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Correction for the ^{17}O interference in $\delta(^{13}\text{C})$ measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report)[*]

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Abstract: Measurements of $\delta(^{13}\text{C})$ determined on CO_2 with an isotope-ratio mass spectrometer (IRMS) must be corrected for the amount of ^{17}O in the CO_2. For data consistency, this must be done using identical methods by different laboratories. This report aims at unifying data treatment for CO_2 IRMS by proposing (i) a unified set of numerical values, and (ii) a unified correction algorithm, based on a simple, linear approximation formula. Because the oxygen of natural CO_2 is derived mostly from the global water pool, it is recommended that a value of 0.528 be employed for the factor λ, which relates differences in ^{17}O and ^{18}O abundances. With the currently accepted $N(^{13}\text{C})/N(^{12}\text{C})$ of 0.011 180(28) in VPDB (Vienna Peedee belemnite) reevaluation of data yields a value of 0.000 393(1) for the oxygen isotope ratio $N(^{17}\text{O})/N(^{16}\text{O})$ of the evolved CO_2. The ratio of these quantities, a ratio of isotope ratios, is essential for the ^{17}O abundance correction: $[N(^{17}\text{O})/N(^{16}\text{O})]/[N(^{13}\text{C})/N(^{12}\text{C})] =$ 0.035 16(8).

The equation $[\delta(^{13}\text{C}) \approx {}^{45}\delta_{\text{VPDB-CO}_2} + 2\ {}^{17}R/{}^{13}R\ ({}^{45}\delta_{\text{VPDB-CO}_2} - \lambda{}^{46}\delta_{\text{VPDB-CO}_2})]$ closely approximates $\delta(^{13}\text{C})$ values with less than 0.010 ‰ deviation for normal oxygen-bearing materials and no more than 0.026 ‰ in extreme cases. Other materials containing oxygen of non-mass-dependent isotope composition require a more specific data treatment. A similar linear approximation is also suggested for $\delta(^{18}\text{O})$. The linear approximations are easy to implement in a data spreadsheet, and also help in generating a simplified uncertainty budget.

Keywords: $\delta(^{13}\text{C})$ correction; $\delta(^{18}\text{O})$ correction; IUPAC Inorganic Chemistry Division; ^{17}O correction; oxygen isotope ratio.

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INTRODUCTION

Measurements of small differences in the ratio of the number of stable carbon isotopes (^{13}C to ^{12}C) in naturally occurring materials are being used in an increasing number of fields including oceanography, atmospheric sciences, biology, paleoclimatology, geology, environmental sciences, food and drug authentication, and forensic applications. These small differences have been reported as isotope delta values, $\delta(^{13}C)$, defined by the relation[a,b]

$$\delta(^{13}\mathrm{C}) = \frac{N\left(^{13}\mathrm{C}\right)_\mathrm{B} / N\left(^{12}\mathrm{C}\right)_\mathrm{B} - N\left(^{13}\mathrm{C}\right)_\mathrm{std} / N\left(^{12}\mathrm{C}\right)_\mathrm{std}}{N\left(^{13}\mathrm{C}\right)_\mathrm{std} / N\left(^{12}\mathrm{C}\right)_\mathrm{std}} \tag{1}$$

where $N(^{13}C)_B$ and $N(^{12}C)_B$ are the numbers of the atoms of two isotopes ^{13}C and ^{12}C in specimen B, and the notation is equivalent for a standard, "std"[c]. The isotope-number ratio, $N(^{13}C)_B/N(^{12}C)_B$, commonly is shortened to isotope ratio and is given by the expression

$$R\left(^{13}\mathrm{C},{}^{12}\mathrm{C}\right)_\mathrm{B} = \frac{N\left(^{13}\mathrm{C}\right)_\mathrm{B}}{N\left(^{12}\mathrm{C}\right)_\mathrm{B}} \tag{2}$$

The determination of the $\delta(^{13}C)$ of a carbon-bearing material usually requires quantitative conversion of carbon in the specimen to CO_2, followed by mass spectrometric measurement. Akin to carbon isotopes above, $\delta(^{17}O)$ values are defined by ratios of $N(^{17}O)$ and $N(^{16}O)$ and $\delta(^{18}O)$ values by ratios of $N(^{18}O)$ and $N(^{16}O)$ for CO_2. In the mass spectrometric analysis of CO_2, the ion currents at mass-to-charge ratio m/z 44, 45, and 46 are measured. These m/z values represent the most abundant of the CO_2 isotopologues, which range from m/z 44 to 49. The symbols for ratios are defined as[d,e]

$$^{13}R_\mathrm{B} = R\left(^{13}\mathrm{C},{}^{12}\mathrm{C}\right)_\mathrm{B} = \frac{N\left(^{13}\mathrm{C}\right)_\mathrm{B}}{N\left(^{12}\mathrm{C}\right)_\mathrm{B}} \tag{3}$$

$$^{17}R_\mathrm{B} = R\left(^{17}\mathrm{O},{}^{16}\mathrm{O}\right)_\mathrm{B} = \frac{N\left(^{17}\mathrm{O}\right)_\mathrm{B}}{N\left(^{16}\mathrm{O}\right)_\mathrm{B}} \tag{4}$$

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[a] Throughout the manuscript, we use the full form of the delta expression (e.g., "$\delta(^{13}C)$"), in order to write equations in compliance with international rules for quantities and symbols (generally, the quantity δ should be a single letter in italic font with the further qualification (^{13}C) in brackets). The common and historical short form (e.g., "$\delta^{13}C$") might lead to ambiguities in international trade and technology issues, but has been acceptable for scientific audiences and publications. Please note also that the extraneous factor 1000 in the traditional δ-equation has been omitted to make this equation coherent in compliance with international recommendations.

[b] For easier reading, $N(^{13}C)/N(^{12}C)$ can be expressed in short as ^{13}R (see eq. 3). Similarly, the expression $[N(^{17}O)/N(^{16}O)]/[N(^{13}C)/N(^{12}C)]$ can be written in a simplified form as $^{17}R/^{13}R$.

[c] The international scale for $\delta(^{13}C)$ and also for $\delta(^{18}O)$ of carbonates is the VPDB (Vienna Peedee belemnite) scale. CO_2 evolved with 100 % H_3PO_4 at 25 °C from virtual VPDB calcite, termed VPDB-CO_2, assumes an oxygen isotopic fractionation between CO_2 and calcite of 1.010 25. To avoid the uncertainty associated with the VPDB to VPDB-CO_2 scale conversion, the VPDB-CO_2 oxygen scale is used both for data treatment (^{17}O-correction) and for ^{18}O data reporting.

[d] The upper left-hand superscript on a symbol is the sum of the mass numbers of the atoms in each species.

