Chemical Geology 441 (2016) 83–96

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Absolute isotopic abundance ratios and the accuracy of Δ_{47} measurements

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ARTICLE INFO

Article history:
Received 17 April 2016
Received in revised form 1 August 2016
Accepted 8 August 2016
Available online 12 August 2016

Keywords:
Clumped isotopes
Triple oxygen isotopes
Oxygen-17 anomalies
Absolute isotopic abundance ratios

ABSTRACT

Clumped isotope measurements aim to quantify some statistical properties of the isotopologue population in a given sample, which requires prior knowledge of the absolute isotopic abundance ratios in reference materials such as VSMOW or VPDB. In the case of CO_2, matters are further complicated by the need to define a mass-dependent fractionation law linking the three stable isotopes of oxygen. Conversion from raw mass spectrometric data to mass-47 anomalies (Δ_{47}) thus relies on four external parameters: the ($^{13}C/^{12}C$) ratio of VPDB, the ($^{17}O/^{16}O$) and ($^{18}O/^{16}O$) ratios of VSMOW (or VPDB-CO_2), and the slope of the triple oxygen isotope line (λ). Here we investigate the influence that these isotopic parameters exert on measured Δ_{47} values, using (a) real-world data corresponding to seven months of measurements; (b) simple simulations based on randomly generated data; (c) precise comparisons between water-equilibrated CO_2 samples and between carbonate standards believed to share quasi-identical Δ_{47} values; and (d) reprocessing of two carbonate calibration data sets with different slopes of Δ_{47} versus T.

We demonstrate that the use of different sets of isotopic parameters generally produces systematic offsets as large as 0.04‰ in measured Δ_{47} values, even after following the established standardization procedures. What's more, even using a single set of isotopic parameters can produce intra- and inter-laboratory discrepancies in measured Δ_{47} values, if some of these parameters are inaccurate, and depending on the isotopic compositions of the standards used for conversion to the absolute scale of Dennis et al. (2011), these errors should correlate strongly with either $\delta^{13}C$ or $\delta^{18}O$, or more weakly with both. Based on measurements of samples expected to display quasi-identical Δ_{47} values, such as 25 °C water-equilibrated CO_2 with different carbon and oxygen isotope compositions, or high-temperature standards ETH-1 and ETH-2, we conclude that the traditional set of isotopic parameters used in all early clumped isotope studies produces large, systematic errors controlled by the relative bulk isotopic compositions of samples and standards. These errors are likely to be one of the key factors responsible for current inter-laboratory discrepancies, but cannot easily explain the conflicting carbonate calibration slopes obtained by different groups. By contrast, the isotopic parameters of Brand et al. (2010) appear to yield accurate Δ_{47} values regardless of bulk isotopic composition. Based on these findings, we offer recommendations aiming to minimize errors related to the choice of isotopic parameters.

1. Introduction

In natural molecular materials, to a first-order approximation, stable isotopes combine into isotopologues according to a stochastic distribution. As a result, if "bulk" isotopic abundance ratios such as ($^{13}C/^{12}C$) or ($^{18}O/^{16}O$) are known, the abundance of each isotopologue may be computed, using only statistical distribution rules, to a reasonably good level of accuracy. Conversely, bulk isotope ratios can be directly calculated from the abundances of singly-substituted isotopologues such as $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$. Although this approximation remains valid for most measurements of bulk isotope ratios, many types of materials are nevertheless expected to display detectable deviations from stochastic distribution in multiply-substituted isotopologues (e.g., Wang et al., 2004; Schauble et al., 2006). Clumped isotope geochemistry is the study of such stochastic anomalies in natural materials, and has experienced rapid progress over the past decade (e.g., Eiler and Schauble, 2004; Ghosh et al., 2006; Eiler, 2007, 2011; Yeung et al., 2012; Stolper et al., 2014), along with significant methodological advances (e.g., Huntington et al., 2009; Dennis et al., 2011; He et al., 2012).

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http://dx.doi.org/10.1016/j.chemgeo.2016.08.014

So far, a majority of clumped isotope studies have targeted carbonate minerals and CO_2, with a wide range of scientific applications including paleoclimatology, thermal and diagenetic histories of crustal rocks, biomineralization processes, and atmospheric CO_2 studies. Such applications rely on measurements of Δ_{47}, a statistical parameter closely related to the stochastic anomaly in $^{16}O^{13}C^{18}O$. Today, these measurements are routinely standardized either by comparison to CO_2 samples with a known Δ_{47} value (thermodynamic gas standards), as described by Dennis et al. (2011), or using a set of *ad hoc* international carbonate standards whose composition has been tied to that of thermodynamic gas standards (Meckler et al., 2014). In theory, this ensures that all modern clumped isotope measurements of CO_2 and carbonates are reported in the same metrological framework, allowing direct comparison of results from different laboratories. In practice, inter-laboratory differences remain larger than expected from instrumental precision alone (S. Bernasconi, panel discussion on interlaboratory comparisons, Fifth International Clumped Isotope Workshop, 2016). Strikingly, the calibration functions for low-temperature carbonate clumped isotope thermometry published by various groups suffer from large discrepancies (up to 0.08‰ for carbonates formed at 25 °C, which is equivalent to a difference of 20–30 °C), and the corresponding calibration slopes (i.e. temperature sensitivity of Δ_{47}) range from 2.6 to 4.4 ppm/K at 20 °C (Fig. 4 from Spencer and Kim, 2015). Even within a single laboratory, thermodynamic gas standards prepared from CO_2 of very different bulk isotope compositions can show large discrepancies, as reported by Schauer et al. (2016b). In the present study, we investigate one of the potential causes for these discrepancies, namely the effects that different data reduction procedures may have on reported, "absolute" Δ_{47} values.

Clumped isotope measurements in CO_2, and by extension in carbonate minerals, have so far relied on precise determination of relative isotopologue abundances using dual-inlet mass spectrometry (e.g., Eiler and Schauble, 2004; Huntington et al., 2009). One inherent limitation of this approach is that some independent assumptions are needed to constrain the relationship between the $\delta^{17}O$ and $\delta^{18}O$ values of any given sample. Traditionally, such ^{17}O "corrections" assume that triple oxygen isotope differences between a sample and a given reference material (e.g., VSMOW) follow a mass-dependent relationship of the form

$$\Delta^{17}O = \ln\left(R^{17}/R^{17}_{ref}\right) - \lambda\ \ln\left(R^{18}/R^{18}_{ref}\right) = 0 \tag{1}$$

where R^{17}, R^{18}, R^{17}_{ref} and R^{18}_{ref} refer to the ($^{17}O/^{16}O$) and ($^{18}O/^{16}O$) abundance ratios in the sample and an international reference material, respectively (e.g., Brand et al., 2010, and references therein). In the above equation, λ can be described as a phenomenological constant linking the oxygen isotope compositions of materials related to each other through similar fractionation processes, such as for instance most carbonates precipitated from oceanic or meteoric waters (Assonov and Brenninkmeijer, 2003a). Although the use of such a mass-dependent law is almost universal, there is no consensus regarding the choice of a reference material, nor the numerical values of R^{17}_{ref} and λ. In some cases, this is a natural consequence of studying different types of samples, such as tropospheric CO_2 (e.g., Hofmann et al., 2012) versus surface carbonate minerals. In other cases, different laboratories analyzing similar types of samples nevertheless use different ^{17}O correction parameters (e.g., for historical reasons, or because of different default software values) and rely on established standardization procedures to correct for any resulting discrepancies.

With respect to clumped isotopes, the use of a mass-dependent ^{17}O correction may bring about two different kinds of problems. Firstly, some samples may deviate significantly from the assumed mass-dependent law, exhibiting large ^{17}O anomalies ($\Delta^{17}O$ in Eq. (1)). If not taken into account in the computation of isotopologue abundance ratios, such anomalies lead to small, systematic errors in estimates of Δ_{47} (Olack and Colman, 2016), but these effects are not the focus of the present study. A second issue concerns the comparison of measurements between laboratories using slightly different ^{17}O correction parameters (or, similarly, slightly different values for R^{13}_{VPDB}). Although these differences in data processing are known to have a non-negligible effect on "raw Δ_{47}" values (Olack et al. 2013), one might expect that they would cancel out after subsequent conversion to "absolute" Δ_{47} (Affek and Eiler, 2006). Our objective here is to assess the validity of this assumption, by processing a large set of raw mass spectrometric data using different numerical values of R^{13}_{VPDB}, R^{17}_{ref}, R^{18}_{ref} and λ (hereafter collectively referred to as "isotopic parameters"). In order to focus on this specific issue, within the scope of this work we make the conventional assumption that all carbonate samples conform strictly to some version of Eq. (1), i.e., that $\Delta^{17}O = 0$ for all carbonate measurements. Although this might not be strictly the case for some samples in our data set, it should have no bearing on our conclusions regarding the use of different isotopic parameters.

2. Methods

2.1. Overview

Fig. 1 presents a schematic overview of our methodology. The raw data set is composed of "working gas" delta values for various carbonate samples and thermodynamic gas standards. These raw numbers are processed using several independent sets of isotopic parameters (R^{13}_{VPDB}, R^{17}_{ref}, R^{18}_{ref} and λ), to compute corresponding, independent sets of $\delta^{13}C$, $\delta^{18}O$ and Δ^{raw}_{47} values for each analysis. Each data set is then converted to absolute Δ_{47} values based on the thermodynamic gas standards. The final computed values for each sample are compared in order to characterize potential bias

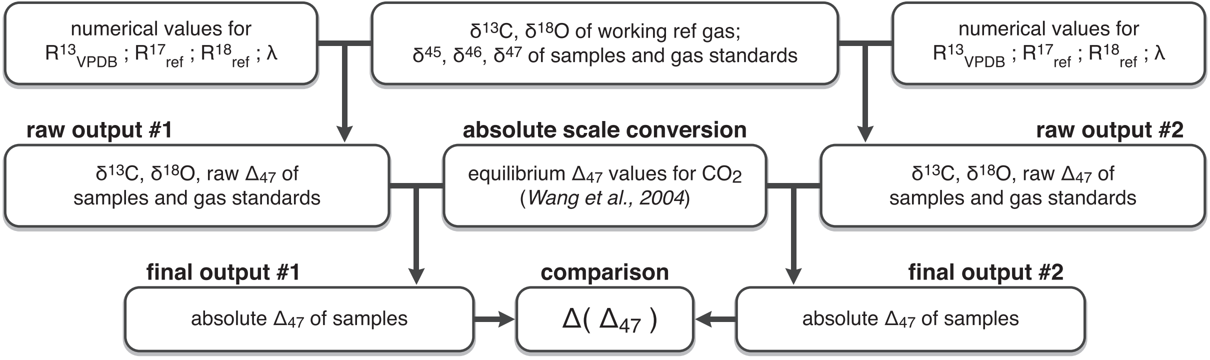

Fig. 1. Schematic overview of our data processing methodology.

introduced by the choice of isotopic parameters. Calculations are performed sequentially, using Python scripts provided as supplementary material, ensuring that all other aspects of data processing are strictly the same.

