Determination of ^{16}O and ^{18}O abundance ratios in natural carbon dioxide reservoirs

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Abstract

A mathematical formalism is presented that, based on the relative proportions of the $^{18}O/^{16}O$-distinctive CO_2 species $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in a given CO_2 pool, allows the calculation of $^{18}O/^{16}O$ ratios for the two different oxygen positions in the CO_2 molecules of this particular pool. The quantities of the isotopically distinctive CO_2 species can be determined as mass peak intensities ^{44}I (for $C^{16}O_2$), ^{46}I (for $C^{16}O^{18}O$), and ^{48}I (for $C^{18}O_2$) by suitable adaptations of conventional mass spectrometric techniques. The $\delta^{18}O_{(1,2)}$ values obtained for each of the above positions furnish information as to either a probabilistic ("homogeneous"; with $\delta^{18}O_{(1)} = \delta^{18}O_{(2)}$) or a nonprobabilistic ("nonhomogeneous") $^{18}O/^{16}O$ distribution (with $\delta^{18}O_{(1)} \neq \delta^{18}O_{(2)}$) in the respective CO_2 pool. Using $\delta^{18}O_{(1,2)}$, we may consequently obtain information pertaining to the oxygen sources of the CO_2 molecules in the pool as well as to reservoir changes reflected by differential diffusion rates of the isotopically distinctive CO_2 species that have left and entered the reservoir. This approach may become potentially important for an assessment of the sources and the reservoir dynamics of the atmospheric CO_2 pool. (Int J Mass Spectrom 203 (2000) 83–92) © 2000 Elsevier Science B.V.

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1. Introduction

Recently, we have published a formalism [1] reflecting the relationship between the ^{16}O and ^{18}O contents of a given carbon dioxide reservoir and its composition in terms of the three most abundant $^{16}O/^{18}O$-distinctive carbon dioxide molecules (i.e., $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$). On the basis of this formalism, we have used the quantitative proportions of the above isotopically different CO_2 species to ascertain whether the oxygen component of a partic-

ular CO_2 pool is characterized by a probabilistic or "homogeneous" oxygen isotope distribution, indicating an equilibrium of oxygen isotopes between the different CO_2 isotopomers (suggestive of a CO_2 derivation from a single source), or by a nonprobabilistic ("nonhomogeneous" or nonequilibrium) distribution pattern, such as that resulting from an oxygen supply to the respective CO_2 pool from two or more isotopically different sources.

A typical example of a nonhomogeneous oxygen isotope distribution in carbon dioxide is provided by the CO_2 species produced by the oxidation of carbon monoxide by iodine pentoxide (I_2O_5) as oxidizing agent [2,3]. In this reaction, the original oxygen atom

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of CO is being retained and a second oxygen atom is added from the oxidant to the newly generated CO_2 molecules. Natural examples are furnished by the temperature-dependent oxygen isotope composition of stratospheric and mesospheric carbon dioxide. According to Yung et al. [4] and Barth and Zahn [5], photolysis of stratospheric ozone results in a preferential release of $^{18}O(^1D)$ atoms that are effectively incorporated into CO_2 via reprocessing of the latter as an electronically excited CO_3^* complex. This leads to the formation of CO_2 molecules whose two oxygen atoms are of different pedigree, one stemming from the original CO_2 and the other from ozone-derived $O(^1D)$. Likewise, the oxidation of atmospheric CO by hydroxyl radical ($CO+OH^. \rightarrow CO_2+H^.$) [6] gives rise to CO_2 molecules whose oxygen constituents are derived from two different sources.

Moreover, we had pointed out before [1] that primarily homogeneous distribution patterns of $^{18}O/^{16}O$-distinctive molecules in a CO_2 pool may undergo differentiation to nonhomogeneous states as a result of isotope fractionations during removal or addition of CO_2 from or to the original pool. Applied to the atmospheric CO_2 reservoir, this would mean that distribution patterns of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ actually observed might hold potential information as to both the oxygen sources of atmospheric CO_2 and its reservoir dynamics (involving CO_2 fluxes into and out of this reservoir).

In the wake of a previous theoretical approach to these questions [1], the following discourse elaborates on practical details of the argument and summarizes the principal methods applied in a theoretical and practical assessment of the oxygen isotope geochemistry of closed and open CO_2 pools.

2. Systematics of oxygen isotope distribution in a carbon dioxide pool

2.1. Absolute abundances of ^{16}O and ^{18}O in homogeneous distribution patterns

If x and y are the abundances of ^{16}O and ^{18}O, their homogeneous (probabilistic) distribution in a given CO_2 pool can be expressed [7] by the equation

$$(x+y)^2 = x^2 + 2xy + y^2 = 1, \tag{1}$$

where x^2, $2xy$, and y^2 represent the probabilities of occurrence of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$, respectively, in this pool. If the quantities $[C^{16}O_2]$, $[C^{16}O^{18}O]$, and $[C^{18}O_2]$ are determined by mass spectrometric analysis, we may write the equation

$$[C^{16}O_2]/\Sigma + [C^{16}O^{18}O]/\Sigma + [C^{18}O_2]/\Sigma$$
$$= I_0 + I_1 + I_2 = 1, \tag{2}$$

where I_0, I_1, and I_2 are the relative intensities of the 44, 46, and 48 mass peaks in the CO_2 mass spectrum, and $\Sigma=[C^{16}O_2]+[C^{16}O^{18}O]+[C^{18}O_2]$. Considering Eqs. (1) and (2), we obtain the equalities

$$x^2 = I_0$$
$$2xy = I_1 \tag{3}$$
$$y^2 = I_2.$$

The equalities expressed by (3) constitute a criterion of, or define respectively, a homogeneous or probabilistic distribution of the ^{16}O and ^{18}O isotopes in our CO_2 pool. Such distribution is also reflected by the following relationships between the peak intensities derived from (3) by substitutions $x=(I_0)^{1/2}$ and $y=(I_2)^{1/2}$, that is,

$$I_1 = 2xy = 2 \cdot (I_0)^{1/2} \cdot (I_2)^{1/2} \tag{4}$$

or

$$(I_1)^2 = 4 \cdot I_0 \cdot I_2. \tag{5}$$

Any violation of criterion (5) by measured mass peak intensities $I_{0,1,2}$ (reflecting the relative proportions of the three $^{16}O/^{18}O$-distinctive CO_2 species) is indicative of a nonhomogeneous distribution of the ^{16}O and ^{18}O isotopes in the investigated CO_2 pool.

