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# Choice of $^{17}\text{O}$ correction affects clumped isotope ( $\Delta_{47}$ ) values of $\text{CO}_2$ measured with mass spectrometry

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**RATIONALE:** The clumped isotope composition of  $\text{CO}_2$  ( $\Delta_{47}$ ) derived from carbonate is widely used as a paleotemperature proxy with broad applications in geoscience. Its accuracy is, however, limited by inter-laboratory discrepancies of reference materials and disagreement among carbonate geothermometer calibrations. Here we show how the correction for the abundance of  $^{17}\text{O}$  influences these discrepancies.

**METHODS:** We used  $\text{CO}_2\text{-H}_2\text{O}$  equilibration at known temperatures and phosphoric acid digested carbonates to generate  $\text{CO}_2$  samples with a wide range in  $^{13}\text{C}$  and  $^{18}\text{O}$  compositions. All samples were purified using an offline vacuum line. We used a Thermo MAT 253 isotope ratio mass spectrometer with a Faraday collector array for  $m/z$  44–49, to measure  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{47}$ , and  $\Delta_{47}$  values. Data were compiled using a traditional correction ('Santrock') for the  $^{17}\text{O}$  interference in  $m/z$  45 as well as a more recently proposed correction ('Brand') for  $^{17}\text{O}$  interference. Two reference frames using  $\text{CO}_2$  with distinct  $^{13}\text{C}$  compositions were constructed to simulate an inter-laboratory comparison.

**RESULTS:** The traditional Santrock  $^{17}\text{O}$  correction leads to a simulated  $\Delta_{47}$  inter-laboratory comparison offset of 0.06 ‰, and a 0.1 ‰  $\Delta_{47}$  range in  $\text{CO}_2\text{-H}_2\text{O}$  23°C equilibrations that is dependent on the  $^{13}\text{C}$  composition. The more recent Brand  $^{17}\text{O}$  correction removes these discrepancies. The traditional  $^{17}\text{O}$  correction yields distinct temperature- $\Delta_{47}$  calibration curves for synthetic carbonates precipitated using different methods to degas  $\text{CO}_2$ , while the more recent  $^{17}\text{O}$  correction collapses all calibration data onto a single curve.

**CONCLUSIONS:** The  $^{17}\text{O}$  correction strategy employed by  $\text{CO}_2$  and carbonate clumped-isotope researchers can have a large effect on the accuracy of  $\Delta_{47}$  values. Use of the traditional  $^{17}\text{O}$  correction may have caused errors in published studies as large as 0.1 ‰ and may account for  $\Delta_{47}$  differences among laboratories and disagreement among previously published carbonate clumped isotope thermometry calibrations. Copyright © 2016 John Wiley & Sons, Ltd.

Measurements of the clumped-isotope composition of  $\text{CO}_2$  ( $\Delta_{47}$ ) have broad applications in geosciences, most of which use the temperature dependence of  $\Delta_{47}$  in  $\text{CO}_2$  derived from acid-digested carbonate for geothermometry (e.g., [1–6]). The parameter  $\Delta_{47}$  represents the ratio of the measured abundance of  $\text{CO}_2$  isotopologues with  $m/z$  47 (mostly  $\text{CO}_2$  molecules containing  $^{13}\text{C}\text{-}^{18}\text{O}$  bonds,  $^{13}\text{C}\text{-}^{18}\text{O}\text{-}^{16}\text{O}$ ) and the calculated abundance of  $m/z$  47 isotopologues that would be expected for the sample if all isotopes were distributed randomly among isotopologues.<sup>[7]</sup> The full signal of  $\Delta_{47}$  representing  $\text{CO}_2$  or carbonate formation temperatures from 0 to 1000°C is of the order of 1 ‰ and hence  $\Delta_{47}$  values require careful measurement and calibration to achieve a useful precision. Significant progress has been made to standardize laboratory methods<sup>[8]</sup> and data reporting using a reference frame of  $\text{CO}_2$  equilibrated at different temperatures.<sup>[9]</sup> Several subsequent workers have suggested further improvements to the measurement.<sup>[10,11]</sup> However, inter-laboratory discrepancies and disagreement among carbonate geothermometer

calibrations based on analyses of synthetic carbonates remain (e.g. [12–14]). Data from synthetic carbonates precipitated at known temperatures using different strategies and analyzed using identical methods rule out most of the sample synthesis, preparation and analysis differences that have been proposed to cause the calibration discrepancies.<sup>[14]</sup> Colman<sup>[15]</sup> recently raised the possibility that there may be a very basic problem with the assumption made regarding the quantity of  $^{17}\text{O}$  in a  $\text{CO}_2$  sample, which would influence  $\Delta_{47}$  and therefore the reference frame calibration. The  $\Delta_{47}$  value relies heavily on the estimates of  $^{13}\text{C}$  and  $^{18}\text{O}$ ,<sup>[8]</sup> which must be corrected for mass interference from  $^{17}\text{O}$  when measured by isotope ratio mass spectrometry (IRMS). Specifically, IRMS estimates of  $^{13}\text{C}$  and  $^{18}\text{O}$  in  $\text{CO}_2$  are calculated from measurements of  $m/z$  44, 45, and 46 that are affected by a mass interference from  $^{17}\text{O}$ , which is traditionally corrected for using an assumed relationship between  $^{17}\text{O}$  and  $^{18}\text{O}$ :<sup>[16–18]</sup>

$$^{17}\text{R} = \text{K} \cdot ^{18}\text{R}^\lambda \quad (1)$$

where  $\lambda$  describes the fractionation process of  $^{17}\text{O}$  and  $^{18}\text{O}$ , and K is a coefficient relating the  $^{17}\text{R}$  and  $^{18}\text{R}$  of the reference material (typically VSMOW or VPDB), where  $^i\text{R}$  is the abundance ratio of the heavier isotopic species of interest to the more abundant lighter isotopic species. The definition of

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$\Delta_{47}$  (as in [7,8]) shows the dependence of clumped isotopic values of  $\text{CO}_2$  on the estimates of  $^{13}\text{C}$  and  $^{18}\text{O}$ , and therefore on Eqn. (1):

$$\Delta_{47} = \left[ \left( \frac{^{47}\text{R}}{^{47}\text{R}^*} - 1 \right) - \left( \frac{^{46}\text{R}}{^{46}\text{R}^*} - 1 \right) - \left( \frac{^{45}\text{R}}{^{45}\text{R}^*} - 1 \right) \right] \quad (2)$$

where

$$^{47}\text{R}^* = 2^{13}\text{R} \cdot ^{18}\text{R} + 2^{17}\text{R} \cdot ^{18}\text{R} + ^{13}\text{R} \cdot (^{17}\text{R})^2 \quad (3)$$

$$^{46}\text{R}^* = 2^{18}\text{R} + 2^{13}\text{R} \cdot ^{17}\text{R} + (^{17}\text{R})^2 \quad (4)$$

$$^{45}\text{R}^* = ^{13}\text{R} + 2^{17}\text{R} \quad (5)$$

Calculating the random (stochastic) distribution of isotopologues (given as  $^i\text{R}^*$  in Eqns. (2)–(5)) for a given bulk isotopic composition requires  $^{13}\text{R}$ ,  $^{17}\text{R}$  and  $^{18}\text{R}$  to be determined. If the  $^i\text{R}$  values are accurate, the calculated  $\Delta_{47}$  values should reflect sample formation/equilibration temperature or other chemical or physical processes independent of the  $^{13}\text{C}$  and  $^{18}\text{O}$  composition of a sample.