2.2. Real-world data set

The 327 measurements considered here were performed over a seven-month period from May to December 2015. All of them were analyzed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) using the same equipment and procedures. Carbonate samples between 2.6 and 4.0 mg were dissolved in a common acid bath held at 90 °C. After cryogenic removal of water, the evolved CO_2 passed through a Porapak Q column (50/80 mesh, 1 m length, 2.1 mm ID) held at −20 °C under helium 6.0 flow (25 mL/min). CO_2 was then quantitatively recollected by cryogenic trapping, and transferred by gas expansion into an Isoprime 100 dual-inlet mass spectrometer equipped with six Faraday collectors (m/z 44 to 49). Each analysis lasted about 3 h, during which sample and working reference gas were allowed to flow from matching, 10 mL reservoirs into the source, through a pair of fused silica capillaries (65 cm length, 110 μm ID). Every 20 min, gas pressures were adjusted to achieve a mass 44 current of 40 nA, with differences between sample and reference gas generally below 0.1 nA. Background currents were measured in all high-gain collectors (m/z 45 to 49) before and after each pressure adjustment, with gas flowing into the source, and are found to correlate strongly with mass 44 current.

High-temperature thermodynamic gas standards were prepared by sealing 30–35 μmol CO_2 into quartz tubes (12 cm length, 6 mm OD), heating them to 1000 °C for 2 h, followed by quenching in liquid nitrogen immediately before analysis. Low-temperature thermodynamic gas standards were prepared by sealing 30–35 μmol CO_2 into borosilicate tubes pre-loaded with 60 μL water, followed by equilibration in a water bath at 25 °C for a minimum of three full days. All thermodynamic gas standards were prepared from a single tank of CO_2, and thus had very similar $\delta^{13}C_{VPDB}$ values around −3.6‰. $\delta^{18}O_{VPDB\text{-}CO_2}$ values (including those of 1000 °C standards) varied from −28‰ to +11‰ as a result of equilibration with waters of different isotopic composition, either collected from high-latitude precipitation or prepared by evaporative enrichment of local deionized water. To the best of our knowledge, all published Δ_{47} studies have so far assumed that water-equilibrated and carbonate-evolved CO_2 conform to the same triple oxygen isotope law. Although this is unlikely to be strictly the case, this discrepancy is expected to manifest as a small, constant error (Fig. 2) between water-equilibrated CO_2 and carbonate-derived samples, and initially we do not attempt to address this particular issue. We do, however, take into account ^{17}O anomalies (ranging from −88 to +15 ppm relative to VSMOW, with $\lambda = 0.528$) in all waters used to prepare the 1000 °C and 25 °C gas standards. These $\Delta^{17}O$ values were measured at LSCE by A. Landais using water fluorination (Barkan and Luz, 2005; Landais et al., 2012), and are explicitly accounted for in subsequent calculations.

Owing to the use of a fully automated preparation system, sample trapping and purification protocols did not significantly differ between gas standards and carbonates, nor between individual samples. Analyses are grouped into four distinct "sessions", each corresponding to several weeks of continuous measurements. For each of the 327 measurements, the following information is recorded: a unique identification number; a session identifier; for thermodynamic gas standards, the temperature of CO_2 equilibration (25 °C or 1000 °C); the carbon and oxygen isotopic composition of the working reference gas relative to VPDB-CO_2 (defined as CO_2 produced by reacting virtual VPDB calcite with phosphoric acid at 25 °C); and the differences in background-corrected ion beam intensity ratios between analyte and working reference gases, noted δ^{45} to δ^{49}.

2.3. Random data simulations

In addition to the raw data set described in the previous section, we can randomly generate raw data corresponding to an arbitrary number of simulated measurements. In order to do so, we start with random "true" values for $\delta^{13}C_{VPDB}$, $\delta^{18}O_{VPDB\text{-}CO_2}$, Δ_{47}, and, in some cases (see below), for bulk isotopic composition of the working reference gas. Thermodynamic gas standards can be generated in the same way, but with non-random Δ_{47} based on the theoretical values of Wang et al. (2004). Using an arbitrarily chosen set of isotopic parameters, these numbers are then converted to "working gas" delta values (δ^{45} to δ^{49}), and can be subsequently processed following the exact same procedures as for real-world measurements. In order to focus purely on data processing effects (as opposed to machine-specific analytical artifacts), we assume "perfect" mass spectrometric measurements with no compositional nonlinearities and no isotopic scrambling ($\Delta_{47}^{raw} = \Delta_{47}$).

2.4. Choice of isotopic parameters

Each set of isotopic parameters considered hereafter is defined by the numerical values of R^{13}_{VPDB}, R^{18}_{ref}, R^{17}_{ref}, and λ.

R^{13}_{PDB} was initially determined by Craig (1957), based on earlier measurements of isotope abundance ratios in air and limestone-derived CO_2 by Nier (1950), and assuming a mass-dependent oxygen fractionation exponent of $\lambda = 0.5$ between them. Subsequently, Chang and Li (1990) reported a slightly lower value based on comparisons between NBS carbonate standards and precisely calibrated mixtures of ^{13}C-depleted and ^{13}C-enriched $BaCO_3$. The latter was accepted as reference value by the International Union of Pure and Applied Chemistry (Rosman and Taylor, 1998).

Similarly, R^{18}_{VSMOW} was measured by Baertschi (1976) by comparison with calibrated mixtures of $D_2^{18}O$ and $H_2^{16}O$. Although VSMOW may be used to anchor the mass-dependent oxygen fractionation law defined by Eq. (1), a more natural reference for CO_2 and carbonate samples is VPDB-CO_2, whose R^{18} value can be computed from the oxygen isotope composition of VPDB relative to VSMOW

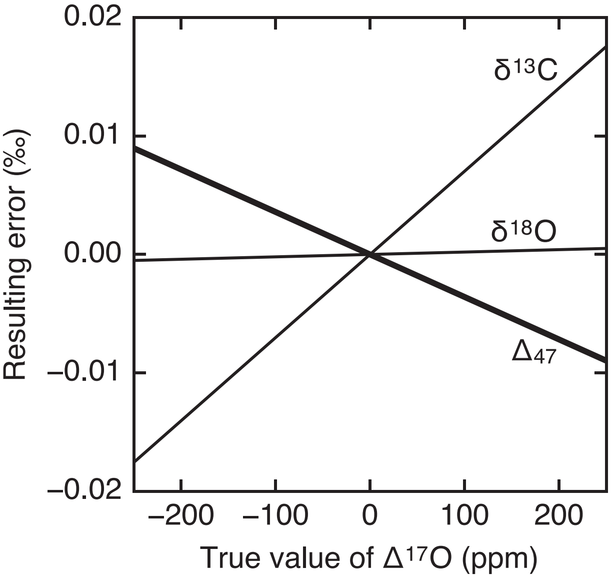

Fig. 2. Errors resulting from wrongly assuming $\Delta^{17}O = 0$. An ^{17}O anomaly of +0.1‰, if not accounted for, causes computed $\delta^{13}C$, $\delta^{18}O$ and Δ_{47} values to be off by +0.0070‰, +0.0002‰ and −0.0036‰ respectively. These errors are calculated for a stochastic sample with the same bulk isotopic composition as VPDB-CO_2, using the isotopic parameters of Brand et al. (2010), but would not change much for different values of $\delta^{13}C$, $\delta^{18}O$ and Δ_{47} nor for different sets of isotopic parameters. Source code provided as supplementary material.

($\delta^{18}O = 30.92‰$, Coplen et al., 1983) and the 25 °C acid fractionation factor of 1.01025 from Friedman and O'Neil (1977):

$$R^{18}_{\text{VPDB-CO}_2} = R^{18}_{\text{VSMOW}} \times 1.03092 \times 1.01025 \qquad (2)$$

Several values for R^{17}_{VSMOW} and $R^{17}_{\text{VPDB-CO}_2}$ have been reported over the years (cf Table 1 from Assonov and Brenninkmeijer 2003a). For example, Li et al. (1988) were able to constrain the ratio (R^{17}/R^{13}) in VSMOW by comparing the abundance of mass-45 isotopologues in CO_2 prepared from isotopically normal and ^{17}O-depleted O_2. Another determination of this ratio was obtained by Assonov and Brenninkmeijer (2003b) using a similar method, updated to correct for known instrumental effects. It should be noted that both of these measurements provide estimates of R^{17}_{VSMOW} which scale linearly with the value of R^{13}_{VPDB}.

Finally, as noted above, the λ parameter should not be interpreted as reflecting a single fractionation process but rather as a phenomenological description of a population of samples. For example, Gonfiantini et al. (1995) recommended the use of $\lambda = 0.5164$ based on the oxygen isotope compositions of 35 terrestrial samples including waters and rocks (Matsuhisa et al., 1978). Alternatively, Assonov and Brenninkmeijer (2003a) argued that the oxygen isotope composition of most carbonates is ultimately derived from the global water pool, so that the corresponding value $\lambda = 0.528$ (Meijer and Li, 1998; Barkan and Luz, 2005) should be used instead, and they subsequently assumed a mass-dependent oxygen fractionation exponent of $\lambda = 0.528$ between VMOW and VPDB-CO_2 (Assonov and Brenninkmeijer, 2003b):

$$R^{17}_{\text{VPDB-CO}_2} = R^{17}_{\text{VSMOW}} \times (1.03092 \times 1.01025)^{\lambda} \qquad (3)$$

In the present study, we consider the following combinations of isotopic parameters. The [*Gonfiantini*] parameters are those originally used by the Caltech group (Huntington et al., 2009, online supporting information), and, to the best of our knowledge, by most clumped isotope laboratories today. It uses the R^{13}_{PDB} value of Craig (1957), and defines VSMOW as the reference material in the triple oxygen isotope equation, with the R^{17}_{VSMOW} value of Li et al. (1988) and $\lambda = 0.5164$ after Matsuhisa et al. (1978). The other combinations of parameters considered here use a value of $\lambda = 0.528$ and each of them is named according to their choice of values for R^{13}_{VPDB} and R^{17}_{VSMOW}. For instance, the [*Craig* + *Li*] combination uses the R^{13}_{PDB} value of Craig (1957) and the R^{17}_{VSMOW} value of Li et al. (1988). It should be noted that the [*Chang* + *Assonov*] parameters are identical to those proposed by Brand et al. (2010), and for the sake of brevity we may use [*Chang* + *Assonov*] and [*Brand*] as equivalent labels.

