55.6	-1.9	0.319	0.021	0.042
IPGP_80-1	Bonifacie	Protodolomite	Lab	80.2	10	-6.9	14.1	0.582	0.015	0.029
ETH-1-1100	(This study)	Calcite	Lab	1000	10	2	36.9	0.263	0.022	0.043
ETH-2-1100	(This study)	Calcite	Lab	1000	10	-10.1	20	0.277	0.021	0.041
HT_25C	Kluge	Calcite	Lab	25	9	2.1	32.6	0.696	0.016	0.031
HT_80C	Kluge	Calcite	Lab	80	9	1.1	23.5	0.574	0.015	0.03
AQUA_BORRA	Kele	Calcite	Natural	36.1	11	1.7	30.3	0.663	0.014	0.028
BUK_4	Kele	Calcite	Natural	54.9	9	2.2	23.5	0.628	0.015	0.03
CANARIAN	Kele	Calcite	Natural	33.8	9	0.1	28.5	0.672	0.016	0.031
CANNATOPA	Kele	Calcite	Natural	11	9	-4.1	33.6	0.718	0.016	0.032
IGAL	Kele	Calcite	Natural	75	10	0.6	25.1	0.562	0.015	0.029
LA PIGNA	Kele	Calcite	Natural	12.5	8	-11.4	33.4	0.706	0.017	0.033
NG_2	Kele	Calcite	Natural	60.4	10	3.6	13.8	0.592	0.015	0.03
P5_SUMMER	Kele	Calcite	Natural	12	9	5.4	24.3	0.72	0.016	0.031
P5_WINTER	Kele	Calcite	Natural	5	10	5.1	25.9	0.723	0.016	0.031
SARTEANO	Kele	Calcite	Natural	20.7	9	0.4	31.5	0.681	0.016	0.031
SZAL	Kele	Calcite	Natural	11	9	-10.3	30.5	0.742	0.016	0.032
TURA	Kele	Calcite	Natural	95	10	3.7	15.1	0.496	0.015	0.029
LF2012-9.7-A	(This study)	Calcite	Natural	2.5	4	2.6	10.9	0.751	0.027	0.054
LF2012-D1-A	(This study)	Calcite	Natural	2.5	4	3.4	11	0.745	0.027	0.053
LJ2010-12A-Z1A	(This study)	Calcite	Natural	0.5	13	7.7	-1.7	0.757	0.017	0.034
LJ2010-12A-Z2A	(This study)	Calcite	Natural	0.5	6	8.1	-0.3	0.762	0.024	0.047
LJ2010-5B-A	(This study)	Calcite	Natural	0.5	11	8.1	0.2	0.767	0.017	0.032
LV26NOV10-2A	(This study)	Calcite	Natural	4	6	11.2	9.1	0.74	0.022	0.042
UWCP14.20C_9	Kelson	Calcite	Lab	23	8	-21.1	27.8	0.691	0.017	0.033
UWCP14.20C_CA_11	Kelson	Calcite	Lab	23	10	-14.1	27.7	0.702	0.015	0.03
UWCP14.21C_1	Kelson	Calcite	Lab	22	8	-18.6	27.6	0.698	0.017	0.033
UWCP14.4C_3	Kelson	Calcite	Lab	6	8	-21.3	32.2	0.737	0.017	0.034
UWCP14.4C_4	Kelson	Calcite	Lab	6	9	-23.4	32.1	0.746	0.016	0.031
UWCP14.50C_2	Kelson	Calcite	Lab	51	9	-18.4	22.1	0.622	0.016	0.031
UWCP14.50C_7	Kelson	Calcite	Lab	54	9	-0.2	21.1	0.605	0.015	0.03
UWCP14.50C_CA_11	Kelson	Calcite	Lab	50	9	-18.5	22.6	0.614	0.016	0.032
UWCP14.60C_2	Kelson	Calcite	Lab	66	9	-12.5	20.2	0.578	0.016	0.031
UWCP14.70C_4	Kelson	Calcite	Lab	72	8	-17.7	19.6	0.577	0.017	0.034
UWCP14.70C_CA_4	Kelson	Calcite	Lab	71	9	-0.2	18.8	0.58	0.015	0.03
UWCP14.80C_2	Kelson	Calcite	Lab	78	9	-6.9	17.4	0.57	0.016	0.03
UWCP14.8C_2	Kelson	Calcite	Lab	9	9	-15.1	31	0.72	0.016	0.031
UWCP14.8C_6	Kelson	Calcite	Lab	9	9	0.4	29.9	0.735	0.016	0.031
UWCP14.8C_CA_4	Kelson	Calcite	Lab	9	8	-17.4	30.6	0.734	0.017	0.033

- 354 doi: 10.1016/j.gca.2016.11.028
- 355 Brand, W. A., Assonov, S. S., & Coplen, T. B. (2010). Correction for the 170
- 356 interference in $\delta^{13}\text{C}$ measurements when analyzing CO_2 with stable isotope
- 357 mass spectrometry (IUPAC Technical Report). *Pure Applied Chemistry*, 82(8),
- 358 1719–1733. doi: 10.1351/PAC-REP-09-01-05
- 359 Breitenbach, S. F., Mleneck-Vautravers, M. J., Grauel, A. L., Lo, L., Bernasconi,
- 360 S. M., Müller, I. A., ... Hodell, D. A. (2018). Coupled Mg/Ca and
- 361 clumped isotope analyses of foraminifera provide consistent water temper-
- 362 atures. *Geochimica et Cosmochimica Acta*, 236, 283–296. doi: 10.1016/
- 363 j.gca.2018.03.010
- 364 Coplen, T. B. (2007). Calibration of the calcite-water oxygen-isotope geothermome-
- 365 ter at Devils Hole, Nevada, a natural laboratory. *Geochimica et Cosmochimica*
- 366 *Acta*, 71(16), 3948–3957. doi: 10.1016/j.gca.2007.05.028
- 367 Daëron, M. (submitted). Full propagation of analytical uncertainties in D47 mea-
- 368 surements. *Geochemistry, Geophysics, Geosystems*.
- 369 Daëron, M., Blamart, D., Peral, M., & Affek, H. P. (2016). Absolute isotopic abun-
- 370 dance ratios and the accuracy of $\Delta 47$ measurements. *Chemical Geology*, 442,
- 371 83–96. Retrieved from <http://dx.doi.org/10.1016/j.chemgeo.2016.08.014>
- 372 doi: 10.1016/j.chemgeo.2016.08.014
- 373 Daëron, M., Drysdale, R. N., Peral, M., Huyghe, D., Blamart, D., Coplen,
- 374 T. B., ... Zanchetta, G. (2019). Most Earth-surface calcites precipitate
- 375 out of isotopic equilibrium. *Nature Communications*, 10(1), 1–7. doi:
- 376 10.1038/s41467-019-08336-5
- 377 Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P., & Eiler, J. M. (2011).
- 378 Defining an absolute reference frame for ‘clumped’ isotope studies of
- 379 CO_2 . *Geochimica et Cosmochimica Acta*, 75(22), 7117–7131. Retrieved
- 380 from <http://dx.doi.org/10.1016/j.gca.2011.09.025> doi: 10.1016/
- 381 j.gca.2011.09.025
- 382 Dennis, K. J., & Schrag, D. P. (2010). Clumped isotope thermometry of carbon-
- 383 atites as an indicator of diagenetic alteration. *Geochimica et Cosmochimica*
- 384 *Acta*, 74(14), 4110–4122. Retrieved from [http://dx.doi.org/10.1016/](http://dx.doi.org/10.1016/j.gca.2010.04.005)
- 385 j.gca.2010.04.005 doi: 10.1016/j.gca.2010.04.005
- 386 Drysdale, R. N., Paul, B. T., Hellstrom, J. C., Couchoud, I., Greig, A., Bajo, P.,

