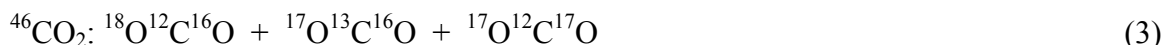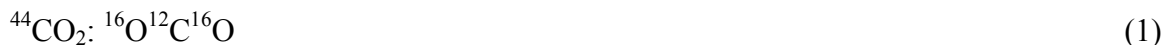# Notation and numerical strategy for conversion of CO_2 isotopomer measurements to standard delta values

Notation

CO_2 isotopomers:

$${}^{44}CO_2:\ {}^{16}O^{12}C^{16}O \tag{1}$$

$${}^{45}CO_2:\ {}^{16}O^{13}C^{16}O\ +\ {}^{17}O^{12}C^{16}O \tag{2}$$

$${}^{46}CO_2:\ {}^{18}O^{12}C^{16}O\ +\ {}^{17}O^{13}C^{16}O\ +\ {}^{17}O^{12}C^{17}O \tag{3}$$

Atomic ratios

$$R13(x) = {}^{13}C/{}^{12}C \text{ of material x (footnote *)} \tag{4}$$

$$R17(x) = {}^{17}O/{}^{16}O \text{ of material x (footnote *)} \tag{5}$$

$$R18(x) = {}^{18}O/{}^{16}O \text{ of material x (footnote *)} \tag{6}$$

Molecular ratios

$$R45(x) = {}^{45}CO_2/{}^{44}CO_2 \text{ of material x} \tag{7}$$

$$R46(x) = {}^{46}CO_2/{}^{44}CO_2 \text{ of material x} \tag{8}$$

Delta notation

The value of an isotope ratio (R) in a sample (sam) relative to a reference (REF) is expressed using the delta (δ) notation (Eq 9), where the *m* term designates the minor isotope of element E in the ratio considered (*e.g.*, $m = 13$ for $^{13}C/^{12}C$, or $m = 18$ for $^{18}O/^{16}O$. For reporting purposes

$$\delta^m E_{sam/REF} = \left[\frac{Rm(sam) - Rm(REF)}{Rm(REF)} \right] \tag{9}$$

the delta value is commonly multiplied by 1000, which is denoted by the symbol *per mill* (‰). Carbon and oxygen isotope compositions are determined through the measurement of carbon dioxide, where the relative differences in isotopomer beam voltage ratios [$^{45}CO_2^+/^{44}CO_2^+$ ($m = 45$), and $^{46}CO_2^+/^{44}CO_2^+$ ($m = 46$)] between sample and reference gases are equated with the bracketed expression in Eq 9. The following equations are also expressions of the delta notation:

$$\delta^{13}C_{x/VPDB\text{-}CO2} = [R13(x)]/[R13(VPDB\text{-}CO2)] - 1 \tag{10}$$

$$\delta^{18}O_{x/VPDB\text{-}CO2} = [R18(x)]/[R18(VPDB\text{-}CO2)] - 1 \tag{11}$$

$$\delta^{45}{}_{x/REF} = [R45(x)]/[R45(REF)] - 1 \text{ (footnote †)} \tag{12}$$

$$\delta^{46}{}_{x/REF} = [R46(x)]/[R46(REF)] - 1 \text{ (footnote †)} \tag{13}$$

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* Material x may denote the sample (sam), reference materials (RM1, RM2), or the reference material representative of the oxygen isotope pool (RM-O).

†.The reference (REF) may be either the working machine gas (WMG) or VPDB-CO_2.

Relationships

Among molecular and atomic ratios:

$$R45(x) = [R13(x)] + 2[R17(x)] \tag{14}$$

$$R46(x) = 2[R18(x)] + 2[R13(x)][R17(x)] + [R17(x)]^2 \tag{15}$$

Among oxygen isotopes:

$$\frac{R17(x)}{R17(_{RM-O})} = \left(\frac{R18(x)}{R18(_{RM-O})}\right)^a \tag{16}$$

or rearranged as:

$$R17(x) = \frac{[R17(_{RM-O})]}{[R18(_{RM-O})]^a} \cdot [R18(x)]^a = K \cdot [R18(x)]^a \tag{17}$$