All numbers corresponding to these five sets of parameters are listed in Table 1, and the corresponding triple oxygen isotope lines are plotted in Fig. 3.

2.5. Calculation of $\delta^{13}C$, $\delta^{18}O$ and Δ^{raw}_{47} values

Regardless of which isotopic parameters are selected, computing the carbon and oxygen isotope composition of a given analyte requires solving an equation of the form

$$-3\,K^2\,(R^{18})^{2\lambda} + 2\,KR^{45}\,(R^{18})^{\lambda} + 2\,R^{18} - R^{46} = 0 \qquad (4)$$

where R^{18} is the ($^{18}O/^{16}O$) ratio in the analyte; R^{45} and R^{46} the CO_2 mass ratios (45/44) and (46/44); and $K = R^{17}_{\text{ref}}(R^{18}_{\text{ref}})^{-\lambda}$

Table 1

All sets of isotopic parameters considered in this study. [*Brand*] and [*Chang* + *Assonov*] are formulated relative to different oxygen reference materials but are nevertheless strictly equivalent. Note that for reasons of consistency, the Brand et al. (2010) value for $R^{18}_{\text{VPDB-CO}_2}$ listed here is slightly greater than that originally reported, but this difference is entirely negligible in the context of the present study.

Designation	Isotopic parameters	Sources
[*Gonfiantini*]	$R^{13}_{\text{PDB}} = 0.0112372$ $R^{18}_{\text{VSMOW}} = 0.0020052$ $R^{17}_{\text{VSMOW}} = 0.0003799$ $\lambda = 0.5164$	Craig (1957) Baertschi (1976) Li et al. (1988) Matsuhisa et al. (1978)
[*Brand*] [*Chang* + *Assonov*]	$R^{13}_{\text{VPDB}} = 0.01118$ $R^{18}_{\text{VSMOW}} = 0.0020052$ $R^{17}_{\text{VSMOW}} = 0.00038475$ $R^{18}_{\text{VPDB-CO}_2} = 0.00208839$ $R^{17}_{\text{VPDB-CO}_2} = 0.00039310$ $\lambda = 0.528$	Chang and Li (1990) Baertschi (1976) Assonov and Brenninkmeijer (2003b), rescaled to R^{13}_{VPDB} Derived from R^{18}_{VSMOW} using Eq. (2) Assonov and Brenninkmeijer (2003b), rescaled to R^{13}_{VPDB} Barkan and Luz (2005)
[*Craig* + *Assonov*]	$R^{13}_{\text{PDB}} = 0.0112372$ $R^{18}_{\text{VSMOW}} = 0.0020052$ $R^{17}_{\text{VSMOW}} = 0.00038672$ $\lambda = 0.528$	Craig (1957) Baertschi (1976) Assonov and Brenninkmeijer (2003b) Barkan and Luz (2005)
[*Chang* + *Li*]	$R^{13}_{\text{VPDB}} = 0.01118$ $R^{18}_{\text{VSMOW}} = 0.0020052$ $R^{17}_{\text{VSMOW}} = 0.0003780$ $\lambda = 0.528$	Chang and Li (1990) Baertschi (1976) Li et al. (1988), rescaled to R^{13}_{VPDB} Barkan and Luz (2005)
[*Craig* + *Li*]	$R^{13}_{\text{PDB}} = 0.0112372$ $R^{18}_{\text{VSMOW}} = 0.0020052$ $R^{17}_{\text{VSMOW}} = 0.0003799$ $\lambda = 0.528$	Craig (1957) Baertschi (1976) Li et al. (1988) Barkan and Luz (2005)
[*Barkan*]	$R^{13}_{\text{VPDB}} = 0.01118$ $R^{18}_{\text{VPDB-CO}_2} = 0.00208839$ $R^{17}_{\text{VPDB-CO}_2} = 0.00039301$ $\lambda = 0.528$	Chang and Li (1990) Derived from R^{18}_{VSMOW} using Eq. (2) $\Delta^{17}O = -0.227$ vs VSMOW (Barkan et al., 2015) Barkan and Luz (2005)
[*Passey*]	$R^{13}_{\text{VPDB}} = 0.01118$ $R^{18}_{\text{VPDB-CO}_2} = 0.00208839$ $R^{17}_{\text{VPDB-CO}_2} = 0.00039305$ $\lambda = 0.528$	Chang and Li (1990) Derived from R^{18}_{VSMOW} using Eq. (2) $\Delta^{17}O = -0.135$ vs VSMOW (Passey et al., 2014) Barkan and Luz (2005)

(Santrock et al., 1985). In the more general case of an independently known or assumed value for Δ^{17}O, the K parameter becomes

$$\mathrm{K} = \exp(\Delta^{17}\mathrm{O})\mathrm{R}^{17}_{\mathrm{ref}}\left(\mathrm{R}^{18}_{\mathrm{ref}}\right)^{-\lambda} \tag{5}$$

Although Eq. (4) generally has no analytical solution, it can be solved to a very good approximation by conversion to a second-order Taylor polynomial, allowing δ^{18}O and δ^{13}C values to be determined with an accuracy better than 0.02 ppm (computational details in Appendix A; Python and Excel implementations provided as supplementary material). Raw Δ_{47} values are then calculated in the usual way, as described by Huntington et al. (2009):

$$\Delta_{47}^{\mathrm{raw}} = \left(\frac{\mathrm{R}^{47}_{\mathrm{measured}}}{\mathrm{R}^{47}_{\mathrm{stochastic}}} - 1\right) - \left(\frac{\mathrm{R}^{46}_{\mathrm{measured}}}{\mathrm{R}^{46}_{\mathrm{stochastic}}} - 1\right) - \left(\frac{\mathrm{R}^{45}_{\mathrm{measured}}}{\mathrm{R}^{45}_{\mathrm{stochastic}}} - 1\right) \tag{6}$$

It might be noted that the last two terms in this formula should both be equal to zero as a consequence of Eq. (4). Using the Taylor polynomial approximation mentioned above, they indeed never exceed 0.02 ppm, so that Eq. (6) can be simplified to

$$\Delta_{47}^{\mathrm{raw}} = \frac{\mathrm{R}^{47}_{\mathrm{measured}}}{\mathrm{R}^{47}_{\mathrm{stochastic}}} - 1 \tag{7}$$

Depending on the context, Δ_{47} values and their uncertainties (both dimensionless) may be expressed in permil or ppm units.

2.6. Computation of absolute Δ_{47} values

Conversion of $\Delta_{47}^{\mathrm{raw}}$ to absolute Δ_{47} values constrained by thermodynamic gas standards can be described by the following relationship:

$$\Delta_{47}^{\mathrm{raw}} = a\ \Delta_{47} + b\ \delta^{47} + c \tag{8}$$

Although the above equation uses a different formalism, the underlying corrections are strictly equivalent to those described by Dennis et al. (2011), with parameters a, b and c being respectively related to scrambling effects, compositional nonlinearity, and non-stochasticity of the working gas. Within each measurement session, numerical values for (a, b, c) can be determined by least-squares fitting of the gas standard results, for which equilibrium Δ_{47} values are derived from the theoretical model of Wang et al. (2004). An example implementation is included in the supplementary material.

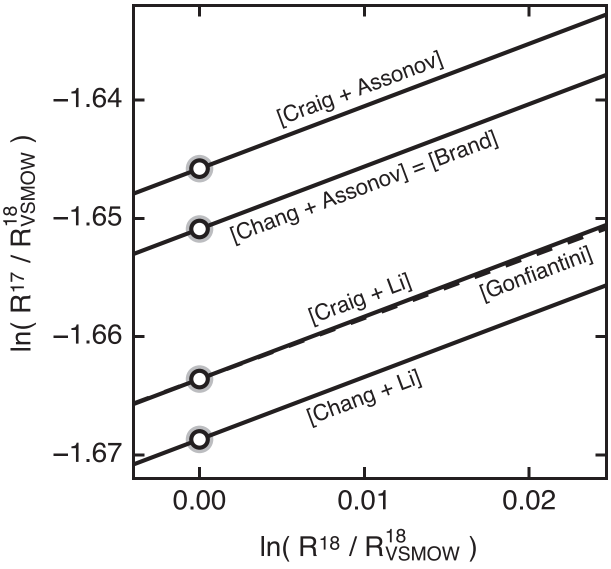

Fig. 3. Triple oxygen isotope lines corresponding to the isotopic parameters listed in Table 1. Round markers correspond to the oxygen isotope composition of VSMOW. Source code provided as supplementary material.

The best-fit values for (a, b, c) are then used to calculate absolute Δ_{47} for all samples in the same session, by simple rearrangement of Eq. (8):

$$\Delta_{47} = \left(\Delta_{47}^{\mathrm{raw}} - b\ \delta^{47} - c\right)/a \tag{9}$$

3. Results and discussion

3.1. Are Δ_{47} values sensitive to the choice of isotopic parameters?

In the context of this study, we define $\Delta(\Delta_{47})$ as the difference, for any single measurement, between the absolute Δ_{47} value computed using one set of parameters and that computed using the [*Gonfiantini*] parameters. It should be noted that this arbitrary choice does not imply that the [*Gonfiantini*] output is more accurate.

3.1.1. Relationship between $\Delta(\Delta_{47})$ and δ^{13}C in real-world measurements

Considering all of the real-world data described above, $\Delta(\Delta_{47})$ values for the [*Brand*] parameters vary from −27 to +12 ppm (Fig. 4a). In this case, although $\Delta(\Delta_{47})$ is poorly correlated with Δ_{47}, there seems to be some structure to their relationship, as illustrated by the clustered distribution of markers in Fig. 4a. The finding that $\Delta(\Delta_{47}) \approx 0$ for all of the thermodynamic gas standards (both at 25 °C and 1000 °C) can be understood simply as a consequence of the conversion to absolute Δ_{47} values, which necessarily assigns a single, temperature-dependent value to the standard gases. It should be noted, however, that the vertical spread of standard gas markers in Fig. 4a is minuscule, which does not appear to be the case for other types of measurements shown here, suggesting that all equilibrated gases share some attribute which dictates the value of $\Delta(\Delta_{47})$.

By contrast, $\Delta(\Delta_{47})$ is strongly correlated with δ^{13}C values (Fig. 4b). Because all of our thermodynamic gas standards are prepared from the same CO$_2$ tank with $\delta^{13}\mathrm{C}_{\mathrm{VPDB}} \approx -3.6$‰, the use of different isotopic parameters affects them all in the same manner, offsetting $\Delta_{47}^{\mathrm{raw}}$ by a uniform amount which cancels out in the conversion to absolute Δ_{47} values.