- ... Woodhead, J. D. (2012). Precise microsampling of poorly laminated speleothems for U-series dating. *Quaternary Geochronology*, 14, 38–47. doi: 10.1016/j.quageo.2012.06.009
- Eiler, J. M. (2007). "Clumped-isotope" geochemistry-The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters*, 262(3-4), 309–327. doi: 10.1016/j.epsl.2007.08.020
- Finnegan, S., Bergmann, K., Eiler, J. M., Jones, D. S., Fike, D. A., Eisenman, I., ... Fischer, W. W. (2011). The magnitude and duration of Late Ordovician- Early Silurian glaciation. *Science*, 331(6019), 903–906. Retrieved from <http://www.sciencemag.org/cgi/doi/10.1126/science.1200803> doi: 10.1126/science.1200803
- Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E. A., ... Eiler, J. M. (2006). ^{13}C - ^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta*, 70(6), 1439–1456. doi: 10.1016/j.gca.2005.11.014
- Guo, W., Mosenfelder, J. L., Goddard, W. A., & Eiler, J. M. (2009). Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochimica et Cosmochimica Acta*, 73(24), 7203–7225. Retrieved from <http://dx.doi.org/10.1016/j.gca.2009.05.071> doi: 10.1016/j.gca.2009.05.071
- Hill, P. S., Tripathi, A. K., & Schauble, E. A. (2014). Theoretical constraints on the effects of pH, salinity, and temperature on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate minerals. *Geochimica et Cosmochimica Acta*, 125, 610–652. Retrieved from <http://dx.doi.org/10.1016/j.gca.2013.06.018> doi: 10.1016/j.gca.2013.06.018
- Horita, J. (2014). Oxygen and carbon isotope fractionation in the system dolomite-water- CO_2 to elevated temperatures. *Geochimica et Cosmochimica Acta*, 129, 111–124. doi: 10.1016/j.gca.2013.12.027
- Jautzy, J., Savard, M., Dhillon, R., Bernasconi, S., Lavoie, D., & Smirnov, A. (2020). Clumped isotope temperature calibration for calcite: Bridging theory and experimentation. *Geochemical Perspective Letters*, 14, 36–41. doi: 10.7185/geochemlet.2021

- 420 Jungblut, A. D., Hawes, I., Mackey, T. J., Krusor, M., Doran, P. T., Sumner, D. Y.,
 421 ... Goroncy, A. K. (2016). Microbial mat communities along an oxygen gra-
 422 dient in a perennially ice-covered Antarctic lake. *Applied and Environmental*
 423 *Microbiology*, 82(2), 620–630. doi: 10.1128/AEM.02699-15
- 424 Kele, S., Breitenbach, S. F., Capezzuoli, E., Meckler, A. N., Ziegler, M., Millan,
 425 I. M., ... Bernasconi, S. M. (2015). Temperature dependence of oxygen- and
 426 clumped isotope fractionation in carbonates: A study of travertines and tufas
 427 in the 6–95°C temperature range. *Geochimica et Cosmochimica Acta*, 168,
 428 172–192. doi: 10.1016/j.gca.2015.06.032
- 429 Kelson, J. R., Huntington, K. W., Schauer, A. J., Saenger, C., & Lechler, A. R.
 430 (2017). Toward a universal carbonate clumped isotope calibration: Di-
 431 verse synthesis and preparatory methods suggest a single temperature
 432 relationship. *Geochimica et Cosmochimica Acta*, 197, 104–131. Re-
 433 trieved from <http://dx.doi.org/10.1016/j.gca.2016.10.010> doi:
 434 10.1016/j.gca.2016.10.010
- 435 Kim, S. T., Mucci, A., & Taylor, B. E. (2007). Phosphoric acid fractionation fac-
 436 tors for calcite and aragonite between 25 and 75 °C: Revisited. *Chemical Geol-*
 437 *ogy*, 246(3–4), 135–146. doi: 10.1016/j.chemgeo.2007.08.005
- 438 Kluge, T., John, C. M., Jourdan, A. L., Davis, S., & Crawshaw, J. (2015). Labora-
 439 tory calibration of the calcium carbonate clumped isotope thermometer in the
 440 25–250°C temperature range. *Geochimica et Cosmochimica Acta*, 157, 213–227.
 441 doi: 10.1016/j.gca.2015.02.028
- 442 Lloyd, M. K., Eiler, J. M., & Nabelek, P. I. (2017). Clumped isotope thermome-
 443 try of calcite and dolomite in a contact metamorphic environment. *Geochimica*
 444 *et Cosmochimica Acta*, 197, 323–344. Retrieved from [http://dx.doi.org/10](http://dx.doi.org/10.1016/j.gca.2016.10.037)
 445 [.1016/j.gca.2016.10.037](http://dx.doi.org/10.1016/j.gca.2016.10.037) doi: 10.1016/j.gca.2016.10.037
- 446 Mackey, T. J., Jost, A. B., Creveling, J. R., & Bergmann, K. D. (2020). A Decrease
 447 to Low Carbonate Clumped Isotope Temperatures in Cryogenian Strata. *AGU*
 448 *Advances*, 1(3). doi: 10.1029/2019av000159
- 449 Mackey, T. J., Sumner, D. Y., Hawes, I., & Jungblut, A. D. (2017). Morpho-
 450 logical signatures of microbial activity across sediment and light microen-
 451 vironments of Lake Vanda, Antarctica. *Sedimentary Geology*, 361, 82–92.
 452 Retrieved from <https://doi.org/10.1016/j.sedgeo.2017.09.013> doi:

