

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

N.T. Anderson<sup>1</sup>, J.R. Kelson<sup>2</sup>, S. Kele<sup>3</sup>, M. Daëron<sup>4</sup>, M. Bonifacie<sup>5</sup>, J.

Horita<sup>6</sup>, T.J. Mackey<sup>7</sup>, C.M. John<sup>8</sup>, T. Kluge<sup>9</sup>, P. Petschnig<sup>11</sup>, A.B. Jost<sup>1</sup>,

K.W. Huntington<sup>10</sup>, S.M. Bernasconi<sup>11</sup>, K. D. Bergmann<sup>1</sup>

<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, 02135

<sup>2</sup>Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109

<sup>3</sup>Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, 1112 Budapest, Hungary

<sup>4</sup>Laboratoire 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

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

<sup>6</sup>Department of Geosciences, Texas Tech University, Lubbock, TX, 79409

<sup>7</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM, 87131

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

<sup>9</sup>Institute of Applied Geosciences, Karlsruhe Institute of Technology-KIT, Adenauerring 20b, 76131 Karlsruhe, Germany

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

<sup>11</sup>Geological 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  $T-\Delta_{47}$  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  $\delta^{47}$  and  $\Delta_{47}$  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  $10^\circ \text{C}$ . 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  $10^\circ$  inclination (hot-end up), which prevents circulation of the gas. Quenching is accomplished via rotating the entire furnace and vessel to a  $90^\circ$  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  $\sim 1860$  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),  $\Delta_{47}$  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 core CD3-12 (Drysdales et al., 2012).

Carbonate samples were converted to  $\text{CO}_2$  by phosphoric acid reaction at  $90^\circ\text{C}$  in a common, stirred acid bath for 15 minutes. Initial phosphoric acid concentration was 103 % ( $1.91 \text{ g/cm}^3$ ) and each batch of acid was used for 7 days. After cryogenic removal of water, the evolved  $\text{CO}_2$  was helium-flushed at  $25 \text{ mL/min}$  through a purification column packed with Porapak Q (50/80 mesh, 1 m length, 2.1 mm ID) and held at  $-20^\circ\text{C}$ , 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 ( $\delta^{45}$  to  $\delta^{49}$ ) were converted to  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and “raw”  $\Delta_{47}$  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  $\Delta_{47}$

values were then converted to the “absolute”  $\Delta_{47}$  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  $\Delta_{47}$  measurements as well as those associated with the conversion to the “absolute”  $\Delta_{47}$  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., Mlonek-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

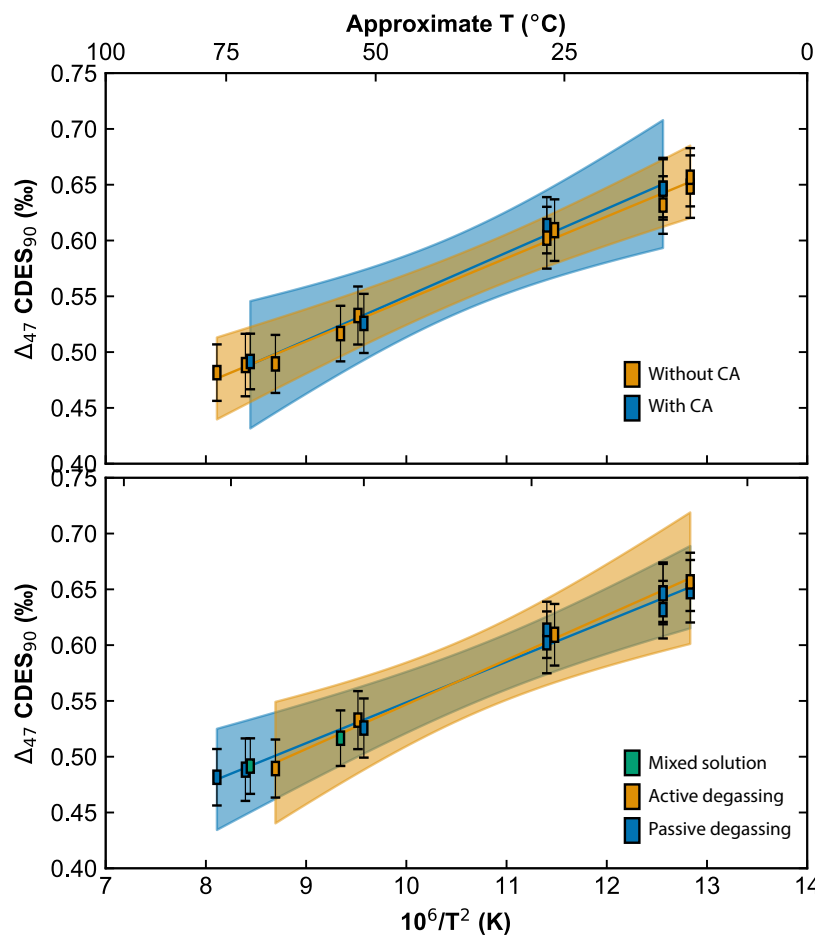
Petersen, S. V., Defliese, W. F., Saenger, C., Daëron, M., Huntington, K. W., John, C. M., ... Winkelstern, I. Z. (2019). Effects of improved  $^{17}\text{O}$  correction on inter-laboratory agreement in clumped isotope calibrations, estimates of mineral-specific offsets, and temperature dependence of 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