[e] The definition of ^{46}R by Craig [1] differs from that in eq. 7 because Craig used a double Faraday cup mass spectrometer instead of a triple Faraday cup mass spectrometer now commonly used.

$$ ^{18}R_{\mathrm{B}} = R\left(^{18}\mathrm{O},^{16}\mathrm{O}\right)_{\mathrm{B}} = \frac{N\left(^{18}\mathrm{O}\right)_{\mathrm{B}}}{N\left(^{16}\mathrm{O}\right)_{\mathrm{B}}} \tag{5} $$

$$ ^{45}R_{\mathrm{B}} = \frac{N\left(^{13}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}\right)_{\mathrm{B}} + N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{17}\mathrm{O}\right)_{\mathrm{B}}}{N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}\right)_{\mathrm{B}}} \tag{6} $$

$$ ^{46}R_{\mathrm{B}} = \frac{N\left(^{12}\mathrm{C}^{18}\mathrm{O}^{16}\mathrm{O}\right)_{\mathrm{B}} + N\left(^{13}\mathrm{C}^{17}\mathrm{O}^{16}\mathrm{O}\right)_{\mathrm{B}} + N\left(^{12}\mathrm{C}^{17}\mathrm{O}^{17}\mathrm{O}\right)_{\mathrm{B}}}{N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}\right)_{\mathrm{B}}} \tag{7} $$

The efficiency of the isotope-ratio mass spectrometer (IRMS) ion source and ion collection varies slightly for the different masses (m/z 44, 45, and 46). Thus, the ratio of ions collected at m/z 44, 45, and 46 differs from the abundance ratio of molecules with these masses. In eqs. 6 and 7, this can be taken into account by expressing the numbers of neutrals by their ionic counterparts, multiplied by the corresponding mass spectrometric sensitivity factors[f] f_x, where x is the value of m/z:

$$ ^{45}R_{\mathrm{B}} = \frac{f_{45}\left[N\left(^{13}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}^{+}\right)_{\mathrm{B}} + N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{17}\mathrm{O}^{+}\right)_{\mathrm{B}}\right]}{f_{44}N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}^{+}\right)_{\mathrm{B}}} \tag{8} $$

and

$$ ^{46}R_{\mathrm{B}} = \frac{f_{46}\left[N\left(^{12}\mathrm{C}^{18}\mathrm{O}^{16}\mathrm{O}^{+}\right)_{\mathrm{B}} + N\left(^{13}\mathrm{C}^{17}\mathrm{O}^{16}\mathrm{O}^{+}\right)_{\mathrm{B}} + N\left(^{12}\mathrm{C}^{17}\mathrm{O}^{17}\mathrm{O}^{+}\right)_{\mathrm{B}}\right]}{f_{44}N\left(^{12}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}^{+}\right)_{\mathrm{B}}} \tag{9} $$

During the differential measurement using IRMS, identical corrections need to be applied automatically to sample and reference gas. For the ratios of ratios that are used to express isotopic deviations from a reference (delta values of $^{45}\delta$ and $^{46}\delta$ expressed analogously to eq. 1), the correction factors f_x cancel out and have therefore been excluded in subsequent considerations.

The ratio of the m/z 45 and m/z 44 ion currents is the primary factor affecting the $\delta(^{13}\mathrm{C})$ value. The ratio of the m/z 46 and m/z 44 ion currents is the principal factor determining the $\delta(^{18}\mathrm{O})$ value. The m/z 44 ion beam consists of the single isotopomer $^{12}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}^{+}$. The m/z 45 ion beam comprises, by number fraction, about 93.5 % $^{13}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}^{+}$ and 6.5 % $^{12}\mathrm{C}^{17}\mathrm{O}^{16}\mathrm{O}^{+}$. The m/z 46 ion beam is composed primarily of $^{12}\mathrm{C}^{18}\mathrm{O}^{16}\mathrm{O}^{+}$ with minor contributions from $^{13}\mathrm{C}^{17}\mathrm{O}^{16}\mathrm{O}^{+}$ (number fraction of ~0.21 %) and $^{12}\mathrm{C}^{17}\mathrm{O}^{17}\mathrm{O}^{+}$ (number fraction of ~0.0036 %). To obtain the $\delta(^{13}\mathrm{C})$ value from the ratio of the m/z 45 and m/z 44 ion currents, one must account for ("correct for") the ^{17}O contribution to the m/z 45 ion beam (see eq. 8). Although an independent analysis of the ^{17}O abundance is feasible by measuring the m/z 47 ion beam (assuming complete isotopic equilibration), the m/z 47 ion beam is in practice not measured routinely due to a lack of precision and accuracy since the number ratio of the m/z 47 to

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[f] For ions, the mass spectrometric sensitivity factors f_{44}, f_{45}, and f_{46} (eqs. 8 and 9) in principle should be incorporated in the correction equations separately for each isotopologue. However, the differences in practice would only matter if the ionization probability for the different isotopologues of the same m/z values (e.g., $^{13}\mathrm{C}^{16}\mathrm{O}^{16}\mathrm{O}$ and $^{12}\mathrm{C}^{17}\mathrm{O}^{16}\mathrm{O}$) would be considerably different, which is not the case for electron impact ionization IRMS. An appropriate scheme linking ratios in a neutral sample gas to those in VPDB via a chain of measured relative $^{45}\delta$- and $^{46}\delta$-values has been given by Allison et al. [3] (eqs. 10 and 11 therein).

m/*z* 44 ion currents is very low (~0.0046 %). Instead, the correction for the ^{17}O abundance of the *m*/*z* 45 ion beam is performed by calculating the ^{17}O abundance from measurement of the $\delta(^{18}\text{O})$ of the sample, which is obtained by determination of the ratio of the *m*/*z* 46 and *m*/*z* 44 ion currents. This method for ^{17}O correction requires detailed information regarding the relationship between the abundance of ^{17}O and ^{18}O in the major terrestrial oxygen pools, as well as knowledge of the value of $X(^{17}\text{O})/X(^{13}\text{C})$ of the material defining the international VPDB $\delta(^{13}\text{C})$ scale, where X is the number fraction. The objective idea is to evaluate the ^{17}O contribution without physically analyzing the ^{17}O abundance of CO_2, based on a "best" and most accurate estimate of the ^{17}O-^{18}O abundance relationship.