In the mass spectrum of any naturally occurring CO_2 quantum, the intensity of the 48 mass peak (I_2) is about five orders of magnitude smaller than that of the 44 mass peak (I_0). Using conventional isotopic mass spectrometry it is, therefore, impossible at present to furnish experimental proof for the validity of Eq. (5). Hence, any application of Eq. (5) for the assessment

of a possible homogeneous or nonhomogeneous condition of a given carbon dioxide reservoir (such as the atmospheric CO_2 burden) has to await the development of a technique allowing a satisfactory mass spectrometric determination of the 48 mass peak.

2.2 ^{16}O and ^{18}O abundances in a CO_2 pool relative to a standard

Let the overall ratio of the relative proportions of ^{16}O (p) and ^{18}O ($1-p$) in the totality of CO_2 molecules of a given carbon dioxide pool be $R=p/(1-p)$. For the two carbon-bound oxygen atoms of the CO_2 molecules, we can write then an equation involving a known and an unknown R, namely,

$$[R - p^*/(1 - p^*)]^2 = 0, \qquad (6)$$

where $p^*/(1-p^*)$ is a known ratio of ^{16}O and ^{18}O abundances in our particular CO_2 pool. Eq. (6) can also be written as

$$R^2 - 2[p^*/(1 - p^*)]R + [p^*/(1 - p^*)]^2 = 0. \qquad (7)$$

Assuming that $(1-p^*)\neq 0$, we obtain from (6) and (7) the equation

$$(1 - p^*)^2 \cdot R^2 - 2 \cdot p^* \cdot (1 - p^*) \cdot R + (p^*)^2 = 0, \qquad (8)$$

where $(1-p^*)^2$, $2p^*(1-p^*)$, and $(p^*)^2$ represent the probabilities of occurrence of the $C^{18}O_2$, $C^{16}O^{18}O$, and $C^{16}O_2$ molecules in our CO_2 pool.

As these values are proportional to intensities $I_{2,1,0}$ of peaks m/z 48, 46, and 44 in the CO_2 mass spectrum, Eq. (8), may be rewritten in terms of mass peak intensities and their respective proportionality factors $\xi_{2,1,0}$, that is,

$$(\xi_2 \cdot I_2) \cdot R^2 - (\xi_1 \cdot I_1) \cdot R + (\xi_0 \cdot I_0) = 0, \qquad (9)$$

where $(1-p^*)^2$, $2p^*(1-p^*)$, and $(p^*)^2$ have been substituted by $(\xi_2 \cdot I_2)$, $(\xi_1 \cdot I_1)$ and $(\xi_0 \cdot I_0)$, respectively. It seems worth noting that Eq. (9) resembles a corresponding equation $I_2 \cdot R_2 - I_1 \cdot R + I_0 = 0$ derived from a geometrical construction (cf. [1], Eq. [5]) if $\xi_0 = \xi_1 = \xi_2$. In the version presented here we have

introduced, however, different coefficients of proportionality ($\xi_{0,1,2}$) for the three peak intensities that reflect the relative abundances of the three principal $^{18}O/^{16}O$-distinctive CO_2 molecules in our reservoir.

For an actual determination of the isotopically different CO_2 species represented by mass peaks 44, 46, and 48, we have to find a possibility either to quantitatively assess or to eliminate the above coefficients $\xi_{0,1,2}$. If R_1 and R_2 are solutions of Eq. (9) and $R_1 \neq R_2$, application of the root theorem of Vieta would give us

$$R_1 + R_2 = (\xi_1 \cdot I_1)/(\xi_2 \cdot I_2), \qquad (10)$$

$$R_1 \cdot R_2 = (\xi_0 \cdot I_0)/(\xi_2 \cdot I_2). \qquad (11)$$

Using a laboratory CO_2 standard with a homogeneous oxygen isotope composition (implying $R_1 = R_2 = R'$), the solutions of Eq. (9) can be expressed in terms of the intensities of the 48, 46, and 44 mass peaks that would transform Eqs. (10) and (11) to the Eqs. (12) and (13):

$$2(R') = (\xi_1 \cdot I_1')/(\xi_2 \cdot I_2'), \qquad (12)$$

$$(R')^2 = (\xi_0 \cdot I_0')/(\xi_2 \cdot I_2'), \qquad (13)$$

with $I'_{0,1,2}$ reflecting the intensities of the above mass peaks in the mass spectrum of our CO_2 standard gas.