The clumped isotope community generally cites Huntington *et al.*[8] when describing data reduction, implicitly assuming the values of  $\lambda$  and  $K$  used therein to calculate  $^i\text{R}$  and  $\Delta_{47}$ . Following Affek and Eiler,[7] the  $\lambda$  value given by Huntington *et al.*[8] is 0.5164, cited to Gonfiantini *et al.*,[19] this  $\lambda$  value originally came from Matsuhisa *et al.*,[20] who derived it from terrestrial water and rock samples for the quartz–water system. The  $K$  value, as derived from Huntington *et al.*,[8] is 0.00922118. Therefore, the  $\lambda$  and  $K$  values used by Affek and Eiler[7] and Huntington *et al.*[8] are indistinguishable from those of Santrock *et al.*,[17] which is a common citation for the correction of  $^{13}\text{C}$  for  $^{17}\text{O}$  interference. The  $K$  value of Santrock *et al.*[17] is based on the work of Nier.[21] These  $\lambda$  and  $K$  values traditionally used by clumped isotope researchers differ from the more recent values suggested by Brand *et al.*,[18] who reasoned that  $\lambda = 0.528$  and  $K = 0.01022461$ , where  $\lambda$  originates from the meteoric water line and  $K$  is calculated from the  $^{17}\text{R}$  and  $^{18}\text{R}$  of VPDB- $\text{CO}_2$ . In the present work, we compare the  $\lambda$  and  $K$  values of Santrock *et al.*[17] (hereafter ‘Santrock method’) and Brand *et al.*[18] (hereafter ‘Brand method’) as they relate to the parameter  $\Delta_{47}$ .

While there is no conclusive evidence that a particular value of  $\lambda$  or  $K$  is most appropriate for  $\Delta_{47}$  calculations, recent work hints at their importance. Affek and Eiler[7] argued that  $\Delta_{47}$  values are relatively insensitive to the choice of  $\lambda$ , noting that  $\lambda$  values of 0.5 to 0.528 result in only a 0.002 ‰ variation in  $\Delta_{47}$ . However, recent preliminary results of Colman[15] suggest that  $\Delta_{47}$  is sensitive to the  $\delta^{17}\text{O}$  value for *some* samples, and Schauer *et al.*[22] observed an unexplained dependence of  $\Delta_{47}$  on  $\delta^{13}\text{C}$ .

Here, we build upon these works with experiments that aim to illustrate the effect of  $^{17}\text{O}$  correction choices on the accuracy of  $\Delta_{47}$  values. In the present work, using the Santrock method, we show (1) two distinct absolute reference frames constructed with reference gases having disparate  $\delta^{13}\text{C}$  values and (2)  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrations from a single temperature that result in  $\Delta_{47}$  values that differ by as much as 0.1 ‰ or  $\sim 20^\circ\text{C}$  depending on the  $\delta^{13}\text{C}$  value. Furthermore, we show the removal of this dependency of calculated  $\Delta_{47}$  values on  $\delta^{13}\text{C}$  values when the  $\lambda$  and  $K$  values of Brand *et al.*[18] are

used. We also show how the choice of  $^{17}\text{O}$  correction influences inter-laboratory calibration carbonates (e.g. ETH reference materials) and synthetic calcite temperature calibration efforts.

## EXPERIMENTAL

### Sample preparation

All samples discussed here were prepared, purified and analyzed at the University of Washington’s IsoLab (Seattle, WA, USA) as described previously[14,23] and summarized here. These samples include  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrations;  $1000^\circ\text{C}$  heated  $\text{CO}_2$  gases; carbonate reference materials; and synthetic calcites synthesized and analyzed by Kelson *et al.*[14] The  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrations used 200  $\mu\text{L}$  of water and 90  $\mu\text{mol}$   $\text{CO}_2$  in a  $\frac{1}{4}$ ” OD Pyrex tube equilibrated for longer than 1 day at 5, 23, or  $60^\circ\text{C}$ . Heated gases were created from a suite of  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrations with subsequent cryogenic removal of water and then heating of the  $\text{CO}_2$  to  $1000^\circ\text{C}$  in  $\frac{1}{4}$ ” OD quartz tubes for at least 2 h. Carbonate reference materials were weighed to approximately 8 mg into silver capsules and digested in a common bath of phosphoric acid (specific gravity 1.9–1.95) held at  $90^\circ\text{C}$  for 10 min.

Whether from a Pyrex/quartz tube or a carbonate,  $\text{CO}_2$  was cryogenically separated from water on an automated stainless steel/nickel vacuum line using an ethanol/dry ice slush trap, isolated in a liquid  $\text{N}_2$  trap, and passed through a Porapak Q trap (50/80 mesh, 122 cm long, 3.2 mm OD) held at  $-20^\circ\text{C}$ . The  $\text{CO}_2$  was transferred through the Porapak Q trap using helium as the carrier gas at a flow rate of  $\sim 35$  mL/min for a total transfer time of 20 min, then isolated cryogenically and transferred into a 6 mm OD Pyrex break seal.

