

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

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Introduction

This supplementary material contains text describing methods used in the associated study, additional supporting figures showing study data broken down in different ways, tables of statistics for regressions described in the text and shown in supplementary figures, and descriptions of large datasets included as separate files.

This study reprocessed data from 14 published studies. Raw, unprocessed data from these studies was gathered from original authors and reprocessed using the same R-code provided below and different values for the absolute abundances of heavy isotopes in the universal standards VPDB and VSMOW defined by four parameters: R^{13}_{VPDB} , R^{17}_{VSMOW} , R^{18}_{VSMOW} and λ . These datasets are also archived in EarthChem using a new template created for this purpose.

Text S1. Comparison of Δ_{47} values calculated from raw voltages or from sample mean δ^{45} - δ^{49} values using R and Easotope

We received published data from study authors in various forms, including 1) original raw voltages; 2) Easotope output sample mean δ^{45} - δ^{49} values and $\delta^{13}C$, $\delta^{18}O$, Δ_{47} to Δ_{49} values; and 3) Sample mean δ^{45} - δ^{49} values, calculated using a lab's code. Easotope calculations and workings are described in John and Bowen (2016) and R code can be found in **Text S4** this study. To test the comparability of these different formats, specifically the final sample mean $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} to Δ_{49} values calculated from these different sources, we took four gas standards two heated gases, two 25°C equilibrated gases and processed the code in five different ways and compared the outputs.

$\delta^{13}C$, $\delta^{18}O$, and Δ_{47} to Δ_{49} values were calculated using:

- 1) *R-raw*: Raw voltages and R code ****preferred method**, used to calculate mean values shown in **Table S1****
- 2) *Easotope-raw*: Raw voltages and Easotope
- 3) *R-shortcut*: Sample mean δ^{45} - δ^{49} values from #1 (R code), kept as long-form decimals, and R code shortcut
- 4) *Easotope-R-shortcut*: Sample mean δ^{45} - δ^{49} values from #3 (Easotope) and R code shortcut
- 5) *R-shortcut-cropped*: Sample mean δ^{45} - δ^{49} values from #1 (R code), rounded to three decimal places to mimic Easotope output and R code shortcut

Calculated using either R code or Easotope, δ^{45} - δ^{49} values were identical when rounded to the third decimal place. $\delta^{13}C$ and $\delta^{18}O$ values were rounded to the second decimal place and Δ_{47} to Δ_{49} values were rounded to the third decimal place.

Easotope-raw was identical to *R-raw* for all values (Easotope-raw minus R-raw = 0.00 or 0.000‰) with the exception of a single IUPAC Δ_{49} value Equilibrated Gas #2 which was 0.001‰ different. This demonstrates that Easotope and our R code produce identical isotope values when working from raw voltages.

R-shortcut was identical to *R-raw* for all values ($R\text{-shortcut} - R\text{-raw} = 0.00$ or 0.000‰), indicating that the shortcut code beginning with a single mean $\delta^{45}\text{-}\delta^{49}$ value for each sample produces the same final isotope values as calculating one $\delta^{45}\text{-}\delta^{49}$ value for each cycle 60 cycles and taking a mean at the end.

Easotope-R-shortcut and *R-shortcut-cropped* were identical for all values, but both had slight differences from *R-raw* and *R-shortcut*. *Easotope-R-shortcut* and *R-shortcut-cropped* had identical $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values to *R-raw* and *R-shortcut* (with the exception of Heated Gas #1, which was off by 0.01), Δ_{47} values within 0.001‰ , identical Δ_{48} values (with the exception of Equilibrated Gas #1, which was off by 0.001‰), and Δ_{49} values within 0.002‰ . These differences are the result of feeding rounded values into the shortcut code, and are smaller than the difference between isotope values calculated using IUPAC vs. Santrock/Gonfiantini parameters (Δ_{47} difference of $+0.009$ to -0.021‰ for these four example samples). This finding suggests Easotope users should change the default number of digits the database outputs if they are planning to do further isotopic calculations.

Text S2. Study-specific notes about reprocessing individual datasets

Table 1 summarizes the published studies compiled and reprocessed here, including information about sample type, sample preparation and measurement techniques. Below, we describe unique features and reprocessing details for each dataset.

S2.1 Synthetically precipitated carbonate studies

S2.1.1 Defliese et al., 2015 and Winkelstern et al., 2016

Synthetic calcite and aragonite precipitate data from Defliese et al. (2015) and synthetic and natural dolomite data from Winkelstern et al. (2016) were collected in the University of Michigan Stable Isotope Laboratory using an off-line manual sample preparation device described in Defliese et al. (2015). Samples were reacted at 75°C in a common acid bath and cleaned using a static PPQ trap with no carrier gas. A subset of acid digestion fractionation data (repeated analyses of four carbonates at different acid digestion temperatures, described below) from Defliese et al. (2015) was also reprocessed where it met our selection criteria regarding sufficient standards for conversion into the absolute reference frame, eliminating $\sim 15\%$ of replicates. Outside of a small number of early samples cleaned using a GC, the bulk of these samples were also cleaned using a static PPQ trap.

Data was reprocessed from raw voltages and ARF parameters were calculated following original publications by using a variable-size moving window (Defliese et al., 2015) or fixed window (Winkelstern et al., 2016) approach to select subsets of gas standard data. ARF parameters were calculated using heated gas (1000°C) and equilibrated gas (25°C , some 50°C standards), mostly made from a single tank with a $\delta^{13}\text{C}$ composition of around -41‰ VPDB, significantly different from the $\delta^{13}\text{C}$ composition of sample unknowns (-10‰ to $+10\text{‰}$) (**Figure S4**).

Since the publication of these two studies, it was discovered that low Porapak trap temperatures used at University of Michigan (-30°C and below) caused fractionations in

$\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and raw Δ_{47} values (Petersen et al., 2016). Therefore, the correction developed by Petersen et al. (2016) was applied to data collected between 2012 and 2014 (the interval in which low Porapak temperatures were used). Prior to 2012 and beginning again in 2015, the Porapak trap temperature was sufficiently warm so as to not require the correction. Although this correction changes raw Δ_{47} values, it has negligible effects on $\Delta_{47\text{-RFAC}}$ values (Petersen et al., 2016).

Where no error in formation temperature was given for synthetically precipitated carbonates (Defliese et al., 2015), an error of $\pm 1^\circ\text{C}$ was assumed. Only synthetic dolomite samples from Winkelstern et al. (2016) were used in the composite synthetic calibration, whereas natural dolomites were investigated separately along with other natural and biogenic data due to greater uncertainty in formation temperature. Acid fractionation factor data was not included in any calibration equations and is presented with no Δ^{*25-75} value applied.

S2.1.2 Kluge et al., 2015 and Garcia de Real., 2016

High-temperature synthetic precipitates (Kluge et al., 2015) and synthetic magnesite and hydromagnesite samples (Garcia de Real et al., 2016) were analyzed in the Qatar Stable Isotope Lab at Imperial College London. Samples were reacted in custom-built individual reaction vessels either at 70°C or at 90°C while continually removing evolved CO_2 , and were cleaned using a static PPQ trap (Kluge et al., 2015). Data was first reprocessed for this study using Easotope (John and Bowen, 2016), and was then reprocessed a second time using the same R script as other data sets using sample mean δ^{45} to δ^{49} values taken from the Easotope initial output. Differences between Easotope and R reprocessing are shown to be negligible (**Text S1**).

Since publication, a small subset ($<10\%$) of sample and standard replicates from the relevant measurement sessions were lost and unrecoverable, resulting in a different number of replicate analyses for some samples compared to the original publications and fewer standard replicates for certain correction intervals. Additionally, the methodology for selecting standards and correction intervals for the ARF conversion was updated from the original publication in line with more recent approaches within the clumped isotope community. This included eliminating the use of a moving-window approach for September 2013 – January 2014 data and reverting to fixed correction intervals, as well as including more carbonate standards in calculation of ARF parameters. The above described data loss resulted in insufficient standard coverage in August and September of 2013. As a result, all sample replicates measured over this interval (5 replicates measured on a single day) produced discordant results and were removed from the dataset in further analysis.

ARF parameters were calculated using a combination of gas and carbonate standards. As in the original works, the SlopeEGL parameter was calculated using only heated gas (1000°C) data, of which there were typically many more replicates than for any equilibrated gas or carbonate standard. In contrast, the two ETF parameters (SlopeETF and IntETF) were calculated using all heated and equilibrated gas (25°C , 50°C , 80°C) and carbonate standard (ETH-3 and an internal Carrara Marble standard) data for a given correction interval, corrected for SlopeEGL. Each correction interval had only a subset of these standard types. The assigned $\Delta_{47\text{-TE}}$ value used for ETH-3 was 0.703‰ for Santrock/Gonfiantini reprocessing (Müller et al., 2017) and 0.691‰ for

IUPAC reprocessing (Bernasconi et al., 2018). The assigned Δ_{47-TE} values used for the in-house Carrara Marble standard were 0.406‰ and 0.410‰ under Santrock/Gonfiantini and IUPAC parameters, respectively, as defined internally against gas standards over a long measurement interval. These assigned values for ETH-3 and Carrara Marble were different than in the original publication (Kluge et al., 2015) due to additional subsequent replicate analysis.

Due to the complexity of precipitating magnesite in the laboratory and the uncertainty in whether these samples represent equilibrium precipitation, synthetic magnesite and hydromagnesite samples from Garcia de Real et al. (2016) were not used in the composite synthetic carbonate calibration. Calcium carbonates precipitated in both high-salt and no-salt solutions were included (Kluge et al., 2015; Kluge and John, 2015), but carbonates precipitated with the addition of CaCl_2 were eliminated because they were shown to deviate from expected equilibrium clumped isotope behavior, possibly due to cation effects (Kluge and John, 2015).

S2.1.3 Kelson et al., 2017

Although synthetic precipitate data from Kelson et al. (2017) was originally published in two forms processed with both Santrock/Gonfiantini and IUPAC parameters, for consistency, we reprocessed all data from sample mean δ^{45} to δ^{49} values using the R code written for this study. Data from Kelson et al. (2017) were produced at the University of Washington IsoLab. Samples were prepared on an independent automated vacuum extraction line described in Burgener et al. (2016). Samples were reacted at either 90°C in a common acid bath (most replicates) or at 25°C in a McCreary-type reaction vessel (fewer replicates), and were cleaned via a packed PPQ trap with a helium carrier gas. Samples were analyzed on a MAT 253 with pressure baseline measurements made prior to each analysis.

ARF parameters were calculated for three correction intervals spanning many months each using heated gases (1000°C) and equilibrated gases (4°C, 60°C), with CO_2 $\delta^{13}\text{C}$ values ranging from -45‰ to 5‰. For samples that were reacted at both 25°C and 90°C, replicates were combined after applying corresponding Δ^{*25-90} values. Samples created using all precipitation methods investigated by Kelson et al. (2017) were included here.

S2.1.4 Tang et al., 2014 and Fernandez et al., 2014

All synthetic siderite samples from Fernandez et al. (2014) and the majority of analyses of synthetic calcites from Tang et al. (2014) were measured in the Stable Isotope Laboratory at Tulane University. Samples were reacted at 100°C in individual reaction vessels, with CO_2 being removed continuously, and were cleaned by passing through a static PPQ trap. Samples from Tulane were analyzed on an Elementar Isoprime 100 mass spectrometer outfitted with six additional Faraday cups. Unlike the Thermo MAT253, the Isoprime mass spectrometer is a small-radius 5kV ion source, which is similar in principle but has a completely different design and geometry.