Subsequent division of Eqs. (10) by (12) and (11) by (13) would give us the expressions

$$A = (1/2) \cdot (R_1/R' + R_2/R') = (I_1/I_1')/(I_2/I_2'), \qquad (14)$$

$$B = (R_1/R') \cdot (R_2/R') = (I_0/I_0')/(I_2/I_2'). \qquad (15)$$

Evidently, coefficients $\xi_{0,1,2}$ have cancelled out during these transformations and are, accordingly, no longer relevant for our argument. From (14) and (15) we may recognize, furthermore, that $X_1 = R_1/R'$ and $X_2 = R_2/R'$ are solutions of the equation

$$X^2 - 2 \cdot A \cdot X + B = 0. \qquad (16)$$

Granting the validity of the foregoing argument, we now may compare the intensities of peaks m/z 44, 46, and 48 in the mass spectrum of any odd CO_2 sample (sa) with the corresponding intensities of our homo-

geneous CO_2 standard (st), with differences quantified in analogy to the conventional δ-notation. For such calculations, measured oxygen isotope abundances must be normalized to one of the isotopically different CO_2 mass fractions, with either the quantity of $C^{16}O_2$ (m/z 44) or $C^{18}O_2$ (m/z 48) having to equal each other in the mass spectra of sample and standard. For instance, if the 48 mass peak intensities in the CO_2 mass spectra of sample ($^{48}I_{sa}$) and standard ($^{48}I_{st}$) are (or are being set) equal (i.e., $^{48}I_{sa}=^{48}I_{st}$), then differences between the 46 and 44 mass peak intensities for the sample relative to standard can be expressed as

$$\Delta^{46}I = (^{46}I_{sa}/^{46}I_{st} - 1) \cdot 1000‰, \qquad (17)$$

$$\Delta^{44}I = (^{44}I_{sa}/^{44}I_{st} - 1) \cdot 1000‰. \qquad (18)$$

Considering Eqs. (17) and (18), A and B from (14) and (15) (where $I_0=^{44}I_{sa}$, $I'_0=^{44}I_{st}$, $I_1=^{46}I_{sa}$, $I'_1=^{46}I_{st}$, $I_2=^{48}I_{sa}$, $I'_2=^{48}I_{st}$, and $I_2/I'_2=1$) may also be expressed in the forms

$$A = I_1/I'_1 = (1 + \Delta^{46}I/1000), \qquad (19)$$

$$B = I_0/I'_0 = (1 + \Delta^{44}I/1000). \qquad (20)$$

Using (19) and (20), the solutions $X_{1,2}$ of Eq. (16) can be consequently rendered as

$$X_{1,2} = (1 + \Delta^{46}I/1000) \pm [1000 \cdot (2 \cdot \Delta^{46}I$$
$$- \Delta^{44}I) + (\Delta^{46}I)^2]^{1/2}/1000. \qquad (21)$$

Generally, the solutions X_1 and X_2 of Eq. (16) prove to be real if the following inequality holds for the determinants

$$D = [1000 \cdot (2 \cdot \Delta^{46}I - \Delta^{44}I) + (\Delta^{46}I)^2] \geq 0, \qquad (22)$$

and if $D<0$, then the solutions X_1 and X_2 consist of complex numbers that have both a real and an imaginary part.

Taking into account that $R=[^{16}O]/[^{18}O]$, the ^{18}O content of the CO_2 in the sample relative to the standard can be expressed in terms of $\delta^{18}O$ by writing the inverse values of X_1 and X_2, that is,

$$\delta^{18}O_{(1)} = (1/X_1 - 1) \cdot 1000‰, \qquad (23)$$

$$\delta^{18}O_{(2)} = (1/X_2 - 1) \cdot 1000‰. \qquad (24)$$

For homogeneous (with $X_1=X_2$) and nonhomogeneous (with $X_1 \neq X_2$) $^{16}O/^{18}O$ distributions in the CO_2 pool, the corresponding expressions (25),

$$\delta^{18}O_{(1)} = \delta^{18}O_{(2)},$$
$$\delta^{18}O_{(1)} \neq \delta^{18}O_{(2)}, \qquad (25)$$

will be valid.

Summarizing the argument, we may state that the approach set out above provides us with a convenient technique to distinguish between a homogeneous and nonhomogeneous distribution of the ^{16}O and ^{18}O isotopes in a given carbon dioxide reservoir. Moreover, this approach also offers the possibility of measuring the $^{18}O/^{16}O$ distribution in such a CO_2 pool by a novel method that is based on the determination of the relative abundance of the three principal $^{18}O/^{16}O$-distinctive CO_2 molecules ($C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) and the employment of mass spectrometric registration systems of different sensitivity for the corresponding mass peaks 44, 46, and 48 (i.e., $\xi_0 \neq \xi_1 \neq \xi_2$).

3. Violations of homogeneous $^{18}O/^{16}O$ distribution patterns in the carbon-bound oxygen of a CO_2 pool

In the following, we shall consider selected processes that may lead to either a violation or degradation of the homogeneous distribution of the carbon-bound oxygen isotopes in a given CO_2 reservoir. As will be shown, both chemical and diffusion processes are capable of imparting nonhomogeneous (nonprobabilistic) $^{18}O/^{16}O$ patterns to a discrete quantity of CO_2 molecules.

3.1. Derivation of CO_2-bound oxygen from different sources as a cause of isotopic inhomogeneity

As we have pointed out, the carbon dioxide produced by the oxidation of carbon monoxide by iodine pentoxide as oxidizing agent [2,3] provides an excel-

lent example for a bimodal (and thus nonhomogeneous) oxygen isotope distribution in the CO_2 pool. In this reaction, the original oxygen atom of the CO molecule is being retained and a second added from the oxidant according to the scheme $CO^* + I_2O_5 \rightarrow COO^*$, with the CO_2-bound oxygen consequently derived from two different sources with specific oxygen isotope ratios R_{CO} (from original CO) and R_{ID} (from I_2O_5), implying $R_{CO} \neq R_{ID}$.

Using our mathematical formalism, we may attempt to quantify the nonhomogeneous ^{16}O and ^{18}O distribution in the resulting CO_2 pool on the basis of the oxygen isotope composition of the two reactants (CO and I_2O_5), for which we shall assume $\delta^{18}O$ values of 41‰ and 35.2‰ (SMOW), respectively, as chosen by Stevens et al. [2]. The CO_2 synthesized in this process will be indexed in the following as $CO_{2(s)}$. As a laboratory standard we shall use a CO_2 sample ($CO_{2(lab)}$) with the $\delta^{18}O$ value of 23.5‰ (SMOW) equal to the isotopic composition of atmospheric oxygen (cf. [8,9]).