- 10.1016/j.sedgeo.2017.09.013
- Mackey, T. J., Sumner, D. Y., Hawes, I., Leidman, S. Z., Andersen, D. T., & Jungblut, A. D. (2018). Stromatolite records of environmental change in perennially ice-covered Lake Joyce, McMurdo Dry Valleys, Antarctica. *Biogeochemistry*, 137(1-2), 73–92. Retrieved from <https://doi.org/10.1007/s10533-017-0402-1> doi: 10.1007/s10533-017-0402-1
- Mangenot, X., Gasparrini, M., Gerdes, A., Bonifacie, M., & Rouchon, V. (2018). An emerging thermochronometer for carbonate-bearing rocks: $\Delta 47$ /(U-Pb). *Geology*, 46(12), 1067–1070. doi: 10.1130/G45196.1
- Meinicke, N., Ho, S. L., Hannisdal, B., Nürnberg, D., Tripathi, A., Schiebel, R., & Meckler, A. N. (2020). A robust calibration of the clumped isotopes to temperature relationship for foraminifers. *Geochimica et Cosmochimica Acta*, 270, 160–183. doi: 10.1016/j.gca.2019.11.022
- Müller, I. A., Rodriguez-blanco, J. D., Storck, J.-c., Santilli, G., Bontognali, T. R. R., Vasconcelos, C., ... Bernasconi, S. M. (2019). Calibration of the oxygen and clumped isotope thermometers for (proto-) dolomite based on synthetic and natural carbonates. *Chemical Geology*, 525(July), 1–17. Retrieved from <https://doi.org/10.1016/j.chemgeo.2019.07.014> doi: 10.1016/j.chemgeo.2019.07.014
- Peral, M., Daëron, M., Blamart, D., Bassinot, F., Dewilde, F., Smialkowski, N., ... Waelbroeck, C. (2018). Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera. *Geochimica et Cosmochimica Acta*, 239, 1–16. doi: 10.1016/j.gca.2018.07.016
- Petersen, S. V., Defliese, W. F., Saenger, C., Daëron, M., Huntington, K. W., John, C. M., ... Winkelstern, I. Z. (2019). Effects of improved 17O correction on interlaboratory agreement in clumped isotope calibrations, estimates of mineral-specific offsets, and temperature dependence of acid digestion fractionation. *Geochemistry, Geophysics, Geosystems*, 3495–3519. doi: 10.1029/2018gc008127
- Piasecki, A., Bernasconi, S. M., Grauel, A. L., Hannisdal, B., Ho, S. L., Leutert, T. J., ... Meckler, N. (2019). Application of clumped isotope thermometry to benthic foraminifera. *Geochemistry, Geophysics, Geosystems*, 20(4), 2082–2090. doi: 10.1029/2018GC007961

- 486 Ross, S. (2003). Peirce's criterion for the elimination of suspect experimental data.
487 *Journal of Engineering Technology*, 20, 1–12.
- 488 Schauble, E. A., Ghosh, P., & Eiler, J. M. (2006). Preferential formation of ^{13}C
489 – ^{18}O bonds in carbonate minerals, estimated using first-principles lattice
490 dynamics. *Geochimica et Cosmochimica Acta*, 70(10), 2510–2529. doi:
491 10.1016/j.gca.2006.02.011
- 492 Schauer, A. J., Kelson, J., Saenger, C., & Huntington, K. W. (2016). Choice of
493 ^{17}O correction affects clumped isotope ($\Delta 47$) values of CO_2 measured with
494 mass spectrometry. *Rapid Communications in Mass Spectrometry*, 30(24),
495 2607–2616. doi: 10.1002/rcm.7743
- 496 Snell, K. E., Thrasher, B. L., Eiler, J. M., Koch, P. L., Sloan, L. C., & Tabor, N. J.
497 (2013). Hot summers in the Bighorn Basin during the early Paleogene. *Geol-*
498 *ogy*, 41(1), 55–58. doi: 10.1130/G33567.1
- 499 Wacker, U., Wacker, U., Fiebig, J., Fiebig, J., Tödter, J., Tödter, J., ... Joachimski,
500 M. M. (2014). Empirical calibration of the clumped isotope paleothermome-
501 ter using calcites of various origins. *Geochimica et Cosmochimica Acta*, 141,
502 127–144. Retrieved from [http://linkinghub.elsevier.com/retrieve/](http://linkinghub.elsevier.com/retrieve/pii/S0016703714004050)
503 [pii/S0016703714004050](http://linkinghub.elsevier.com/retrieve/pii/S0016703714004050){\%}5Cnpapers2://publication/doi/10.1016/
504 [j.gca.2014.06.004](http://linkinghub.elsevier.com/retrieve/pii/S0016703714004050)
- 505 Winkelstern, I. Z., & Lohmann, K. C. (2016). Shallow burial alteration of dolomite
506 and limestone clumped isotope geochemistry. *Geology*, 44(6), 467–470. doi: 10
507 .1130/G37809.1
- 508 Winograd, I. J., Landwehr, J. M., Coplen, T. B., Sharp, W. D., Riggs, A. C., Lud-
509 wig, K. R., & Kolesar, P. T. (2006). Devils Hole, Nevada, $\delta^{18}\text{O}$ record ex-
510 tended to the mid-Holocene. *Quaternary Research*, 66(2), 202–212. doi:
511 10.1016/j.yqres.2006.06.003
- 512 York, D., Evensen, N. M., López, M., & Delgado, J. D. B. (2004). Unified equations
513 for the slope, intercept, and standard errors of the best straight line. *American*
514 *Journal of Physics*, 72(3), 367–373. doi: 10.1119/1.1632486
- 515 Zaarur, S., Affek, H. P., & Brandon, M. T. (2013). A revised calibration of the
516 clumped isotope thermometer. *Earth and Planetary Science Letters*, 382, 47–
517 57. Retrieved from <http://dx.doi.org/10.1016/j.epsl.2013.07.026> doi:
518 10.1016/j.epsl.2013.07.026