### Isotopic analyses

Break seals containing  $\text{CO}_2$  purified on the vacuum line were loaded into an automated 10-port tube-cracker inlet system and analyzed by dual-inlet isotope ratio mass spectrometry (DI-IRMS) on a Thermo MAT 253 mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) configured to measure  $m/z$  44–49 inclusive. The mass spectrometer was fitted with nickel capillaries and a standard MEMCO Faraday cup configuration with additional cups for  $m/z$  47–49. To start each sample analysis, the sample bellows were fully expanded and evacuated. Sample gas was then expanded into the sample bellows and the pressure was measured. Following sample gas introduction, the evacuated reference bellows at 100% expansion were automatically filled to a pressure equal to that measured in the sample bellows with working reference gas  $\text{CO}_2$  ( $\delta^{13}\text{C} = -10.2$  ‰,  $\delta^{18}\text{O} = -6.4$  ‰, both vs NBS19 on the VPDB scale) using a modified ISL script (detailed in the Supporting Information, Schauer\_RCM\_17OCorrectionClumped\_IsodatISLScripts.docx). Following bellow fill, the  $m/z$  45 signal was used for peak centering, and the bellows were compressed for pressure adjustment that produced a  $m/z$  44 signal of 16 V. The pressure baseline (PBL)[10,24] was automatically measured using a modified background ISL script (detailed in the Supporting Information, Schauer\_RCM\_17OCorrectionClumped\_sodatISLScripts.docx) in the mass spectrometer software (Isodat

version 3.0.88.1, Thermo Fisher Scientific; see next section) with the measurement made 0.08 kV left of peak center prior to each sample. The sample  $\text{CO}_2$   $m/z$  44–49 signals were measured against working reference gas  $\text{CO}_2$  for six acquisitions of 10 sample-reference comparison cycles with 26-s integration times. The signals for  $m/z$  44–46 were measured with standard amplification ( $3 \times 10^8$ ,  $3 \times 10^{10}$ ,  $1 \times 10^{11} \Omega$ , respectively), while the signals for  $m/z$  47–49 were measured with  $1 \times 10^{12} \Omega$  amplification. At the end of each six-acquisition sample measurement, the water backgrounds were measured by peak centering on the  $m/z$  45 Faraday collector and measuring the  $m/z$  18 signal of both sample and working reference gas.

### Data processing

A custom Matlab (Mathworks, Natick, MA, USA) script (provided as Supporting Information, Schauer\_RCM\_17OCorrectionClumped\_MatlabScripts.docx) was used to reduce measured mV signals to measured delta values. The measured mV signals were output to a comma separated value file. The measured mV signal output is already corrected for background (PBL in our case) in the mass spectrometer software; the traditional background measurement ISL script is replaced by our modified script such that the background values are passed through Isodat normally with the end result being a PBL corrected mV signal (detailed in Supporting Information, Schauer\_RCM\_17OCorrectionClumped\_IsodatISLScripts.docx). We use the Matlab `fsolve` function to iteratively minimize the result when Eqns. (1), (4), and (5) are set to zero for each measurement of the sample gas and the mean of each of the flanking measurements of the mass spectrometer working reference gas (working gas). For a given  $K$ ,  $\lambda$  and measured  $^{45}\text{R}$  and  $^{46}\text{R}$ , we then obtain estimates of  $^{17}\text{R}$ ,  $^{18}\text{R}$ , and  $^{13}\text{R}$  for both sample and working gases. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values as well as the stochastic predictions for both sample and working gases are calculated. Lastly, the measured  $\Delta_{47}$ ,  $\Delta_{48}$  and  $\Delta_{49}$  are calculated. The above calculations from the measured PBL-corrected mV signals to measured  $\Delta$  values are carried out twice for each sample, once using the Santrock method  $K$  (0.00922118) and  $\lambda$  (0.5164) and a second time using the Brand method  $K$  (0.01022461) and  $\lambda$  (0.528). Further processing of measured  $\Delta_{47}$  values into the absolute reference frame<sup>[9]</sup> is described in detail below.

### Two absolute reference frames

We constructed two absolute reference frames (as in Dennis *et al.*<sup>[9]</sup>) using two isotopically distinct  $\text{CO}_2$  gases contained in compressed gas cylinders to prepare the  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrations and heated  $\text{CO}_2$  gases. One cylinder had  $\text{CO}_2$  that originated from an ethanol/corn-fermentation plant with a  $\delta^{13}\text{C}$  value of  $-10.5 \text{‰}$  VPDB (hereafter referred to as 'FC' for fermented corn). The other cylinder had  $\text{CO}_2$  that originated from fossil fuel combustion with a  $\delta^{13}\text{C}$  value of  $-35.5 \text{‰}$  (hereafter referred to as 'FF' for fossil fuel). These two types of  $\text{CO}_2$  were equilibrated with evaporatively enriched water, local tap water, South Pole ice core water, and mixtures of these waters, which spanned  $\delta^{18}\text{O}$  values ranging from  $-50$  to  $+40 \text{‰}$  VSMOW. The  $\Delta^{17}\text{O}$  values of these waters were measured in our laboratory using the methods described by Schoenemann *et al.*<sup>[25]</sup> the  $\Delta^{17}\text{O}$  values are  $-156$ ,  $+34$ , and  $+9$

permeg, respectively. The reference frame temperatures used were 5, 60, and  $1000^\circ\text{C}$ . The data from heated and water-equilibrated  $\text{CO}_2$  gases prepared using the two respective  $\text{CO}_2$  cylinders were treated independently to construct the two distinct reference frames (FC and FF reference frames). A single slope and three intercepts (for 5, 60, and  $1000^\circ\text{C}$ ) were calculated as per Dennis *et al.*<sup>[9]</sup> for each respective reference frame. Independent empirical transfer functions (ETFs) were created for both of the two reference frames.

### 23°C $\text{CO}_2$ - $\text{H}_2\text{O}$ equilibrations

We created a set of known-temperature  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrated samples at  $23^\circ\text{C}$  using a variety of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. We used both the FF and the FC  $\text{CO}_2$  gas cylinders referred to above as well as phosphoric-acid-digested carbonates to generate a range in  $\text{CO}_2$   $\delta^{13}\text{C}$  values. All the  $\text{CO}_2$  samples were equilibrated with evaporatively enriched water, local tap water, and South Pole ice core water at  $23^\circ\text{C}$ . The  $\Delta_{47}$  values were corrected using both, separately, the FC and the FF  $\text{CO}_2$  reference frames and the associated ETFs, and the apparent equilibration temperature was calculated from the  $\Delta_{47}$  values using Eqn. (A2) from Dennis *et al.*<sup>[9]</sup> (which is derived from Table 4(I) of Wang *et al.*<sup>[26]</sup>) and the Matlab `fsolve` function.

### Carbonate reference materials

We analyzed three in-house carbonate reference materials (C64, C2 and Coral) as well as four inter-laboratory carbonate reference materials (ETH 1, 2, 3, 4). C64 and C2 are reagent grade calcites while Coral is a *Porites* spp. of the Great Barrier Reef similar in growth temperature to the RIB *Porites* presented in Saenger *et al.*<sup>[27]</sup> ETH 1–4 are a collection of carbonates increasingly used by the carbonate clumped isotope community. Meckler *et al.*<sup>[28]</sup> originally published the carbon, oxygen, and clumped isotope composition of the ETH reference materials as 'Iso A' now ETH 1, 'Iso B' now ETH 2, 'Iso C' now ETH 3, and 'Iso R' now ETH 4 (see Table 1 of Meckler *et al.*<sup>[28]</sup>). All the carbonates were digested in a common phosphoric acid bath at  $90^\circ\text{C}$ . We used the carbonate data from these seven materials to create a hypothetical inter-laboratory comparison where one lab used the FC  $\text{CO}_2$  reference frame and the other lab used the FF  $\text{CO}_2$  reference frame to calculate  $\Delta_{47}$  values.