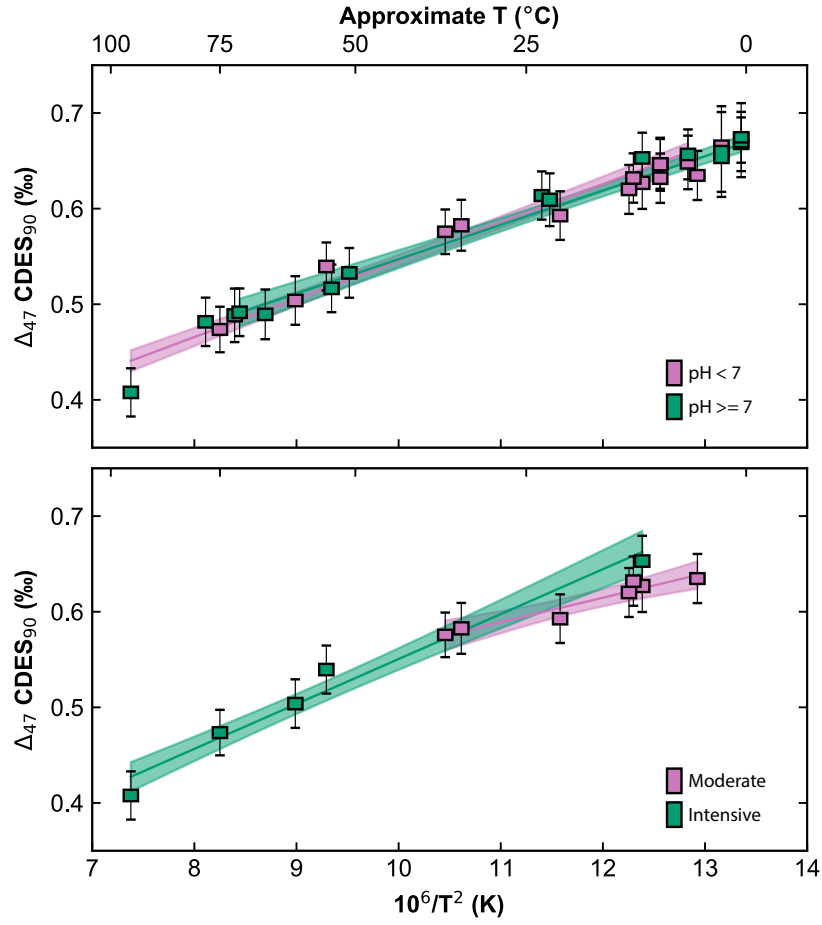
Winograd, I. J., Landwehr, J. M., Coplen, T. B., Sharp, W. D., Riggs, A. C., Ludwig,