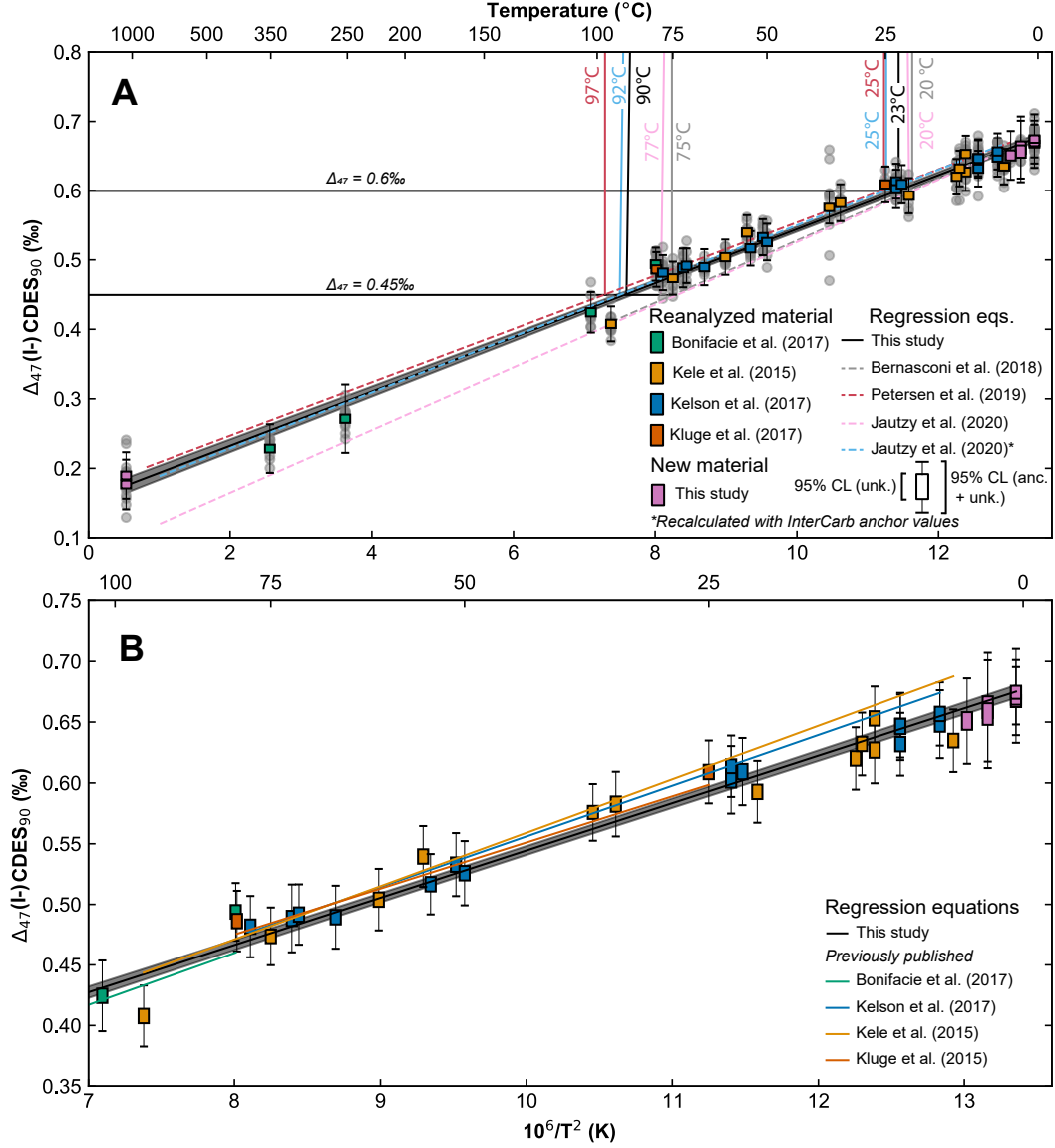


Figure 1. A. Linear $1/T^2$ - Δ_{47} regression and 95% confidence interval (York et al., 2004) for samples (re)analyzed in this study along with recently published calibrations. Solid vertical lines show approximate formation temperature for each calibration when $\Delta_{47} = 0.45\text{‰}$ and $\Delta_{47} = 0.6\text{‰}$. 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).

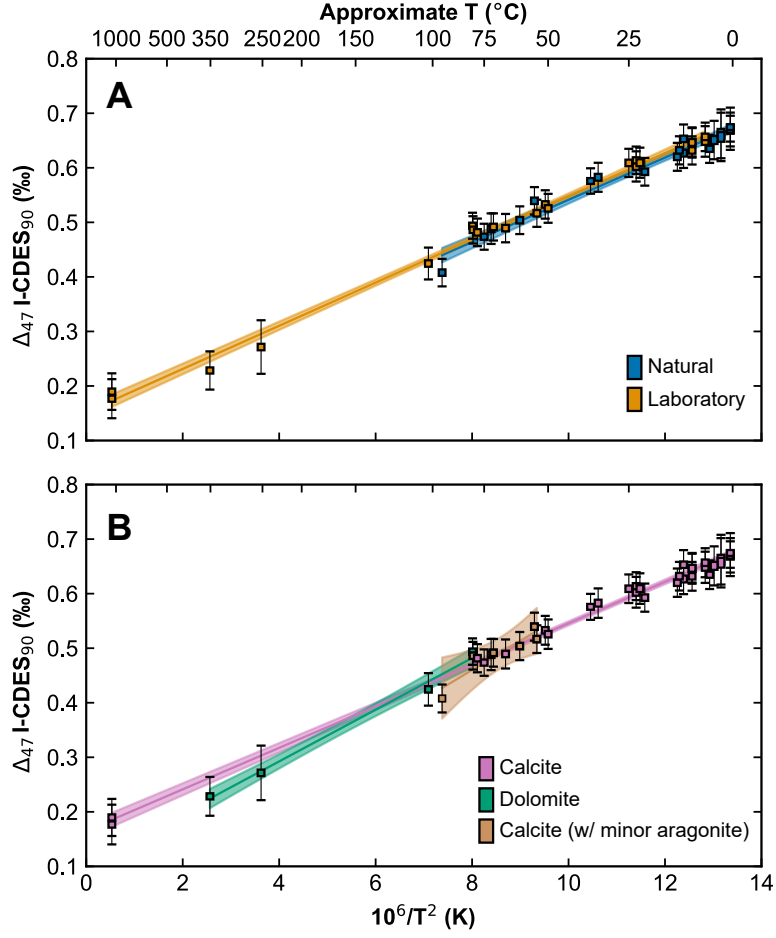


Figure 2. A. $1/T^2$ - Δ_{47} comparison of natural and laboratory precipitated sample material. Error bars correspond to 95% confidence limits accounting for error from both unknown and anchor analyses; boxes correspond to 95% CL not accounting for normalization errors. Natural samples have larger uncertainty 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.