### Synthetic carbonates

The synthetic carbonates discussed in this paper are the same samples that were precipitated at known temperatures using various methods and analyzed as described in detail in Kelson *et al.*<sup>[14]</sup> We present the  $\Delta_{47}$  values that were calculated by Kelson *et al.*<sup>[14]</sup> using the Brand method and reprocess the raw data using the Santrock method for comparison. All the synthetic carbonate  $\Delta_{47}$  values were corrected using the FC  $\text{CO}_2$  reference frame and the associated ETF. The variations in precipitation method resulted in carbonates with a range in  $\delta^{13}\text{C}$  values of  $-25.7$  to  $1.5 \text{‰}$  (VPDB) and a range in  $\delta^{18}\text{O}$  values of  $-20.7$  to  $-6.5 \text{‰}$  (VPDB). Precipitation methods that involved bubbling  $\text{CO}_2$  that was relatively depleted in  $^{13}\text{C}$  into solution resulted in carbonates that were also depleted in  $^{13}\text{C}$  (carbonate  $\delta^{13}\text{C}$  values ranging from  $-25.7$  to  $-6.2 \text{‰}$  VPDB). Carbonates that were precipitated without  $\text{CO}_2$  bubbling have  $\delta^{13}\text{C}$  values that range from  $-2.0$  to  $1.5 \text{‰}$  VPDB.

**Table 1.** CO<sub>2</sub>-H<sub>2</sub>O equilibration and heated gas line regression coefficients from the two reference frames (fermented corn, 'FC', and fossil fuel, 'FF') reduced via the Santrock method and Brand <sup>17</sup>O correction methods

Reference frame	T (°C)	n	Slope	Intercept	r <sup>2</sup>	ETF	r <sup>2</sup>
FC <sup>a</sup>	5	20	-0.0012	0.084	0.818	$\Delta_{47}\text{-ARF} = 1.0528 * \Delta_{47}\text{-WG} + 0.9352$	0.999
	60	20		-0.146	0.436		
	1000	36		-0.867	0.512		
FF <sup>a</sup>	5	8	-0.0012	0.021	0.392	$\Delta_{47}\text{-ARF} = 1.0562 * \Delta_{47}\text{-WG} + 0.9954$	0.999
	60	6		-0.196	0.903		
	1000	17		-0.922	0.713		
FC <sup>b</sup>	5	20	-0.0002	0.083	0.210	$\Delta_{47}\text{-ARF} = 1.0542 * \Delta_{47}\text{-WG} + 0.9354$	0.999
	60	20		-0.146	-0.042		
	1000	36		-0.866	0.024		
FF <sup>b</sup>	5	8	-0.0002	0.076	0.032	$\Delta_{47}\text{-ARF} = 1.0571 * \Delta_{47}\text{-WG} + 0.9375$	0.999
	60	6		-0.142	0.255		
	1000	17		-0.867	0.006		

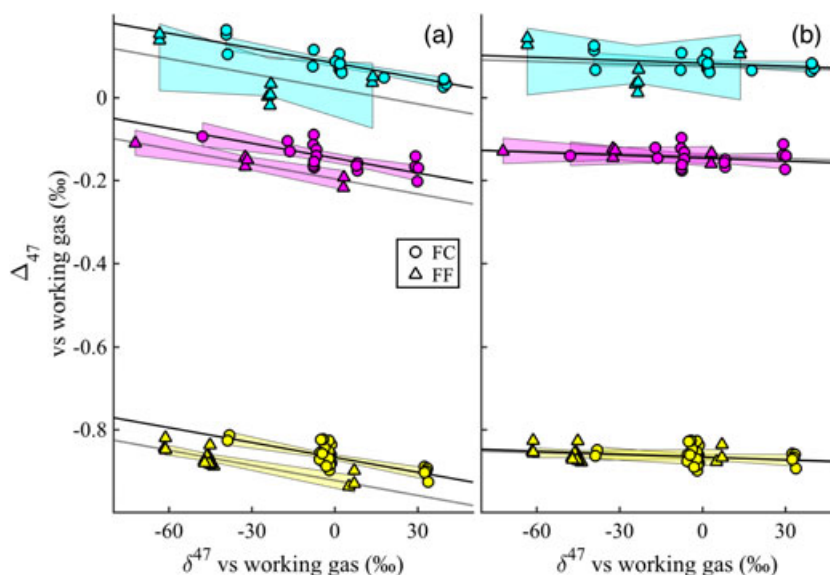
ETF is Empirical Transfer Function and ARF is Absolute Reference Frame, both after Dennis *et al.*<sup>[9]</sup>  
<sup>a</sup>Santrock <sup>17</sup>O correction method.  
<sup>b</sup>Brand <sup>17</sup>O correction method.

## RESULTS

All the isotopic data have been archived at the University of Washington, IsoLab data repository.<sup>[29]</sup> The data processing scripts are also given as Supporting Information (Schauer\_RCM\_17OCorrectionClumped\_Matlab Scripts.docx).

### Two absolute reference frames

The FC and FF reference frames resulted in equilibrated and heated CO<sub>2</sub> gases with a δ<sup>47</sup> value range of approximately 80 ‰. Figure 1(a) shows the two reference frames created with the FC CO<sub>2</sub> and the FF CO<sub>2</sub> using the Santrock method while Fig. 1(b) shows the same data using the Brand method. The slopes and intercepts for these two reference frames under



**Figure 1.** Δ<sub>47</sub> vs δ<sup>47</sup> reference frames created with CO<sub>2</sub>-H<sub>2</sub>O equilibrations. The CO<sub>2</sub> originated from fermented corn (FC, circles) and from fossil fuels (FF, triangles). The H<sub>2</sub>O originated from a South Pole ice core, local Seattle tap water, and evaporatively enriched water. Equilibrations were conducted at 5 °C (cyan), 60 °C (magenta) and 1000°C (yellow). Data compiled with (a) the Santrock <sup>17</sup>O correction method and (b) the Brand <sup>17</sup>O correction method. The shaded regions indicate 95% confidence intervals. Table 1 shows regression coefficients and Table 2 shows statistical test results comparing FC and FF for each temperature and for both the Santrock and the Brand methods. Note FC and FF become indistinguishable using the Brand method.

both <sup>17</sup>O correction methods are given in Table 1. Statistical tests (Table 2) show that the FC and FF reference frames have indistinguishable slopes, but their intercepts are significantly different. [Note the 5°C FF dataset shows more scatter than data at the other temperatures (Fig. 1(a) confidence interval) but remains statistically distinct from the 5°C FC set (Table 2).] The mean  $\Delta_{47}$  offset among identical equilibration-temperature intercepts when the Santrock method is used is approximately 0.056 ‰ – more than five times analytical error. The offset is reduced to 0.001 ‰ when the Brand method is used (Table 1). The Santrock method slopes of both the FC and the FF reference frames are an order of magnitude steeper than those from the Brand method FC and FF reference frames.