The first attempt of a ^{17}O abundance-correction procedure was introduced in 1957 by Craig [1], who related ^{17}O and ^{18}O abundances. Craig approximated the isotope ratios of ^{18}O and ^{17}O in a measured sample by the relation

$$\left[\frac{^{18}R_{\text{B}}}{^{18}R_{\text{std}}}\right]^{\lambda} = \frac{^{17}R_{\text{B}}}{^{17}R_{\text{std}}} \tag{10}$$

with $\lambda = 0.5$. From measurements of CO_2 evolved from carbonate isotopic reference materials in use in 1957 using 100 % H_3PO_4 at 25.3 °C, the relation of ^{45}R and ^{13}R was determined to be

$$\frac{^{45}R_{\text{std}}}{^{13}R_{\text{std}}} = 1.0676 \tag{11}$$

where std represents CO_2 evolved from PDB (Peedee belemnite isotopic reference material used in the 1950s), not the isotopic composition of the PDB solid. In a similar manner, for ^{17}R and ^{13}R, Craig [1] published

$$\frac{^{17}R_{\text{std}}}{^{13}R_{\text{std}}} = 0.0338 \tag{12}$$

The result was a simple quantity equation for correcting measured isotopic differences using the *m*/*z* 44, 45, and 46 ion currents, expressed in the delta notation relative to PDB as

$$\delta(^{13}\text{C}) \approx 1.0676\ {}^{45}\delta - 0.0338\ \delta^{18}\text{O} \tag{13}$$

where $^{45}\delta$ is $(^{45}R_{\text{B}}/^{45}R_{\text{std}}) - 1$. This procedure, although widely used throughout the community since it was first published in 1957, is an oversimplification of the situation for naturally occurring materials and has, with improved instrumentation and analytical procedures, led to considerable scale inconsistencies in some cases. The experimental situation has been investigated for more than two decades by a number of research groups [2–9] with the following general formulae and conclusions, which apply in a strict sense only for neutral species[g]:

$$^{45}R = 2\ {}^{17}R + {}^{13}R \tag{14}$$

$$^{46}R = 2\ {}^{18}R + 2\ {}^{17}R\,{}^{13}R + (^{17}R)^2 \tag{15}$$

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[g] These expressions assume statistical distribution of the isotopes across all isotopologues so that molecular ratios can correctly be described as atom ratios.

and from eq. 10:

$$^{17}R = K\,(^{18}R)^{\lambda} \tag{16}$$

where $K = {}^{17}R_{\mathrm{std}} / ({}^{18}R_{\mathrm{std}})^{\lambda}$.

Using ^{13}R from eq. 14 and ^{17}R from combining eqs. 14 and 16, one finds

$$-3\,K^2\,(^{18}R)^{2\lambda} + 2\,K\,^{45}R\,(^{18}R)^{\lambda} + 2\,^{18}R - {}^{46}R = 0 \tag{17}$$

Equation 17 must be solved iteratively for ^{18}R when λ differs from the Craig [1] assignment of 0.5 exactly. Then, ^{17}R is obtained from eq. 16. Finally, ^{13}R is obtained from the relation

$$^{13}R = {}^{45}R - 2\,^{17}R \tag{18}$$

SELECTION OF LAMBDA

Equation 10 implies that the isotopic compositions of sample and reference material are linked exponentially. The nature of this link can be one of the following cases [8,10]:

(1) Materials linked by a common fractionation process that started from the same material follow an exponential relation characterized by λ. Luz and Barkan [8] demonstrated this for respiration, both mathematically and by accurate measurements. Other examples include Rayleigh distillation and diffusion.

(2) Similar (or the same) fractionation processes starting from a single (or similar) materials give a family of fractionation lines, being close in the three-isotope space (^{17}O-^{18}O-^{16}O). This seems to be the case for natural waters [5] (ocean and precipitation). In this case, the description by eq. 10 is a phenomenological approach [10].

(3) If the value for λ is calculated for two data points (e.g., sample and zero point of a scale) that are not proven to be linked by a common fractionation process, then: λ does not characterize a process; λ has a formal meaning only; and the value of λ may be confusing at best.

It has long been known that λ is not exactly 0.5 for any fractionation process. From theoretical considerations [11,12], the exact relation between isotopic fractionation factors based on ^{17}R and ^{18}R depends predominantly on the formation of the CO bond and on mass-separation processes, such as diffusion or distillation (case 1 above). Thus, one cannot expect a constant value for different oxygen isotopic fractionation processes in nature. This has been confirmed experimentally for the major oxygen-bearing pools in nature [4,5,7,8,11], and thus the ^{17}O correction cannot simply follow a case 1 scenario. However, most carbon-bearing materials analyzed as CO_2 in IRMSs have their oxygen derived from the global water pool, which has a constant λ of 0.528 [5] and which is now known with high precision to be 0.5279 ± 0.0001 [7]. Analyses of numerous samples measured from the Vostok ice core (Antarctic), covering the last 150 000 years, also confirmed a value of 0.528 for λ [13]. Hence, for the global water pool it can be concluded that λ is 0.528 (following a case 2 scenario).

When investigating the $\delta(^{17}\mathrm{O})$–$\delta(^{18}\mathrm{O})$ relationship in carbonates by thermal decomposition, Miller et al. [15] found a λ value of 0.5247 for the CO_2 as well as for the associated residues (CaO and MgO)[h]. The $\delta(^{18}\mathrm{O})$ values in these experiments covered a range of about 30 ‰. Despite a small vertical offset in the data, a value of 0.5247 appears to characterize carbonates—a value that is similar to that found for the global water pool. The same value of 0.5247 was found for a large number of silicates [4] where the ^{17}O-^{18}O partitioning involves high-temperature magmatic processes not directly related to marine carbonates or water.

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[h] Seven different carbonates were analyzed, which may limit statistical significance of the extracted value for λ.

Finally, Thiemens et al. [28] reported the value of $\Delta(^{17}O) = \delta(^{17}O) - 0.52^{*}\ \delta(^{18}O)$ to be zero (within experimental uncertainty) on 20 commercial and 75 tropospheric CO_2 samples from La Jolla (all data on the VSMOW scale[i]). Taking a reasonable range of $\delta(^{18}O)$ (from 20 to 42 ‰ relative to VSMOW, –11 to 0 on the VPDB-CO_2 scale) and translating data to the VPDB-CO_2 scale, the slope in the $\ln[\delta(^{17}O) + 1]$ vs. $\ln[\delta(^{18}O) + 1]$ plot is estimated at ~0.528 (depending slightly on the range of values selected).

Considering the findings above, and given that oxygen of natural CO_2 is rapidly exchanged with liquid water (except for some very specific cases like CO_2 in the stratosphere and in some meteorites), the water value of 0.528 for λ was proposed as the most probable value for the ^{17}O-correction [16]. Equation 10 links the analyzed CO_2 to respective isotope scales in use (VPDB-CO_2 or VSMOW). Hence, the use of 0.528 for λ in combination with VPDB-CO_2 or VSMOW scales (both related to water) is self-consistent. This is in agreement with the purpose of the ^{17}O correction, which is to provide a "best" and most accurate estimate of the ^{17}O-^{18}O relationship without actually analyzing the ^{17}O abundance of CO_2.[j] The choice of 0.528 for λ corresponds to the phenomenological approach, case 2 above.