Data from Tulane was reprocessed from raw voltages using either the Santrock/Gonfiantini or IUPAC parameters. The ARF was established using heated gases (1000°C) and equilibrated gases (4°C, 28°C, 51°C) for two fixed-window intervals constructed around a change in the ion source filament. Changes in the ARF over time

were tracked using heated gases, but a single ETF was calculated for each measurement session. A pressure baseline correction was applied to data collected after January 2013 (in the second correction interval), with the negative baseline being measured for one cycle prior to each acquisition (Rosenheim et al., 2013). Two replicates from early January 2013 could not be corrected because they fell in the transition period when new gas lines were being established. One replicate of sample C9 was also eliminated because reprocessed data was significantly offset from other samples (by $\sim 0.5\%$ in Δ_{47}) for an undetermined reason.

The remainder of the replicates of synthetic calcites from Tang et al. (2014) were measured at the University of California Los Angeles, in the Tripathi Lab on an automated sample preparation device similar to the one described by Passey et al. (2010). Samples were reacted at 90°C in a common acid bath and cleaned through a GC column with a helium carrier gas. The ARF was established using heated (1000°C) and equilibrated gases (25°C) for the single correction interval in which all samples were analyzed.

Although Tang et al. (2014) mentions a small number of replicates that were reacted at 25°C , those data were not included in this study. Additionally, samples C21 and C23 were excluded because they were reported to display deviations from equilibrium clumped isotope behavior due to being precipitated at significantly elevated pH levels ($\text{pH} \geq 10$) (Tang et al., 2014).

S2.1.5 Passey and Henkes, 2012

Passey and Henkes (2012) present data from calcite samples that were heated to sufficiently high temperatures for long enough to completely reset the clumped isotope signal (determined by having Δ_{47} values that ceased to change with additional heating). These samples were analyzed at Johns Hopkins University using an automated sample preparation device described by Passey et al. (2010), which reacted samples at 90°C in a common acid bath and cleaned CO_2 through a GC column with helium carrier gas.

Data from Johns Hopkins was reprocessed from raw voltages and the ARF was established using heated gases (1000°C) and equilibrated gases (27°C or 30°C) for eight correction intervals. ARF parameters were calculated using the moving heated gas line method described by Passey et al. (2010), which fits the gas line slopes and intercepts using a polynomial of either 1st linear or 2nd quadratic order. In this method, heated and equilibrated gas line slopes and intercepts are solved for separately unlike in the traditional method (Dennis et al., 2011), and the polynomial fit results in unique slope and intercept values corresponding to each sample analysis time point. Sample data is first corrected using only the slope of the heated gas line, then using unique ETF parameters calculated for that analysis time point from the corresponding unique heated and equilibrated gas line intercepts.

2nd order solutions were used for longer correction intervals (Series 1 and 2) and linear solutions were used for shorter intervals (Series 3-8). Selection of gas standards used, break points between Series, and choice of polynomial order was made following the detailed supplementary tables found in Henkes et al. (2013), which include the two measurement sessions in which the high temperature calcite samples of Passey and Henkes (2012) were analyzed. In one case (Series 6), a significant jump in gas values mid-Series led the authors to separate one sub-section of data and fit lines using a fixed window method (0th order), a procedure that was reproduced here.

S2.2 Biogenic carbonate studies

S2.2.1 Peral et al., 2018

Peral et al. (2018) analyzed Late Holocene foraminifera collected from 13 marine sediment core-tops, comprising 9 planktonic and 2 benthic species. Calcification temperatures were estimated based on a gridded model of seawater $\delta^{18}\text{O}$ (LeGrande & Schmidt, 2006), assuming the oxygen-18 fractionation law of Kim & O'Neil (1997). All samples were measured at the Laboratoire des Sciences de Climat et de l'Environnement (LSCE) on an Isoprime 100 dual-inlet mass spectrometer. Samples were reacted at 90°C in a common acid bath followed by purification through a Porapak column with helium carrier gas, before being measured on an Isoprime 100 dual-inlet mass spectrometer. Whereas this instrument has the same ion source design and geometry as the mass spectrometer used in Tang et al. (2014) and Fernandez et al. (2014), the instrument at LSCE uses fused silica capillaries delivering CO_2 to the ion source from a fixed volume that is identical between the sample and reference sides.

To compute the ARF parameters, Peral et al. (2018) measured carbonate standards (ETH-1, ETH-2, and ETH-3), with particular emphasis on ETH-3 (i.e. many replicates), whose isotopic composition is very similar to that of the foraminifera. ARF parameters were solved for in a single step, using heated and equilibrated gases and carbonate standards, as described in Daëron et al. (2016). This method ties final $\Delta_{47\text{-RFAC}}$ values to the nominal Δ_{47} values ETH standards assigned (i.e. $\Delta_{47\text{-TE}}$ values). As the $\Delta_{47\text{-TE}}$ values for gas standards are not used in this calculation except implicitly in the definitions of $\Delta_{47\text{-TE}}$ values for ETH standards, updating the $\Delta_{47\text{-TE}}$ values does not have any effect (**Figure 2**). Assigned $\Delta_{47\text{-TE}}$ values for ETH-1 through ETH-4 are taken from Müller et al. (2017) for Santrock/Gonfiantini reprocessing and from Bernasconi et al. (2018) for IUPAC reprocessing.

S2.2.2 Henkes et al., 2013

As with Passey and Henkes (2012) described above, these samples were measured at Johns Hopkins University. All other sample preparation and reprocessing details are the same as above. Henkes et al. (2013) present a biogenic carbonate dataset including mainly bivalve mollusks of both calcite and aragonite mineralogy. Three samples were reacted offline at 25°C in addition to being analyzed using their standard method (90°C automated preparation device). These replicates were combined with the 90°C replicates after applying the acid digestion fractionation correction of either Defliese et al. (2015) or the new values calculated in this study.

S3.2.3 Petrizzo et al., 2014

Bivalve shells live-collected from various locations were analyzed for their clumped isotopic composition in the Young Lab at University of California Los Angeles (Petrizzo et al., 2014). Samples were reacted at 25°C in individual McCrea-style reaction vessels and were cleaned through a GC column with helium carrier gas. The absolute reference frame was established using heated (1000°C) and equilibrated gases (25°C and a few 2°C) and ARF parameters were calculated for a single correction interval combining the “P2” and “P3” intervals from Petrizzo and Young (2014).

Due to erratic behavior of the Faraday cup intended to measure mass-47 CO₂, the Young Lab used only the first three cups (intended to measure masses 44 to 46) and a peak-hopping approach with their Thermo MAT253 mass spectrometer to determine the clumped isotopic composition of the carbonates (Petrizzo and Young, 2014; Petrizzo et al., 2014). This approach first determines $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (via δ^{45} and δ^{46}) with beams in the typical alignment, then adjusts the magnet settings to place the mass-46 and mass-47 beams in the center of the cups usually used to measure masses 45 and 46 in order to accurately determine the 46/47 ratio, correcting for negative background values. Using the 46/47 ratio combined with the 46/44 ratio from the first step, the 47/44 ratio can be determined (Petrizzo and Young, 2014). The authors then use a Monte-Carlo sampling approach to calculate Δ_{47} in order to take errors in the first step measurement ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) into account.

In reprocessing the data using Santrock/Gonfiantini and IUPAC parameters, we recreated as closely as possible the data processing steps described in the supplement of Petrizzo and Young (2014) that are needed for this unique measurement technique, while also trying to conform to the standardized processing steps used for other datasets in this study. For example, we include the Monte-Carlo approach to calculating Δ_{47} and associated errors, but use the same R *solver* function to calculate $\delta^{18}\text{O}$ as was used in all other reprocessing efforts here. Data from Petrizzo et al. (2014) was reprocessed from raw voltage measurements.

S2.2.4 Wacker et al., 2014

Wacker et al. (2014) presents another calibration dataset of mainly biogenic carbonates including foraminifera, one bivalve, one brachiopod, an ostrich egg, and a cold-seep carbonate, analyzed at Goethe University. Samples were reacted at 90°C in a common acid bath, cleaned through a GC column and multiple water traps, and finally measured on a Thermo MAT253 with no baseline correction. Data was originally processed in Excel following Huntington et al. (2009) using a Δ^{*}_{25-90} value of +0.069‰, but was provided as Easotope output after data was uploaded to that database software. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Δ_{47} values were reprocessed for this study using sample mean δ^{45} to δ^{49} values from Easotope for consistency.

ARF parameters are calculated using a combined long-window and moving-window approach (Wacker et al., 2013; Wacker et al. 2014). We followed the window selections defined in the supplementary material of Wacker et al. (2014) as closely as possible. The SlopeEGL parameter was calculated using a moving window of nine heated gases bracketing the sample measurement, with the exception of two longer windows at the beginning and end of the study interval that used a larger number of gases. To calculate the ETF parameters, heated gases were broken into four two-month-long windows. Two groups of equilibrated gases (25°C) measured at the beginning and end of the full study interval were used with the heated gases to calculate the ETF parameters for each of the four ETF windows. Unlike in the original publication, we did not round heated and equilibrated gas line intercepts to two decimal places when calculating the ETF, or round SlopeEGL to four decimal places, instead using the full long-form decimal versions computed by R.

S2.2.5 Katz et al., 2017

Katz et al. (2017) analyzed cultured coccolithophorids grown at various temperatures at the Institut de Physique du Globe de Paris (IPGP) using an off-line manual preparation device described in Bonifacie et al. (2017). Samples were reacted at 90°C in a common acid bath and cleaned through a static PPQ trap. Data was reprocessed from sample mean δ^{45} to δ^{49} values. ARF parameters were calculated using heated (1000°C) and equilibrated gases (25°C) for seven separate correction intervals, all detailed in the original publication.

S2.2.6 Breitenbach et al., 2018

Breitenbach et al. (2018) present analyses of natural cave carbonates that precipitated subaqueously at known temperatures between 3°C and 47°C and of planktonic foraminifera from modern core-top sediments. This data was collected using a micro-sampling measurement scheme and customized Kiel device preparation method similar to that pioneered at ETH-Zurich (Schmid and Bernasconi, 2010). In this scheme, many ($n=6-15$ replicates each) small ($\sim 140-200\mu\text{g}$) replicates are analyzed instead of a few (~ 3) larger (3-8 mg) replicates as is typical in most other studies presented here. Micro-samples were reacted at 70°C in individual Kiel sample vessels and were cleaned through a static PPQ trap before being analyzed on a MAT253.

Data transfer into the absolute reference frame was achieved using exclusively the ETH carbonate standards (Meckler et al., 2014; Breitenbach et al., 2018) over two long correction intervals. This leads to no difference between $\Delta_{47\text{-RFAC}}$ values calculated using Wang/Dennis vs. Petersen $\Delta_{47\text{-TE}}$ values, because this update in $\Delta_{47\text{-TE}}$ values is restricted to gas standards. Although the established ETH standard values are inherently based on the heated/equilibrated gas reference frame, and changing to Petersen $\Delta_{47\text{-TE}}$ values would likely impact established ETH carbonate values slightly, this level of deep reprocessing is beyond the scope of this study.

Data in Breitenbach et al. (2018) was initially processed and published using the new IUPAC parameters. For consistency, it was reprocessed as part of this study from sample mean δ^{45} to δ^{49} values using the same R code as all other datasets. In reprocessing this dataset, a 2‰ error was found in the original Excel template in the cell converting the working gas composition between PDB and SMOW scales. This error affected roughly half the published cave pearl and foraminifera data, causing changes in $\Delta_{47\text{-RFAC}}$ of $\pm 0.016\%$ and changing the cave carbonate calibration slope from ~ 0.045 to 0.041.