### 23°C CO<sub>2</sub>-H<sub>2</sub>O equilibrations

Figure 2 shows  $\Delta_{47}$  data for samples generated from CO<sub>2</sub> cylinder gas and acid-digested carbonates across a 50 ‰ range of  $\delta^{13}\text{C}$  values (128 ‰ range of  $\delta^{47}$  values) that were all equilibrated at 23°C and reduced using the Santrock method (Fig. 2(a)) and the Brand method (Fig. 2(b)). The data processed with the Santrock method projected into the FC reference frame or the FF reference frame produce mean  $\Delta_{47}$  values with a 0.102 ‰ range (temperature estimates with a 20°C range) that are dependent on the  $\delta^{13}\text{C}$  values (least-squares linear model for FC: slope = +0.0021, intercept = 0.964,  $R^2 = 0.960$ ,  $p < 0.001$ ; least-squares linear model for FF: slope = +0.0021, intercept = 1.024,  $R^2 = 0.960$ ,  $p < 0.001$ ). The Brand method, however, shows no distinguishable difference between the  $\Delta_{47}$  values and the calculated  $\Delta_{47}$  value associated with a 23°C equilibration temperature (0.935 ‰) for the full range of  $\delta^{13}\text{C}$  values (least-squares linear model for FC:

slope = -0.0002, intercept = 0.941,  $R^2 = 0.119$ ,  $p = 0.449$ ; least-squares linear model for FF: slope = -0.0002, intercept = 0.943,  $R^2 = 0.192$ ,  $p = 0.325$ ).

### Carbonate reference materials

Table 3 shows the influence of the choice of reference gas  $\delta^{13}\text{C}$  values and choice of <sup>17</sup>O correction method on the  $\Delta_{47}$  values for seven carbonate reference materials. Under the Santrock method, the difference between the FC and FF reference frames across all seven carbonates is approximately 0.06 ‰, which can correspond to 15–65°C discrepancies in temperature estimates depending on the absolute value of  $\Delta_{47}$ . The Brand method, however, yields a negligible difference in  $\Delta_{47}$ . ETH 1 and 2 are considered to have a formation temperature of 600°C,<sup>[28]</sup> and the Brand method produces  $\Delta_{47}$  results for these two materials that are indistinguishable from each other. The calculated  $\Delta_{47}$  values for ETH 1 and 2 are not in agreement if the Santrock method is used.

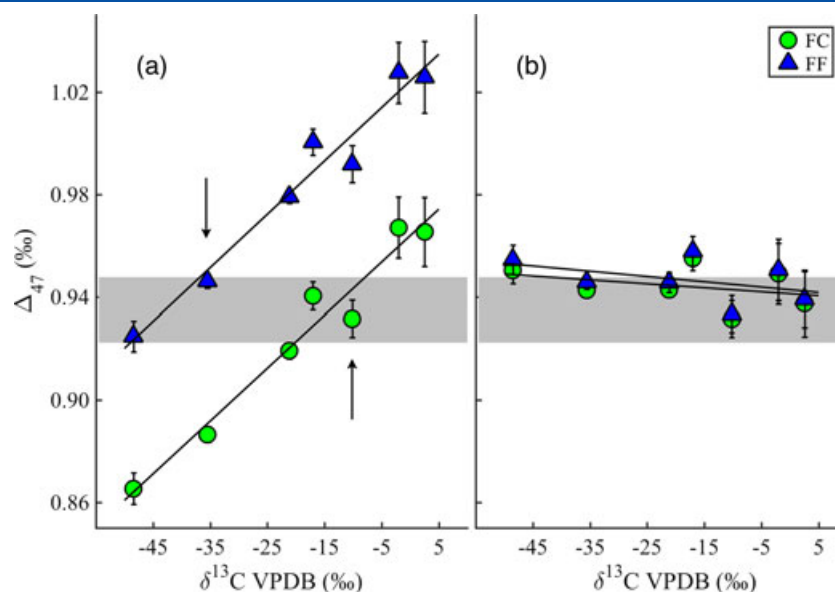
### Synthetic calcites

When the synthetic calcite data are compiled using the Santrock method, samples relatively depleted in <sup>13</sup>C have lower growth temperature  $\Delta_{47}$  values than samples that were relatively enriched in <sup>13</sup>C (Fig. 3(a)). When the data are compiled using the Brand method, as shown by Kelson *et al.*,<sup>[14]</sup> samples grown at the same temperature with widely differing <sup>13</sup>C compositions have  $\Delta_{47}$  values that are within measurement error of each other (Fig. 3(b)). Table 4 shows the regression coefficients for each of the calcite growth experiments. The slopes and intercepts among the different experiments become more similar to each other when the data

**Table 2.** Comparison of fermented corn (FC) and fossil fuel (FF) reference frame regressions by gas equilibration temperature

Gas	Slope	t	t crit	df	p	Intercept	t	t crit	df	p
Santrock										
FC 5 vs	-0.00129	0.155	3.745	24	0.878	0.08437	4.705	3.745	24	<0.0001
FF 5	-0.00137					0.01761				
FC 60 vs	-0.00099	0.730	3.792	22	0.473	-0.14635	4.173	3.792	22	0.0004
FF 60	-0.00129					-0.19831				
FC 1000 vs	-0.00114	0.073	3.500	49	0.942	-0.86745	7.106	3.500	49	<0.0001
FF 1000	-0.00112					-0.91935				
Brand										
FC 5 vs	-0.00033	0.029	3.745	24	0.977	0.08416	0.820	3.745	24	0.420
FF 5	-0.00034					0.07251				
FC 60 vs	-0.00001	0.596	3.792	22	0.557	-0.14644	0.648	3.792	22	0.524
FF 60	-0.00026					-0.14355				
FC 1000 vs	-0.00018	0.308	3.500	49	0.759	-0.86650	0.129	3.500	49	0.898
FF 1000	-0.00010					-0.86391				

The test statistic (t), critical value (t crit), degrees of freedom (df), and probability (p) of rejecting the null hypothesis when it should have been accepted. The null hypotheses being tested are that the slopes are equal or that the intercepts are equal. This table shows that the FC and FF reference gases exhibit equal slopes but different intercepts for all temperatures when the Santrock method is used. The FC and FF gases exhibit equal slopes and intercepts under the Brand method. Note that for a given reference frame (FC or FF) the formal calculation of a reference frame slope<sup>[9]</sup> takes into account all the gases at all temperatures (n = 76 for the FC reference frame, and n = 31 for the FF reference frame to calculate a single slope). Here, for the purposes of this statistical test, we have taken a more conservative approach and used only single temperature gases to calculate the slope.