This strong correlation with δ^{13}C is a systematic feature of our real-world data set, as can be verified by modifying the original [*Gonfiantini*] parameters in various ways (Fig. 4b), such as changing $\mathrm{R}^{13}_{\mathrm{VPDB}}$ to the value of Chang and Li (1990) and/or changing λ to the meteoric water value of 0.528. The respective effects of these various changes are additive, and, as expected, the intersection of all regression lines corresponds to the gas standards ($\delta^{13}\mathrm{C}_{\mathrm{VPDB}} = -3.6$‰ and $\Delta(\Delta_{47}) = 0$).

3.1.2. Random data simulation results

The random data simulations described in Section 2.3 provide us with a more general view of the observations described above.

As a starting point, we computed $\Delta_{47}^{\mathrm{raw}}$ values, using either the [*Gonfiantini*] or the [*Brand*] parameters, for 100 simulated measurements with $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ values between −30‰ and +30‰, Δ_{47} between 0‰ and 1‰, and working reference gas $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ between −30‰ and +30‰ (all of which were randomly generated from uniform distributions). By analogy with $\Delta(\Delta_{47})$, here we define $\Delta(\Delta_{47}^{\mathrm{raw}})$ as the difference, for each measurement, between $\Delta_{47}^{\mathrm{raw}}$ computed from the [*Brand*] parameters and $\Delta_{47}^{\mathrm{raw}}$ computed from [*Gonfiantini*].

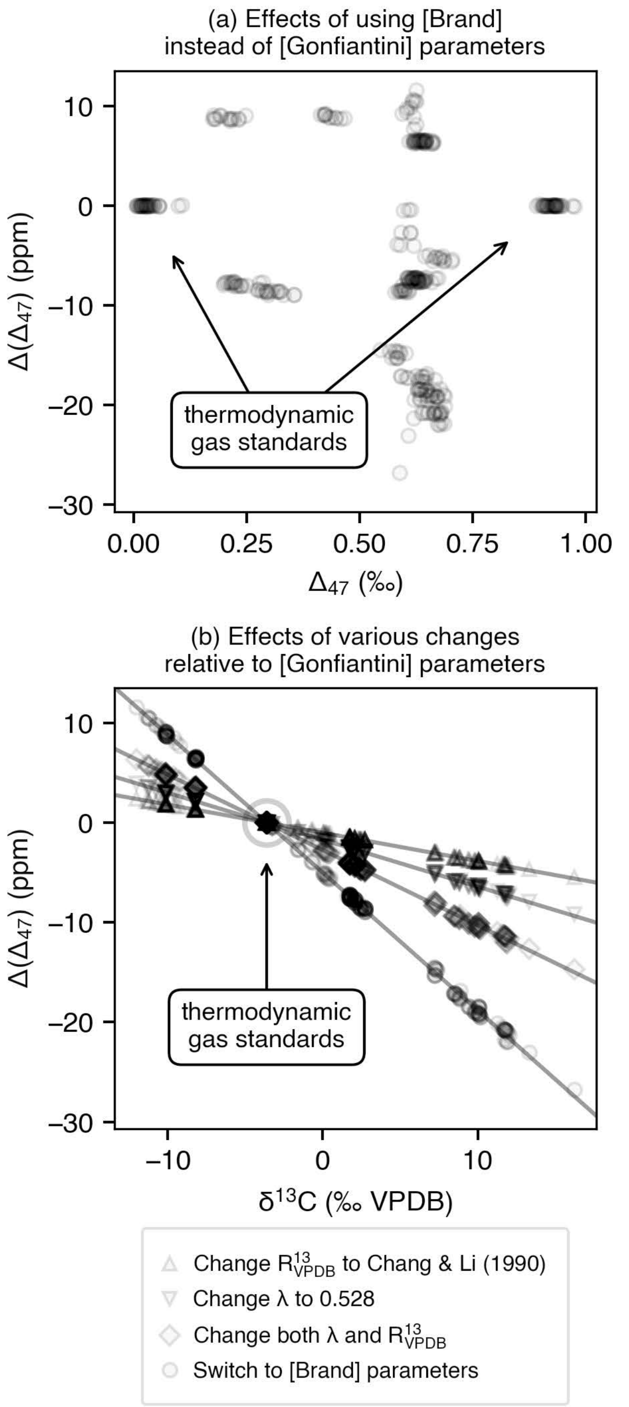

Fig. 4. Effects of performing raw data reduction using different isotopic parameters. $\Delta(\Delta_{47})$ is the sample-to-sample difference in final, absolute Δ_{47} values, relative to the [*Gonfiantini*] parameters. Source code provided as supplementary material.

The exact analytical formulation of $\Delta(\Delta_{47}^{\mathrm{raw}})$ is extremely cumbersome. Alternatively, as shown in Fig. 5, $\Delta(\Delta_{47}^{\mathrm{raw}})$ can be described to a very good approximation (with a root-mean-square error of 0.3 ppm), by the following relationship:

$$\Delta\left(\Delta_{47}^{\mathrm{raw}}\right) = \mathrm{A}\left(\delta^{13}\mathrm{C}[\mathrm{s}] - \delta^{13}\mathrm{C}[\mathrm{wg}]\right) + \mathrm{B}\left(\delta^{18}\mathrm{O}[\mathrm{s}] - \delta^{18}\mathrm{O}[\mathrm{wg}]\right) \qquad (10)$$

where δ^{13}C[s] and δ^{13}C[wg] are the respective $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ values of the sample and working gas, δ^{18}O[s] and δ^{18}O[wg] their respective $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ values. Coefficients A and B were computed by least-squares fitting of the 100 simulated measurements, yielding $A = -5.38 \times 10^{-4}$ and $B = +6.95 \times 10^{-4}$. Because this equation reflects a purely mathematical effect, the best-fit values for (A,B) would not change significantly for a different (sufficiently large) set of random data.

Although using different isotopic parameters thus affects $\Delta_{47}^{\mathrm{raw}}$ in a simple, systematic manner, it should be noted that these effects have a dimensionality of 2, i.e. $\Delta(\Delta_{47}^{\mathrm{raw}})$ varies as a function of two independent parameters. Subsequent conversion to the absolute scale also behaves as a function of two independent parameters (δ^{47} and $\Delta_{47}^{\mathrm{raw}}$), but only the former is directly linked to bulk isotope compositions ($\delta^{47} \approx \delta^{13}\mathrm{C} + \delta^{18}\mathrm{O}$). To illustrate this point, let us consider a situation where all thermodynamic gas standards share the same δ^{13}C value. In that case, δ^{47} only varies with δ^{18}O, so that the conversion to absolute values will also cancel the effects of parameter B in Eq. (10). The δ^{13}C effects (parameter A), however, are left uncorrected, as displayed in Fig. 4b. Conversely, if all thermodynamic gas standards share the same δ^{18}O value, conversion to the absolute scale will correct for parameter A but not for B.

In order to test this prediction, we generated a second set of 50 simulated measurements, with random, uniformly distributed $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ values between −15‰ and +15‰ and random Δ_{47} values between 0.05‰ and 0.9‰. In this case, the working gas composition was assigned constant values ($\delta^{13}\mathrm{C}_{\mathrm{VPDB}} = 0‰, \delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}} = 0‰$) to imitate real-world measurement conditions. We then arbitrarily assumed that the [*Brand*] parameters are the "true" ones and used these parameters to compute the working gas delta values (δ^{45} to δ^{49}) for each of the 50 simulated samples. We can then convert these samples to the absolute scale using the [*Gonfiantini*] parameters, based on three hypothetical sets of 16 thermodynamic gas standards. All gas standards in the first set have identical $\delta^{13}\mathrm{C}_{\mathrm{VPDB}} = 0‰$ and variable $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ values (Fig. 6a); gases from the second one have random $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ and $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}}$ values (Fig. 6b); and all gases in the third set have variable $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ values and identical $\delta^{18}\mathrm{O}_{\mathrm{VPDB\text{-}CO_2}} = 0‰$ (Fig. 6c).

As predicted, the resulting measurement errors (defined as the difference between the Δ_{47} value measured using [*Gonfiantini*] and the "true" starting value) are perfectly correlated with δ^{13}C in the first case, weakly correlated with both δ^{13}C and δ^{18}O in the second one, and perfectly correlated with δ^{18}O in the third one (Fig. 6). In all three cases, the amplitude of Δ_{47} errors remains the same, on the

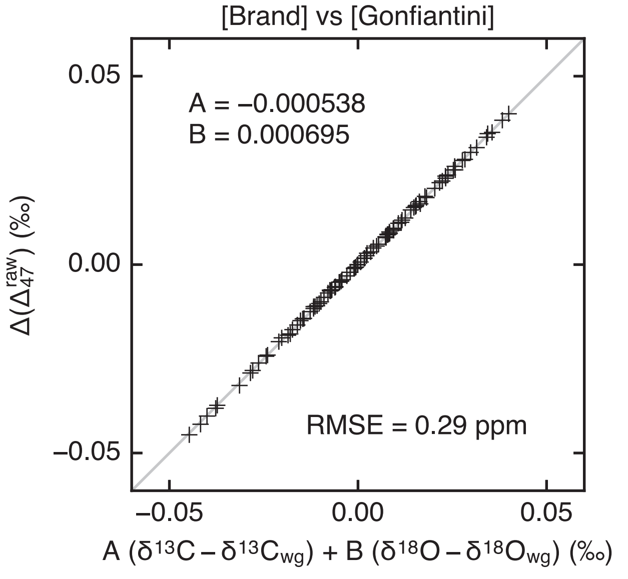

Fig. 5. Relationship between $\Delta(\Delta_{47}^{\mathrm{raw}})$, δ^{13}C and δ^{18}O based on random simulation data for 100 measurements. RMSE: root mean square error. Source code provided as supplementary material.