S2.3 Additional studies

We compare data from two additional studies to our reprocessed data. Data from these studies was not reprocessed in the same manner as the rest of the datasets using the methods described here. As a result, these studies are exclusively plotted for comparison, and are not included in any of the composite calibration regressions or investigations of the effects of switching from S/G to IUPAC parameters and from Wang/Dennis to Petersen $\Delta_{47\text{-TE}}$ values.

S2.3.1 Kele et al. 2015

Kele et al. (2015) published a calibration of natural travertine carbonates. This is another study in which samples were prepared on a customized Kiel IV device, measuring many micro-replicates instead of a few larger replicates (Schmid and

Bernasconi, 2010). Samples were reacted at 70°C in individual Kiel-device sample vessels and were cleaned through a static PPQ trap, before being measured on a MAT253. Conversion to the absolute reference frame was achieved using exclusively carbonate standards, as in Breitenbach et al. (2018).

Data from Kele et al. (2015) was not provided in sufficiently raw format with enough supporting information (voltages/currents or sample mean δ^{45} to δ^{49} values with details of ARF window selection and filtering of outliers) to be reprocessed using the methods described here. However, this dataset was reprocessed using IUPAC parameters as part of another study (Bernasconi et al., 2018), and replicate-level $\Delta_{47\text{-RFAC}}$ values can be found in the supplementary material for that paper. Additionally, this dataset, termed "Kele+" includes three newly added biogenic samples an ostrich egg, a bivalve and brachiopod (Bernasconi et al., 2018).

There may be small differences between their calculated $\Delta_{47\text{-RFAC}}$ values and what would have been calculated using our methodology, such as those introduced by programming language used, rounding, method of calculating isotopic values, etc. that we cannot control for. Nevertheless, we can compare the final values with our reprocessed IUPAC calibration, while not including these points in our composite fit. We do not expect choice of $\Delta_{47\text{-TE}}$ values to make a difference because the Kele dataset was converted into the absolute reference frame using ETH standards and another in-house carbonate, the $\Delta_{47\text{-TE}}$ values of which would not change with recalculation of WD values. In order to achieve the best comparison, we update this published data to use the Δ^{*25-70} value derived in this study.

S2.3.2 Bonifacie et al., 2017

The synthetic dolomite data from Bonifacie et al. (2017) was collected partially at Caltech and partially at IPGP, using similar techniques and measurement intervals to the biogenic coccolith study described above (Katz et al., 2017). The raw data from this study was not available to reprocess, and the portion of data measured at Caltech was collected prior to the establishment of the absolute reference frame and therefore also does not meet our data selection criteria. However, based on the fact that other data measured at IPGP (Katz et al., 2017) seems to show very little change as a result of updating to the IUPAC parameters, we can reasonably compare the published dolomite data of Bonifacie et al. (2017) to our updated data compilation, while not including it in the compilation itself. In order to achieve the best comparison, we add our updated value of Δ^{*25-90} to published CDES90 values (i.e. +0.088‰).

Text S3. Recalculating “true” $\Delta_{47\text{-TE}}$ values used to calculate the empirical transfer function

One integral part of transferring data into the absolute reference frame is calculating the empirical transfer function (ETF), which requires knowledge (or assignment) of the “true value” of Δ_{47} at a given temperature, defined as the theoretical equilibrium value or $\Delta_{47\text{-TE}}$. In the original paper defining the procedure for calculating the ETF (Dennis et al., 2011), this was done using equation A2 (below), which is a 4th order polynomial fit through data from Wang et al. (2004), where T_K is the temperature in Kelvin.

$$\Delta_{47-RF} = 0.003 \left(\frac{1000}{T_K} \right)^4 - 0.0438 \left(\frac{1000}{T_K} \right)^3 + 0.02553 \left(\frac{1000}{T_K} \right)^2 - 0.2195 \left(\frac{1000}{T_K} \right) + 0.0616$$

Equation A2 from Dennis et al., 2011

The Δ_{47-TE} values calculated by Wang et al. (2004) represent the expected abundances of isotopologues in thermodynamic equilibrium at a given temperature for a gas with an R^{13} value equivalent to the VPDB standard and R^{17} and R^{18} values equivalent to VSMOW. At the time that Wang and coauthors made these calculations, these R values were defined by the Santrock/Gonfiantini parameters (Huntington et al., 2009). As part of this study to update published calibrations to use the new and improved IUPAC parameters (Brand et al., 2010), we went back to recalculate the thermodynamic equilibrium predictions using the new parameters.

S3.1 Original Wang et al. 2004/Dennis et al. 2011 calculation of Δ_{47-TE} values

When attempting to reconstruct the published values given in the appendix of Dennis et al. (2011) using the equations defined by Wang et al. (2004), it was not possible to exactly match the published values. This may be due to limitations to the input data we have access to. For example, we are using zero point energies and normal mode wave numbers from Table 3 of Wang et al. (2004), which are rounded to the third decimal place, but Wang et al. may have been working from longer decimals originally. Additionally, we don't know the exact values used by Wang et al. (2004) for the universal constants that are required by the calculation (Planck's constant, speed of light, Boltzmann's constant). We achieved the closest match to their published values when using values for the universal constants that were rounded to two significant digits listed below.

$h = 6.63 \times 10^{-34}$	<i>Planck's constant</i>
$c = 3 \times 10^8$	<i>Speed of light</i>
$b = 1.38 \times 10^{-23}$	<i>Boltzmann's constant, listed as b instead of traditional k to avoid confusion with other equilibrium constants K_{eq} in code</i>

It was also discovered that Wang/Dennis used a conversion from Celsius to Kelvin that involved adding 273 instead of 273.15 degrees, which also causes a small difference. This rounding in conversion between temperatures also causes problems for users of equation A2. If a user attempts to calculate a Δ_{47-TE} value for a given temperature in Celsius using equation A2 and uses the correct conversion +273.15, they will end up with a value that is both incorrect, and slightly different from published in Table 1 by Dennis et al. (2011). For example, for an equilibrium temperature of 25°C, Dennis et al. (2011) report a Δ_{47-TE} value of 0.9252‰ in their Table 1, which is what you calculate if you plug in 25+273=298 into their equation A2. If you plug in 25+273.15=298.15, you instead get 0.9244‰. The difference caused by the extra 0.15 degrees is zero at 1000°C to the 4th decimal place, with both methods of calculation giving 0.0266‰, and is greatest at 0°C, where the difference is 0.0009‰.

Wang et al. (2004) describe how to calculate the abundances of all possible isotopologue at thermodynamic equilibrium. To calculate the Δ_{47-TE} value as measurable, all three isotopologues of mass 47 ($^{16}\text{O}^{13}\text{C}^{18}\text{O}$, $^{17}\text{O}^{12}\text{C}^{18}\text{O}$, and $^{17}\text{O}^{13}\text{C}^{17}\text{O}$) must be combined. This is defined by Equation 28 in Wang et al. (2004), which relates the calculated abundance of three relevant isotopologues [X] to their stochastic abundances $[\text{X}]_r$.

$$\Delta_{47} = \left(\frac{\frac{[^{16}\text{O}^{13}\text{C}^{18}\text{O}] + [^{17}\text{O}^{12}\text{C}^{18}\text{O}] + [^{17}\text{O}^{13}\text{C}^{17}\text{O}]}{[^{16}\text{O}^{12}\text{C}^{16}\text{O}]}}{\frac{[^{16}\text{O}^{13}\text{C}^{18}\text{O}]_r + [^{17}\text{O}^{12}\text{C}^{18}\text{O}]_r + [^{17}\text{O}^{13}\text{C}^{17}\text{O}]_r}{[^{16}\text{O}^{12}\text{C}^{16}\text{O}]_r}} - 1 \right) * 1000$$

Equation 28 from Wang et al., 2004

However, at another point, Wang et al. (2004) state that Δ_{47} is “equal to the weighted sum of $\Delta_{16\text{O}13\text{C}18\text{O}}$, $\Delta_{17\text{O}12\text{C}18\text{O}}$, and $\Delta_{17\text{O}13\text{C}17\text{O}}...$ ”. Dennis et al. (2011) used the later definition, weighting the three isotopologues based on their natural abundances (46 ppm, 1.6 ppm, 1.6 ppb), as given by Table 1 of Eiler and Schauble (2004).

$$\Delta_{47} = \frac{46 * (\Delta_{16\text{O}13\text{C}18\text{O}}) + 1.6 * (\Delta_{17\text{O}12\text{C}18\text{O}}) + 0.0016 * (\Delta_{17\text{O}13\text{C}17\text{O}})}{46 + 1.6 + 0.0016}$$

Weighted Average equation used by Dennis et al., (2011) (personal communication)

The weighted average does not give the same value as Equation 28 of Wang et al. (2004), and differs by 0.0002-0.0008‰ in the range of 0-1000°C. Dennis et al. (2011) may have used the weighted average method because they were only provided with the final abundances of the three isotopologues of mass 47 and not the corresponding stochastic distributions, so were unable to use Equation 28.

Another source of uncertainty is the 4th order polynomial fit to the Wang data carried out by Dennis et al. (2011). Comparing the raw Δ_{47} data in the supplementary table (Wang et al. (2004) Δ_{47-TE} value calculated as weighted average of three isotopologues of mass 47) to values calculated by the polynomial fit plugging in a given temperature to Equation A2, the calculated Δ_{47} value can be off from the thermodynamic prediction by -0.0018‰ to +0.0022‰ in the range of 0-1000°C. A higher order polynomial fit, with coefficients carried out to more than 4 decimal places would allow a user to reliably calculate the thermodynamic equilibrium values to the 4th decimal place without introducing additional error.

S3.2 Recalculation of Δ_{47-TE} values in this study

Our new calculation of theoretical equilibrium Δ_{47} values uses the correct conversion between Celcius and Kelvin (+273.15) and the following, long-form versions of universal constants:

$$h = 6.626070040 \times 10^{-34} \quad \text{Planck's constant}$$

$$c = 299792458 \quad \text{Speed of light}$$

$$b = 1.38064852 \times 10^{-23}$$

Boltzmann's constant, listed as b instead of traditional k to avoid confusion with other equilibrium constants Keq in code

These new values are taken from Fisher and Ullrich (2016), which are both the most up-to-date standard international unit values, and are presented to many additional decimal places compared to the values that appear to have been used in the original Wang/Dennis calculations, improving the overall accuracy of the calculations.

To calculate Δ_{47-TE} values, we choose to use Equation 28 (Wang et al., 2004) because it is the explicit definition of Δ_{47} and, since we are calculating isotopologue abundances from scratch, we can easily calculate the corresponding stochastic distribution at the same time. We calculate the Δ_{47-TE} value using both methods and provide them in the supplementary table. We also calculate Δ_{47-TE} values using both Santrock/Gonfiantini and IUPAC parameters.

Ideally, users would calculate the thermodynamic equilibrium value from scratch for the exact temperature of interest instead of using a polynomial fit. As this is not feasible, we present a read-off table (**Table S2**) of Δ_{47-TE} values for many temperatures between -12°C and 1100°C (each degree between -12°C and 100°C, every 2 degrees between 102°C and 350°C, every 5 degrees between 355°C and 1100°C). We recommend that users employ the provided 4-digit Δ_{47-TE} value that corresponds to their equilibrated gas equilibration temperature. The attached supplementary table also includes full long-form decimal values for $\Delta_{16O13C18O}$, $\Delta_{17O12C18O}$, and $\Delta_{17O13C17O}$, and long-form versions of the Δ_{47-TE} value calculated two ways (Eq. 28 and weighted average method) using both Santrock/Gonfiantini and IUPAC parameters.