We note two cases where deviations from the more general relation between $\delta(^{17}O)$ and $\delta(^{18}O)$ in terrestrial waters have been documented. The oxygen isotopic composition of O_2 in air is generated mainly by photosynthesis and respiration. The latter has a considerable isotope fractionation effect characterized by a λ value of 0.518 [8], resulting in O_2 gas with a composition below the water fractionation line (the line with a λ value of 0.528 starting from VSMOW, where VSMOW by definition has $\delta(^{17}O) \equiv 0$ and $\delta(^{18}O) \equiv 0$). In addition, ^{17}O is removed in part by accumulation in stratospheric ozone, giving a somewhat enhanced ^{17}O depletion of air O_2 relative to the water line. As a consequence, the oxygen isotopic composition of O_2 in air expressed on the VSMOW scale [7,8] can be characterized by a (formal, case 3) value for λ of 0.509, representing the steady state among ocean water, photosynthesis, and respiration with some ^{17}O accumulation in stratospheric ozone.

Moreover, an increasing number of studies investigate the deviation of the ^{17}O-^{18}O relationship from a mass-dependent fractionation in its general form $\Delta(^{17}O)$; ^{17}O anomaly or non-mass dependent fractionation[k]. The materials usually originate from reactions of ozone in the stratosphere, which is extremely enriched in ^{17}O. The correction in this case is starting at first with an approximation using the water line ($\lambda = 0.528$). This usual ^{17}O correction then needs to be refined by introducing $\Delta(^{17}O)$ (scaled to the VPDB-CO_2 scale using $\lambda = 0.528$) into the correction equations [6,9,10,16]. We stress here that using a value for λ other than the default value used for the ^{17}O-correction, 0.528, is confusing, leads to potential scale inconsistencies, and cannot be recommended. For example, $\lambda = 0.509$, which characterizes air-O_2 on the VSMOW scale, inflates to an artificial 0.555 on the VPDB-CO_2 oxygen scale [10,16] (case 3 considered above).

Summarizing, a value of 0.528 for λ appears to be the best estimate for general use in the ^{17}O correction of CO_2 originating from the relevant most abundant natural oxygen pools. The $\delta(^{13}C)$ bias arising from atmospheric O_2 with its negative $\Delta(^{17}O)$ vs. the $\lambda = 0.528$ line is limited (and the same can be expected for commercial oxygen produced from atmospheric O_2), but can reach a maximum value of 0.032 ‰. While this value may seem large for some applications, biases will tend to cancel when reference material and sample material are treated using the same oxygen source. However, when CO_2 samples with oxygen from different sources are compared to each other directly, as would be the case

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[i] VSMOW = Vienna Standard Mean Ocean Water, available from the IAEA in Vienna. The VSMOW international reference material defines the scale origins for $\delta(^{2}H)_{VSMOW}$ and $\delta(^{18}O)_{VSMOW}$.

[j] In this context, it is important to note that the VSMOW oxygen three-isotope scale and the VPDB-CO_2 oxygen isotope scale must be linked using the same $\lambda = 0.528$ [16].

[k] $\Delta(^{17}O)$ is considered here as the vertical distance (deviation) from the water fractionation line, namely $\Delta(^{17}O) = \delta(^{17}O) - [\delta(^{18}O) + 1]^{\lambda}$. For more details, see ref. [10].

for CO_2 from carbonates and from combustion, the bias needs to be taken into consideration. This bias is close to the total combined uncertainty (see below) and may be tolerable for many applications (e.g., online combustion techniques) where utmost precision is not a requirement.

SELECTION OF REFERENCE RATIOS

The second unknown in eq. 16 is K, which describes the relation of ^{17}R and ^{18}R in the reference material. The value of ^{17}R in CO_2 evolved from international reference carbonates by treatment with 100 % H_3PO_4 at 25 °C has been determined repeatedly with variable accuracy.[1] The original result adopted by Craig [1] (0.000 3800) was constructed from mass spectrometric measurements made by A. O. Nier on oxygen from an O_2 high-pressure cylinder gas with unknown origin that was calibrated using mixtures of Ar isotopes. The ^{17}R value of CO_2 evolved from virtual VPDB carbonate derived by Santrock et al. [2], from experiments where a known CO_2 gas was equilibrated with water samples of varying isotopic composition, marks the high end of the measurement values (0.000 410 85). It should be noted that the difference between these two extreme cases is equivalent to a ^{17}R span of about 80 ‰. The uncertainty in the value of ^{17}R is probably one of the largest sources of uncertainty in comparing ^{17}O-corrected results of $\delta(^{13}C)$ measurements from different laboratories. Li et al. [18] determined ^{17}R by converting O_2 gases (O_2 released from VSMOW and $H_2{}^{16}O$) to CO_2 and comparing the isotopic results before and after the conversion step. They determined a value for $^{17}R_{VSMOW}$ of 0.000 3799(8) and stressed the importance of using a newly determined value for ^{13}R [19]. However, Li et al. [18] did not report on tests or on corrections for instrumental effects and have not considered use of ^{17}R in the ^{17}O correction.

A careful redetermination of the $^{17}R/^{13}R$ relationship has been carried out by Assonov and Brenninkmeijer [17]. By using essentially the same approach as that used by Li et al. [18] of converting O_2 gases (a normal O_2 and an O_2 gas depleted in ^{17}O and ^{18}O) to CO_2 and comparing the isotopic results before and after the conversion step, including a thorough investigation of and correction for known instrumental effects, they determined a value of 0.000 395 11(94) for the ^{17}R value of CO_2 evolved from virtual VPDB calcite at 25 °C with 100 % H_3PO_4 (VPDB-CO_2). This value is about halfway between the value adopted by Craig [1] and the value of Santrock et al. [2]. Because this experiment only yields the ratio of $R(^{17}O)$ and $R(^{13}C)$ in the CO_2 measurement, Assonov and Brenninkmeijer [17] calculated the value above assuming the original ^{13}R of Craig [1] ($^{13}R_{PDB}$ = 0.011 2372). Using instead the revised value of $^{13}R_{VPDB}$ of 0.011 80(28), as determined from the measurement of NBS 19 calcite by Chang and Li [19] and accepted as the reference value for $x(^{13}C)$ and $x(^{12}C)$ by IUPAC [20], the assigned ^{17}R value shifts to 0.000 393 10(94), which can be represented as 0.000 393(1). It is important to recognize that any value assigned to ^{17}R in VPDB-CO_2 gas based on the Assonov and Brenninkmeijer measurements [17] will change with a revised, more accurate determination of ^{13}R. However, the ^{17}O correction calculation does not require absolute values [9,16]. Quantitatively, it is sufficient to use a consistent $^{17}R/^{13}R$ value, such as 0.035 16(8), for the experiments done by Assonov and Brenninkmeijer [17]. Thereafter, we propagate the uncertainty of the $^{17}R/^{13}R$ ratio to the scale of ^{13}R; for calculating $\delta(^{13}C)$, the uncertainty of ^{13}R does not need to be considered.