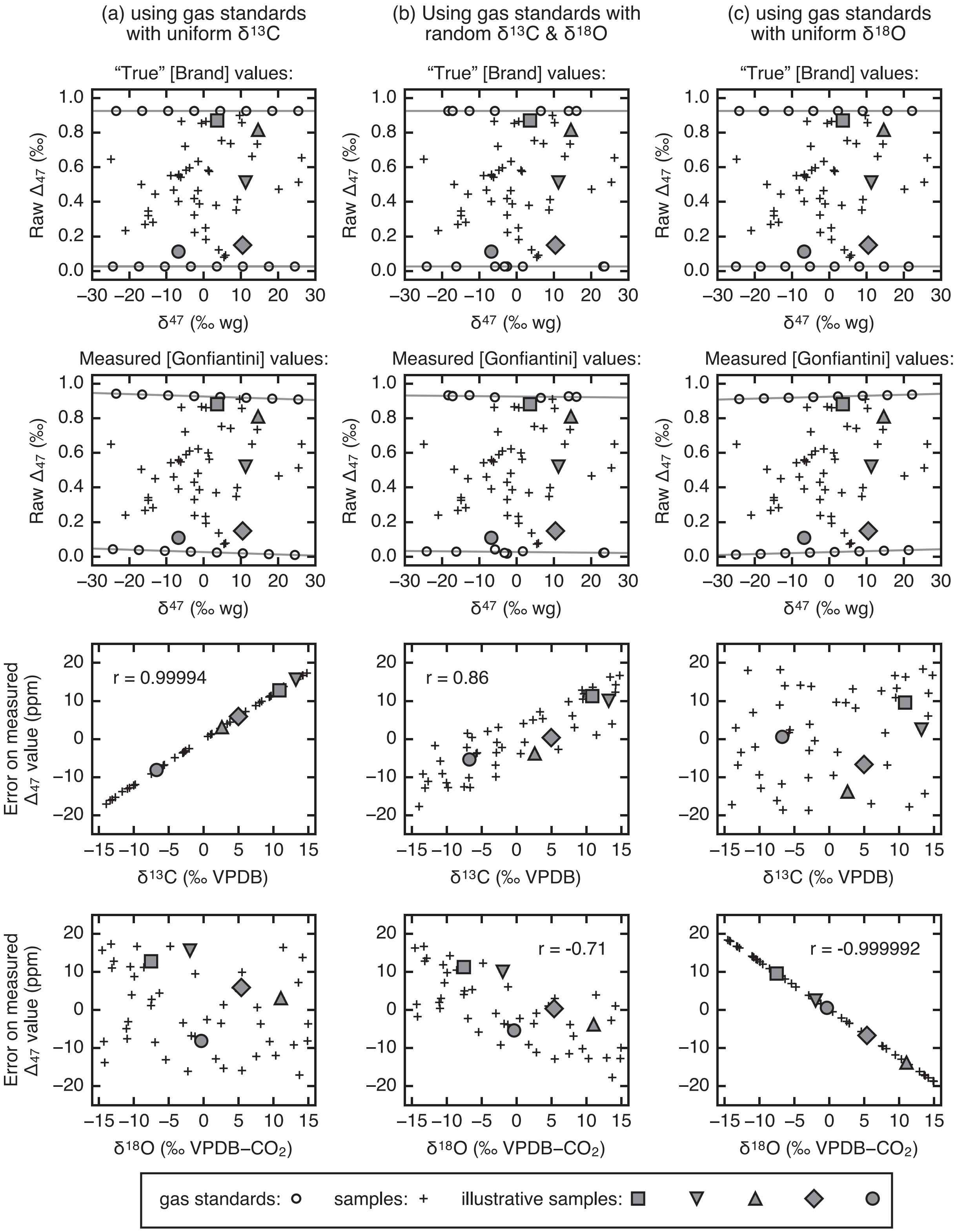

Fig. 6. Computation of errors resulting from the use of inaccurate isotopic parameters, based on random simulation data for 50 samples. Raw measurement data are generated by arbitrarily assuming that the [*Brand*] parameters are accurate, then processed using the [*Gonfiantini*] parameters in three different hypothetical situations: (a) data corrected using 16 thermodynamic gas standards with identical values of $\delta^{13}C$; (b) data corrected using 16 gas standards with random $\delta^{13}C$ and $\delta^{18}O$ values; and (c) data corrected using 16 gas standards with identical values of $\delta^{18}O$. r: Pearson correlation coefficient. Source code provided as supplementary material.

order of 40 ppm. One important result of this simulation is that using a single set of isotopic parameters does not ensure that Δ_{47} measurements remain consistent through time or between laboratories: if these isotopic parameters are inaccurate, the resulting Δ_{47} errors are significant, and vary strongly with the bulk isotopic compositions of the standards used for conversion to the absolute scale.

3.1.3. *Variability between sessions in real-world measurements*

Going back to our real-world data, residuals for the regression of $\Delta(\Delta_{47})$ as a linear function of $\delta^{13}C_{VPDB}$ (Fig. 4b, [*Brand*] versus [*Gonfiantini*]) are plotted in Fig. 7. Due to strong correlation between the two variables, these residuals remain extremely small, within ±0.5 ppm. However, all residuals within a single analytical session (defined as a continuous period of stable instrumental/analytical conditions) are themselves well correlated with $\delta^{13}C$. In other words, data from each session would yield slightly different regression slopes in Fig. 4b, although differences from one session to another would remain within ±0.5 ppm.

These differences can be understood as a consequence of Eqs. (9) and (10). Differences in isotopic parameters affect Δ_{47}^{raw} in a mathematically predictable way. As discussed in the previous section, conversion to the absolute scale partially corrects for these effects, but the remaining Δ_{47} offsets are scaled by a factor of $1/a$ in the conversion (Eq. (9)). We would thus expect that session-to-session variability of the a parameter manifests as small differences in the regression slope of $\Delta(\Delta_{47})$ versus $\delta^{13}C$. This prediction is consistent with the observations from our real-world data set, where session-specific regression slopes are indeed proportional to $1/a$ (Fig. 7).

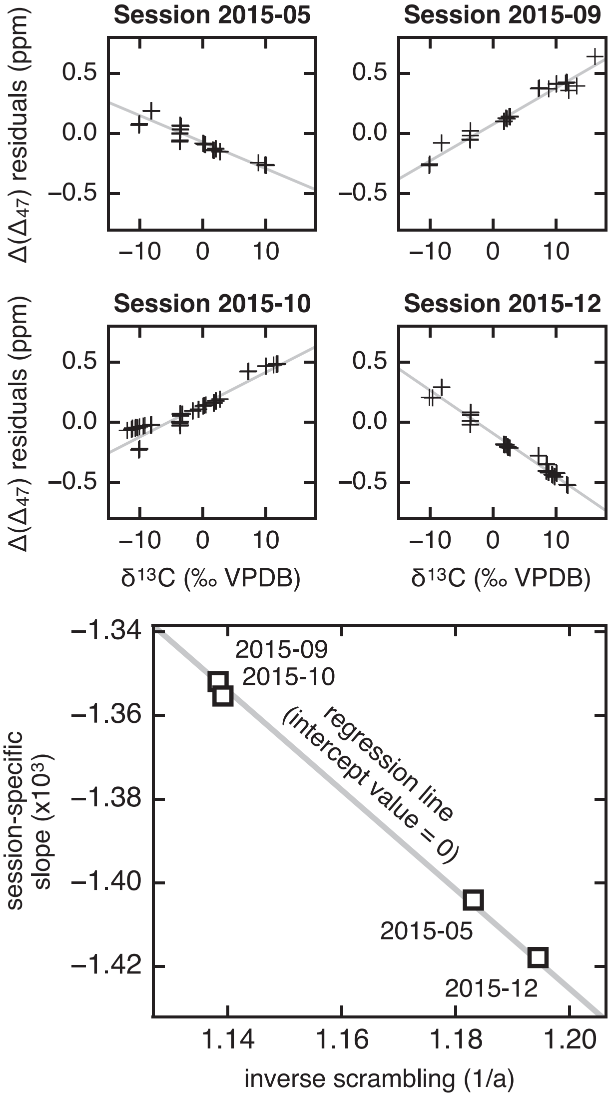

Fig. 7. Residuals of $\Delta(\Delta_{47})$ for the [*Brand*] parameters relative to the corresponding trend line in Fig. 4b. Although these residuals remain very small, they are not random. Instead, they appear tightly correlated to $\delta^{13}C$ within each analytical session (defined as a continuous period of instrumental stability), meaning that data from different sessions follow slightly different trends. As discussed in Section 3.1.3, this behavior reflects session-to-session variability in the scrambling correction (parameter a in Eq. (9)). Source code provided as supplementary material.

3.1.4. *Methodological implications*

The findings described above have serious implications regarding modern analytical protocols. For one thing, it is clear that the use of different parameters in different research groups is likely to produce Δ_{47} discrepancies up to several tens of ppm (e.g., Fig. 4). Furthermore, even if Δ_{47} measurements were universally processed using identical but inaccurate parameters, the random data simulations summarized in Fig. 6 still predict significant errors which will strongly depend on the bulk isotopic compositions of the standards used for conversion to the absolute scale, again resulting in notable discrepancies between different research groups. Incidentally, the large, ^{13}C-dependent offsets in thermodynamic gas standard measurements recently reported by Schauer et al. (2016b) can be simply interpreted as a result of isotopic parameter effects such as those described above (see also Olack and Colman, 2016 and Schauer et al. 2016a, in review).

In the strictest sense, theory predicts that equilibrium Δ_{47} values will vary slightly with $\delta^{13}C$ and $\delta^{18}O$, because mass-47 CO_2 includes three isotopologues with different stochastic anomalies at a given temperature (Wang et al., 2004). However, this effect remains out of reach of current precision limits (computation details and example values are provided in Appendix B). Therefore we expect, using accurate isotopic parameters, that samples with different bulk isotope compositions but known to have quasi-identical mass-47 anomalies will yield identical Δ_{47} values within analytical uncertainties, providing us with an empirical basis for testing the accuracy of various sets of isotopic parameters.

3.2. *Optimal isotopic parameters for water-equilibrated CO_2*

As discussed above, it is possible to search for isotopic parameters which would result in quasi-identical measured Δ_{47} values for CO_2 samples with different bulk isotope compositions and equilibrated at a known temperature. We thus prepared three sample groups with $\delta^{13}C_{VPDB}$ values of −37.8, −23.8 and −3.7‰, respectively, and equilibrated them at 25 °C with 60 μL aliquots of the same deionized water whose ^{17}O excess was independently measured by water fluorination ($\delta^{18}O_{VSMOW} = +10.5‰, \Delta^{17}O_{water} = +5$ ppm relative to VSMOW). Samples in the most ^{13}C-enriched and ^{13}C-depleted groups ("eEG" and "CdEG-B", respectively) were prepared from two different commercial tanks of CO_2, while those from the third group ("CdEG-A") were produced by acid digestion of commercial, reagent-grade calcium carbonate (Rhône-Poulenc Prolabo). Molar ratios of CO_2 to H_2O were on the order of 1:100, ensuring quasi-identical triple oxygen isotope compositions for all equilibrated samples. In the conversion to absolute Δ_{47} values, only the samples in the ^{13}C-enriched group (eEG) were treated as thermodynamic gas standards.