In addition, we provide a 7th order polynomial fit, with coefficients rounded to eight decimal places, where T_K is the temperature in Kelvin, calculated correctly as $T_C + 273.15$. This polynomial fit equation can be used to calculate the thermodynamic equilibrium values for any temperature between 0 and 1000°C with to within 0.0001%. We recommend only using this polynomial fit if a Δ_{47-TE} value is needed for a temperature that is not included in the read-off table (eg. a non-cardinal temperature such as 4.5°C). In this case, calculate Δ_{47-RF} using all long-form coefficients and rounding the final value to 4 digits as the final step.

$$\begin{aligned} \Delta_{47-RF} = & 0.00050479 \left(\frac{1000}{T_K}\right)^7 - 0.00885734 \left(\frac{1000}{T_K}\right)^6 + 0.06385048 \left(\frac{1000}{T_K}\right)^5 \\ & - 0.23891768 \left(\frac{1000}{T_K}\right)^4 + 0.46854990 \left(\frac{1000}{T_K}\right)^3 - 0.34158204 \left(\frac{1000}{T_K}\right)^2 \\ & + 0.12940422 \left(\frac{1000}{T_K}\right) - 0.01752753 \end{aligned}$$

“True Δ_{47} ” calculated using Eq. 28 from Wang et al. (2004) and IUPAC parameters
*****Preferred equation to replace Dennis et al. (2011) Eq. A2*****

$$\begin{aligned} \Delta_{47-RF} = & 0.00050456 \left(\frac{1000}{T_K}\right)^7 - 0.00885331 \left(\frac{1000}{T_K}\right)^6 + 0.06382147 \left(\frac{1000}{T_K}\right)^5 \\ & - 0.23881029 \left(\frac{1000}{T_K}\right)^4 + 0.46834474 \left(\frac{1000}{T_K}\right)^3 - 0.34142554 \left(\frac{1000}{T_K}\right)^2 \\ & + 0.12934099 \left(\frac{1000}{T_K}\right) - 0.01751806 \end{aligned}$$

“True Δ_{47} ” calculated using weighted average method used by Dennis et al. (2011) and IUPAC parameters

S3.3 Effects of Santrock vs. IUPAC parameters on Δ_{47-TE} values

The use of Santrock/Gonfiantini vs. IUPAC parameters has very minimal effect on the calculated Δ_{47-TE} values, with differences of 0-0.0001‰ for the weighted average method and 0-0.0005‰ for the Equation 28 method of calculating Δ_{47-TE} in the temperature range of 0-1000°C. These differences are smaller than changes due to using full, unrounded values of universal constants h , c , and b and the +273.15 Celsius-to-Kelvin conversion. Overall, the final new true Δ_{47-TE} values this study differ from the Wang/Dennis values by 0.0006-0.0037‰ over the temperature range 0-1000°C, with the largest discrepancies occurring at the coldest temperatures. The final preferred Δ_{47-TE} differ from values calculated using the Dennis et al. (2011) polynomial fit equation A2 by even more (0-0.0056‰). In fact, the largest discrepancies occur in the 0-50°C range, with the largest discrepancy (0.0056‰) occurring at 25°C, a near-room-temperature value at which many labs produce equilibrated gases (**Figure S1**).

Text S4. R-code of main functions used in reprocessing.

** Found in a separate R file named “SupplementaryTextS4_Rcode_FUNCTIONS.R” **

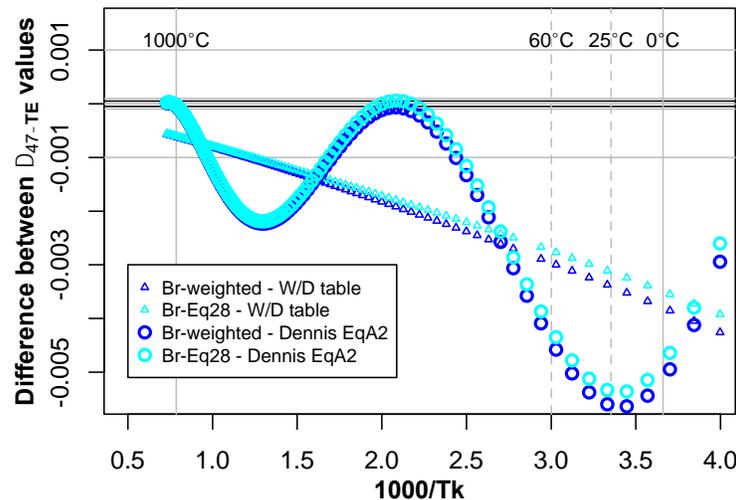


Figure S1. Differences between Δ_{47-TE} values calculated with various methods, plotted vs. equilibration temperature. “Br-weighted” and “Br-Eq28” are newly calculated Δ_{47-TE} values from this study using either the weighted average approach or Equation 28 of Wang et al. (2004). “W/D table” and “Dennis EqA2” are values from Dennis et al. (2011), taken from either their Table S1 or calculated using their polynomial fit through

said data given by their equation A2. The largest differences from our preferred recalculated Δ_{47-TE} values (Br-Eq28) occurs with the polynomial fit of Dennis et al. (2011) around 25°C.

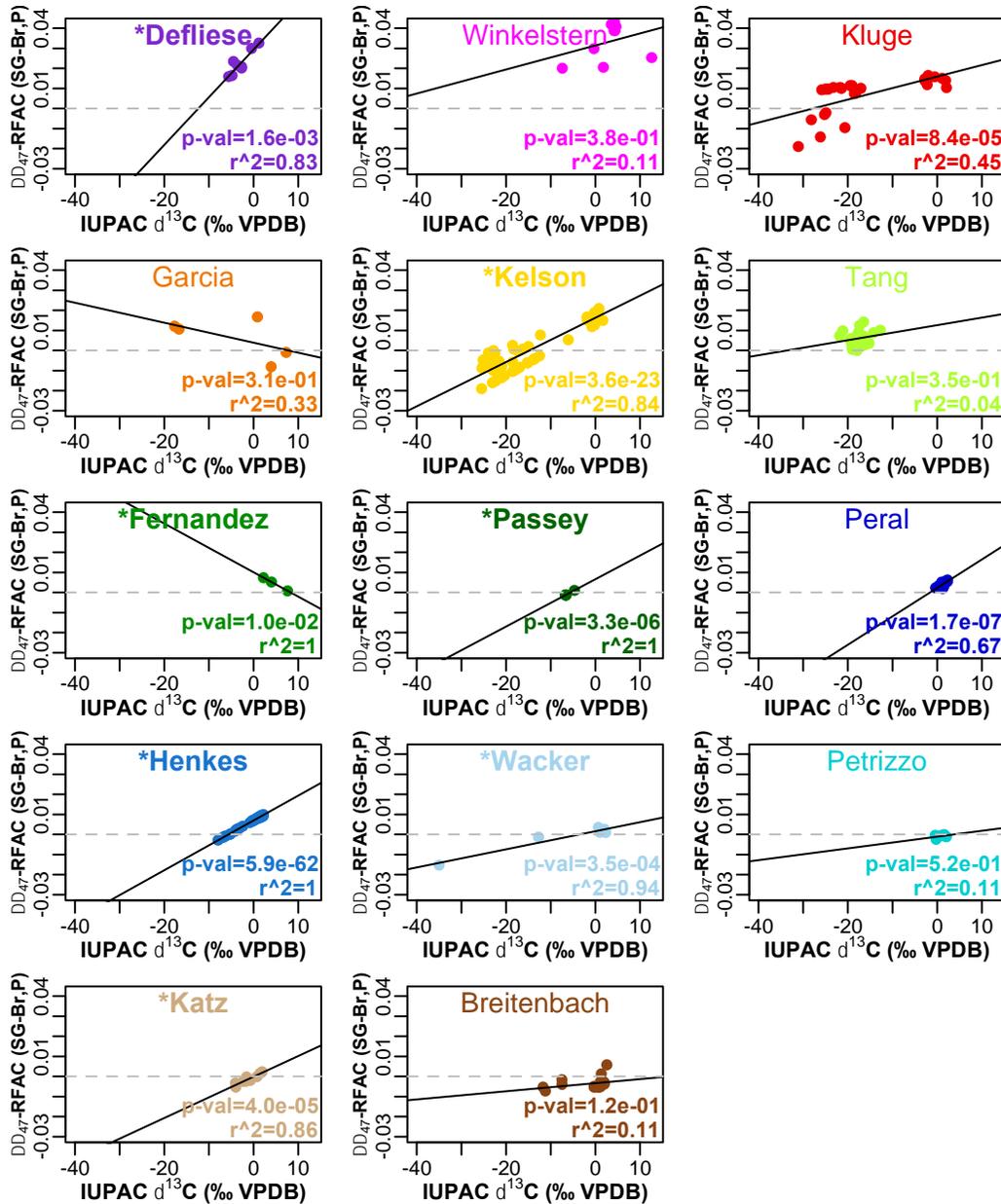


Figure S2. The offset between $\Delta_{47-RFAC}$ values calculated using SG vs. IUPAC parameters ($\Delta\Delta_{47-RFAC}$ SG-Br, P) vs. IUPAC $\delta^{13}C$ for each study individually showing the correlation strength p -value and r^2 value. If the study name is preceded by an asterisk *, this means that study has a strong correlation as defined by an $r^2 > 0.75$, and a p -value < 0.05 . 7 out of 14 studies show a strong correlation between $\Delta\Delta_{47-RFAC}$ values (SG-Br, P) and $\delta^{13}C$. In 6 of 8 of these, the correlation is positive, excluding Fernandez.