**Figure 2.** Mean  $\Delta_{47}$  values for gases equilibrated at 23°C across a range of  $^{13}\text{C}$  compositions: data compiled with (a) the Santrock  $^{17}\text{O}$  correction method and (b) the Brand  $^{17}\text{O}$  correction method. Green circles are data projected into the FC reference frame while blue triangles are data projected into the FF reference frame. Error bars are standard error of the mean. The horizontal gray bar shows the calculated  $\Delta_{47}$  value for 23°C (0.935 ‰) with a thickness of the largest standard error (0.013 ‰). Arrows in (a) indicate the samples that have identical  $^{13}\text{C}$  composition to that of the  $\text{CO}_2$  used to build the reference frame. Furthermore, those arrowed samples are indistinguishable from the expected 23°C value of 0.935 ‰.

**Table 3.** In-house and inter-laboratory carbonate reference materials calibrated under four regimes: the fermented corn reference frame (FC) using Santrock, the fossil fuel reference frame (FF) using Santrock, and then both FC and FF using the Brand  $^{17}\text{O}$  correction method

Carbonate Reference Material	n	$\Delta_{47}$ 1 $\sigma$ (‰)	$\Delta_{47}$ Mean FC Santrock (‰)	$\Delta_{47}$ Mean FF Santrock (‰)	$\Delta_{47}$ Mean FC Brand (‰)	$\Delta_{47}$ Mean FF Brand (‰)
Coral	11	0.017	0.721	0.780	0.703	0.704
C64	16	0.019	0.624	0.683	0.606	0.607
C2	7	0.017	0.514	0.572	0.598	0.602
ETH 1	8	0.017	0.314	0.372	0.287	0.287
ETH 2	12	0.017	0.280	0.338	0.280	0.281
ETH 3	6	0.021	0.719	0.779	0.694	0.694
ETH 4	7	0.015	0.533	0.592	0.533	0.535

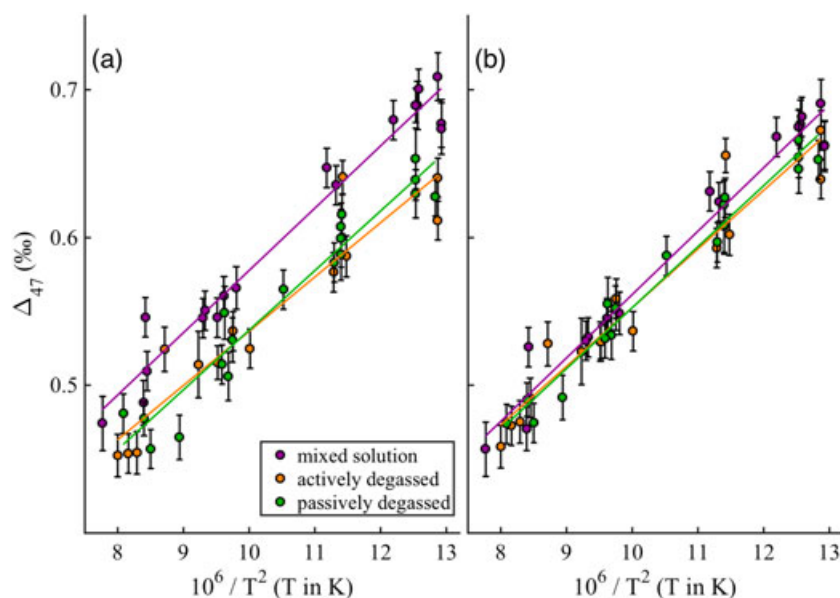
The reference frame details and ETF for each of these four reference frames are provided in Table 1. The standard deviation (1 $\sigma$ ) is shown and is identical to the fourth decimal place among all regimes, respective to the specific carbonate material. All samples were digested in 90°C acid, and the data have been corrected to 25°C acid digestions using an acid fractionation factor of 0.082 ‰.<sup>[32]</sup>

are calculated using the Brand method. Note that when the Brand method is used, the slope increases for all experiments compared with the Santrock method.

## DISCUSSION

The choice of  $^{17}\text{O}$  correction can significantly affect the accuracy of  $\Delta_{47}$  estimates by IRMS. A basic property of clumped isotope geochemistry is that samples with the same

state of ordering have the same  $\Delta_i$  value, independent of bulk isotopic composition over the range of natural abundances of rare isotopes.<sup>[26]</sup> Thus, the  $\text{CO}_2$  gases equilibrated at the same temperature in this study have nominally the same  $\Delta_{47}$  value, independent of the  $\delta^{47}$ ,  $\delta^{18}\text{O}$  or  $\delta^{13}\text{C}$  values of the  $\text{CO}_2$ . However, when the  $^{17}\text{O}$  correction scheme traditionally used for  $\Delta_{47}$  data reduction is used (Santrock method), we observe that  $\text{CO}_2$  gases equilibrated at the same temperature but with  $\delta^{13}\text{C}$  values across a 50 ‰ range produce calculated  $\Delta_{47}$  values that differ by >0.1 ‰, corresponding to a 20°C apparent



**Figure 3.** Synthetic calcites grown using a suite of methods and across a range of temperatures by Kelson *et al.*<sup>[14]</sup> and reprocessed using the Santrock method (a) and presented as published with the Brand method (b). Note that all precipitation methods collapse onto a single calibration when the Brand method is used.

difference in equilibration temperature. This discrepancy practically disappears when the more recent <sup>17</sup>O correction scheme is used (Brand method).