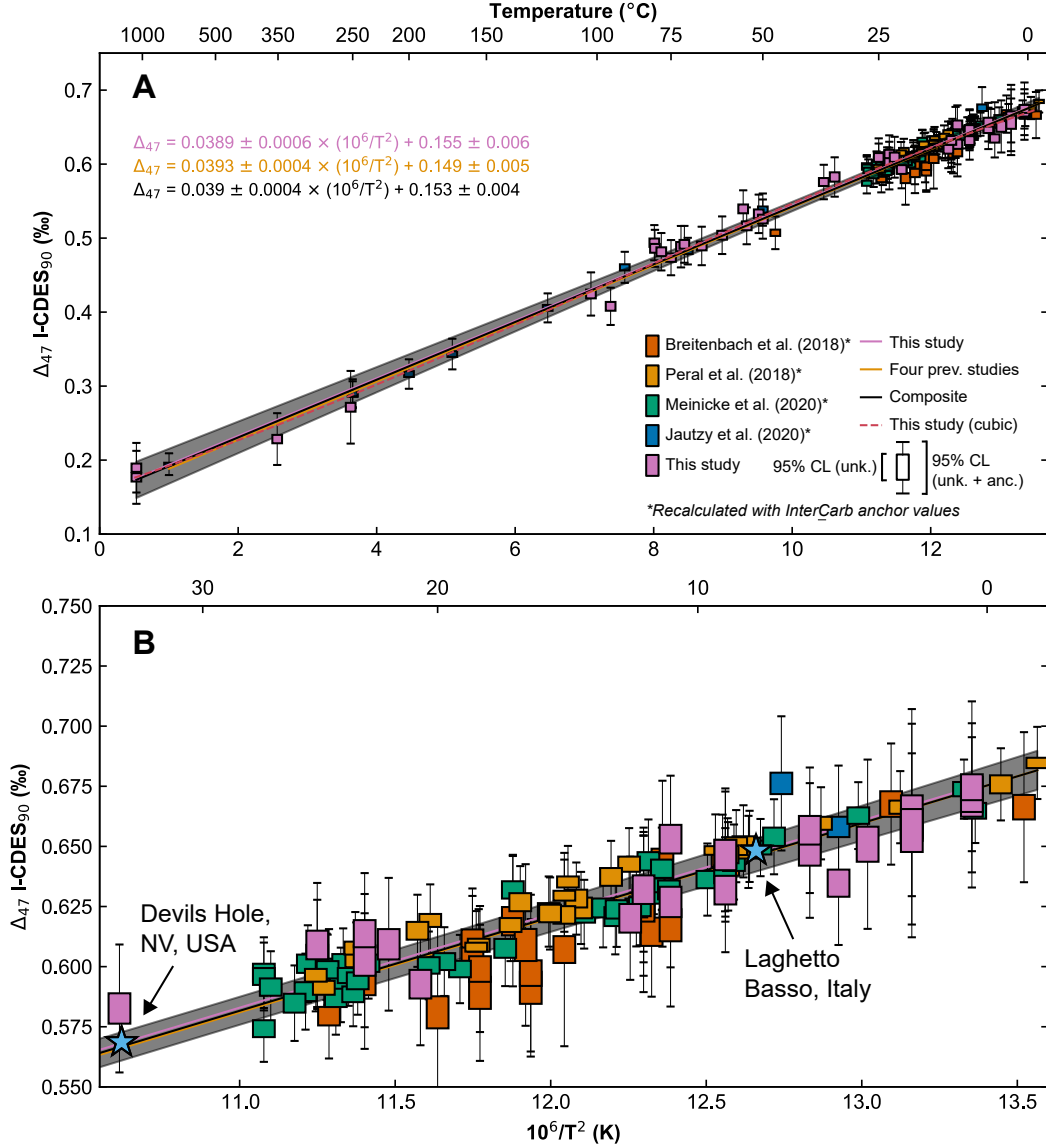


Figure 3. A. All Δ_{47} results from this study shown with data from four recent studies using carbonate-based standardization using laboratory precipitates (Jautzy et al., 2020) and foraminifera (Breitenbach et al., 2018; Peral et al., 2018; Meinicke et al., 2020), recalculated here with InterCarb anchor 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.

Supporting Information for ”A unified clumped isotope calibration (0.5–1100°C) using carbonate-based standardization”

N.T. Anderson¹, J.R. Kelson², S. Kele³, M. Daëron⁴, M. Bonifacie⁵, J.

Horita⁶, T.J. Mackey⁷, C.M. John⁸, T. Kluge⁹, P. Petschnig¹¹, A.B. Jost¹,

K.W. Huntington¹⁰, S.M. Bernasconi¹¹, K. D. Bergmann¹

¹Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, 02135

²Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109

³Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, 1112 Budapest, Hungary

⁴Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Orme des Merisiers, F-91191, Gif-sur-Yvette Cedex, France

⁵Institut de Physique du Globe de Paris, Sorbonne Paris Cite, Université Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France

⁶Department of Geosciences, Texas Tech University, Lubbock, TX, 79409

⁷Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, 87131

⁸Department of Earth Science and Engineering, Imperial College, Prince Consort Road, London SW7 2AZ

⁹Institute of Applied Geosciences, Karlsruhe Institute of Technology-KIT, Adenauerring 20b, 76131 Karlsruhe, Germany

¹⁰Department of Earth and Space Sciences and Quaternary Research Center, University of Washington, Seattle, WA, USA

¹¹Geological Institute, ETH Zurich, CH-8092 Zurich, Switzerland

December 10, 2020, 8:31pm

Contents of this file

1. Text S1 to S3
2. Figures S1 to S4
3. Table S1

Additional Supporting Information (Files uploaded separately)

1. Captions for Datasets S1-S2

Introduction

This supporting information document contains supplemental text on high-temperature calcite formation procedure (S1), information on the measurement of two slow-growing carbonate samples from Devils Hole and Laghetto Basso (S2), and details of reprocessing of data from previous studies (S3). Table S1 summarizes analysis of covariance (ANCOVA) results for this study. Summary isotopic data, including all relevant sample information (e.g., percent aragonite, fluid $\delta^{18}\text{O}$) is included in Dataset S1 (.csv). Replicate-level isotopic data are provided as separately uploaded Dataset S2 (.csv); these data will be uploaded to the EarthChem database pending acceptance of the manuscript. Figure S1 and S2 respectively shows comparison of T- Δ_{47} regressions with addition of CA and by

Corresponding author: N. T. Anderson, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Building 54, Cambridge, MA 02139, USA. (nanderso@mit.edu)

precipitation method and $T-\Delta_{47}$ with low vs. high and moderate vs. intensive precipitation rates. Figure S3 compares regressions for sample reanalyzed for this study compared to regressions from their originally published studies. Figure S4 shows the range of δ^{47} and Δ_{47} values of (re)analyzed samples and carbonate anchors used in this study.

Text S1.

Both high-temperature calcite samples (ETH-1-1100, ETH-2-1100) were synthesized in externally heated pressure vessels (EHPV or “cold-seal” apparatus) with argon as a pressure medium at the Institute of Geochemistry and Petrology, ETH Zurich. Both equilibration experiments were done in $\text{Au}_{90}\text{Pd}_{10}$ capsules with a length of 40mm and 4mm outer diameter. The sample material was filled and compressed in the capsule and welded shut under an Ar stream using a Lampert PUK arc welder. Run conditions for both experiments were 1100°C and 2000 bar (200 MPa) with 24h runtime at final run conditions. The temperature gradient within the (extended) hot zone of the vessel is $\pm 10^\circ \text{C}$ and the accuracy of the temperature measurement is better than 10°C . Pressure conditions were stable within 10 bars for the entire run duration. At run conditions the hot end of the EHPV is in a subhorizontal position of 10° inclination (hot-end up), which prevents circulation of the gas. Quenching is accomplished via rotating the entire furnace and vessel to a 90° vertical position. The capsule drops to the cold-end and is quenched to room temperature within seconds. Prior heating, the pressure was set to 1000 bar at room temperature. The experimental capsules were loaded directly in the hot-end of the vessel and heated to final temperature within six hours. At final run temperature

(1100°C), pressure was adjusted from ~ 1860 bar to final run conditions (2000 bar) and held at there for 24h.

Text S2.

Publicly available mass spectrometer data from five previous calibration studies (Peral et al., 2018; Breitenbach et al., 2018; Piasecki et al., 2019; Meinicke et al., 2020; Jautzy et al., 2020) were acquired from the EarthChem database. To follow the data processing procedure of samples analyzed in this study, analyses were split into sessions of 50 analyses each and raw data were converted to the I-CDES using the 'D47crunch' package using InterCarb anchor values (Bernasconi et al., submitted) for the standards ETH-1, ETH-2, ETH-3, ETH-4, and, when available, IAEA-C2 and MERCK. IAEA-C1 was used as a consistency check. No cycle-level data processing was performed. Full details of the data reduction process in 'D47crunch' are detailed in Daëron (submitted).

To reflect the design of the original study, data from Peral et al. (2018) were initially processed with each size fraction of foraminifera of the same species and from the same core as distinct samples; after processing via the pooled regression model of Daëron (submitted), Δ_{47} values for each size fraction were computed by a weighted average.

Text S3.

Two slowly-growing carbonates (DVH-2 and LGB-2) were measured on an Isoprime 100 dual-inlet mass spectrometer at the Laboratoire des Sciences du Climat et de l'Environnement, Université Paris-Saclay. DVH-2 is a Holocene mammillary cave calcite from Devil's Hole, Nevada, USA, and is the outer surface of sample DHC2-8 as described in Winograd et al. (2006); Coplen (2007). Laghetto Basso calcite (LGB-2) is a

subaqueous calcite coating found at the bottom of Laghetto Basso, a small lake in Corchia Cave (Italy). LGB-2 was collected from the top of of core CD3-12 (Drysedale et al., 2012).