As oxygen isotope compositions of a sample (sa) are commonly reported as $\delta^{18}O_{sa} = (r_{sa}/r_{st} - 1) \cdot 1000‰$ (with $r_{sa} = {}^{18}O/{}^{16}O$ and $r_{st} = r_{SMOW}$) [10], we have adapted our values of R (cf. Eq. [6]) accordingly, calculating R_{CO}, R_{ID}, and R_{lab} on the basis of the $\delta^{18}O$ values of CO, I_2O_5, and our laboratory standard yielding $R_{CO} = 960.615 \cdot 10^{-3} \cdot r^{-1}{}_{SMOW}$, $R_{ID} = 965.997 \cdot 10^{-3} \cdot r^{-1}{}_{SMOW}$, and $R_{lab} = 977.040 \cdot 10^{-3} \cdot r^{-1}{}_{SMOW}$, respectively. Consequently, we can calculate the I_1 (m/z 46) and I_0 (m/z 44) mass peak intensities of the $CO_{2(s)}$ mass spectrum according to Eqs. (10) and (11) (where $R_1 = R_{CO}$ and $R_2 = R_{ID}$) as well as the $CO_{2(lab)}$ mass spectrum according to (12) and (13) (where $R' = R_{lab}$). Calculated intensities are then expressed relative to the I_2 (m/z 48) mass peak intensity of the $CO_{2(s)}$ mass spectrum obtained as a result of the reaction between CO and I_2O_5. Comparison of the 46 and 44 mass peak intensities in the $CO_{2(s)}$ and $CO_{2(lab)}$ mass spectra according to (17) and (18) finally gives us the $\Delta^{46}I$ and $\Delta^{44}I$ values of the $CO_{2(s)}$ sample relative to the $CO_{2(lab)}$ standard (i.e., $\Delta^{46}I = -14.0565‰$ and $\Delta^{44}I = -27.9229‰$). Using (21) and the $\Delta^{46}I$ and $\Delta^{44}I$ values, the two solutions of Eq. (16) can be calculated as $X_{1,2} = (1 - 14.0565/1000) \pm 2.7543/1000$, yielding

$X_1 = 0.98891$ and $X_2 = 0.98287$. With solutions $X_{1,2}$ at hand we may, in turn, calculate the $\delta^{18}O_{(1,2)}$ values of the $CO_{2(s)}$ pool of mixed oxygen derivation according to (23) and (24), obtaining $\delta^{18}O_{(1)} = 11.43‰$ and $\delta^{18}O_{(2)} = 17.10‰$ relative to our laboratory standard $\delta^{18}O_{lab} = 23.5‰$ (SMOW). Then, the $\delta^{18}O_{(1,2)}$ values can be expressed relative to the SMOW standard using the expression

$$\delta^{18}O_{sa-SMOW} = \delta^{18}O_{sa-lab}(1 + \delta^{18}O_{lab-SMOW}/1000) + \delta^{18}O_{lab-SMOW}, \quad (26)$$

where $\delta^{18}O_{sa-SMOW}$ and $\delta^{18}O_{lab-SMOW}$ are the $\delta^{18}O$ values of samples and laboratory standard relative to SMOW and $\delta^{18}O_{sa-lab}$ is the $\delta^{18}O$ value relative to our laboratory standard. Applying Eq. (26), we can show that the $\delta^{18}O$ values of the two oxygen sources of our $CO_{2(s)}$ pool (11.43‰ and 17.10‰ relative to the laboratory standard) would translate into $\delta^{18}O_{(1)} = 35.2‰$ and $\delta^{18}O_{(2)} = 41‰$ versus SMOW. Assuming that the measurements of $\Delta^{46}I$ and $\Delta^{44}I$ values are beset with a standard error of about $\pm 0.0006‰$ on the 95% confidence level, the $\delta^{18}O_{(1,2)}$ values probably have a standard error of $\pm 0.18‰$.

Summing up, we may state that the two above solutions $X_{1,2}$ of Eq. (16) and the correspondingly different values of $\delta^{18}O_{(1,2)}$ for $CO_{2(s)}$ derived from Eqs. (23) and (24) constitute indicators of a nonhomogeneous distribution of ^{16}O and ^{18}O isotopes in the CO_2 pool under consideration.

3.2. Degradation of homogeneous $^{18}O/^{16}O$ distribution patterns in CO_2-bound oxygen by diffusion processes

We may reasonably assume that the kinetic isotope effects that come to bear during the diffusional differentiation of a pool of oxygen isotopically distinctive CO_2 molecules will disturb any primary homogeneity in the oxygen isotope distribution of the latter. A good example of a system passing from a homogeneous to a nonhomogeneous state as a result of diffusion processes is a carbon dioxide reservoir suffering efflux and influx of discrete CO_2 quanta.

Table 1
Intensities of the ^{44}I ($C^{16}O_2$), ^{46}I ($C^{16}O^{18}O$), and ^{48}I ($C^{18}O_2$) peaks in the CO_2 mass spectrum and corresponding changes in the oxygen isotope characteristics of a CO_2 model reservoir as result of a progressive efflux of CO_2 (f_t is the fraction that has left the initial reservoir by time t)