Two other types of thermodynamic gas standards were prepared from the same ^{13}C-enriched CO_2, either equilibrated at 25 °C with a mixture of high-latitude meteoric waters ($\delta^{18}O_{VSMOW} = -20.6‰, \Delta^{17}O_{water} = -34$ppm), or heated to 1000 °C after equilibration at room temperature with a different mixture of high-latitude meteoric waters ($\delta^{18}O_{VSMOW} = -28.7‰, \Delta^{17}O_{water} = -88$ppm). Although δ^{47}-enriched heated gases were also analyzed over the course of the experiment, they were excluded from this particular dataset so that the "compositional slope" (parameter b in Eq. (8)) is exclusively constrained by the 25 °C gas standards.

Table 2 lists the average isotopic compositions of these five different gases. All samples were analyzed within a single session in February 2016, following the same protocols as those described in Section 2. For each measurement, the calculation of $\delta^{18}O$ from Eq. (4) was based on an assumed $\Delta^{17}O$ value (relative to VSMOW) inherited from its equilibration water, with an additional modifier

Table 2
Results of the water equilibration experiment. Sample groups eEG, dEG and dHG are treated as thermodynamic gas standards (and thus have constant Δ_{47} values), while groups CdEG-A and CdEG-B are treated as unknown samples. Standard errors are based on the overall external reproducibility (SD=13.5 ppm) of all replicate measurements in this data set.

Group	Eq. T (°C)	$\Delta^{17}O_{water}$ (ppm, VSMOW)	Parameters	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB\text{-}CO_2}$ (‰)	Δ_{47} (ppm, ±1SE)
eEG (n = 4)	25	+5	[*Gonfiantini*]	−3.60	10.81	925.0 ± 6.7
			[*Craig + Li*]	−3.62	10.81	925.0 ± 6.7
			[*Chang + Li*]	−3.62	10.81	925.0 ± 6.7
			[*Craig + Assonov*]	−3.64	10.81	925.0 ± 6.7
			[*Chang + Assonov*]	−3.64	10.81	925.0 ± 6.7
dEG (n = 5)	25	−34	[*Gonfiantini*]	−3.63	−20.22	925.0 ± 6.0
			[*Craig + Li*]	−3.62	−20.22	925.0 ± 6.0
			[*Chang + Li*]	−3.62	−20.22	925.0 ± 6.0
			[*Craig + Assonov*]	−3.62	−20.22	925.0 ± 6.0
			[*Chang + Assonov*]	−3.62	−20.22	925.0 ± 6.0
dHG (n = 3)	1000	−88	[*Gonfiantini*]	−3.61	−27.43	26.6 ± 7.8
			[*Craig + Li*]	−3.60	−27.43	26.6 ± 7.8
			[*Chang + Li*]	−3.60	−27.43	26.6 ± 7.8
			[*Craig + Assonov*]	−3.59	−27.43	26.6 ± 7.8
			[*Chang + Assonov*]	−3.59	−27.43	26.6 ± 7.8
CdEG-A (n = 8)	25	+5	[*Gonfiantini*]	−23.71	10.48	897.9 ± 4.8
			[*Craig + Li*]	−23.73	10.48	907.8 ± 4.8
			[*Chang + Li*]	−23.73	10.48	908.5 ± 4.8
			[*Craig + Assonov*]	−23.77	10.48	926.1 ± 4.8
			[*Chang + Assonov*]	−23.77	10.48	926.9 ± 4.8
CdEG-B (n = 4)	25	+5	[*Gonfiantini*]	−37.63	10.16	874.4 ± 6.7
			[*Craig + Li*]	−37.65	10.16	891.2 ± 6.7
			[*Chang + Li*]	−37.65	10.16	892.4 ± 6.7
			[*Craig + Assonov*]	−37.71	10.16	922.5 ± 6.7
			[*Chang + Assonov*]	−37.71	10.16	923.7 ± 6.7

of −205.1 ppm based on the oxygen isotope fractionation factors reported by Barkan and Luz (2012) for CO_2-H_2O equilibrium at 25 °C:

$$^{18}\alpha = 1.041036$$
$$\ln(^{17}\alpha)/\ln(^{18}\alpha) = 0.5229$$
$$\ln(^{17}\alpha) - 0.528 \times \ln(^{18}\alpha) = -0.0002051$$

Raw data for this water equilibration experiment were processed using the [*Chang + Assonov*], [*Chang + Li*], [*Craig + Assonov*], and [*Craig + Li*] parameters, and for comparison purpose also using those of [*Gonfiantini*]. The results are summarized in Table 2 and Fig. 8. By design, the samples treated as thermodynamic standards (eEG, dEG and dHG) retain their nominal Δ_{47} values for all sets of isotopic parameters. By contrast, Δ_{47} values for the ^{13}C-depleted samples CdEG-A and CdEG-B vary by up to 50 ppm, and, as predicted, these offsets are almost perfectly proportional to the difference in $\delta^{13}C$ relative to eEG. All three sets of parameters using the Li et al. (1988) value for R^{17}_{VSMOW} (including [*Gonfiantini*]), yield non-zero slopes of Δ_{47} versus $\delta^{13}C$. By contrast, both [*Assonov*] sets produce Δ_{47} values between 922.5 and 926.9 ppm, statistically indistinguishable from the equilibrium value of 925.0 ppm. As can be verified using the source code for Fig. 8 (provided in the supplementary material), these results do not depend in any significant way on the $\Delta^{17}O$ modifier used to account for $CO_2 - H_2O$ equilibrium fractionation.

Based on the plots in Fig. 8, it appears that Δ_{47} versus $\delta^{13}C$ slopes are not very sensitive to the numerical value of R^{13}_{VPDB}, but vary significantly with the ratio of $R^{13}_{VPDB}/R^{17}_{VSMOW}$. Assuming that our values for R^{18}_{VSMOW} and λ are correct, these results imply that the determination of $R^{13}_{VPDB}/R^{17}_{VSMOW}$ by Assonov and Brenninkmeijer (2003b) is more accurate than the previous estimate by Li et al. (1988).

3.3. Optimal isotopic parameters for carbonate samples

A conceptually similar experiment can be made by comparing the Δ_{47} values computed for the ETH-1 and ETH-2 carbonate standards.

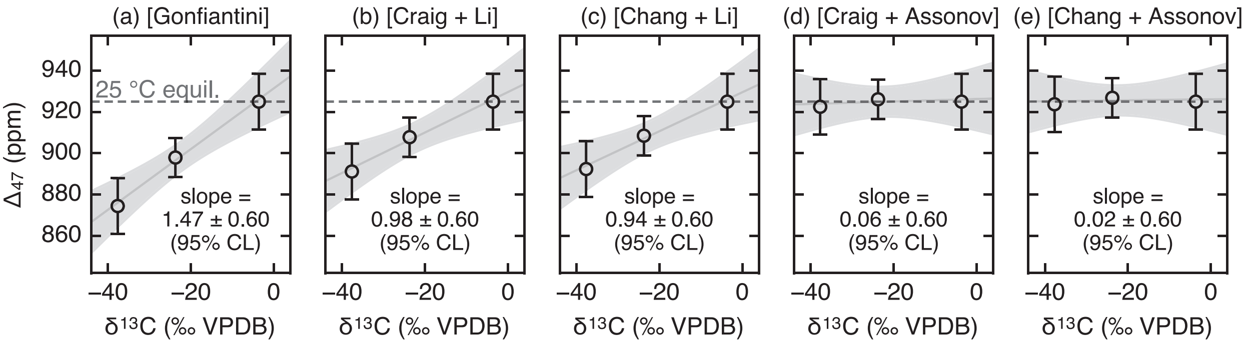

Fig. 8. Results of our water equilibration experiment. Three CO_2 samples with quasi-identical $\delta^{18}O$ and $\Delta^{17}O$ values but very different $\delta^{13}C$ were all isotopically equilibrated at 25 °C. Although their true Δ_{47} values are expected to be undistinguishable, their measured values appear different unless raw data are processed using the [*Craig + Assonov*] or the [*Chang + Assonov*] parameters. Measurement error bars correspond to ±2SE. CL: confidence limits. Source code provided as supplementary material.

To the best of our knowledge, these two standards, whose $\delta^{13}C_{VPDB}$ values differ by 12‰, were produced through identical heating experiments (10 h, 600 °C, 155 MPa, from Table 1 in Meckler et al. (2014)). Assuming that their bond reordering kinetics are similar (which is probably not strictly true but remains a reasonable first-order assumption), one would thus expect their true Δ_{47} values to be very close. To test this prediction, we computed average Δ_{47} for ETH-1 ($n = 18$) and ETH-2 ($n = 13$) based on the real-world data set described in Section 2.2.

As pointed out by Assonov and Brenninkmeijer (2003a), triple oxygen isotope parameters applicable to CO_2 produced by acid digestion of carbonates should be closely related to those applicable to natural surface waters. We might assume, for instance, as did Brand et al. (2010), that VPDB-CO_2 plots on the same triple oxygen isotope line as VSMOW ($\Delta^{17}O = 0$). Alternatively, one may assign carbonates a constant but non-zero value to $\Delta^{17}O$ (relative to VSMOW), based on analyses of CO_2 produced from NBS-19. Two such experiments were reported by Passey et al. (2014) and Barkan et al. (2015), with respective results of $\Delta^{17}O = -0.135$‰ and $\Delta^{17}O = -0.227$‰. These three options correspond to three different triple oxygen isotope lines, hereafter referred to as [*Brand*], [*Passey*] and [*Barkan*] (see Table 1).

In this round of calculations, we thus explicitly account for a $\Delta^{17}O$ difference between carbonates ($\Delta^{17}O = 0$, -135 or -227 ppm relative to [*Chang* + *Assonov*]) and water-equilibrated CO_2 ($\Delta^{17}O = -205.1$ ppm). As before, we also account for independently measured water ^{17}O anomalies in our thermodynamic gas standards.

Table 3 lists the average Δ_{47} values and the difference between ETH-1 and ETH-2, computed for each set of isotopic parameters (including [*Gonfiantini*] for comparison). The [*Gonfiantini*] parameters yield a statistically significant difference of 21 ± 9 ppm (1SE), which compares well with the 18 ppm (1SE) systematic error predicted for the [*Gonfiantini*] parameters, based on the slope from Fig. 4b and the difference in $\delta^{13}C$.

Because [*Brand*], [*Passey*] and [*Barkan*] assume different ^{17}O anomalies between the carbonates and the thermodynamic gas standards, the resulting Δ_{47} values of ETH-1 and ETH-2 covary by up to 10 ppm, consistent with the small effects predicted in Fig. 2. However, as shown in Fig. 9, these three options yield much smaller Δ_{47} differences on the order of 4 ± 9 ppm, demonstrating that all three sets of parameters derived from [*Chang* + *Assonov*] produce quasi-identical Δ_{47} values for ETH-1 and ETH-2.