Carbonate samples were converted to CO_2 by phosphoric acid reaction at 90°C in a common, stirred acid bath for 15 minutes. Initial phosphoric acid concentration was 103 % (1.91 g/cm^3) and each batch of acid was used for 7 days. After cryogenic removal of water, the evolved CO_2 was helium-flushed at 25 mL/min through a purification column packed with Porapak Q (50/80 mesh, 1 m length, 2.1 mm ID) and held at -20°C , then quantitatively recollected by cryogenic trapping and transferred into an Isoprime 100 dual-inlet mass spectrometer equipped with six Faraday collectors (m/z 44–49). Each analysis took about 2.5 hours, during which analyte gas and working reference gas were allowed to flow from matching, 10 mL reservoirs into the source through deactivated fused silica capillaries (65 cm length, $110 \mu\text{m}$ ID). Every 20 minutes, gas pressures were adjusted to achieve $m/z = 44$ current of 80 nA, with differences between analyte gas and working gas generally below 0.1 nA. Pressure-dependent background current corrections were measured 12 times for each analysis. All background measurements from a given session are then used to determine a mass-specific relationship linking background intensity (Z_m), total $m/z = 44$ intensity (I_{44}), and time (t): $Z_m = a + bI_{44} + ct + dt^2$. Background-corrected ion current ratios (δ^{45} to δ^{49}) were converted to $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and “raw” Δ_{47} values as described by (Daëron et al., 2016), using the IUPAC oxygen-17 correction parameters. The isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of our working reference gas was computed based on the nominal isotopic composition of carbonate standard ETH-3 (Bernasconi et al., submitted) and an oxygen-18 acid fractionation factor of 1.00813 (Kim et al., 2007). Raw Δ_{47}

values were then converted to the “absolute” Δ_{47} reference frame defined by the “ETH” carbonate standards (Bernasconi et al., submitted) using a pooled regression approach (Daëron, submitted). Full analytical errors are derived from the external reproducibility of unknowns and standards ($N_f = 101$) and conservatively account for the uncertainties in raw Δ_{47} measurements as well as those associated with the conversion to the “absolute” Δ_{47} reference frame.

Data Set S1.

Summarized isotopic data and uncertainty along with associated sample information when available (i.e. precipitation rate, pH).

Data Set S2.

Replicate-level raw isotopic data for all samples and anchors analyzed in this study. This dataset 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.

References

- Bernasconi, S. M., Daëron, M., Bergmann, K. D., Bonifacie, M., Meckler, A. N., Affek, H. P., ... Ziegler, M. (submitted). InterCarb: A community effort to improve inter-laboratory standardization of the carbonate clumped isotope thermometer using carbonate standards. *Geochemistry, Geophysics, Geosystems*. doi: DOI:10.1002/essoar.10504430.2
- Breitenbach, S. F., Mlencek-Vautravers, M. J., Grauel, A. L., Lo, L., Bernasconi, S. M., Müller, I. A., ... Hodell, D. A. (2018). Coupled Mg/Ca and clumped isotope analyses

- of foraminifera provide consistent water temperatures. *Geochimica et Cosmochimica Acta*, 236, 283–296. doi: 10.1016/j.gca.2018.03.010
- Coplen, T. B. (2007). Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. *Geochimica et Cosmochimica Acta*, 71(16), 3948–3957. doi: 10.1016/j.gca.2007.05.028
- Daëron, M. (submitted). Full propagation of analytical uncertainties in D47 measurements. *Geochemistry, Geophysics, Geosystems*.
- Daëron, M., Blamart, D., Peral, M., & Affek, H. P. (2016). Absolute isotopic abundance ratios and the accuracy of $\Delta 47$ measurements. *Chemical Geology*, 442, 83–96. Retrieved from <http://dx.doi.org/10.1016/j.chemgeo.2016.08.014> doi: 10.1016/j.chemgeo.2016.08.014
- Drysdale, R. N., Paul, B. T., Hellstrom, J. C., Couchoud, I., Greig, A., Bajo, P., ... Woodhead, J. D. (2012). Precise microsampling of poorly laminated speleothems for U-series dating. *Quaternary Geochronology*, 14, 38–47. doi: 10.1016/j.quageo.2012.06.009
- Jautzy, J., Savard, M., Dhillon, R., Bernasconi, S., Lavoie, D., & Smirnov, A. (2020). Clumped isotope temperature calibration for calcite: Bridging theory and experimentation. *Geochemical Perspective Letters*, 14, 36–41. doi: 10.7185/geochemlet.2021
- Kelson, J. R., Huntington, K. W., Schauer, A. J., Saenger, C., & Lechler, A. R. (2017). Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship. *Geochimica et Cosmochimica Acta*, 197, 104–131. Retrieved from <http://dx.doi.org/10.1016/>

j.gca.2016.10.010 doi: 10.1016/j.gca.2016.10.010

- Kim, S. T., Mucci, A., & Taylor, B. E. (2007). Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited. *Chemical Geology*, *246*(3-4), 135–146. doi: 10.1016/j.chemgeo.2007.08.005
- Meinicke, N., Ho, S. L., Hannisdal, B., Nürnberg, D., Tripathi, A., Schiebel, R., & Meckler, A. N. (2020). A robust calibration of the clumped isotopes to temperature relationship for foraminifers. *Geochimica et Cosmochimica Acta*, *270*, 160–183. doi: 10.1016/j.gca.2019.11.022
- Peral, M., Daëron, M., Blamart, D., Bassinot, F., Dewilde, F., Smialkowski, N., ... Waelbroeck, C. (2018). Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera. *Geochimica et Cosmochimica Acta*, *239*, 1–16. doi: 10.1016/j.gca.2018.07.016
- Petersen, S. V., Defliese, W. F., Saenger, C., Daëron, M., Huntington, K. W., John, C. M., ... Winkelstern, I. Z. (2019). Effects of improved ^{17}O correction on inter-laboratory agreement in clumped isotope calibrations, estimates of mineral-specific offsets, and temperature dependence of acid digestion fractionation. *Geochemistry, Geophysics, Geosystems*, 3495–3519. doi: 10.1029/2018gc008127
- Piasecki, A., Bernasconi, S. M., Grauel, A. L., Hannisdal, B., Ho, S. L., Leutert, T. J., ... Meckler, N. (2019). Application of clumped isotope thermometry to benthic foraminifera. *Geochemistry, Geophysics, Geosystems*, *20*(4), 2082–2090. doi: 10.1029/2018GC007961
- Winograd, I. J., Landwehr, J. M., Coplen, T. B., Sharp, W. D., Riggs, A. C., Ludwig,

K. R., & Kolesar, P. T. (2006). Devils Hole, Nevada, $\delta^{18}\text{O}$ record extended to the mid-Holocene. *Quaternary Research*, 66(2), 202–212. doi: 10.1016/j.yqres.2006.06.003