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[1] The PDB scale and, later, the VPDB scale are linked to solid carbonates. The only analyte is CO_2 evolved from the reference carbonate. Though for many years VPDB was the only recommended scale, data reporting and comparisons were always based on VPDB-CO_2. Moreover, all experimental determinations of ^{17}R until now have been based on CO_2 gas [1,2,17,18]. For the reasons discussed above and in order to avoid uncertainties associated with the VPDB/VPDB-CO_2 conversion, both data treatment (^{17}O-correction) and ^{18}O data reporting have to be made on the VPDB-CO_2 scale; it is useful to state the value assumed for the oxygen isotopic fractionation factor between evolved CO_2 and calcite, the purity of the phosphoric acid, and the reaction temperature.

A SIMPLIFIED ^{17}O CORRECTION SUFFICIENTLY ACCURATE FOR MANY CASES

The fact that eq. 17 must be solved iteratively has led to difficulties when implementing the full ^{17}O correction in a data spreadsheet and to potential inconsistencies in data treatment. M. Verkouteren attempted to unify data treatment with an interactive web tool created and maintained by NIST [21]. However, this tool cannot be introduced in data spreadsheets and, because of iterative equation solving, scenarios cannot be evaluated easily.

Following arguments in Gonfiantini et al. [22] and in Kaiser [9], it is worth simplifying the equations given above using the delta notation and the $^{17}R/^{13}R$ ratio instead of the individual ratios. The $^{46}\delta$ value represents the $\delta(^{18}\mathrm{O})$ deviation at the 99.8 % level, depending slightly on the ^{13}C content (see above). Hence, subtraction of the respective interfering ion currents does not need to be extremely accurate in order to achieve the desired precision requirement for the ^{17}O correction. To a first approximation, the measured $^{46}\delta$ value relative to $\mathrm{CO_2}$ evolved from virtual VPDB carbonate with 100 % $\mathrm{H_3PO_4}$ at 25 °C ($^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$) can be equated with $\delta(^{18}\mathrm{O})$. Assuming that $\Delta(^{17}\mathrm{O})$ is zero (an absence of non-mass-dependent fractionation)$^{\mathrm{k}}$ and assuming that $\delta(^{17}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}}$ can be expressed as ($\lambda\,^{46}\delta_{\mathrm{VPDB}}$), eq. 22 in Kaiser [9] can be simplified further, yielding

$$\delta\left(^{13}\mathrm{C}\right) \approx {}^{45}\delta_{\mathrm{VPDB\text{-}CO_2}} + 2\frac{^{17}R\left({}^{45}\delta_{\mathrm{VPDB-CO_2}} - \lambda^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}\right)}{^{13}R} \tag{19}$$

where $^{17}R/^{13}R = 0.035\,16(8)$ as given above.

A very similar equation was previously proposed by Gonfiantini et al.[m] [22]. Equation 19 shares its simplicity with that of Craig [1], which is eq. 13 herein, with the notation also given in delta terms, but it avoids the oversimplification of the $^{17}\mathrm{O}$-$^{18}\mathrm{O}$ relation in the world oxygen pools. Equation 19 also avoids the necessity to build an iterative procedure into the evaluation calculation. Equation 19 deviates from the complete correction by less than 0.010 ‰ in most cases and no more than 0.026 ‰ in extreme cases (see Table 1). We note that the extreme cases given in Table 1 are far from everyday analytical practice.

The difference between $\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}}$ and $^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$ can reach 0.1 ‰ when $\delta(^{13}\mathrm{C})_{\mathrm{VPDB}}$ is large. While this is sufficient for the ^{17}O correction (eq. 19), it is not satisfactory for the $\delta(^{18}\mathrm{O})$ value itself. Gonfiantini et al. [22] also proposed to determine $\delta(^{18}\mathrm{O})$ from $^{46}\delta$ by correcting the $^{46}\delta$ value for ^{13}C and ^{17}O contributions and pointed out that these correction terms are small. For a more accurate representation of $\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}}$, the ratio set given in Table 2 can be used, resulting in the approximation

$$\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}} \approx [{}^{46}\delta_{\mathrm{VPDB\text{-}CO_2}} - 0.0021\ \delta\,^{13}\mathrm{C}_{\mathrm{VPDB}}\ ]/0.99904 \tag{20}$$

The deviations between $\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}}$ calculated using eq. 20 and fully rigorous equations remain well below 0.002 ‰ (Table 1).

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[m] The Gonfiantini et al. [22] equation has essentially the same form as the Kaiser [9] equation. The main difference is the proposed use of $\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO2}}$ instead of the measured $^{46}\delta_{\mathrm{VPDB\text{-}CO2}}$ for the ^{17}O correction.

Table 1 Comparison of ^{17}O correction results between the exact solution (after Assonov and Brenninkmeijer [16,17]) and eq. 19.

Values after numerical solution of eq. 17, the full correction [16]		Linear approximation in this work, eqs. 19 and 20		Deviation from exact solution/bias	
1000 $\delta(^{13}C)$	1000 $\delta(^{18}O)$	1000 $\delta(^{13}C)$	1000 $\delta(^{18}O)$	1000 $\delta(^{13}C)$	1000 $\delta(^{18}O)$
1.950	–2.200	1.9497	–2.1999	–0.0003	0.0001
25.000	–25.000	24.992	–25.000	–0.008	0.000
0.000	–25.000	–0.006	–24.999	–0.006	0.001
–25.000	–25.000	–25.005	–24.999	–0.005	0.001
–50.000	–25.000	–50.003	–24.998	–0.003	0.002
25.000	0.000	24.998	0.000	–0.002	0.000
0.000	0.000	0.000	0.000	0.000	0.000
–25.000	0.000	–24.998	0.000	0.002	0.000
–50.000	0.000	–49.996	0.000	0.004	0.000
25.000	25.000	24.994	25.000	–0.006	0.000
0.000	25.000	–0.004	24.999	–0.004	–0.001
–25.000	25.000	–25.003	24.998	–0.003	–0.002
–50.000	25.000	–50.001	24.998	–0.001	–0.002
Extreme cases:					
25.000	–50.000	24.974	–50.001	–0.026	–0.001
0.000	–50.000	–0.024	–49.999	–0.024	0.001
–25.000	–50.000	–25.022	–49.998	–0.022	0.002
–50.000	–50.000	–50.020	–49.996	–0.020	0.004
25.000	50.000	24.978	49.999	–0.022	–0.001
0.000	50.000	–0.020	49.998	–0.020	–0.002
–25.000	50.000	–25.018	49.997	–0.018	–0.003
–50.000	50.000	–50.016	49.995	–0.016	–0.005

Table 2 Relevant ratios for correcting the ^{17}O contribution to the *m/z* 45 ion current.