At face value, these findings appear to be at odds with those of Meckler et al. (2014), who reported quasi-identical values for ETH-1 and ETH-2 despite using the [*Gonfiantini*] parameters (A. Meckler, pers. comm.). It is difficult to offer anything but conjecture without reprocessing the corresponding raw data set, but we note that the Meckler et al. values could result from using thermodynamic gas standards with bulk isotopic compositions different from ours. For example, in the purely hypothetical case where 1000 °C gas standards (heated gases) were prepared from ETH-1 and ETH-2 themselves, the final Δ_{47} values for these standards are expected to be independent from the choice of isotopic parameters.

Table 3
Comparison of Δ_{47} values for ETH-1 and ETH-2 computed using different isotopic parameters. Except for the [*Gonfiantini*] parameters, which are included for comparison only, these values take into account ^{17}O differences between carbonate-derived CO_2 and water-equilibrated gases. Standard errors are based on the external reproducibility (SD=24 ppm) of each standard over the course of seven months.

Parameters	ETH-1 (ppm, ±1SE) n = 18	ETH-2 (ppm, ±1SE) n = 13	ETH-1–ETH-2 (ppm, ±1SE)
[*Gonfiantini*]	228.1 ± 5.6	207.4 ± 6.8	20.7 ± 8.8
[*Brand*]	229.0 ± 5.6	224.4 ± 6.8	4.5 ± 8.8
[*Passey*]	223.3 ± 5.6	219.0 ± 6.8	4.3 ± 8.8
[*Barkan*]	219.4 ± 5.6	215.3 ± 6.8	4.2 ± 8.8

All values are unmodified Δ_{47} for 90 °C acid reaction.

Our ETH results are consistent with those of the water equilibration experiment described in Section 3.2. However, these ETH measurements suffer from one potential limitation: they are strongly constrained by the measured values of our 1000 °C gas standards (heated gases), whose ^{17}O anomalies are not as robustly constrained as those of water-equilibrated CO_2 standards. Although our heated gases are initially prepared from CO_2 equilibrated with waters with well-known $\Delta^{17}O$ values, there have been numerous observations (e.g. Huntington et al., 2009) that the subsequent heating protocol can cause $\delta^{18}O$ values to change by up to several permil, possibly due to oxygen exchange between CO_2 and the quartz tube. Such oxygen exchange reactions potentially modify ^{17}O anomalies, so that heated gas measurements may be slightly less accurate than those of water-equilibrated gas standards. However, to the best of our knowledge, this remains for now a purely hypothetical issue, and testing it will require high-precision, direct measurements of $\Delta^{17}O$ in CO_2.

3.4. Carbonate calibration discrepancies

In order to assess the influence of different isotopic parameters on carbonate calibration lines from different research groups, we reprocessed the raw data used by Zaarur et al. (2013), and compared the results with those obtained for unpublished synthetic carbonates precipitated at LSCE. Experimental details of the precipitation techniques are not directly relevant here, but the protocols used at Yale and LSCE were very similar, apart from the isotopic composition of the CO_2 used to prepare saturated solutions, resulting in carbonates with different $\delta^{13}C_{VPDB}$ values (−32.6 and +9.9‰ on average, respectively).

Although the Yale measurements predate the widespread adoption of the absolute scale of Dennis et al. (2011), we can still perform the corresponding corrections for each session, based on repeated analyses of heated gases (1000 °C) and of three internal laboratory standards (one CO_2 tank, one speleothem and one Carrara marble),

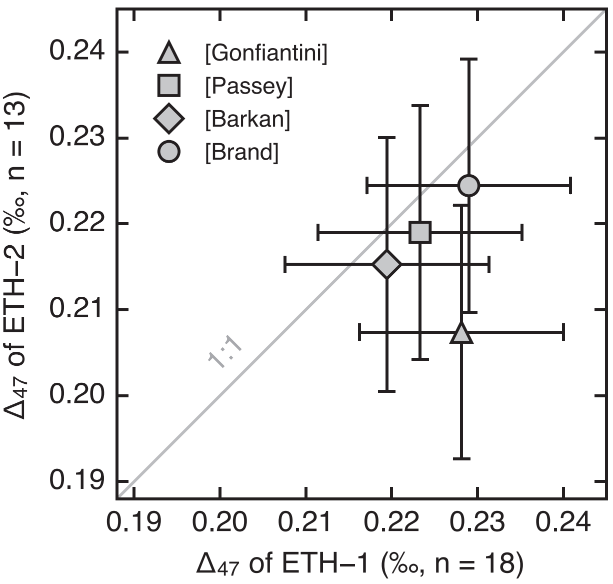

Fig. 9. Comparison of absolute Δ_{47} values for ETH-1 and ETH-2 computed using different sets of isotopic parameters. These two standards have different bulk isotopic compositions but their clumped isotope signatures are expected to be very similar (see Section 3.3). All parameters except [*Gonfiantini*] yield statistically indistinguishable Δ_{47} values for ETH-1 and ETH-2 (Table 3). Error bars correspond to 95% confidence limits, based on 18 analyses of ETH-1 and 13 analyses of ETH-2. Source code provided as supplementary material.

whose absolute Δ_{47} values were determined for different isotopic parameters by comparison with thermodynamic gas standards at 1000 °C and 25 °C. Five out of the seven Zaarur et al. calibration samples, precipitated at temperatures ranging from 5 to 65 °C, were robustly constrained by these internal standards, and the two unconstrained samples were found to have very little influence on the best-fit calibration line itself.

Fig. 10 illustrates the contrast between the Yale and LSCE calibration lines. In an effort to remain as close as possible to the raw data, here we report measured Δ_{47} values without any correction for acid reaction temperatures (25 °C at Yale versus 90 °C at LSCE), resulting in a large Δ_{47} difference at a given temperature (0.084‰ and 0.118‰ at 25 °C for [*Gonfiantini*] and [*Brand*], respectively). Strikingly, the distance between the Yale and LSCE calibrations increase by 36 ppm when switching from the [*Gonfiantini*] to the [*Brand*] parameters. These large shifts do not significantly affect the calibration slopes, however. The [*Brand*] slope for Yale (4.4 ppm/K at 20 °C, consistent with the findings of Zaarur et al., 2013) is 40% steeper than the [*Brand*] slope for LSCE (3.1 ppm/K at 20 °C), and these values barely change when using the [*Gonfiantini*] parameters.

Generally speaking, each calibration data set for the carbonate clumped isotope thermometer will differ in terms of the relative bulk isotope compositions of samples and standards. Thus, as implied by the random data simulations described in Section 3.1.2 and summarized in Fig. 6, it is difficult to predict how each published calibration would change (or not) for a different set of parameters. Nevertheless, from the Yale/LSCE comparison reported here, we infer that some aspects of the current discrepancies between published carbonate calibrations (e.g., Fig. 4 from Spencer and Kim, 2015) can be explained by such sample/standard compositional differences and/or by the use of different isotopic parameters. These effect, however, do not appear to provide an explanation for the large reported differences in carbonate calibration slopes.

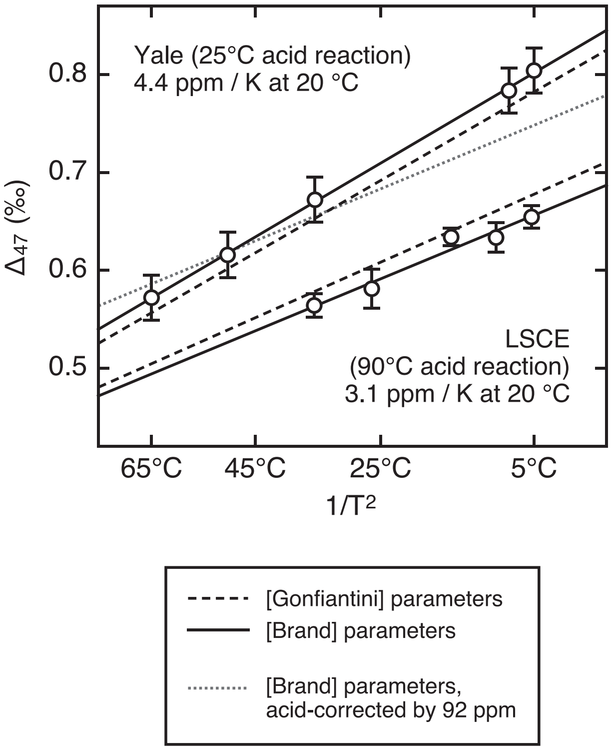

Fig. 10. Comparison of two carbonate calibration lines processed using [*Gonfiantini*] (dashed lines) versus [*Brand*] (solid lines and round markers, error bars correspond to ±2SE). Source code provided as supplementary material.

4. Recommendations

Based on all the results presented above, it appears likely that data reduction procedures contribute significantly to current interlaboratory discrepancies. This is not simply a matter of agreeing on a single set of isotopic parameters: the choice of certain values, including the [*Gonfiantini*] parameters originally used by the Caltech group, demonstrably leads to spurious effects such as those displayed in Fig. 8a. To make matters worse, these effects will manifest in very different ways depending on the relative bulk isotope compositions of samples and of the standards used for conversion to the absolute scale (Fig. 6).

A natural way forward would be to establish consensus on a set of isotopic parameters known to make Δ_{47} measurements quasi-independent of bulk isotope compositions. Based on the observations reported here, and with the caveat that these results require independent confirmation, we offer the following recommendations:

(1) Raw data processing should use the [*Brand*] isotopic parameters listed below. Note that with these numbers, the choice of VSMOW or VPDB-CO_2 as a triple oxygen isotope reference material is of no consequence, because they are both assumed to belong to the [*Chang* + *Assonov*] water line.

$$R^{13}_{\text{VPDB}} = 0.01118 \qquad \text{(Chang and Li, 1990)}$$

$$R^{18}_{\text{VSMOW}} = 0.00200520 \qquad \text{(Baertschi, 1976)}$$

$$R^{17}_{\text{VSMOW}} = 0.00038475$$

(Assonov and Brenninkmeijer, 2003b, re-scaled)

$$R^{18}_{\text{VPDB-CO}_2} = 0.00208839$$

(derived from Baertschi, 1976 using Eq. (2))

$$R^{17}_{\text{VPDB-CO}_2} = 0.00039310$$

(Assonov and Brenninkmeijer, 2003b, re-scaled)

$$\lambda = 0.528 \qquad \text{(Barkan and Luz, 2005)}$$

Using these parameters, the measurements reported here yield statistically indistinguishable Δ_{47} values for ETH-1 and ETH-2, with a combined average value of 218.3 ± 4.4 ppm (1SE, N = 31, 90 °C acid reaction, no acid temperature correction).