f_t	[a]$\xi_0 \cdot ^{44}I$, V	$\xi_1 \cdot ^{46}I$, V	$\xi_2 \cdot ^{48}I$, V	$\Delta^{46}I$ ‰	$\Delta^{48}I$ ‰	A	B	$\delta^{18}O_{(1)}$ ‰	$\delta^{18}O_{(2)}$ ‰
0.0	10.000	4.2393	4.4931	0.0000	0.0000	1.0000	1.0000	0.000	0.0000
0.1	10.000	4.2492	4.5132	2.3353	4.4735	0.99787	0.99555	−11.895	16.566
0.2	10.000	4.2602	4.5359	4.9301	9.5257	0.99545	0.99056	−14.009	23.870
0.3	10.000	4.2727	4.5618	7.8787	15.2901	0.99270	0.98494	−15.127	30.885
0.4	10.000	4.2872	4.5918	11.2990	21.9670	0.98956	0.97851	−16.246	38.844
0.5	10.000	4.3044	4.6276	15.3563	29.9348	0.98585	0.97094	−16.482	47.194
0.6	10.000	4.3256	4.6717	20.3573	39.7498	0.98135	0.96177	−16.776	57.490
0.7	10.000	4.3530	4.7293	26.8205	52.5695	0.97554	0.95006	−15.497	69.140
0.8	10.000	4.3920	4.8116	36.0201	70.8865	0.96744	0.93381	−13.489	85.529
0.9	10.000	4.4594	4.9557	51.9190	102.9579	0.95665	0.90665	−7.877	111.715

$\Delta^{46}I_{f_t} = (^{46}I_{ft}/^{46}I_{init} - 1) \cdot 1000$‰, where $^{46}I_{init}$ is the peak intensity at $f_t = 0$. $\Delta^{48}I_{f_t} = (^{48}I_{ft}/^{48}I_{init} - 1) \cdot 1000$‰, where $^{48}I_{init}$ is the peak intensity at $f_t = 0$. A, B, $\delta^{18}O_{(1)}$ and $\delta^{18}O_{(2)}$ have been calculated from Eqs. (31), (32), (23), and (24) (see text).

[a] Coefficients ξ_0, ξ_1, ξ_2 are 1, 10^2, and 10^5, respectively.

3.2.1. $^{18}O/^{16}O$ evolution of a carbon dioxide reservoir undergoing diffusional depletion

Assuming a model reservoir of CO_2 that is subjected to continuous depletion with an efflux rate proportional to its CO_2 concentration, the removal of the three principal $^{18}O/^{16}O$-distinctive CO_2 species may be described in terms of the differential equations

$$dC^{(0)}/dt = -k_1 C^{(0)}$$

$$dC^{(1)}/dt = -k_2 C^{(1)}$$

$$dC^{(2)}/dt = -k_3 C^{(2)}, \tag{27}$$

where $C^{(0,1,2)}$ are the concentrations of the $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ molecules in the pool and $k_{1,2,3}$ the corresponding rate constants.

Integration of Eq. (27) and consideration of the relationship

$$C_t^{(0)}/C^{(0)} = \exp(-k_1 \cdot t) = 1 - f_t \tag{28}$$

gives us a next set of equations that reflect the change in the content of the residual $C^{16}O^{18}O$ and $C^{18}O_2$ molecules relative to $C^{16}O_2$ in our model reservoir as a function of the fraction f_t of CO_2 that has left the reservoir by time t; that is,

$$r_t^{(0)} = 1.0$$

$$r_t^{(1)} = r_0^{(1)} \cdot (1 - f_t)^{(1-a2)/a2} \tag{29}$$

$$r_t^{(2)} = r_0^{(2)} \cdot (1 - f_t)^{(1-a3)/a3}$$

where ratios $r_o^{(1,2)}$ reflect the initial proportions of the two "heavy" CO_2 species to $C^{16}O_2$ in our reservoir at time $t=0$; that is, $r_o^{(0)}=C_o^{(0)}/C^{(0)}=1$, $r_o^{(1)}=C_o^{(1)}/C^{(0)}$, and $r_o^{(2)}=C_o^{(2)}/C^{(0)}$. $\alpha_2=k_1/k_2=1.0224747$ and $\alpha_3=k_1/k_3=1.0444659$ are the fractionation coefficients of the $C^{16}O^{18}O$ and $C^{18}O_2$ molecules relative to $C^{16}O_2$ (see [1])

Changes in the content of the $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ molecules in the residual reservoir in response to a progressive removal of CO_2 are expressed as changes in the intensities of the ^{44}I, ^{46}I, and ^{48}I mass peaks and presented in Table 1, with intensities of peaks ^{46}I and ^{48}I always normalized to the ^{44}I peak of the mass spectrum obtained at a particular depletion state f_t. The intensities of the $C^{16}O_2$ peaks (m/z 44) in the CO_2 mass spectra of the initial ($^{44}I_{init}$) and the progressively depleted pool at various states $f_t (^{44}I_{f_t})$ have been set equal (i.e., $^{44}I_{init}=^{44}I_{f_t}$). As a consequence, $\Delta^{44}I=0$, and the numerical values for $\Delta^{46}I$ and $\Delta^{48}I$ reflecting the abundances of the $C^{16}O^{18}O$ and $C^{18}O_2$ molecules for any depletion state f_t (relative to the initial reservoir at $t=0$) can be calculated as

$$\Delta^{(46,48)}I(f_t) = (r_t^{(1,2)}/r_0^{(1,2)} - 1) \cdot 1000$$

$$= \{(1 - f_t)^{[(1-a_{2,3})/a_{2,3}]} - 1\} \cdot 1000‰. \tag{30}$$

Considering Eqs. (14) and (15) (where $I_2 \equiv {}^{48}I_{f_t}$, $I'_2 \equiv {}^{48}I_{init}$, $I_1 \equiv {}^{46}I_{f_t}$, $I'_1 \equiv {}^{46}I_{init}$, $I_0 \equiv {}^{44}I_{f_t}$, and $I'_0 \equiv {}^{44}I_{init}$) and using the $\Delta^{46}I_{f_t}$ and $\Delta^{48}I_{f_t}$ values from Table 1, the dependence of the terms A_{f_t} and B_{f_t} on f_t is given by the expressions

$$A_{f_t} = ({}^{46}I_{f_t}/{}^{46}I_{init})/({}^{48}I_{f_t}/{}^{48}I_{init})$$

$$= (1 + \Delta^{46}I_{f_t}/1000)/(1 + \Delta^{48}I_{f_t}/1000) \quad (31)$$

$$B_{f_t} = 1/({}^{48}I_{f_t}/{}^{48}I_{init} = 1/(1 + \Delta^{48}I_{f_t}/1000). \quad (32)$$