The constant K is dependent upon the value of the exponent a, as well as the oxygen isotope ratios of the reference material chosen to be representative of the applicable oxygen pool. Existing conversion algorithms have utilized various fixed values of $R17(_{RM-O})$, $R18(_{RM-O})$, and a. The historical "Craig approach" [Craig 1957] commonly sets $a = 0.5$, $R17(_{RM-O}) = 0.0003775$, and $R18(_{RM-O}) = 0.0020514$ (where RM-O is a sample of tank oxygen). The "Santrock approach" [Stantrock et al 1985] uses $a = 0.516$ and values of $R17(_{RM-O})$ and $R18(_{RM-O})$ so that $K = 0.0099235$. It was shown, at least for the IRMS on which the measurements were made, that these values of a and K avoided a co-variance between the resulting $\delta^{13}C$ and $\delta^{18}O$ values. Allison et al 1995, in order that VPDB-CO_2 oxygen assignments be consistent with those of VSMOW, adopted $R17(_{RM-O}) = 0.0003808033420$, $R18(_{RM-O}) = 0.002088349077$, $a = 0.5$, and $R13(_{VPDB}) = 0.0112372$, and recommended that the delta measurements be related to the VPDB scale *before* applying the data algorithm. For general use, this approach is currently recommended by the IAEA, although each approach has advantages when utilized correctly. The algorithm in this Website has been designed to encompass all these approaches, as well as to accommodate modifications to the values of the variables for other specialized purposes.

The conversion algorithm described here may utilize user-selected values or the default values recommended by the IAEA. Upon selection of the values, the R45(x) and R46(x) values of underlying reference standards are recalculated to provide internal consistency. However, this algorithm differs from other algorithms in one important aspect. No knowledge is required regarding the isotopic composition of the working machine gas (WMG). The WMG is used to relate the measurements of a sample to one or two reference gases that are also measured on the sample side of the inlet. This avoids uncertainties arising from differences in isotopic fractionation behavior of the gases across the inlets. Measuring repeatedly the sample and reference gases against the WMG within a short timespan minimizes uncertainties from instrumental drift.

The delta measurements are related to the VPDB-CO_2 scale through either a single reference material (Eq 18):

$$\delta^m_{sam/VPDB-CO2} = \left[\frac{\left(\delta^m_{sam/WMG} + 1\right)\left(\delta^m_{RM/VPDB-CO2} + 1\right)}{\left(\delta^m_{RM/WMG} + 1\right)} - 1 \right] \tag{18}$$

Or two reference materials (Eq 19):

$$\delta^m_{sam.norm/VPDB-CO2} = \delta^m_{RM1/VPDB-CO2} + \left[\frac{\delta^m_{sam/WMG} - \delta^m_{RM1/WMG}}{\delta^m_{RM2/WMG} - \delta^m_{RM1/WMG}} \right] \cdot \left[\delta^m_{RM2/VPDB-CO2} - \delta^m_{RM1/VPDB-CO2} \right] \tag{19}$$

The $\delta^m_{RM/VPDB-CO2}$ reference values are internally calculated from the $\delta^{13}C$ and $\delta^{18}O$ value assignments using the specified values of R17(RM-O), R18(RM-O), and a. Upon relating the sample $\delta^{45}CO_2$ and $\delta^{46}CO_2$ measurements to the VPDB-CO_2 scale, the R45(sam) and R46(sam) values may be calculated through Eqs 12 and 13. The conversions to $\delta^{13}C$ and $\delta^{18}O$ values are then performed via Eq (20) by successive approximations:

$$R18(sam)_{i+1} = [-B_i + (B_i^2 - 4 \cdot A_i \cdot C)^{+0.5}]/(2 \cdot A_i) \tag{20}$$

where

$$A = 2 \cdot K \cdot [R45(sam)] \cdot [R18(sam)_i]^{a-2} \tag{21}$$

$$B = (-3 \cdot K^2 \cdot [R18(sam)_i]^{2a-1}) + 2 \tag{22}$$

$$C = -R46(sam) \tag{23}$$

The value [R46(sam)/2] is used as the first approximation [R18(sam)$_1$], and successive approximations (i = 2, 3, 4, …) of R18(sam)$_i$ are calculated until the absolute difference between successive values is less than $1 \cdot 10^{-12}$. The final value of R18(sam) is used to determine the value of R17(sam) through Eq (17). In turn, R17(sam) is used to determine R13(sam) through Eq (14). The final results are calculated through Eq 10 and Eq 11.

References

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Santrock J, Studley SA, Hayes JM (1985) Anal Chem 57: 1444-1448

Allison CE, Francey RJ, Meijer HAJ (1995) In: Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA-TECDOC-825: 155-162