When the sample gas <sup>13</sup>C composition is similar to that of the reference frame gas, the difference between the Santrock and Brand methods is negligible. Figure 2(a) shows the same 23°C CO<sub>2</sub>-H<sub>2</sub>O equilibration samples projected, independently, into both the FC and the FF reference frames. Note that the correct Δ<sub>47</sub> value reflecting 23°C is obtained when the sample <sup>13</sup>C composition is most similar to that of the reference frame gas (i.e. a sample equilibrated at 23°C with FF cylinder CO<sub>2</sub> yields a Δ<sub>47</sub> value corresponding to 23°C equilibration only when projected into the FF reference frame). Similarly, the lack of sensitivity of Δ<sub>47</sub> values to the choice of <sup>17</sup>O-correction parameters found by Affek and Eiler<sup>[7]</sup> (variation of ±0.002 ‰ when λ varies from 0.5 to 0.528) might be explained by the sample gas having a bulk isotopic composition similar to that of the mass spectrometer working gas. Figure 4 shows the difference between the Santrock and

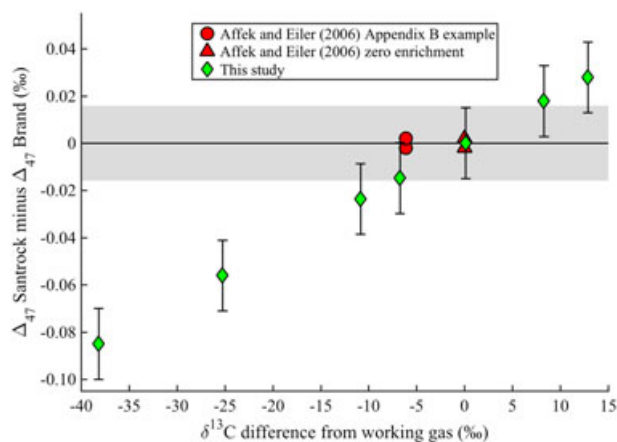
Brand methods for the 23°C CO<sub>2</sub>-H<sub>2</sub>O equilibration samples expressed against the difference from the mass spectrometer working gas. While it is unclear exactly what the sample and working gases were in Affek and Eiler<sup>[7]</sup> to calculate the ±0.002 ‰, Fig. 4 also shows two possible scenarios: (1) the sample and reference gas are identical (zero-enrichment), or (2) the sample is that of the example calculation in appendix B of the said paper. When the mass spectrometer working gas and reference frame gas are considered, Affek and Eiler<sup>[7]</sup> and this study are in agreement.

Another example showing how the choice of <sup>17</sup>O correction, the choice of reference frame gas, and the choice of mass spectrometer working gas can all produce inter-laboratory inconsistencies is illustrated by our FC and FF hypothetical inter-laboratory comparison (Table 3). The two hypothetical labs constructed distinct reference frames (Fig. 1 and Table 2). Use of the traditional Santrock <sup>17</sup>O correction elicits a difference between the two hypothetical labs when they constructed reference frames with FC or FF gases while the

**Table 4.** Regression coefficients for the synthetic calcite experiments

Regression	Slope ± 1 SE	Intercept ± 1 SE	r <sup>2</sup>	T Range (°C)	n
<i>Santrock <sup>17</sup>O correction</i>					
actively degassed	0.0367 ± 0.0039	0.169 ± 0.040	0.888	6 to 80	13
passively degassed	0.0403 ± 0.0026	0.133 ± 0.028	0.937	6 to 80	18
mixed solution	0.0421 ± 0.0012	0.156 ± 0.024	0.963	6 to 85	18
<i>Brand <sup>17</sup>O correction</i>					
actively degassed	0.0369 ± 0.0035	0.155 ± 0.035	0.921	6 to 80	13
passively degassed	0.0412 ± 0.0018	0.139 ± 0.019	0.970	6 to 80	18
mixed solution	0.0429 ± 0.0020	0.132 ± 0.021	0.967	6 to 85	18

The acid digestion temperature was 90 °C and no acid fractionation factor has been used. The p-value for every regression regardless of data compilation method is <0.001. Data are from Kelson *et al.*<sup>[14]</sup> and descriptions of the precipitation methods can be found therein.

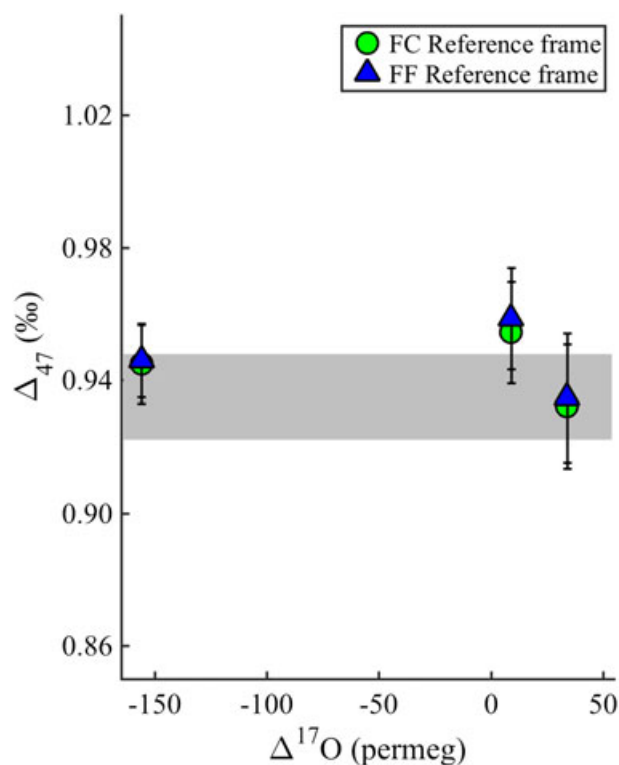


**Figure 4.** 23°C CO<sub>2</sub>-H<sub>2</sub>O equilibration data (FC reference frame) from Figs. 2(a) and 2(b) recast (green diamonds) as the Δ<sub>47</sub> difference between the Santrock and Brand <sup>17</sup>O correction methods on the y-axis and the δ<sup>13</sup>C difference of those samples from the mass spectrometer working gas on the x-axis. Error bars are a typical/nominal 0.015 ‰ standard deviation on Δ<sub>47</sub>. Note the Brand and Santrock methods do not differ from each other when the sample gas is similar to the mass spectrometer working gas. Affek and Eiler<sup>[7]</sup> state a variation of ±0.002 ‰ in Δ<sub>47</sub> across a range in λ from 0.5 to 0.528. We do not know what sample was used to make this estimate and as such we have plotted this variation under two scenarios: (1) the Affek and Eiler<sup>[7]</sup> example calculation from Appendix B uses a sample with a δ<sup>13</sup>C value of -9.801 ‰ VPDB with a working gas of δ<sup>13</sup>C value of -3.698 ‰ VPDB, and (2) assuming a zero-enrichment, the working gas measured against itself.

more recently proposed Brand <sup>17</sup>O correction provides indistinguishable results for carbonate reference materials. Even if all laboratories constructed the reference frame using identical methods, inaccurate Δ<sub>47</sub> values that depend on sample <sup>13</sup>C composition could still result from the traditional Santrock <sup>17</sup>O correction. Similarly, for a single laboratory using equilibrated CO<sub>2</sub> with differing <sup>13</sup>C compositions, the traditional <sup>17</sup>O correction could lead to reference frame scatter, change in slope or departures from a linear δ<sup>47</sup>-Δ<sub>47</sub> relationship, systematic scale compression, or all the above.