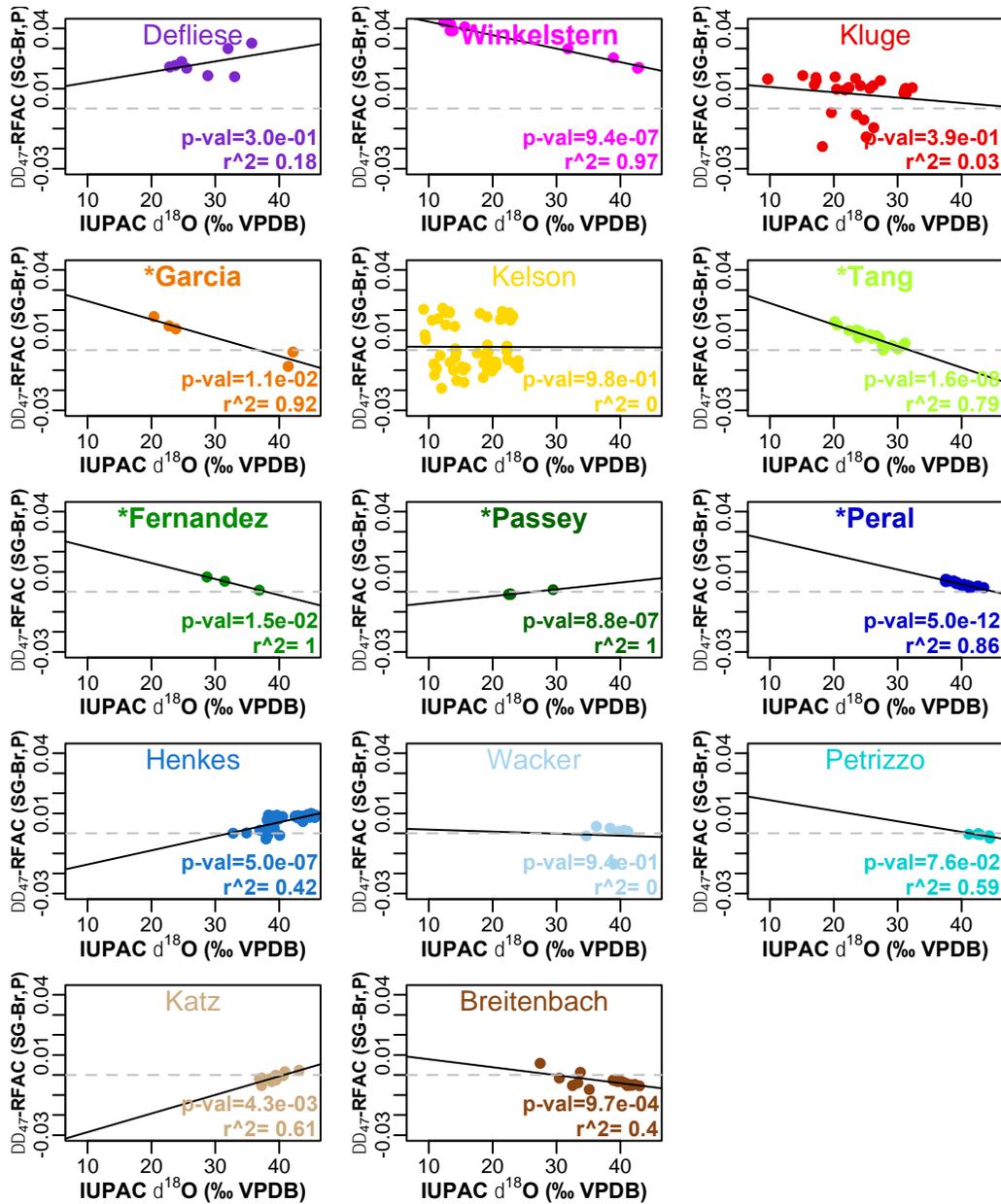


Figure S3. The offset between $\Delta_{47}\text{-RFAC}$ values calculated using SG vs. IUPAC parameters ($\Delta\Delta_{47}\text{-RFAC SG-Br, P}$) vs. IUPAC $\delta^{18}\text{O}$ for each study individually showing the correlation strength p -value and r^2 . If the study name is preceded by an asterisk*, this means that study has a strong correlation, as defined by an $r^2 > 0.8$ and a p -value < 0.05 . 6 out of 14 studies show a strong correlation between $\Delta\Delta_{47}\text{-RFAC}$ values SG-Br, P and $\delta^{18}\text{O}$, 5 of which are negative (excluding Passey).

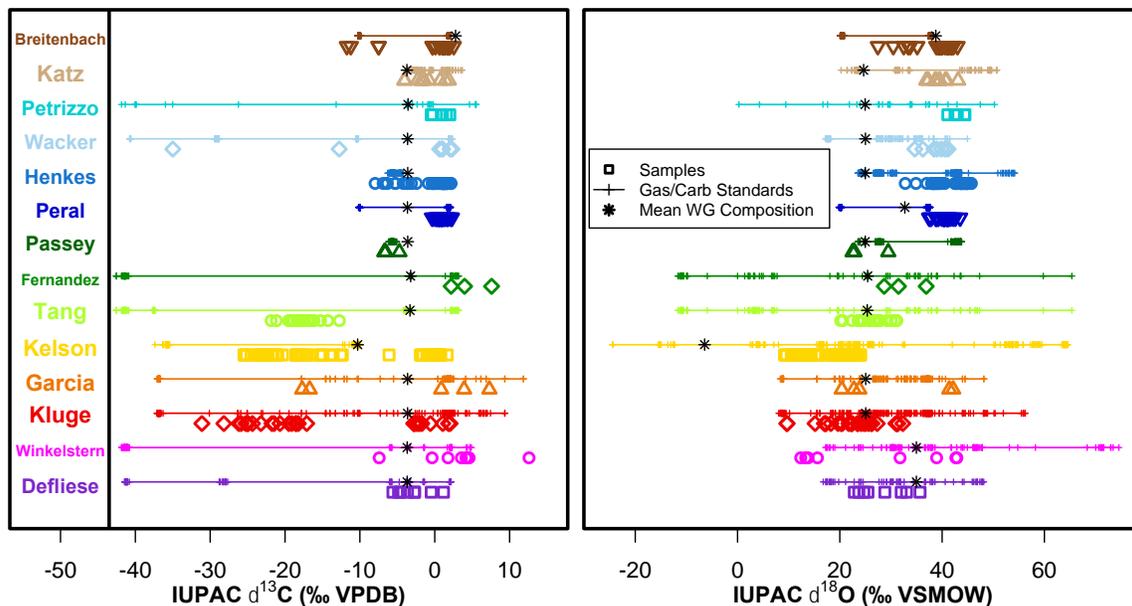


Figure S4. $\delta^{13}\text{C}$ (left) and $\delta^{18}\text{O}$ (right) values of gas and carbonate standards used to convert calibration samples to the absolute reference frame. Horizontal lines show full range of compositions and individual standard measurements (tick marks) compared to samples compositions (symbols). Black * denotes mean working gas composition for each study. Coincidentally, biogenic/natural inorganic studies (top 6, Peral to Breitenbach) tend to have smaller ranges in standard compositions than the synthetic studies (bottom 8, Defliese to Passey), resulting in a smaller effect when updating from SG to IUPAC parameters.

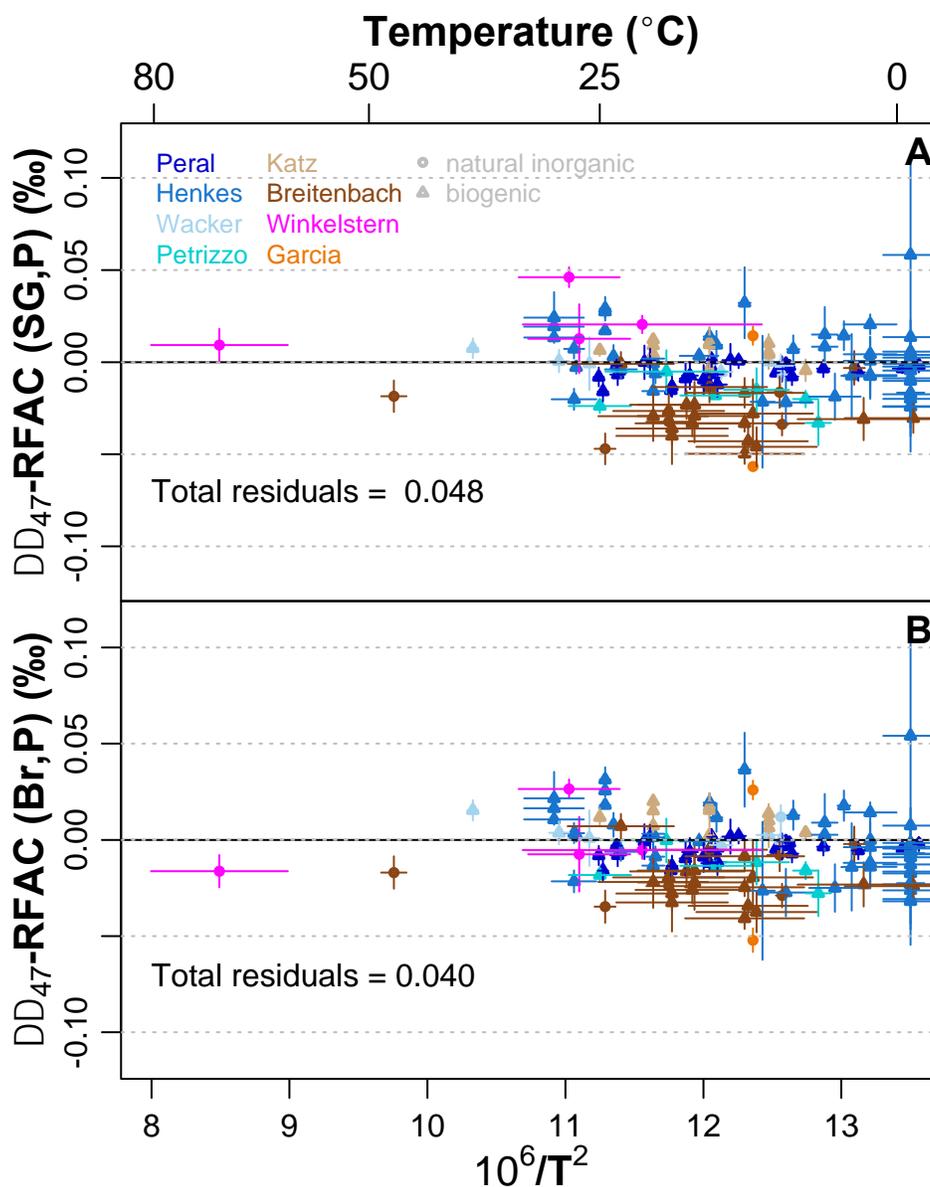


Figure S5. Offset between biogenic and natural inorganic sample mean $\Delta_{47}\text{-RFAC}$ values and the synthetic composite calibrations shown in **Figure 4** and defined in **Equation 1**, processed using either Santrock/Gonfiantini (**A**) or IUPAC (**B**) parameters and new $\Delta_{47}\text{-TE}$ values (Petersen) and Δ^{*25-X} values (this study). Error bars represent 1SE external error on sample mean $\Delta_{47}\text{-RFAC}$ (vertical) or reported uncertainty in formation temperature (horizontal). Colors correspond to study, with first author name listed in corresponding color more details given in **Table 1**. Total residuals are calculated as the sum of the square of the absolute value of the offset between observed and predicted from the synthetic composite calibration.