The function $F(X)$ that determines the isotopic fractionation of the CO_2-bound oxygen in the course of the CO_2 efflux from the initial model reservoir can be given in analogy to Eq. (16) as

$$F(X) = X^2 - 2 \cdot A_{f_t} \cdot X + B_{f_t}, \quad (33)$$

where X is equal to the ratio of R_{f_t}/R_{init}. As had been previously pointed out (Fig. 3 in [1]), function $F(X)$ has one extremum point for the case $X = A_{f_t}$ where $F(A_{f_t}) = B_{f_t} - A_{f_t}^2$. Like the analogous Eq. (16), function $F(X) = 0$ can have two identical solutions $X_{(1)f_t} = X_{(2)f_t}$ (for $[A_{f_t}^2 - B_{f_t}] = 0$) or two different solutions $X_{(1)f_t} \neq X_{(2)f_t}$ (for $[A_{f_t}^2 - B_{f_t}] > 0$).

Using the values of $X_{(1,2)f_t}$ we may, with the help of Eqs. (23) and (24), calculate the oxygen isotope composition of our CO_2 pool for increasing fractions f_t in terms of the $\delta^{18}O_{(1)f_t}$ and $\delta^{18}O_{(2)f_t}$ values (see Table 1) for the two different sites of oxygen in the CO_2 molecule. The average of X_{f_t} reflecting the mean for both oxygen positions in dependence of f_t can be calculated as $X_{aver(f_t)} = (X_{(1)f_t} + X_{(2)f_t})/2$. Considering Eq. (31) and the relationship $2A_{f_t} = X_{(1)f_t} + X_{(2)f_t}$, we obtain

$$X_{aver(f_t)} = A_{f_t}$$

$$= (1 + \Delta^{46}I_{f_t} 1000)/(1 + \Delta^{48}I_{f_t} 1000). \quad (34)$$

With the resulting values of $X_{aver(f_t)}$ at hand, the $\delta^{18}O_{aver(f_t)}$ for the pool as a whole can be calculated for any state of reservoir depletion as

$$\delta^{18}O_{aver(f_t)} = (1/X_{aver(f_t)} - 1) \cdot 1000$$

$$= (\Delta^{48}I_{f_t} - \Delta^{46}I_{f_t})/(1 + \Delta^{46}I_{f_t}/1000). \quad (35)$$

As can be readily inferred from Table 1, the differences between $\delta^{18}O_{(1)f_t}$ and $\delta^{18}O_{(2)f_t}$ increase in the residual pool with increasing efflux of CO_2, implying that the departure from a probabilistic (homogeneous) ${}^{18}O/{}^{16}O$ distribution towards a nonhomogeneous state becomes more pronounced with increasing removal of CO_2 from the initial reservoir.

3.2.2. ${}^{18}O/{}^{16}O$ evolution during buildup of a juvenile carbon dioxide reservoir from an extraneous source with a homogeneous ${}^{18}O/{}^{16}O$ distribution

In analogy to the above reservoir depletion model, we may also envision an influx model (see [1]) involving the buildup of a new carbon dioxide reservoir by a steady flow of CO_2 quanta from an external source with a homogeneous ${}^{18}O/{}^{16}O$ distribution pattern. Assuming that the influx rates of the isotopically distinctive CO_2 species $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ will depend on their respective concentrations in the external reservoir, changes in the relative proportions of these molecules during their transfer to the newly evolving CO_2 pool can be quantified by the following set of equations:

$$P_t^{(0)} = C^{(0)} - C_t^{(0)} = C^{(0)} \cdot [1 - \exp(-k_1 \cdot t)],$$

$$P_t^{(1)} = C^{(1)} - C_t^{(1)} = C^{(1)} \cdot [1 - \exp(-k_2 \cdot t)], \quad (36)$$

$$P_t^{(2)} = C^{(2)} - C_t^{(2)} = C^{(2)} \cdot [1 - \exp(-k_3 \cdot t)].$$

Here $P_t^{(0,1,2)}$ are the quantities of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ that have been transferred to the new reservoir by time t; $C^{(0,1,2)}$ and $C_t^{(0,1,2)}$ are the concentrations of the isotopically different CO_2 molecules in the feeder reservoir at times $t=0$ and t, respectively, and $k_{1,2,3}$ are the corresponding rate constants.

Taking into account that the fraction f_t of the feeder pool transferred to the new reservoir by time t can be defined as

$$P_t^{(0)}/C^{(0)} = 1 - \exp(-k_1 \cdot t) = f_t, \quad (37)$$

Table 2

Intensities of the ^{44}I ($C^{16}O_2$), ^{46}I ($C^{16}O^{18}O$), and ^{48}I ($C^{18}O_2$) peaks in the CO_2 mass spectrum and corresponding changes in the oxygen isotope characteristics of a newly evolving (juvenile) CO_2 reservoir fed by cumulative quantities (f_t) of CO_2 from an external pool with a primarily homogeneous $^{18}O/^{16}O$ distribution