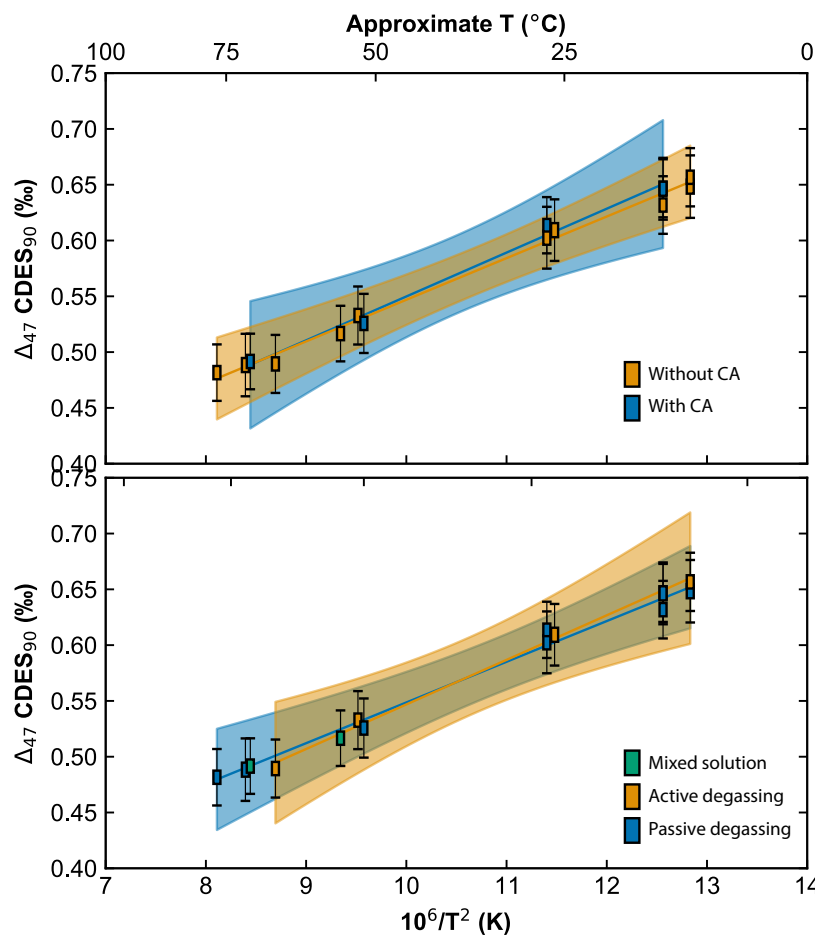


Figure S1. A. Comparison of samples from Kelson et al. (2017) with and without addition of carbonic anhydrase (CA) during precipitation. We see no statistically significant offset between these groups; this confirms the findings of Kelson et al. (2017). B. Comparison of samples from Kelson et al. (2017) with different precipitation methods; active degassing, passive degassing, and mixed solution. We confirm the findings of Kelson et al. (2017) by finding no statistically significant offset between passively and actively degassed samples; not enough data are available to determine the agreement with mixed solution samples.

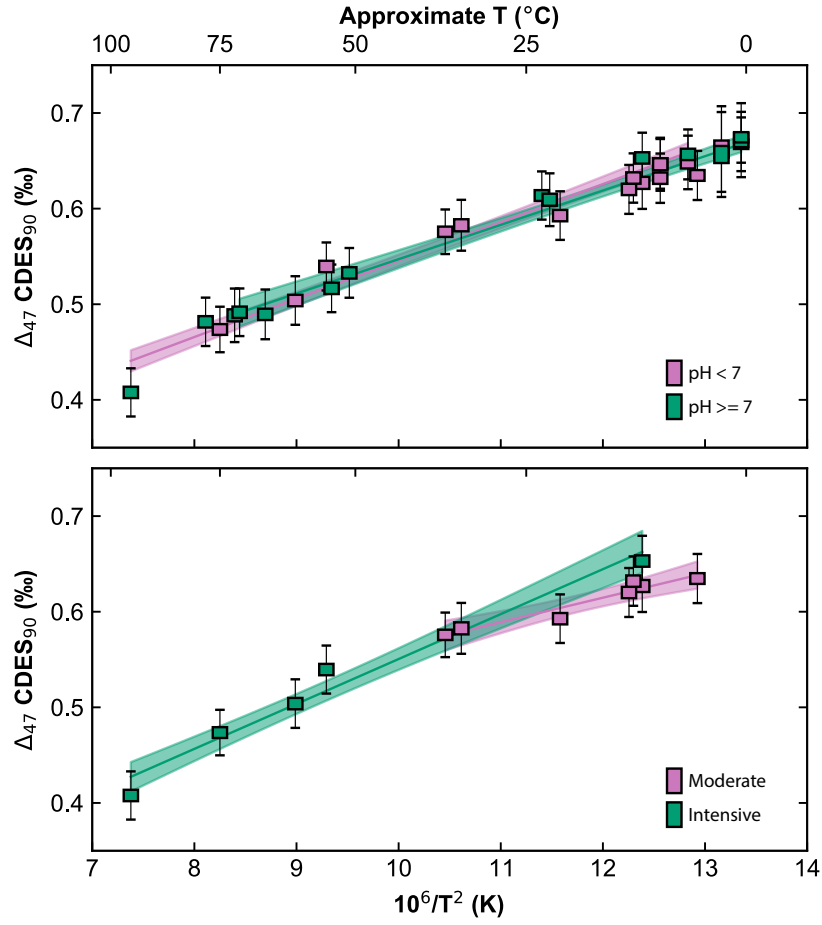


Figure S2. A. Comparison between sample material precipitated from fluid with pH < 7 and pH ≥ 7; no significant difference is evident. B. Comparison between samples with 'moderate' and 'intensive' precipitation rates (after Kele et al., 2015). The regression lines visually diverge, but it is unclear if this is due to the relatively small number of samples with precipitation rate data, the limited amount of rapidly precipitated cold-water carbonates, or a true effect of precipitation rate. ANCOVA accepts the null hypothesis of no significant difference between the two regressions ($p_{\text{slope}} = 0.12$, $p_{\text{intercept}} = 0.54$)