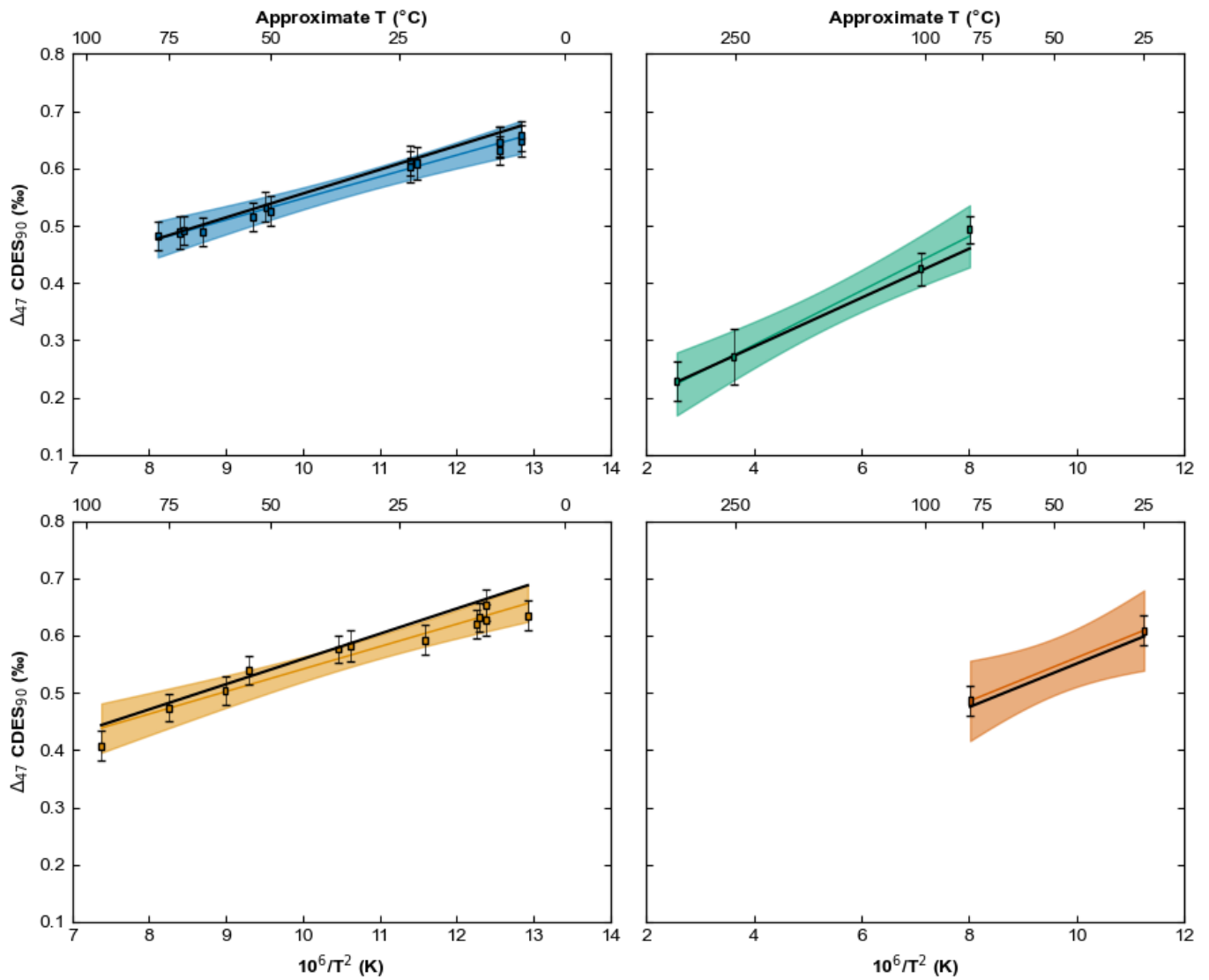
K. R., & Kolesar, P. T. (2006). Devils Hole, Nevada,  $\delta^{18}\text{O}$  record extended to the mid-Holocene. *Quaternary Research*, 66(2), 202–212. doi: 10.1016/j.yqres.2006.06.003