f_t	$^{a}\xi_0 \cdot {}^{44}I, V$	$\xi_1 \cdot {}^{46}I, V$	$\xi_2 \cdot {}^{48}I, V$	$\Delta^{46}I$ ‰	$\Delta^{48}I$ ‰	A	B	$\delta^{18}O_{(real)}$ ‰	$\pm i \cdot \delta^{18}O$ ‰
0.1	10.000	4.1509	4.3111	−20.8525	−40.5066	1.02048	1.04222	−20.85	27.64
0.2	10.000	4.1560	4.3215	−19.6495	−38.1919	1.01928	1.03971	−19.65	26.85
0.3	10.000	4.1615	4.3326	−18.3521	−35.7214	1.01801	1.03704	−18.35	25.42
0.4	10.000	4.1675	4.3448	−16.9368	−33.0062	1.01661	1.03413	−16.94	24.09
0.5	10.000	4.1743	4.3584	−15.3327	−29.9793	1.01610	1.03091	−15.33	21.24
0.6	10.000	4.1818	4.3738	−13.5636	−26.5518	1.01334	1.02728	−13.56	19.78
0.7	10.000	4.1906	4.3917	−11.4878	−22.5679	1.01134	1.02309	−11.49	16.60
0.8	10.000	4.2012	4.4133	−8.9873	−17.7606	1.00893	1.01808	−8.99	11.55
0.9	10.000	4.2114	4.4416	−5.7557	−11.4620	1.00577	1.01159	−5.76	4.02
1.0	10.000	4.2393	4.4931	0.0000	0.0000	1.00000	1.00000	0.00	0.00

$\Delta^{46}I_{ft} = ({}^{46}I_{ft}/{}^{46}I_{init} - 1) \cdot 1000$‰, where $^{46}I_{init}$ is the peak intensity at $f_t = 1$. $\Delta^{48}I_{ft} = ({}^{48}I_{(ft)}/{}^{48}I_{init} - 1) \cdot 1000$‰, where $^{48}I_{init}$ is the peak intensity at $f_t = 1$. $A, B, \delta^{18}O_{(1)}$ and $\delta^{18}O_{(2)}$ have been calculated from Eqs. (40), (41), (44), and (45) (see text).

^{a} Coefficients ξ_0, ξ_1, ξ_2 are 1, 10^2, and 10^5, respectively.

the quantities $[C^{16}O_2]$, $[C^{16}O^{18}O]$, and $[C^{18}O_2]$ relative to $[C^{16}O_2]$ in the new reservoir at time t can be presented as $\rho_t^{(0,1,2)}$; that is,

$$\rho_t^{(0)} = 1.0,$$
$$\rho_t^{(1)} = r_0^{(1)} \cdot [1 - (1 - f_t)^{(1/a_2)}]/f_t, \qquad (38)$$
$$\rho_t^{(2)} = r_0^{(2)} \cdot [1 - (1 - f_t)^{1/a_3}]/f_t,$$

where $r_o^{(1)} = [C^{(1)}]/[C^{(0)}]$ and $r_o^{(2)} = [C^{(2)}]/[C^{(0)}]$ are the ratios $[C^{16}O^{18}O]/[C^{16}O_2]$ and $[C^{18}O_2]/[C^{16}O_2]$ in the external feeder pool of CO_2 at time $t=0$.

Table 2 shows the quantitative evolution of the $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ molecule fractions in the newly generated CO_2 pool as a result of increasing fractions f_t of the source reservoir that have been transferred to the evolving pool by time t. Again, these changes are expressed in terms of the magnitudes of the $^{44}I_{f_t}$, $^{46}I_{f_t}$, and $^{48}I_{f_t}$ peaks as they would appear in the mass spectrum obtained for the new reservoir with rising influx values f_t. As in the case of the efflux model (Table 1), intensities $^{46}I_{f_t}$ and $^{48}I_{f_t}$ have been normalized to the intensity of peak $^{44}I_{f_t}$ for each state of f_t. Also, the intensities of the $C^{16}O_2$ (^{44}I) peaks in the mass spectra of the primary feeder pool at $t=0$ ($^{44}I_{init}$) and of the new reservoir at different times t ($^{44}I_{f_t}$) have been set equal ($^{44}I_{init} = {}^{44}I_{f_t}$). As a consequence, $\Delta^{44}I_{f_t} = 0$. Then, the $\Delta^{46}I_{f_t}$ and $\Delta^{48}I_{f_t}$ values for each cumulative state f_t can be calculated

relative to the primary abundances of the $C^{16}O^{18}O$ and $C^{18}O_2$ molecules in the external source reservoir at time $t=0$ as

$$\Delta^{(46,48)}I_{f_t} = (P_t^{(1,2)}/P_0^{(1,2)} - 1)1000$$
$$= \{[1 - (1 - f_t)^{(1/a_{2,3})}]/f_t - 1\} \cdot 1000. \qquad (39)$$

As in our foregoing efflux model, we can calculate the values A_{f_t} and B_{f_t} (cf. Eqs. [31] and [32]) for rising values f_t as

$$A_{f_t} = (1 + \Delta^{46}I_{f_t}/1000)/(1 + \Delta^{48}I_{f_t}/1000), \qquad (40)$$

$$B_{f_t} = 1/(1 + \Delta^{48}I_{f_t}/1000). \qquad (41)$$

Af and Bf are coefficients of the function

$$F(Y) = Y^2 - 2A_{f_t} \cdot Y + B_{f_t}, \qquad (42)$$

where Y equals both the ratios R_{f_t} in the evolving reservoir at time t and R_{init} in the source reservoir at time $t=0$. The above function $F(Y)$ has an extremum point for each f_t value at $Y=A_{f_t}$ where its value is $F(A_{f_t}) = B_{f_t} - A_{f_t}^2$. However, for the case of $F(Y)=0$, we obtain for our influx model reservoir solutions with real numbers only if $f_t=1$ and $Y_{(1)f_t} = Y_{(2)f_t}$. In all cases ($f_t < 1$), the solutions $Y_{(1,2)f_t}$ of Eq. (42), that is,

$$Y_{(1,2)f_t} = A_{f_t} \pm i \cdot (B_{f_t} - A_{f_t}^2)^{1/2} \tag{43}$$

are complex numbers and $Y_{(1)f_t} \neq Y_{(2)f_t}$, with A_{f_t} and $i \cdot (B_{f_t} - A_{f_t2})^{1/2}$ being a real and an imaginary part of $Y_{(1,2)f_t}$, respectively.