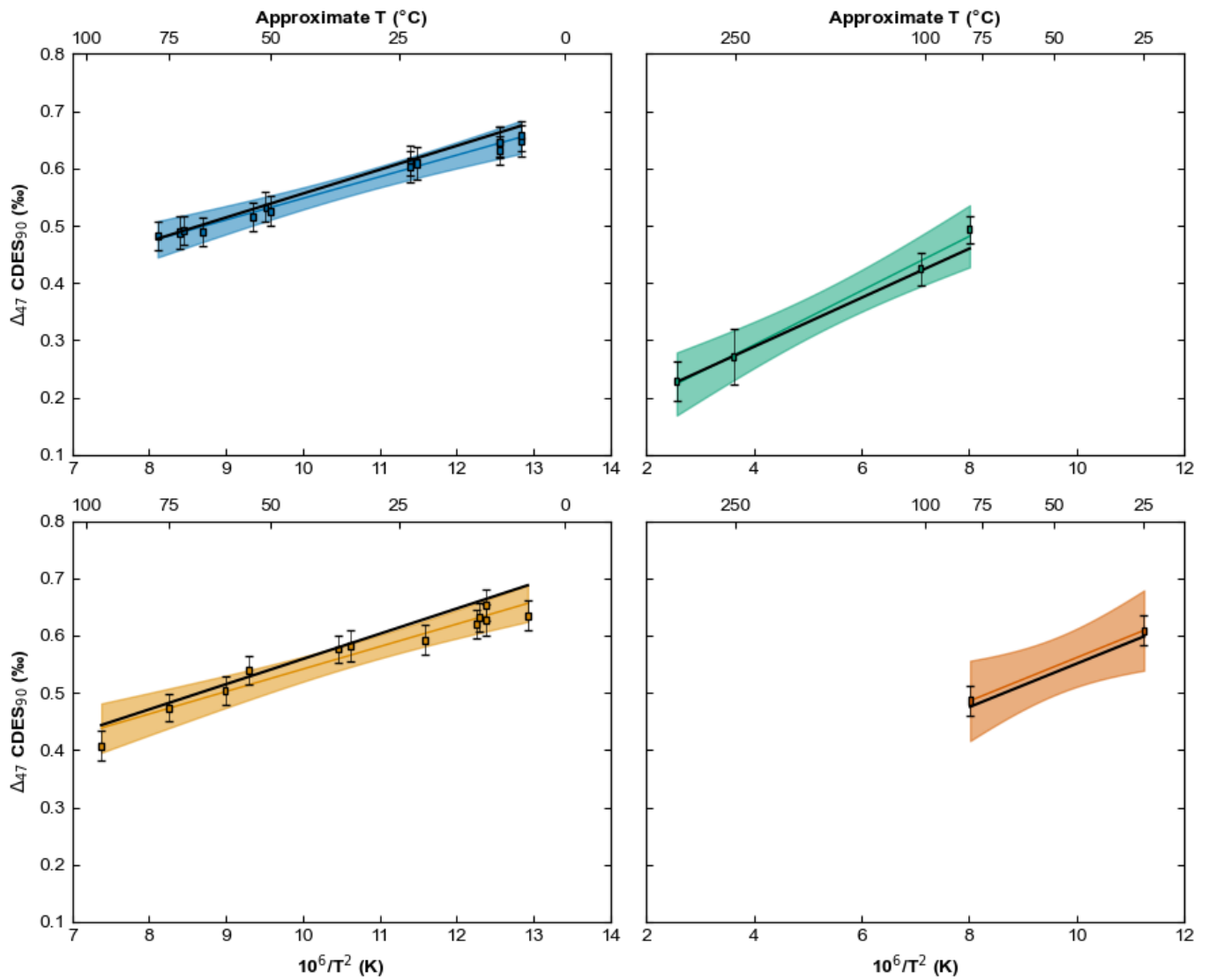


Figure S3. Comparison between published regressions from studies with sample material re-analyzed in this study (black lines) and regressions developed from their constituent samples in this study (colored lines and confidence envelopes). All previously published regressions are projected to the 90°C CDES using AFF values from Petersen et al. (2019), whereas regressions from this study are in the 90°C I-CDES. Previously published regressions agree well with regressions based on the same sample material reanalyzed in this study.

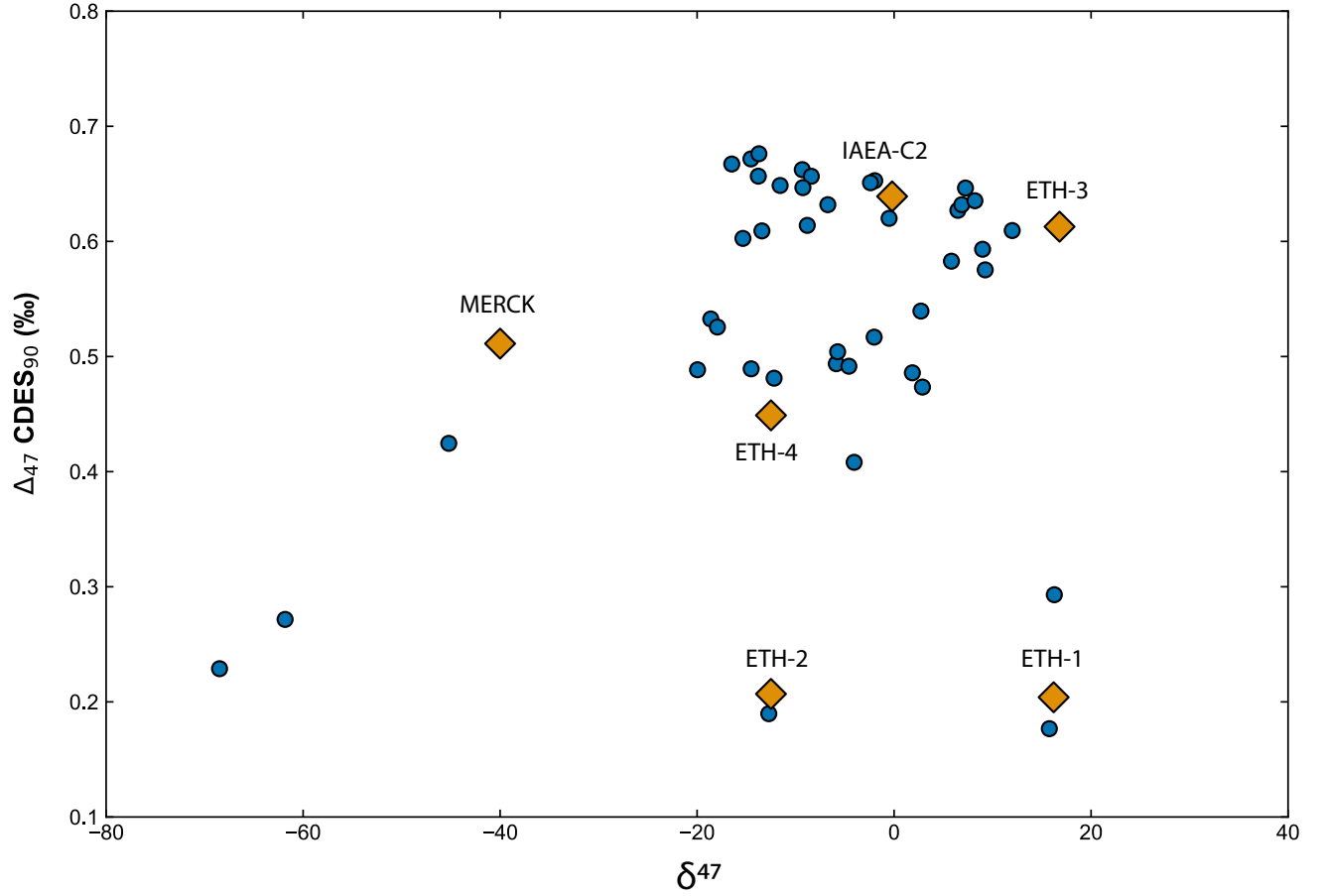


Figure S4. δ^{47} and Δ_{47} values of carbonates measured in this study, with 'InterCarb' anchor samples shown as orange diamonds. Material measured in this study spans an extremely wide range of δ^{47} (-70‰ – 15‰) and is well-bracketed by the anchor materials.

Table S1. ANCOVA p -values for null hypothesis of similar regression slope and intercept.

Category A	Category B	p_{slope}	$p_{intercept}$
Bonifacie et al. (2017)	Kele et al. (2015)	0.06	0.27
Bonifacie et al. (2017)	Kelson et al. (2017)	0.01	0.77
Bonifacie et al. (2017)	Kluge et al. (2015)	0.19	0.41
Kele et al. (2015)	Kelson et al. (2017)	0.56	0.99
Kele et al. (2015)	Kluge et al. (2015)	0.8	0.08
Kelson et al. (2017)	Kluge et al. (2015)	0.99	0.07
Calcite	Dolomite	0.002	0.47
Calcite	Aragonite	0.16	0.59
Passive degassing	Active Degassing	0.19	0.79
Carbonic anhydrase	No carbonic anhydrase	0.79	0.32
Moderate precip. rate	Intensive precip. rate	0.12	0.54
Laboratory	Natural	0.41	0.19