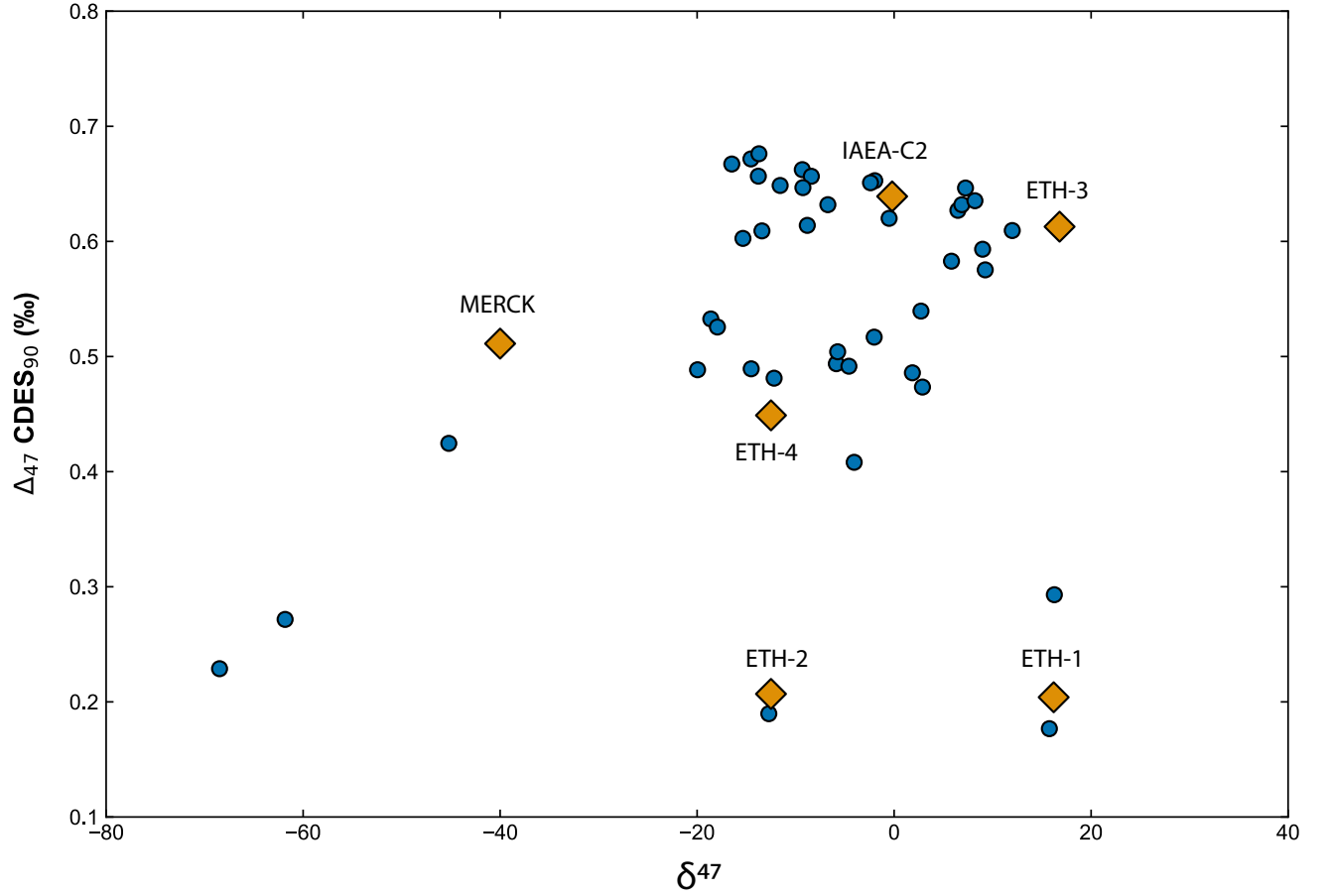
**Figure S1.** A. Comparison of samples from Kelson et al. (2017) with and without addition of carbonic anhydrase (CA) during precipitation. We see no statistically significant offset between these groups; this confirms the findings of Kelson et al. (2017). B. Comparison of samples from Kelson et al. (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.**  $\delta^{47}$  and  $\Delta_{47}$  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  $\delta^{47}$  ( $-70\text{‰}$ – $15\text{‰}$ ) 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)	<b>0.01</b>	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	<b>0.002</b>	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