Adapting Eqs. (23) and (24) to $Y_{(1,2)f_t}$, we obtain

$$\delta^{18}O_{(1)f_t} = (1/Y_{(1)f_t} - 1) \cdot 1000‰, \tag{44}$$

$$\delta^{18}O_{(2)f_t} = (1/Y_{(2)f_t} - 1) \cdot 1000‰. \tag{45}$$

Using Eqs. (43), (44), and (45), $\delta^{18}O_{(1,2)f_t}$ can be calculated as

$$\delta^{18}O_{(1)f_t} = (A_{f_t}/B_{f_t} - 1) \cdot 1000 - i$$
$$\cdot (1000 \cdot (B_{f_t} - A_{f_t}^2)^{1/2})/B_{f_t}, \tag{46}$$

$$\delta^{18}O_{(2)f_t} = (A_{f_t}/B_{f_t} - 1) \cdot 1000 + i$$
$$\cdot (1000 \cdot (B_{f_t} - A_{f_t}^2)^{1/2})/B_{f_t}. \tag{47}$$

The resulting numerical values for $\delta^{18}O_{(1,2)f_t}$ contain a real and an imaginary part and are presented in Table 2 as $\delta^{18}O_{(real)f_t}$ and $\pm i \cdot \delta^{18}O_{f_t}$, respectively. While $\delta^{18}O_{(1,2)}$ reflect separately the oxygen isotope compositions of the two oxygen-hosting sites of all CO_2 molecules in our pool, the average $\delta^{18}O$ value for both sites $(\delta^{18}O_{(aver)f_t} = [\delta^{18}O_{(1)f_t} + \delta^{18}O_{(2)f_t}]/2)$, and thus, for the CO_2 pool as a whole. can be calculated as

$$\delta^{18}O_{(aver)f_t} = (A_{f_t}/B_{f_t} - 1) \cdot 1000 = \Delta^{46}I_{f_t} ‰. \tag{48}$$

Substituting Af_t and Bf_t in Eq. (48) by Eqs. (31) and (32), we can rewrite Eq. (48) in the form

$$\delta^{18}O_{(aver)f_t} = \Delta^{46}I_{f_t} ‰. \tag{49}$$

From Eq. (49) it is obvious that changes in the average oxygen isotope composition of our CO_2 pool in response to increasing fractions f_t added by time t from an external feeder reservoir are monitored by the $\Delta^{46}I_{f_t}$ values, provided the mass peaks for $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in the new reservoir at time t are normalized to the $C^{16}O_2$ quantities in both CO_2 pools. In the case of the feeder pool, this normalization

refers to the initial $C^{16}O_2$ content of the latter at time $t=0$.

4. Summary and conclusions

A mathematical formalism has been developed for the calculation of $^{18}O/^{16}O$ abundances in a CO_2 pool relative to a standard that uses the quantities of the $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ molecules occurring in this pool. These $^{18}O/^{16}O$-distinctive CO_2 species can be measured by conventional mass spectrometric techniques with Faraday cups and electron multiplier-based ion registration systems of different sensitivity as mass peaks ^{44}I, ^{46}I, and ^{48}I that differ by about five orders of magnitude. This approach allows a calculation of the $^{18}O/^{16}O$ distributions for both oxygen-hosting sites of the CO_2 molecules of the respective pool. With the $^{18}O/^{16}O$ ratios for these two sites at hand, we may assess whether or not the pool is characterized by a probabilistic (homogeneous) or by a nonprobabilistic (nonhomogeneous) $^{18}O/^{16}O$ distribution.

Violations of homogeneous distribution patterns of $^{18}O/^{16}O$ in assemblages of CO_2 molecules may be caused by various processes. For instance, the oxygen constituents of CO_2 may have been derived from two $^{18}O/^{16}O$-distinctive sources. Also, a leakage with different diffusion rates of the isotopically different CO_2 molecules from a reservoir with a homogeneous $^{18}O/^{16}O$ distribution will give rise to nonhomogeneous $^{18}O/^{16}O$ patterns in both the residual and the newly generated CO_2 pools. In the case of the reservoir undergoing depletion, departures from the probabilistic state increase with increasing quantities of CO_2 that have left the reservoir, whereas the growth of the new reservoir will start with an extreme degree of nonhomogeneity that progressively grades into less nonhomogeneous states during its subsequent buildup, attaining the homogeneous state of the source reservoir with the complete exhaustion of the latter. The $\delta^{18}O_{(1,2)}$ values for the two oxygen-hosting sites of the CO_2 molecules of the respective pools serve as an index for the type of $^{18}O/^{16}O$ distribution, with $\delta^{18}O_{(1)} = \delta^{18}O_{(2)}$ indicating a homogeneous and

$\delta^{18}O_{(1)} \neq \delta^{18}O_{(2)}$ a nonhomogeneous state. The $\delta^{18}O_{(1,2)}$ values are represented either by two real numbers, as in the case of CO_2 whose oxygen was derived from two isotopically different sources (cf. section 3.1) and in our efflux model (section 3.2.1), or by two complex numbers. as in the case of our juvenile reservoir (section 3.2.2). Establishing a quantitative relationship between the relative proportions of the three $^{18}O/^{16}O$-distinctive CO_2 species within a given CO_2 reservoir and the influx to, and efflux from, the latter of discrete CO_2 quanta, the new formalism advanced could be potentially useful for quantitative estimates of the reservoir dynamics of natural CO_2 pools (inclusive of the atmospheric CO_2 reservoir).

Acknowledgements

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