[$^{13}R_{VPDB} = R(^{13,12}C)_{VPDB}$, $^{17}R_{VPDB–CO_2} = R(^{17,16}O)_{VPDB–CO_2}$, and $^{18}R_{VPDB–CO_2} = R(^{18,16}O)_{VPDB–CO_2}$.]

	Assonov and Brenninkmeijer [16]	This work	Reference (this work)
$^{13}R_{VPDB}$	0.011 237 2	0.011 180(28)	[19]
$^{17}R_{VPDB\text{-}CO_2}$	0.000 395 11(94)	0.000 3931(9)	derived from [16]
$^{17}R_{VPDB\text{-}CO_2}/^{13}R_{VPDB}$	0.035 16(8)	0.035 16(8)	derived from [16,19]
λ	0.528	0.528	[5,7,13]
K	0.010 276 89	0.010 224 61**	
$^{18}R_{VPDB\text{-}CO_2}$*	0.002 088 35	0.002 088 35	[3] (derived from [24])

[*] This value is derived from $^{18}R_{VSMOW}$ using a conversion of 1.030 92 for the VSMOW/VPDB (solid calcite) relation [25,26]. In addition, the conversion at 25 °C from calcite to CO_2 is taken into account using an oxygen isotopic fractionation factor of 1.010 25 between calcite and CO_2 (Friedman and O'Neil, 1977) [27].

[**] $K = 0.010\,224\,48$ when using rounded values for $^{17}R_{VPDB\text{-}CO_2}$ (= 0.000 3931) and $^{18}R_{VPDB\text{-}CO_2}$ (= 0.002 0884).

EXPRESSING $^{45}\delta$ AND $^{46}\delta$ ON THE VPDB-CO_2 SCALE

Equation 19 requires $^{45}\delta_{\text{VPDB-CO}_2}$ and $^{46}\delta_{\text{VPDB-CO}_2}$. Conceptually, VPDB-$CO_2$ defines a virtual scale realized via CO_2 evolved from NBS 19 carbonate with 100 % H_3PO_4 at 25 °C. The VPDB scale is defined for the virtual solid carbonate material by assigning a consensus $\delta(^{13}C)$ value of +1.95 ‰ and assigning a $\delta(^{18}O)$ value of –2.2 ‰ exactly to NBS 19 carbonate (not CO_2 evolved from this carbonate) [23]. By definition, the uncertainty of both of these consensus values is zero.

For any sample analyzed, $^{45}\delta$ and $^{46}\delta$ values are obtained by comparison with a reference precisely calibrated for $\delta(^{13}C)_{\text{VPDB}}$ and $\delta(^{18}O)_{\text{VPDB-CO}_2}$. From these measurements, the composite $^{45}\delta_{\text{VPDB-CO}_2}$ and $^{46}\delta_{\text{VPDB-CO}_2}$ values have to be calculated in order to apply eq. 19 during correction for the ^{17}O contribution. This is essentially the same relation, applied in reverse order. It can be shown that

$$^{45}\delta_{\text{VPDB-CO}_2} = [\delta(^{13}C)_{\text{VPDB}} + \lambda\, Q\, \delta(^{18}O)_{\text{VPDB-CO}_2}]/(Q + 1) \tag{21}$$

or

$$^{45}\delta_{\text{VPDB-CO}_2} = 0.9343\ \delta(^{13}C)_{\text{VPDB}} + 0.0347\ \delta(^{18}O)_{\text{VPDB-CO}_2} \tag{22}$$

where $Q = 2\ (^{17}R/^{13}R)$ and is 0.070 32 ± 0.000 17 (following Assonov [17]), and $\lambda = 0.528$. Again, the individual ^{17}R and ^{13}R values are not needed. Rather, their ratios enter the correction equation.

It should be noted that eq. 21 and any correction for ^{17}O are intimately linked and must be used in a consistent fashion in order to avoid artefacts in the data. While this sounds simple, it often is difficult in practice, particularly when using secondary reference materials that have an uncertain history regarding the ^{17}O correction applied during the initial assignments of $\delta(^{13}C)_{\text{VPDB}}$ and $\delta(^{18}O)_{\text{VPDB-CO}_2}$.

Similarly, $^{46}\delta_{\text{VPDB-CO}_2}$ can be calculated from eq. 20 by using the assigned $\delta(^{13}C)_{\text{VPDB}}$ and $\delta(^{18}O)_{\text{VPDB-CO}_2}$ values

$$^{46}\delta_{\text{VPDB-CO}_2} \approx 0.0021\ \delta(^{13}C)_{\text{VPDB}} + 0.99904\ \delta(^{18}O)_{\text{VPDB-CO}_2} \tag{23}$$

Applying eqs. 22 and 23 to NBS 19 itself, we obtain

$$^{45}\delta_{\text{NBS19-CO}_2\text{,VPDB-CO}_2} = 1.746\ ‰ \tag{24}$$

and

$$^{46}\delta_{\text{NBS19-CO}_2\text{,VPDB-CO}_2} = -2.194\ ‰. \tag{25}$$

The VPDB-CO_2 scale is defined via NBS 19 with $\delta(^{13}C)_{\text{NBS19}} \equiv 1.95$ ‰, and $\delta(^{18}O)_{\text{NBS19,VPDB}} \equiv -2.2$ ‰ exactly. Both values by definition have an uncertainty of zero. The scale is *not* defined in terms of $^{45}\delta$ and $^{46}\delta$, although the values above could serve this purpose. One important consequence is that the origin of the VPDB scale for $\delta(^{13}C)$ cannot be fixed independently, and it depends on the numerical parameters used for the ^{17}O correction applied when CO_2 is the measured gas.[n] While this effect in general is not large, it cannot be ignored in applications where high precision and accuracy is a requirement. In comparison with the full correction, the shift of the VPDB $\delta(^{13}C)$ origin is very small when using the linear approximation for ^{17}O correction, as can be inferred from the first example in Table 1 with the NBS 19 calcite values defining the VPDB scale. In contrast, when comparing the Craig [1]-vs.-Santrock [2] correction, the relative deviation of the $\delta(^{13}C)$-zero point amounts to 0.018 ‰, a value which can exceed the larger deviations given in Table 1 for extreme isotopic compositions. The relative deviation of the $\delta(^{13}C)$-zero point is also large when compared to the accuracy required, for instance, for air-CO_2 research where the inter-laboratory compatibility should be