In light of these observations, we echo the recommendation of Brand *et al.*<sup>[18]</sup> that all researchers measuring CO<sub>2</sub> via IRMS use a λ value of 0.528 and K value of 0.01022461 to correct for <sup>17</sup>O interference on measurements of δ<sup>13</sup>C values unless <sup>17</sup>O has been measured and/or alternative λ and K values are warranted. While we have shown a higher level of Δ<sub>47</sub> accuracy with the Brand method, it is likely that further improvements will come with measurement of <sup>17</sup>O for each CO<sub>2</sub> analyzed. The <sup>17</sup>O composition of equilibration waters should also be considered as it may have an effect.<sup>[30]</sup> Here we use waters with very different Δ<sup>17</sup>O values but see no evidence of a detectable influence on the Δ<sub>47</sub> values (Fig. 5). It is unclear if future improvements will arise when one controls for the <sup>17</sup>O composition of equilibration waters. A good physical basis exists<sup>[18]</sup> and the empirical observations presented here support use of the Brand method now.

Our synthetic carbonate data comparison showcases the effect of <sup>17</sup>O correction method on carbonate Δ<sub>47</sub>-temperature calibrations. Using the traditional <sup>17</sup>O correction scheme, data for synthetic carbonates<sup>[14]</sup> precipitated using a suite of



**Figure 5.** Mean Δ<sub>47</sub> values for gases equilibrated at 23°C grouped by the equilibration waters (evaporatively enriched, local deionized tap water, and South Pole ice core water) compiled with the Brand <sup>17</sup>O correction method. Green circles are data projected into the FC reference frame while blue triangles are data projected into the FF reference frame. Error bars are standard deviation. The horizontal gray bar is as in Fig. 2.

methods, including those used in previous calibration studies (e.g.,<sup>[12,31]</sup>), define Δ<sub>47</sub>-temperature calibrations that differ significantly from one another. The systematic offset in calibration lines could be interpreted as a function of CO<sub>2</sub> degassing rate during carbonate precipitation, with more slowly degassed 'mixed solution' carbonates showing the highest Δ<sub>47</sub> values. However, this apparent relationship is an artifact of the difference in δ<sup>13</sup>C values for carbonates synthesized with and without CO<sub>2</sub> bubbling through the precipitating solution. Using the proposed <sup>17</sup>O correction coefficients of Brand *et al.*,<sup>[18]</sup> all the synthetic carbonate data collapse onto a single calibration curve. A full reevaluation of previously published calibration data is beyond the scope of this study, particularly given that the <sup>13</sup>C compositions of synthetic carbonates are rarely reported, not to mention the bulk isotopic compositions of the reference frame gases and mass spectrometer working gases. Furthermore, if ever completed, a reevaluation of some previously published data might yield no difference given the early result of Affek and Eiler<sup>[7]</sup> showing no sensitivity to the choice of λ. Nevertheless, our results show that the traditional <sup>17</sup>O correction method potentially leads to inaccurate Δ<sub>47</sub> values, including systematic errors for different carbonate precipitation methods and reference frames. We suggest the <sup>17</sup>O correction coefficients may be partially responsible for discrepancies among previously published Δ<sub>47</sub>-T calibrations.



## CONCLUSIONS

The data presented in this study, along with those previously presented<sup>[15]</sup> and associated new work,<sup>[30]</sup> clearly demonstrate the potential for a dependence of calculated  $\Delta_{47}$  values on the choice of <sup>17</sup>O correction. The <sup>17</sup>O correction scheme originally proposed for  $\Delta_{47}$  data reduction can result in inter-laboratory discrepancies and inaccurate calculated  $\Delta_{47}$  values. Examples highlighted here include systematic,  $\delta^{13}\text{C}$ -dependent errors in the calculated  $\Delta_{47}$  of CO<sub>2</sub> gases equilibrated at the same temperature; equilibrated CO<sub>2</sub> reference frame gases; ETH and intra-laboratory carbonate reference materials; and synthetic calcites precipitated using different methods. The more recently proposed <sup>17</sup>O correction scheme of Brand *et al.*<sup>[18]</sup> eliminates the discrepancy among  $\Delta_{47}$  values for CO<sub>2</sub> gases equilibrated at the same temperature and provides consistent results for carbonate reference materials formed at the same temperature, regardless of the sample or reference frame gas <sup>13</sup>C composition.

Our results imply that discrepancies among previous carbonate clumped isotope thermometer calibrations might have been caused by the choice of <sup>17</sup>O correction methods and associated artifacts that result from differences among sample, reference frame, and/or working gas bulk isotopic compositions. The potential magnitude of such effects is illustrated by both the hypothetical inter-laboratory comparison exhibiting better agreement and the Kelson *et al.*<sup>[14]</sup> synthetic carbonate dataset showing that disparate precipitation methods collapse onto a single calibration curve when Brand *et al.*<sup>[18]</sup> values are used. Lack of discrepancies among clumped isotope thermometers spanning a large range in <sup>13</sup>C composition is also possible as recently suggested by Daëron *et al.*<sup>[30]</sup> Our results suggest that it is the choice of <sup>17</sup>O correction, the <sup>13</sup>C composition of the reference frame gas, and the <sup>13</sup>C composition of the mass spectrometer working gas that might contribute to a discrepancy.

Ideally, we would measure the <sup>17</sup>O composition of all materials and provide sample- and standard-specific  $\lambda$  values to correct for <sup>17</sup>O mass interference. However, until such measurements are practical, our conclusion is aligned with that of Brand *et al.*<sup>[18]</sup> who proposed that researchers measuring CO<sub>2</sub> via IRMS should use a  $\lambda$  value of 0.528 and K value of 0.01022461 because these are the most reasonable values for a species such as CO<sub>2</sub> whose oxygen composition is largely determined by water. We recommend that the CO<sub>2</sub> and carbonate clumped isotope community begin to critically consider the choice of  $\lambda$  and K and its impact on the accuracy of  $\Delta_{47}$  values. To evaluate the potential <sup>17</sup>O correction sensitivity of previously published works, researchers should consider the data processing method (Santrock, Brand, or other) as well as the isotopic difference among sample gas, reference frame gas, and mass spectrometer working gas, where larger differences among these gases coupled with the Santrock <sup>17</sup>O correction might make for larger discrepancies in  $\Delta_{47}$  values. While it seems impractical to reevaluate the entire body of CO<sub>2</sub> clumped isotope data, perhaps a first step could be to reevaluate all  $\Delta_{47}$ -T calibrations as this dataset is used most heavily. Furthermore, until improved  $\lambda$  and K values are available and <sup>17</sup>O measurement in CO<sub>2</sub> samples is routine for clumped isotopes, we advocate using those values reasoned by Brand *et al.*<sup>[18]</sup>

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