Technically, it would be possible to take into account the respective ^{17}O anomalies of water-equilibrated and carbonate-evolved CO_2. However, the discrepancy between the results of Passey et al. (2014) and Barkan and Luz (2012) implies that the ^{17}O composition of VPDB-CO_2 is not well constrained enough to do so with confidence. For now, we recommend that all types of measurements be processed using the unmodified parameters listed above, keeping in mind that doing so will produce a systematic, quasi-constant bias of a few ppm in carbonate samples relative to water-equilibrated gases.

(2) H_2O-equilibrated gas standards should be produced using water with small ^{17}O anomalies relative to VSMOW. In practice, pure meteoric waters and mixtures of meteoric waters should meet these requirements, with expected $\Delta^{17}O$ values ranging from −0.1‰ (corresponding to a Δ_{47} offset of +3.6 ppm based on Fig. 2) to +0.05‰ (Δ_{47} offset of −1.8 ppm). By contrast, isotopic enrichment by evaporation may potentially produce large negative ^{17}O anomalies (e.g., −0.4‰ was observed at LSCE under rapid evaporation conditions). Thus, if possible, $\Delta^{17}O$ in such evaporatively enriched waters should be measured independently.

(3) Raw data processing software should be able to solve Eq. (4) to a level of precision better than 0.1 ppm, which would allow two-way, lossless conversion between working gas delta values (δ^{45} to δ^{49}), bulk isotope compositions and clumped isotope

anomalies, and ensure that the simpler definition of Δ_{47} (Eq. (7)) is mathematically equivalent to the traditional one. Using the Taylor polynomial approximation described in Appendix A, such precision is easily achieved in virtually any software environment. By way of example, two reference implementations for Python and Excel are provided as supplementary material, which also allow taking into account potential ^{17}O anomalies for each analyte. We also provide an online application (http://daeron.fr/clumpycrunch), based on the algorithms described above, which makes it simple to process new raw data sets using any combination of isotopic parameters, and allows conversion to absolute Δ_{47} values.

(4) Conversion of past measurements from one set of isotopic parameters to a different one can be done in two ways. If working gas delta values (δ^{45} to δ^{49}) are available (including those of all related thermodynamic gases and/or carbonate standards), one may directly reprocess the raw data based on the new parameters. Alternatively, one could use a relationship between $\Delta_{47}^{\mathrm{raw}}$, $\delta^{13}C$ and $\delta^{18}O$ similar to that of Eq. (10), but a requirement of this approach is that the reported values for $\delta^{13}C$ and $\delta^{18}O$ must conform to Eq. (4) to a very good approximation, which is not necessarily the case for existing commercial software.

5. Conclusions

The mathematical treatment of raw data produced by IRMS analyses of CO_2 has evolved over time. Instrumental precision improvements and the increasing need for inter-laboratory consistency prompted a shift from the original Craig (1957) equations to the more accurate Santrock et al. (1985) correction procedure and its successors (e.g., Brand et al., 2010). Clumped isotopes require increased precision, at the level of a few ppm, and present new, specific challenges in terms of linearity correction and standardization procedures. Because of these requirements, however, clumped isotopes also offer new opportunities to test the accuracy of absolute isotopic ratios in reference materials.

Based on the observations reported above, the isotopic parameters reported by Brand et al. (2010) appear to yield accurate Δ_{47} values regardless of bulk isotopic composition. The recommendations offered here rely critically on measurements of samples believed to share quasi-identical Δ_{47} values. Pending independent confirmation of these results, we expect that systematic use of the isotopic parameters listed above will help reduce inter-laboratory discrepancies, particularly for samples with “exotic” bulk isotopic compositions.

Acknowledgments

We are indebted to A. Schauer, whose presentation at the Fifth International Clumped Isotope Workshop (Schauer et al., 2016b) provided the original motivation for this work. This article was significantly improved thanks to the thoughtful comments of an anonymous reviewer. We also thank A. Landais for performing analyses of ^{17}O excess in water, and E. Michel for providing us with a tank of ^{13}C-depleted CO_2. The Yale data reprocessed here was originally measured by S. Zaarur and various members of the Affek group. The clumped isotope facility at LSCE was established with the help of many former members of the Eiler group at Caltech, most particularly B. Passey, and with financial support from the following institutions: Région Ile-de-France; Direction des Sciences de la Matière du Commissariat à l’Energie Atomique; Institut National des Sciences de l’Univers, Centre National de la Recherche Scientifique; Universtité de Versailles/Saint-Quentin-en-Yvelines. This is LSCE contribution #5802.

Appendix A. Taylor polynomial calculation of $\delta^{18}O$ and $\delta^{13}C$

Computing $\delta^{18}O$ requires solving the following equation (generalized from Santrock et al. (1985)):

$$-3K^2(R^{18})^{2\lambda} + 2K(R^{45})(R^{18})^{\lambda} + 2R^{18} - R^{46} = 0$$
$$\text{with}: K = \exp(\Delta^{17}O)R^{17}_{\mathrm{ref}}(R^{18}_{\mathrm{ref}})^{-\lambda} \tag{A.1}$$

We may define x as the dimensionless value of $\delta^{18}O_{\mathrm{VPDB\text{-}CO_2}}$:

$$R^{18} = (1+x)R^{18}_{\mathrm{VPDB\text{-}CO_2}} \tag{A.2}$$

Combining Eqs. (A.1) and (A.2) yields

$$A(1+x)^{2\lambda} + B(1+x)^{\lambda} + C(1+x) + D = 0 \tag{A.3}$$

with

$$A = -3K^2(R^{18}_{\mathrm{VPDB\text{-}CO_2}})^{2\lambda}$$
$$B = 2KR^{45}(R^{18}_{\mathrm{VPDB\text{-}CO_2}})^{\lambda}$$
$$C = 2R^{18}_{\mathrm{VPDB\text{-}CO_2}}$$
$$D = -R^{46}$$

Because $x \ll 1$, we can use the following second-order Taylor polynomials:

$$(1+x)^{2\lambda} \approx 1 + 2\lambda x + \lambda(2\lambda-1)x^2$$
$$(1+x)^{\lambda} \approx 1 + \lambda x + \frac{1}{2}\lambda(\lambda-1)x^2 \tag{A.4}$$

Substitution of Eq. (A.4) into Eq. (A.3) yields

$$ax^2 + bx + c \approx 0 \tag{A.5}$$

with

$$a = A\lambda(2\lambda-1) + B\lambda(\lambda-1)/2$$
$$b = 2A\lambda + B\lambda + C$$
$$c = A + B + C + D$$

which is solved trivially by

$$x \approx \frac{-b+\sqrt{b^2-4ac}}{2a} \approx \delta^{18}O_{\mathrm{VPDB-CO_2}} \tag{A.6}$$

$\delta^{13}C$ may then be computed directly:

$$R^{17} = K(R^{18})^{\lambda}$$
$$R^{13} = R^{45} - 2R^{17}$$
$$\delta^{13}C_{\mathrm{VPDB}} = R^{13}/R^{13}_{\mathrm{VPDB}} - 1 \tag{A.7}$$

Using this method, the errors on computed values of $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}^{\mathrm{raw}}$ remain smaller than 0.02 ppm for all $\delta^{13}C_{\mathrm{VPDB}}$ and $\delta^{18}O_{\mathrm{VPDB-CO_2}}$ values between −50‰ and +50‰.

Table 4
Δ_{47} difference between our water-equilibrated samples and VPDB-CO_2, for 300 K equilibrium. See Appendix B for computation details.

Sample	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB-CO_2}$ (‰)	Δ_{47} difference (ppm)
eEG	−3.64	10.81	−0.24
dEG	−3.62	−20.22	+0.18
CdEG-A	−23.77	10.48	−0.76
CdEG-B	−37.71	10.16	−1.13

Appendix B. Influence of bulk isotopic composition on equilibrium values of Δ_{47} in CO_2

According to Table 4 in Wang et al. (2004), equilibrium values for mass-47 isotopologues of CO_2 at 300 K are

$$\begin{aligned}\Delta_{^{16}O^{13}C^{18}O} &= \Delta_{638} = 0.9384‰\\ \Delta_{^{17}O^{12}C^{18}O} &= \Delta_{728} = 0.1681‰\\ \Delta_{^{17}O^{13}C^{17}O} &= \Delta_{737} = 1.0738‰\end{aligned} \tag{B.1}$$

Let us consider the case of a CO_2 sample with known $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB\text{-}CO_2}$. The following equations use the dimensionless expression of delta values, so that

$$\begin{aligned}R^{13} &= R^{13}_{VPDB} \times (1+\delta^{13}C)\\ R^{18} &= R^{18}_{VPDB\text{-}CO_2} \times (1+\delta^{18}O)\\ R^{17} &= R^{17}_{VPDB\text{-}CO_2} \times (1+\delta^{18}O)^{\lambda}\end{aligned} \tag{B.2}$$

Stochastic isotopologue abundance ratios are then

$$\begin{aligned}R(^{16}O^{13}C^{18}O)_{stoch} &= 2R^{13}R^{18}\\ R(^{17}O^{12}C^{18}O)_{stoch} &= 2R^{17}R^{18}\\ R(^{17}O^{13}C^{17}O)_{stoch} &= R^{13}(R^{17})^2\end{aligned} \tag{B.3}$$

so that

$$\Delta_{47} = \frac{(2R^{13}R^{18}(1+\Delta_{638}) + 2R^{17}R^{18}(1+\Delta_{728}) + R^{13}(R^{17})^2(1+\Delta_{737}))}{(2R^{13}R^{18} + 2R^{17}R^{18} + R^{13}(R^{17})^2)} - 1 \tag{B.4}$$

By combining Eqs. (B.1), (B.2) and (B.4), equilibrium Δ_{47} values may be computed for a given bulk isotopic composition ($\delta^{13}C_{VPDB}$, $\delta^{18}O_{VPDB-CO_2}$) at 300 K. For example, the compositional differences in equilibrium Δ_{47} values between samples in our ^{13}C-depleted CO_2 equilibration experiment (Table 2) and VPDB-CO_2 are listed in Table 4.

Appendix C. Supplementary data

Supplementary material associated with this article (http://dx.doi.org/10.1016/j.chemgeo.2016.08.014) includes source code for generating all figures except Fig. 1, and, by way of example, Python scripts and an Excel spreadsheet intended to facilitate the conversion of past and future measurements from one set of isotopic parameters to another.

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