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[n] If one were to use a gas such as CF_4 with fluorine being mono-isotopic, this ambiguity would not occur during the measurement of $\delta(^{13}C)$ values.

in the range of 0.01 ‰. The VPDB zero point offset arises exclusively from the small isotopic abundance difference of NBS 19 from the VPDB origin. When based on different ratio sets, the deviations in measured $\delta(^{13}\mathrm{C})$ values increase with the $^{45}\delta_{\mathrm{sample,NBS19\text{-}CO_2}}$ deviation from zero and depend on actual $\delta(^{13}\mathrm{C})$ and $\delta(^{18}\mathrm{O})$ values (Assonov and Brenninkmeijer [17]); note that the only measurands are the $^{45}\delta$ and $^{46}\delta$ differences between a sample and NBS 19-CO$_2$.

In daily routine measurement practice, the raw isotopic differences $^{45}\delta$ and $^{46}\delta$ between a CO$_2$ sample and a working reference CO$_2$ must be converted to the respective VPDB-CO$_2$ values ($^{45}\delta_{\mathrm{VPDB\text{-}CO_2}}$ and $^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$) before the ^{17}O correction can be applied. While this is no different than the earlier requirements using the Craig [1] equation, the order has often been reversed in published data. Making use of eqs. 21 and 22 may be of help in avoiding further inconsistencies within the final data.

ACCURACY OF THE LINEARIZED ^{17}O CORRECTION

By using a simplified uncertainty budget, one can demonstrate that the errors due to a linear approximation of the ^{17}O correction are much less than or, in extreme cases, at least comparable to the analytical errors produced during measurement using the best IRMS instruments available. We start with the singular point having zero uncertainty on the VPDB scale, and with the respective VPDB-CO$_2$ scale anchor[o]: NBS 19 calcite (for VPDB) and NBS 19-CO$_2$ (for VPDB-CO$_2$). Next, all measured values are linked to the scale via a chain of measurements done on CO$_2$ gases, each measurement having its own uncertainty. For establishing a complete calibration or traceability chain, a simple equation can be derived [3].

Using the general delta equation (eq. 1; $\delta_{\mathrm{B,S}x} = R_{\mathrm{B}}/R_{\mathrm{S}x} - 1$) and using the relation $R_{\mathrm{B}}/R_{\mathrm{S0}} = R_{\mathrm{B}}/R_{\mathrm{S1}} \times R_{\mathrm{S1}}/R_{\mathrm{S2}} \times R_{\mathrm{S2}}/R_{\mathrm{S3}} \ldots \times R_{\mathrm{S}x}/R_{\mathrm{S0}}$ with B representing the sample and Sx referring to the various levels of reference material in the chain, one can write

$$(\delta_{\mathrm{B,S0}} + 1) = (\delta_{\mathrm{B,S1}} + 1) \times (\delta_{\mathrm{S1,S2}} + 1) \times (\delta_{\mathrm{S2,S3}} + 1)\ldots \times (\delta_{\mathrm{S}x\mathrm{,S0}} + 1) \tag{26}$$

Equation 26 is valid for all delta expressions. The benefit of the linearized ^{17}O correction described in this work can be demonstrated by a simplified uncertainty budget. The combined uncertainty of the $^{45}\delta$ values of a sample, $U_{\mathrm{c}}(^{45}\delta)$, then can be expressed as

$$U_{\mathrm{c}}(^{45}\delta) \approx \{\Sigma\,[U(^{45}\delta)]^2\}^{0.5} \tag{27}$$

where the $U(^{45}\delta)$ are the uncertainties of the $^{45}\delta$ values. The same form is valid for determining $U_{\mathrm{c}}(^{46}\delta)$ from values of $U(^{46}\delta)$.

For the highest-accuracy IRMS instruments running in dual inlet mode, a typical analytical error in $^{45}\delta$ is about ±0.01 ‰ (1σ). For three consecutive measurement steps (NBS 19-CO$_2$ → working ref. CO$_2$ → sample), $U_{\mathrm{c}}(^{45}\delta)$ is ±0.017 ‰. Using eq. 19 and assuming $\Delta(^{17}\mathrm{O})$ equals 0 and $^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$ is close to zero, the error in $\delta(^{13}\mathrm{C})$ is ±0.019 ‰. This value is higher than any uncertainty (bias) introduced by the linearized ^{17}O correction (see Table 1). For the case when a secondary/tertiary-level reference material is distributed as combustible material, the error budget is more complicated. As a consequence, the traceability chain to NBS 19-CO$_2$ grows longer and errors will be enhanced.

Equation 19 can also be used to estimate how the uncertainty in the $^{17}R_{\mathrm{VPDB\text{-}CO_2}}/^{13}R_{\mathrm{VPDB}}$ ratio affects calculated $\delta(^{13}\mathrm{C})$ values. The value 0.035 16(8) in Table 2 is based on a 95 % confidence interval of measured values and a conservative assessment of other values included in the ^{17}R calculations [17]. For a measured $^{45}\delta_{\mathrm{VPDB\text{-}CO_2}}$ deviating up to ±25 ‰ from zero and $^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$ deviating up to

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[o] As the VPDB-CO$_2$ scale is anchored to VPDB by CO$_2$ evolved from virtual VPDB calcite by reaction with 100 % phosphoric acid at 25 °C, the uncertainty can be made very low; it is, however, not zero, as has been demonstrated recently by a series of NBS 19-CO$_2$ extractions performed independently in three laboratories, under well-controlled conditions [29].

±25 ‰ from zero, the effect of the uncertainty on $\delta(^{13}C)$ amounts to ±0.006 ‰ (depending on combination of $\delta^{13}C$ and $\delta^{18}O$; for the most critical application, air CO_2 with $\delta(^{13}C)$ from –10 to –7 ‰ and $\delta(^{18}O)$ from –10 to +2 ‰, the effect is within ±0.001 ‰). The uncertainty in λ cannot be illustrated in this way.