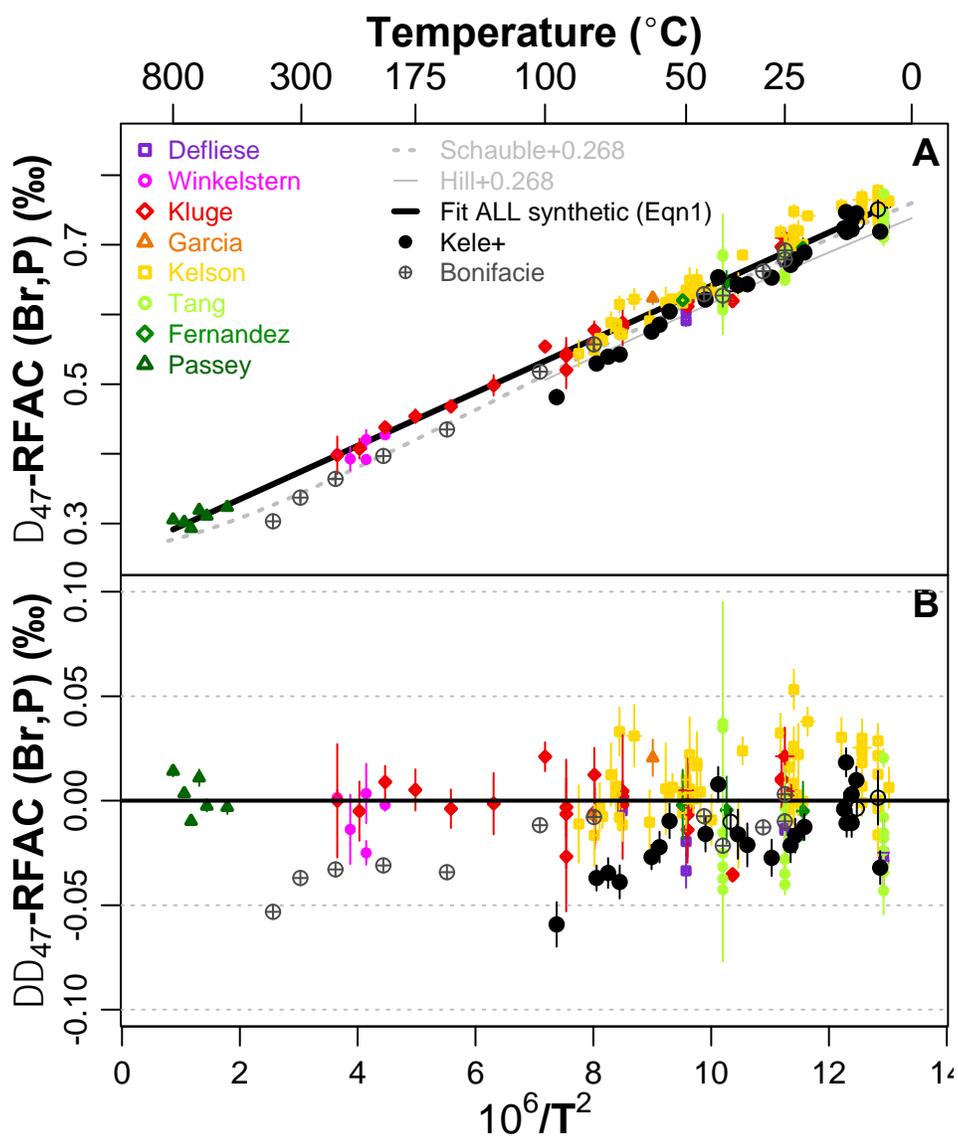


Figure S6. Same as **Figure 4cd**, but including data from Bonifacie et al. (2017) and Kele et al. (2015) for comparison. Data from Kele et al. (2015) was updated using IUPAC parameters by Bernasconi et al. (2018) and three additional samples were included ("Kele+"). Bonifacie et al. (2017) data uses older SG parameters, but is not expected to change much based on the limited change in data from Katz et al. (2017) and the composition of standards used at IPGP. Both Kele+ and Bonifacie data have been updated to use new Δ^{*25-X} values.

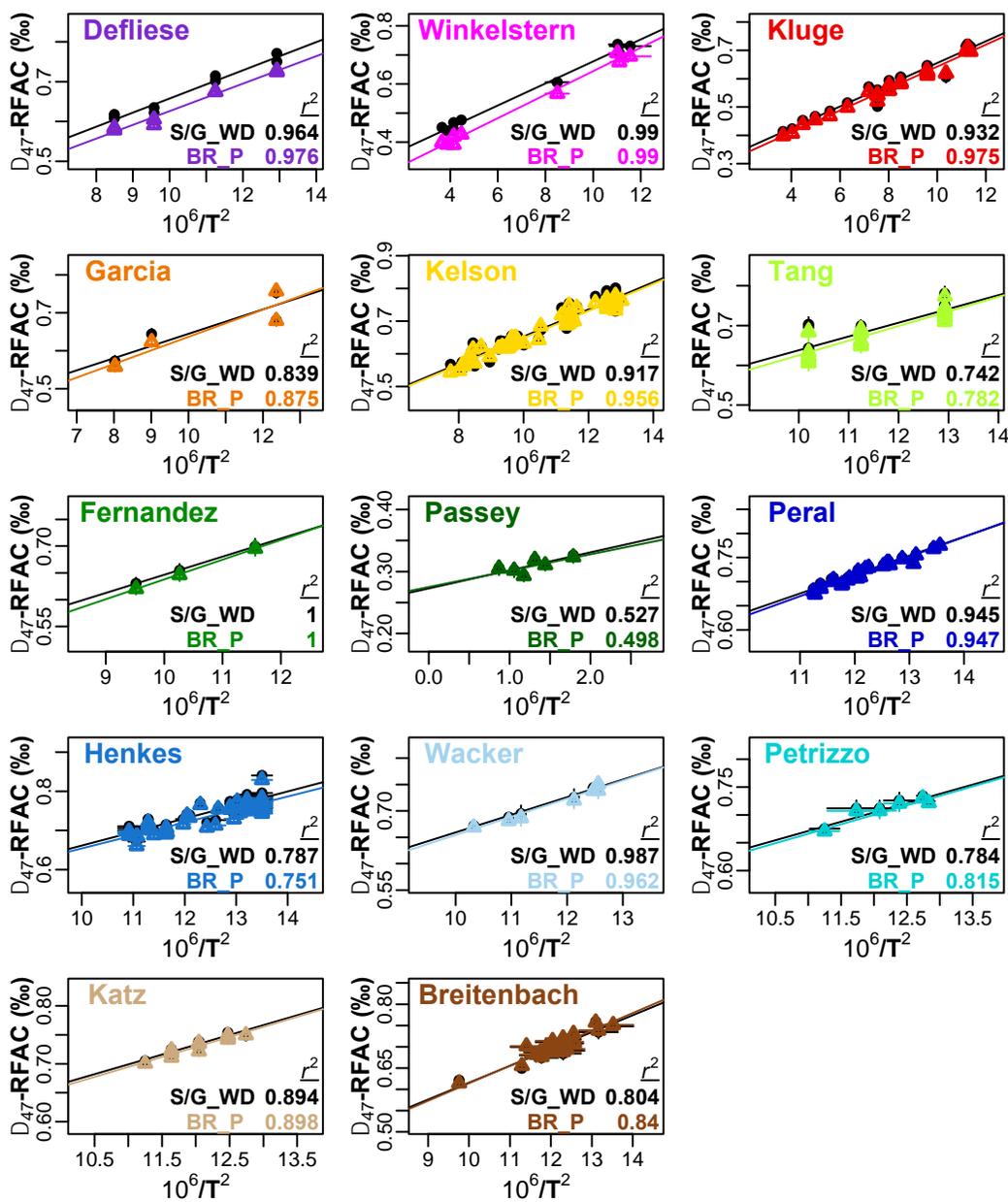


Figure S7. Comparison of $\Delta_{47}\text{-RFAC}$ values calculated two ways ($\Delta_{47}\text{-RFAC}(\text{S/G,WD,newAFF})$ and $\Delta_{47}\text{-RFAC}(\text{Br,P,newAFF})$) vs. formation temperature for each study taken individually. r^2 values for the Deming regressions take into account error in x and y plotted through each dataset are shown in the bottom corner. In 11 out of 14 studies reprocessed here, r^2 values improved or were unchanged (i.e. including Winkelstern and Fernandez) with the use of IUPAC parameters. Note that axes differ for each plot according to the range of data. Deming regression computed with the ‘Deming’ package in R.

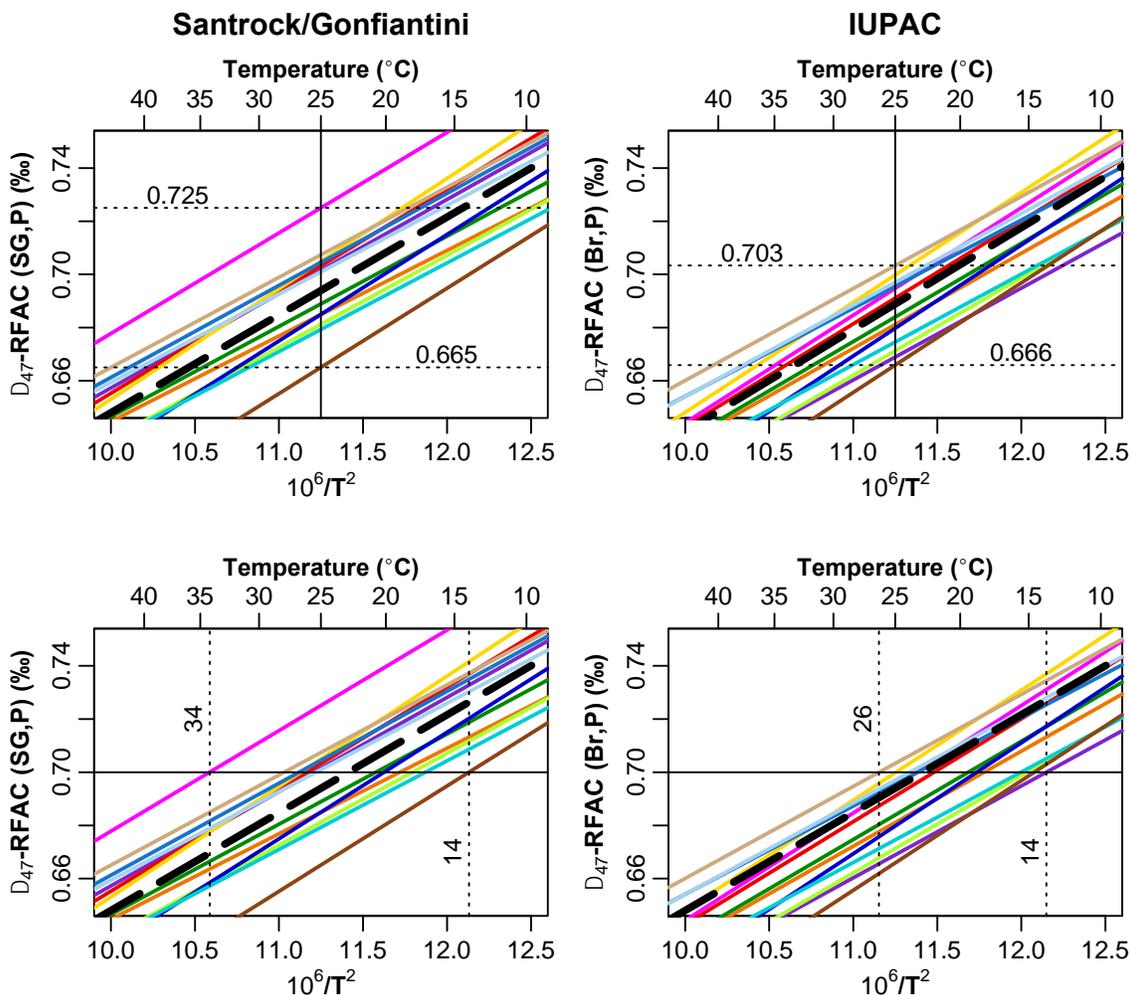


Figure S8. Comparison of individual laboratory fits (as listed in **Table S5**) around a formation temperature of 25°C showing improved agreement between calibrations with the use of IUPAC parameters. The range in Δ_{47} values predicted for a temperature of 25°C decreases from 0.060‰ to 0.037‰ (top left vs. top right) and the range in temperature predicted for a Δ_{47} value of 0.700‰ decreases from 20°C to 12°C (bottom left vs. bottom right) with the adoption of IUPAC parameters. Colored lines correspond to study colors following **Table S5** and many other figures. **Equation 1** or **Equation 2** composite synthetic calibration shown in thick black dashed line for comparison.