SUMMARY AND PRACTICAL IMPLEMENTATION OF THE LINEARIZED ^{17}O CORRECTION

This report aims at unifying raw data treatment for CO_2 IRMS by proposing (i) a unified set of numerical values in use and (ii) a unified calculation algorithm, based on a simple linear approximation formula. In this way, users can easily check calculations performed by mass-spectrometry software. In practice, the approach aims at bringing users making CO_2 isotope determinations by IRMS to the same scale realization. As the value of ^{17}R has been determined on the scale of the fixed ^{13}R in current use; only the ratio $^{17}R/^{13}R$ matters. Therefore, the error propagation does not include the error in the ^{13}R determination; the error of $^{17}R/^{13}R$ in use is sufficiently small not to affect $\delta(^{13}C)$ determinations further.[p]

The calculation scheme includes measured (raw) $^{45}\delta$ and $^{46}\delta$ values only, and links a sample to a primary reference material via a chain of relative/delta measurements. The scheme is based on a consistent set of numerical values (^{13}R, ^{17}R, and ^{18}R values and a general value for λ). In addition to the data treatment unification, the approach helps getting transparent and simple estimation of uncertainties. Errors introduced by the linearization formula are typically less than 0.008 ‰ as tabulated in Table 1. If needed, users can apply numerical calculation methods to solve the whole set of equations without approximation.

The data treatment includes the following sequence of steps:

1. All calculation steps must be based on the numerical values listed in Table 2 (unless new recommendations are released and agreed upon).
2. Values of $^{45}\delta$–$^{46}\delta$, obtained by mass spectrometric measurement of a sample CO_2 gas, must be scaled to $^{45}\delta$–$^{46}\delta$ of VPDB-CO_2 using $^{45}\delta$–$^{46}\delta$ values of the calibration chain traceable to NBS 19-CO_2; furthermore, the CO_2 gas must be evolved from NBS 19 calcite by reaction with 100 % H_3PO_4 at 25 °C. The traceability chain for substance B and reference materials S0 to S*x* is given by eq. 26:

   $$(\delta_{B,S0} + 1) = (\delta_{B,S1} + 1) \times (\delta_{S1,S2} + 1) \times (\delta_{S2,S3} + 1)\ldots \times (\delta_{Sx,S0} + 1)$$

   Use of $^{45}\delta_{NBS19\text{-}CO_2,VPDB\text{-}CO_2}$ of 1.746 ‰ and $^{46}\delta_{NBS19\text{-}CO_2,VPDB\text{-}CO_2}$ of –2.194 ‰ is recommended (eqs. 24 and 25). Alternatively, for a combustible reference material, $^{45}\delta$–$^{46}\delta$ values may be based on certificate $\delta(^{13}C)$ values and actual $\delta(^{18}O)$ values through use of eqs. 22 and 23 with analyses of CO_2 generated from NBS 22 oil, for example, and CO_2 that has been independently calibrated for oxygen isotopic composition.
3. Finally, $\delta(^{13}C)_{VPDB}$ can be calculated from eq. 19

$$\delta\left(^{13}C\right) \approx {}^{45}\delta_{VPDB\text{-}CO_2} + 2\frac{^{17}R\left(^{45}\delta_{VPDB-CO_2} - \lambda^{46}\delta_{VPDB\text{-}CO_2}\right)}{^{13}R}$$

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[p] The so-constructed $\delta(^{13}C)$ scale itself still suffers from the remaining uncertainties/errors in ^{13}R, ^{17}R, and ^{18}R values as well as errors in assuming a general value for the slope λ. These errors matter when, and only when data are propagated to the primary SI-scale, not when comparing data on the (relative) VPDB-CO_2 scale. As a consequence, the effect of these uncertainties is excluded from the error propagation for $\delta(^{13}C)$ values.

To a first approximation, $\delta(^{18}\mathrm{O})$ can be equated with $^{46}\delta_{\mathrm{VPDB\text{-}CO_2}}$. Newly determined $\delta(^{13}\mathrm{C})$ and $\delta(^{18}\mathrm{O})$ values can then be reevaluated more accurately using eq. 20

$$\delta(^{18}\mathrm{O})_{\mathrm{VPDB\text{-}CO_2}} \approx [^{46}\delta_{\mathrm{VPDB\text{-}CO_2}} - 0.0021\ \delta(^{13}\mathrm{C})_{\mathrm{VPDB}}]/0.99904$$

4. When sample and reference materials are $\mathrm{CO_2}$ gases (and not combustible materials), one can consider a simplified uncertainty budget based on all measurement steps by tracing the calibration from NBS 19-$\mathrm{CO_2}$ to a sample using eq. 27

$$U_{\mathrm{c}}(^{45}\delta) \approx \{\Sigma\ [U(^{45}\delta)]^2\}^{0.5}$$

From this evaluation, the combined uncertainty in $\delta(^{13}\mathrm{C})$, $U_{\mathrm{c}}[\delta(^{13}\mathrm{C})]$, can be approximated as 1.07 $U_{\mathrm{c}}(^{45}\delta)$, where $U_{\mathrm{c}}(^{45}\delta)$ is the combined uncertainty of $^{45}\delta$. The same form is valid for determining $U_{\mathrm{c}}(^{46}\delta)$ from values of $U(^{46}\delta)$ and results in $U_{\mathrm{c}}(\delta^{18}\mathrm{O}) \approx U_{\mathrm{c}}(^{46}\delta)$.

APPENDIX I

The general form of the delta definition is given by

$$\delta\left({}^{i}\mathrm{E}\right)_{\mathrm{std}} = \frac{R\left({}^{i}\mathrm{E},{}^{j}\mathrm{E}\right)_{\mathrm{B}} - R\left({}^{i}\mathrm{E},{}^{j}\mathrm{E}\right)_{\mathrm{std}}}{R\left({}^{i}\mathrm{E},{}^{j}\mathrm{E}\right)_{\mathrm{std}}} = \frac{\dfrac{N\left({}^{i}\mathrm{E}\right)_{\mathrm{B}}}{N\left({}^{j}\mathrm{E}\right)_{\mathrm{B}}} - \dfrac{N\left({}^{i}\mathrm{E}\right)_{\mathrm{std}}}{N\left({}^{j}\mathrm{E}\right)_{\mathrm{std}}}}{\dfrac{N\left({}^{i}\mathrm{E}\right)_{\mathrm{std}}}{N\left({}^{j}\mathrm{E}\right)_{\mathrm{std}}}}$$

where $N(^{i}\mathrm{E})_{\mathrm{B}}$ and $N(^{j}\mathrm{E})_{\mathrm{B}}$ are the numbers of the two isotopes $^{i}\mathrm{E}$ and $^{j}\mathrm{E}$ of chemical element E in specimen B, $R(^{i}\mathrm{E}, {}^{j}\mathrm{E})_{\mathrm{B}}$ is $N(^{i}\mathrm{E})_{\mathrm{B}}/N(^{j}\mathrm{E})_{\mathrm{B}}$ in specimen B, and equivalent parameters follow for the *international measurement standard*, "std". Superscripts *i* and *j* denote mass numbers of a heavier and a lighter isotope, respectively, so that the quantity of the heavier isotope is in the numerator and that of the lighter isotope is in the denominator.

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