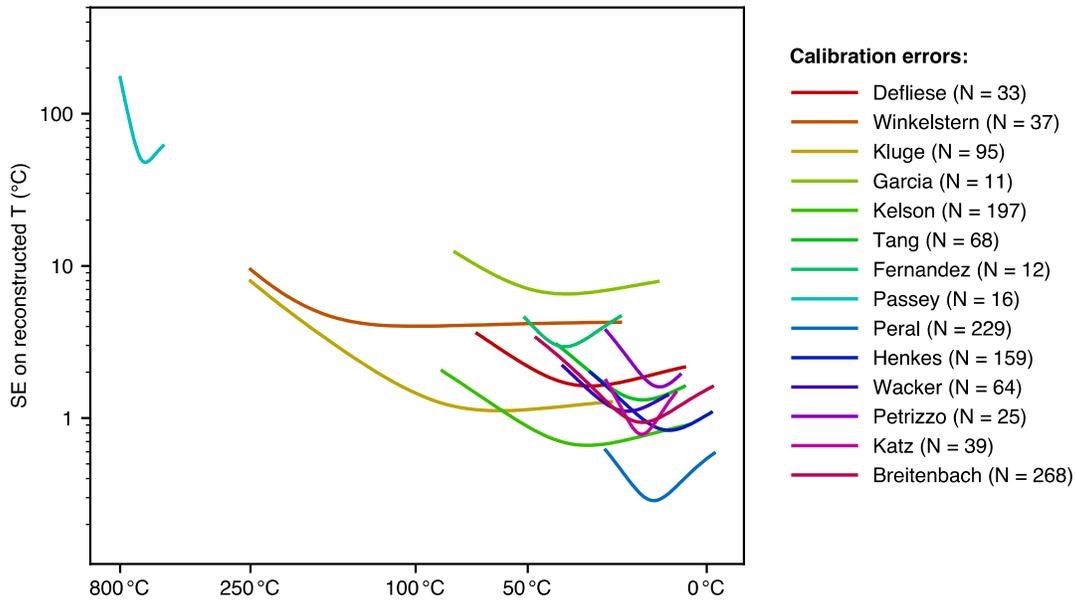


Figure S9. Formation temperature vs. error on reconstructed temperature (1SE) on a log scale showing the relative contributions of different sources of error to total uncertainty on a reconstructed clumped isotope temperature. Similar to **Figure 8**, but including all individual studies. Assuming a long-term reproducibility of 0.020‰ (1sd) on Δ_{47} (which is achieved by most labs - see **Table 1**), grey dashed lines show the purely instrumental or analytical error (ignoring all calibration uncertainties) 1SE error for N=1, 4, or 10 replicates at different formation temperatures. Colored lines show the error introduced by the calibration (from uncertainty in slope and intercept values, computed in the same way as in **Figure 6**) for each individual study calibrations spanning different temperature ranges and containing different numbers of replicate analyses (see legend). For well-constrained calibrations (e.g. N>30 replicates), error from uncertainty in the slope and intercept of the calibration is much less than the analytical error, even with >10 replicates of the unknown.

	δ^{45}	δ^{46}	δ^{47}	δ^{48}	δ^{49}
Equil. Gas #1	-0.164	-2.580	-2.523	0.722	-209.904
Equil. Gas #2	-34.930	-16.029	-52.832	-41.474	-36.017
Heated Gas #1	-6.810	-9.233	-17.356	-24.983	1.673
Heated Gas #2	-0.323	-6.409	-7.720	-16.421	-6.500
	IUPAC	IUPAC	IUPAC	IUPAC	IUPAC
	$\delta^{13}\text{C VPDB}$	$\delta^{18}\text{O VSMOW}$	Raw Δ_{47}	Raw Δ_{48}	Raw Δ_{49}
Equil. Gas #1	-3.77	32.31	0.182	5.095	-205.745
Equil. Gas #2	-40.35	18.45	-1.694	-9.991	33.549
Heated Gas #1	-10.61	25.43	-1.338	-6.726	27.555
Heated Gas #2	-3.80	28.34	-1.094	-3.691	6.480
	Santrock/ Gonfiantini	Santrock/ Gonfiantini	Santrock/ Gonfiantini	Santrock/ Gonfiantini	Santrock/ Gonfiantini
	$\delta^{13}\text{C VPDB}$	$\delta^{18}\text{O VSMOW}$	Raw Δ_{47}	Raw Δ_{48}	Raw Δ_{49}
Equil. Gas #1	-3.77	32.31	0.184	5.095	-205.742
Equil. Gas #2	-40.33	18.45	-1.703	-9.991	33.528
Heated Gas #1	-10.62	25.43	-1.335	-6.726	27.561
Heated Gas #2	-3.81	28.34	-1.089	-3.691	6.489

Table S1. Isotopic composition of four example standard gases used to demonstrate calculability of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Δ_{47} to Δ_{49} values from small delta values δ^{45} - δ^{49} or raw voltages using different calculation programs and schemes. Data here calculated using R code from raw voltages our “best” method.

Table S2. Read-off Table of new theoretical equilibrium $\Delta_{47\text{-TE}}$ values

** Found in a separate Excel file named “SupplementaryTableS2_D47TEvalues.xlsx” **

Rxn Temp	Defliese et al., 2015	Reprocessed data $\Delta_{47\text{-RFAC SG,WD}}$ C/A/D <i>n</i>=151	Reprocessed data $\Delta_{47\text{-RFAC SG,P}}$ C/A/D <i>n</i>=151	Reprocessed data $\Delta_{47\text{-RFAC Br,WD}}$ calcite only <i>n</i>=87	Reprocessed data $\Delta_{47\text{-RFAC Br,P}}$ C/A/D <i>n</i>=151**
100°C	0.091‰	0.105 ± 0.006‰	0.105 ± 0.006‰	0.099 ± 0.006‰	0.098 ± 0.006‰
90°C	0.082‰	0.095 ± 0.006‰	0.094 ± 0.006‰	0.089 ± 0.006‰	0.088 ± 0.006‰
75°C	0.067‰	0.078 ± 0.005‰	0.077 ± 0.005‰	0.073 ± 0.005‰	0.072 ± 0.005‰
70°C	0.062‰	0.071 ± 0.004‰	0.071 ± 0.004‰	0.067 ± 0.004‰	0.066 ± 0.004‰

Table S3. Summary of the temperature dependence on the acid digestion fractionation ($\Delta_{25\text{-X}}$) discussed in this study with 1SE errors, processed with different parameter sets.

** indicates recommended $\Delta_{25\text{-X}}$ to use with updated IUPAC parameters and Petersen $\Delta_{47\text{-TE}}$ values. C/A/D = Calcite/Aragonite/Dolomite combined.

Data	slope	slope s.e.	intercept	intercept s.e	r ²
<i>Only synthetic n=451</i>					
Δ_{47} -RFACSG,WD,DeflieseAFF	0.0370	1.7E-06	0.270	1.7E-05	0.92
Δ_{47} -RFACSG,P,DeflieseAFF	0.0368	1.7E-06	0.270	1.7E-05	0.92
Δ_{47} -RFACSG,WD,newAFF	0.0370	1.7E-06	0.281	1.7E-05	0.92
Δ_{47} -RFACSG,P,newAFF	0.0368	1.7E-06	0.280	1.7E-05	0.92
Δ_{47} -RFACBr,WD,DeflieseAFF	0.0384	1.7E-06	0.249	1.7E-05	0.93
Δ_{47} -RFACBr,P,DeflieseAFF	0.0382	1.7E-06	0.249	1.7E-05	0.93
Δ_{47} -RFACBr,WD,newAFF	0.0387	1.7E-06	0.257	1.7E-05	0.94
Δ_{47}-RFACBr,P,newAFF	0.0383	1.7E-06	0.258	1.7E-05	0.94
<i>Only synthetic below 100°C n=379</i>					
Δ_{47} -RFACSG,WD,DeflieseAFF	0.0371	3.3E-06	0.269	3.4E-05	0.79
Δ_{47} -RFACSG,P,DeflieseAFF	0.0367	3.3E-06	0.269	3.4E-05	0.79
Δ_{47} -RFACSG,WD,newAFF	0.0373	3.2E-06	0.277	3.4E-05	0.80
Δ_{47} -RFACSG,P,newAFF	0.0370	3.2E-06	0.277	3.4E-05	0.80
Δ_{47} -RFACBr,WD,DeflieseAFF	0.0376	3.2E-06	0.258	3.4E-05	0.82
Δ_{47} -RFACBr,P,DeflieseAFF	0.0372	3.3E-06	0.259	3.4E-05	0.82
Δ_{47} -RFACBr,WD,newAFF	0.0380	3.3E-06	0.265	3.4E-05	0.82
Δ_{47} -RFACBr,P,newAFF	0.0376	3.2E-06	0.265	3.4E-05	0.82
<i>All data n=1253</i>					
Δ_{47} -RFACSG,WD,DeflieseAFF	0.0352	1.4E-06	0.281	1.6E-05	0.86
Δ_{47} -RFACSG,P,DeflieseAFF	0.0352	1.5E-06	0.280	1.6E-05	0.86
Δ_{47} -RFACSG,WD,newAFF	0.0353	1.5E-06	0.293	1.6E-05	0.86
Δ_{47} -RFACSG,P,newAFF	0.0353	1.4E-06	0.290	1.6E-05	0.87
Δ_{47} -RFACBr,WD,DeflieseAFF	0.0368	1.5E-06	0.260	1.6E-05	0.88
Δ_{47} -RFACBr,P,DeflieseAFF	0.0367	1.5E-06	0.259	1.6E-05	0.89
Δ_{47} -RFACBr,WD,newAFF	0.0372	1.5E-06	0.268	1.6E-05	0.89
Δ_{47} -RFACBr,P,newAFF	0.0370	1.4E-06	0.267	1.6E-05	0.89
<i>All data below 100°C n=1181</i>					
Δ_{47} -RFACSG,WD,DeflieseAFF	0.0341	2.6E-06	0.294	3.0E-05	0.70
Δ_{47} -RFACSG,P,DeflieseAFF	0.0342	2.6E-06	0.291	3.0E-05	0.71
Δ_{47} -RFACSG,WD,newAFF	0.0344	2.6E-06	0.303	3.0E-05	0.71
Δ_{47} -RFACSG,P,newAFF	0.0345	2.6E-06	0.300	3.0E-05	0.72
Δ_{47} -RFACBr,WD,DeflieseAFF	0.0352	2.6E-06	0.280	2.9E-05	0.74
Δ_{47} -RFACBr,P,DeflieseAFF	0.0352	2.6E-06	0.277	3.0E-05	0.74
Δ_{47} -RFACBr,WD,newAFF	0.0357	2.6E-06	0.285	2.9E-05	0.74
Δ_{47} -RFACBr,P,newAFF	0.0357	2.6E-06	0.283	3.0E-05	0.75

Table S4. Summary of Monto Carlo regression parameters mean values and standard errors for fits through different subsets of synthetic, biogenic, and natural inorganic data, corrected using Santrock/Gonfiantini (SG) or IUPAC (Br) parameters, Wang/Dennis (WD) or Petersen (P) Δ_{47} -TE values, and Defliese et al. (2015) (DeflieseAFF) or updated Δ_{25-90}^* values from this study (newAFF) calculated with corresponding parameters and Δ_{47} -TE values. See **Figure 1** for a summary of abbreviations. Errors on slopes and

intercepts are taken from Monto Carlo sampling, as described in Section 2.4. The suggested calibration equation through all synthetic data, $\Delta_{47-RFACBr,P,newAFF}$ is highlighted in grey. Note: When choosing which calibration equation to use, unknown data must be processed with the same parameters as selected calibration choice of SG vs. Br, WD vs. P, new vs. Defliese Δ^*_{25-90} . p -values not shown, but all are $\lll 0.0001$.

Study	Parameter Set	(<i>n</i>) N	Slope	Slope SE	Intercept	Intercept SE	R ²
Defliese	SG,WD,newAFF	(33)	0.0354	0.0032	0.303	0.035	0.96
	Br,P,newAFF	8	0.0345	0.0020	0.280	0.024	0.98
Winkelstern	SG,WD,newAFF	(37)	0.0378	0.0025	0.300	0.014	0.99
	Br,P,newAFF	9	0.0404	0.0027	0.240	0.015	0.99
Kluge	SG,WD,newAFF	(95)	0.0383	0.0010	0.272	0.008	0.93
	Br,P,newAFF	28	0.0387	0.0008	0.256	0.006	0.98
Garcia	SG,WD,newAFF	(11)	0.0321	0.0125	0.323	0.107	0.84
	Br,P,newAFF	5	0.0357	0.0131	0.279	0.110	0.88
Kelson	SG,WD,newAFF	(197)	0.0415	0.0018	0.238	0.019	0.92
	Br,P,newAFF	56	0.0414	0.0011	0.234	0.012	0.96
Tang	SG,WD,newAFF	(68)	0.0345	0.0042	0.293	0.052	0.74
	Br,P,newAFF	23	0.0367	0.0040	0.259	0.049	0.78
Fernandez	SG,WD,newAFF	(12)	0.0339	0.0016	0.307	0.016	1.00
	Br,P,newAFF	3	0.0369	0.0020	0.268	0.021	1.00
Passey	SG,WD,newAFF	(16)	0.0291	0.0131	0.273	0.020	0.53
	Br,P,newAFF	6	0.0264	0.0112	0.275	0.018	0.50
Peral	SG,WD,newAFF	(229)	0.0392	0.0018	0.244	0.022	0.94
	Br,P,newAFF	27	0.0409	0.0018	0.220	0.023	0.95
Henkes	SG,WD,newAFF	(159)	0+.0346	0.0029	0.315	0.036	0.79
	Br,P,newAFF	49	0.0332	0.0030	0.323	0.037	0.75
Wacker	SG,WD,newAFF	(64)	0.0333	0.0032	0.327	0.037	0.99
	Br,P,newAFF	7	0.0344	0.0053	0.310	0.065	0.96
Petrizzo	SG,WD,newAFF	(25)	0.0333	0.0180	0.305	0.225	0.78
	Br,P,newAFF	6	0.0340	0.0168	0.292	0.211	0.82
Katz	SG,WD,newAFF	(39)	0.0339	0.0037	0.326	0.043	0.89
	Br,P,newAFF	11	0.0346	0.0036	0.314	0.043	0.90
Breitenbach	SG,WD,newAFF	(268)	0.0396	0.0145	0.219	0.178	0.80
	Br,P,newAFF	24	0.0412	0.0097	0.202	0.119	0.84
Defliese/ Winkelstern U of M	SG,WD,newAFF	(70)	0.0350	0.0011	0.310	0.010	0.98
	Br,P,newAFF	17	0.0372	0.0011	0.254	0.010	0.99
Kluge/Garcia Imperial	SG,WD,newAFF	(106)	0.0376	0.0013	0.277	0.010	0.93
	Br,P,newAFF	33	0.0383	0.0012	0.259	0.009	0.96
Tang/Fernandez Tulane/UCLA	SG,WD,newAFF	(80)	0.0333	0.0029	0.308	0.035	0.77
	Br,P,newAFF	26	0.0350	0.0029	0.280	0.034	0.80
Passey/Henkes JHU	SG,WD,newAFF	(175)	0.0388	0.0004	0.262	0.005	0.99
	Br,P,newAFF	55	0.0379	0.0005	0.263	0.005	0.98

Table S5. Regression parameters for Deming regression (similar to York regression that takes error in X and Y into account) through individual studies using either updated parameters (Br, P, newAFF) or older parameters (SG, WD, newAFF), as well as single-lab fits combining multiple studies per lab. These regressions are shown in **Figure S7 and S8** in colored lines. (*n*) = # replicates and N = # samples.

	Breitenbach	Katz	Petrizzo	Wacker	Henkes	Peral	Passey	Fernandez	Tang	Kelson	Garcia	Kluge	Winkler
Katz	Defliese	Winkelstern	Kluge	Garcia	Kelson	Tang	Fernandez	Passey	Peral	Henkes	Wacker	Petrizzo	Breitenbach
Ps = 0.31 Pi = 4e-17	Ps = 0.12 Pi = 0.14	Ps = 0.84 Pi = 3e-03	Ps = 0.65 Pi = 7e-09	Ps = 0.25 Pi = 0.05	Ps = 0.99 Pi = 2e-24	Ps = 0.36 Pi = 0.84	Ps = 0.66 Pi = 5e-02	Ps = 0.30 Pi = 0.24	Ps = 0.89 Pi = 3e-9	Ps = 5e-2	Ps = 0.16 Pi = 5e-10	Ps = 0.40 Pi = 3e-02	Ps = 0.12 Pi = 0.14
	Ps = 1.00 Pi = 9e-07	Ps = 0.31 Pi = 0.92	Ps = 0.37 Pi = 0.50	Ps = 0.85 Pi = 1e-02	Ps = 0.23 Pi = 0.25	Ps = 0.68 Pi = 1e-17	Ps = 0.82 Pi = 4e-02	Ps = 0.58 Pi = 0.26	Ps = 0.20 Pi = 1e-6	Ps = 0.84 Pi = 2e-03	Ps = 0.98 Pi = 0.10	Ps = 0.95 Pi = 2e-03	Ps = 1.00 Pi = 9e-07
	Ps = 0.94 Pi = 0.18	Ps = 0.42 Pi = 0.16	Ps = 0.48 Pi = 2e-02	Ps = 0.83 Pi = 0.70	Ps = 0.35 Pi = 1e-05	Ps = 0.71 Pi = 2e-02	Ps = 0.80 Pi = 0.75	Ps = 0.63 Pi = 0.43	Ps = 0.32 Pi = 0.12	Ps = 0.94 Pi = 0.09	Ps = 0.96 Pi = 0.07		Ps = 0.94 Pi = 0.18
	Ps = 0.96 Pi = 8e-05	Ps = 0.10 Pi = 0.85	Ps = 0.12 Pi = 0.98	Ps = 0.76 Pi = 3e-02	Ps = 4e-2	Ps = 0.52 Pi = 1e-09	Ps = 0.79 Pi = 5e-02	Ps = 0.58 Pi = 0.12	Ps = 4e-2	Ps = 0.78 Pi = 0.60			Ps = 0.96 Pi = 8e-05
	Ps = 0.69 Pi = 5e-05	Ps = 3e-3	Ps = 7e-4	Ps = 0.50 Pi = 2e-02	Ps = 4e-6	Ps = 0.24 Pi = 1e-11	Ps = 0.70 Pi = 4e-02	Ps = 0.62 Pi = 2e-03	Ps = 3e-4				Ps = 0.69 Pi = 5e-05
	Ps = 1e-2	Ps = 0.57 Pi = 4e-2	Ps = 0.24 Pi = 7e-3	Ps = 0.08 Pi = 0.90	Ps = 0.75 Pi = 5e-17	Ps = 0.14 Pi = 1e-9	Ps = 0.60 Pi = 0.94	Ps = 0.28 Pi = 5e-2					Ps = 1e-2
	Ps = 0.56 Pi = 0.26	Ps = 0.32 Pi = 0.34	Ps = 0.35 Pi = 0.50	Ps = 0.51 Pi = 0.45	Ps = 0.29 Pi = 2e-02	Ps = 0.45 Pi = 0.87	Ps = 0.53 Pi = 0.63						Ps = 0.56 Pi = 0.26
	Ps = 0.80 Pi = 0.65	Ps = 0.70 Pi = 0.21	Ps = 0.77 Pi = 0.11	Ps = 0.90 Pi = 0.96	Ps = 0.64 Pi = 3e-02	Ps = 0.99 Pi = 0.16							Ps = 0.80 Pi = 0.65
	Ps = 0.48 Pi = 0.25	Ps = 0.31 Pi = 1e-02	Ps = 0.40 Pi = 3e-08	Ps = 0.74 Pi = 0.12	Ps = 0.14 Pi = 3e-25								Ps = 0.48 Pi = 0.25
	Ps = 7e-3	Ps = 0.68 Pi = 0.44	Ps = 0.14 Pi = 0.82	Ps = 0.08 Pi = 4e-02									Ps = 7e-3
	Ps = 0.76 Pi = 0.61	Ps = 0.19 Pi = 0.42	Ps = 0.23 Pi = 0.14										Ps = 0.76 Pi = 0.61
	Ps = 0.05 Pi = 2e-03	Ps = 0.67 Pi = 0.97											Ps = 0.05 Pi = 2e-03
	Ps = 5e-2												Ps = 5e-2

Table S6. Results of the ANCOVA tests for each pair of calibration studies. P_s is the probability that the null hypothesis is true at the 95% confidence level, that the two calibration slopes are identical taking into account errors. P_i is the probability that the intercepts of the two calibrations are identical if fit to a single slope (this analysis was only done in cases where the pair passed the first test if identical slope). Green shading indicates that two calibrations are identical within error in slope and intercept. Light orange shading indicates two calibrations are identical within error in slope, but differ in intercept. Pink shading indicates two calibrations differ in both slope and intercept. This table shows the statistics for $\Delta_{47}\text{-RFAC (Br, P, newAFF)}$: 42 green pairs, 39 orange, and 10 red, but results are very similar for other combinations not shown. $\Delta_{47}\text{-RFAC (Br, WD, newAFF)}$ has 40 green pairs, 41 orange, and 10 red. $\Delta_{47}\text{-RFAC SG, P, newAFF}$ has 42 green pairs, 38 orange, and 11 red. $\Delta_{47}\text{-RFAC (SG, WD, newAFF)}$ has 42 green pairs, 39 orange, and 10 red.

Data Set S1. All studies, all replicates samples + standards

***Uploaded separately in a file named “ds01_ALLstudies_SAMPSTDreplicates.txt”.*

A text file containing all sample and standard replicates from all 14 studies reprocessed here (n=5448 replicates). Columns include identifying information (study author, time, date, run#, or similar) and replicate mean small delta values ($\delta^{45}\text{-}\delta^{49}$) and isotopic compositions ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\Delta_{47}\text{-}\Delta_{49}$) calculated with both SG and IUPAC parameters, as well as working gas composition at the time of that replicate analysis.

For sample replicates, columns include sample information (sample type as biogenic, synthetic, or natural inorganic, mineralogy, formation temperature and error) and information/values needed to convert raw values into the absolute reference frame (measurement session or window indicator, SlopeEGL two sets: SG and Br, SlopeETF and IntETF four sets: SG/WD, SG/P, Br/WD, Br/P, and acid temperature and $\Delta^{*25\text{-X}}$ value used five sets: Defliese, SG/WD, SG/P, Br/WD, Br/P). This results in eight different $\Delta_{47}\text{-RFAC}$ values, depending on the combination of parameters and values chosen.

For standard replicates, columns include assigned $\Delta_{47}\text{-TE}$ values two sets: WD and P, a measurement session/window indicator and an indicator of whether that particular standard was used to calculate ARF parameters or not.

The data combined here will also be archived through the EarthChem database, with one file and doi number for each study. This will happen at the time of publication of this manuscript.

Data Set S2. All studies, sample means unknowns only

*** Uploaded separately in a file named “ds02_ALLstudies_SAMPmeans.txt” ***

A text file containing sample mean values from all 14 studies reprocessed here (n=262 sample means). Columns include identifying information (study author, sample name, sample type, sample number, formation temperature and error, mineralogy, acid temperature), and number of replicates included in the mean, as well as sample mean stable isotopic compositions ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, with 1sd: 2 sets, SG and IUPAC) and clumped isotopic compositions ($\Delta_{47}\text{-RFAC}$ with 1 SE: 8 sets with different combinations of SG/IUPAC parameters, WD/P $\Delta_{47}\text{-TE}$ values, Defliese/new $\Delta^{*25\text{-X}}$ values) and external 1 SE error on the mean independent on parameter choice.

Supplementary References

** Includes only references cited exclusively in the supplementary material. All other references in this document can be found in the main manuscript reference list. **

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