

Isotopic Analyses Based on the Mass Spectrum of Carbon Dioxide

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Measurements of carbon and oxygen isotopic abundances are commonly based on the mass spectrum of carbon dioxide, but analysis of that spectrum is not trivial because three isotope ratios ($^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$, and $^{13}\text{C}/^{12}\text{C}$) must be determined from only two readily observable ion-current ratios (45/44 and 46/44). Here, approaches to the problem are reassessed in the light of new information regarding the distribution of oxygen isotopes in natural samples. It is shown that methods of calculation conventionally employed can lead to systematic errors in the computed abundance of ^{13}C and that these errors may be related to incorrect assessment of the absolute abundance of ^{17}O . Further, problems arising during the analysis of samples enriched by admixture of ^{18}O -labeled materials are discussed, and it is shown (i) that serious inaccuracies arise in the computed abundance of ^{17}O and ^{13}C if methods of calculation conventionally employed in the analysis of natural materials are applied to material labeled with ^{18}O but (ii) that computed fractional abundances of ^{18}O are always within 0.4% of the correct result. Methods for exact calculation of two isotope ratios when the third is known are presented and discussed, and a more exact approach to the computation of all three isotope ratios in natural materials is given.

Measurement of the mass spectrum of a molecule can quantify only the relative abundances of *molecular species* of differing mass. Elemental isotope ratios are not measurable directly and must be determined by calculations based on the observed molecular spectrum (1). In the case of carbon dioxide, for example, ion currents appear at m/z 44 through m/z 49. With the exception of m/z 44 ($^{12}\text{C}^{16}\text{O}_2$), all measurable ion currents represent sums of multiple isotopic contributions (e.g., $^{13}\text{C}^{17}\text{O}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}^{16}\text{O} + ^{12}\text{C}^{17}\text{O}_2$ at m/z 46). A problem common to all mathematical formulations (2-4) is that a measurement of two ion-current ratios ($[45]/[44]$ and $[46]/[44]$) does not provide sufficient information to obtain unique solutions for three isotope ratios ($^{13}\text{C}/^{12}\text{C}$, $^{17}\text{O}/^{16}\text{O}$, and $^{18}\text{O}/^{16}\text{O}$).

The oxygen-isotope ratios have, therefore, commonly been treated as functionally related; that is, an expression for $^{17}\text{O}/^{16}\text{O}$ as a function of $^{18}\text{O}/^{16}\text{O}$ has been employed as the third equation required for solution of the problem. This approach is based on the fact that processes (other than admixture of separated isotopes) which have affected the abundance of ^{18}O must also have affected the abundance of ^{17}O , and vice versa (5). Recently, however, it has been shown (i) that no single, fixed relationship correctly describes the fractionation of ^{17}O relative to ^{18}O in all processes and (ii) that the relationship commonly employed by isotopic mass spectrometrists does not correctly describe even the "average relationship" prevailing in natural systems (6). Here, we

explore the significance of these findings for isotopic analysis and show that a simple system of equations for accurate calculation of isotopic abundances can be developed.

MASS SPECTROMETRIC MEASUREMENT OF ISOTOPIC ABUNDANCES

Notation. We will consistently employ the letter R to designate the *ratio* of a particular isotopic species to the related isotopic species of lowest mass

$$^nR = \frac{\text{isotopic species of mass } n}{\text{base species related to } n} \quad (1)$$

Left superscripts will be used to designate isotopic species by mass. For $n = 13$, the base species is ^{12}C ; for $n = 17$ or 18 , ^{16}O ; and, for $45 \leq n \leq 49$, the base species is $^{12}\text{C}^{16}\text{O}_2$. The letter F is used in the same way to designate *fractional abundances*

$$^nF = \frac{\text{isotopic species of mass } n}{\text{sum of all species related to } n} \quad (2)$$

for $n = 13$, the denominator is the sum ($^{12}\text{C} + ^{13}\text{C}$); for $n = 17$ or 18 , ($^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O}$); and, for $44 \leq n \leq 49$, the denominator is the sum of all species of carbon dioxide. The symbol α is used to designate the fractionation factor; a ratio of isotope ratios characteristic of an isotope effect associated with a physical or chemical process

$$^n\alpha = ^nR_{\text{products}} / ^nR_{\text{reactants}} \quad (3)$$

for $n = 13, 17$, or 18 .

Mass Spectrum of Carbon Dioxide. Since the vibrational modes in CO_2 are nearly harmonic and coupling between modes is weak (7), the distribution of isotopes among molecules at equilibrium is accurately described by a simple probability function (1). The abundances of the various molecular species are, therefore, related to the isotopic abundances by the following equations:

$$^{44}F = ^{12}F \cdot ^{16}F \cdot ^{16}F \quad (4)$$

$$^{45}F = ^{13}F \cdot ^{16}F \cdot ^{16}F + 2 \cdot ^{12}F \cdot ^{16}F \cdot ^{17}F \quad (5)$$

$$^{46}F = ^{12}F \cdot ^{17}F \cdot ^{17}F + 2 \cdot ^{12}F \cdot ^{16}F \cdot ^{18}F + 2 \cdot ^{13}F \cdot ^{16}F \cdot ^{17}F \quad (6)$$

$$^{47}F = ^{13}F \cdot ^{17}F \cdot ^{17}F + 2 \cdot ^{13}F \cdot ^{16}F \cdot ^{18}F + 2 \cdot ^{12}F \cdot ^{17}F \cdot ^{18}F \quad (7)$$

$$^{48}F = ^{12}F \cdot ^{18}F \cdot ^{18}F + 2 \cdot ^{13}F \cdot ^{17}F \cdot ^{18}F \quad (8)$$

$$^{49}F = ^{13}F \cdot ^{18}F \cdot ^{18}F \quad (9)$$

In practice, it is most convenient to express these relationships in terms of ratios. Dividing eq 5 through 9 by eq 4 yields

$$^{45}R = ^{13}R + 2 \cdot ^{17}R \quad (10)$$

$$^{46}R = 2 \cdot ^{18}R + 2 \cdot ^{13}R \cdot ^{17}R + ^{17}R^2 \quad (11)$$

$$^{47}R = ^{13}R \cdot ^{17}R^2 + 2 \cdot ^{13}R \cdot ^{18}R + 2 \cdot ^{17}R \cdot ^{18}R \quad (12)$$

$$^{48}R = ^{18}R^2 + 2 \cdot ^{13}R \cdot ^{17}R \cdot ^{18}R \quad (13)$$

$$^{49}R = ^{13}R \cdot ^{18}R^2 \quad (14)$$

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For samples with isotopic abundances near natural levels, ion currents large enough to allow precise, rapid measurement occur only at masses 44, 45, and 46. Modern instruments employ a triple collector system to facilitate simultaneous measurement of ^{45}R and ^{46}R .

Relationships between ^{17}R and ^{18}R . *Theoretical Considerations.* Fractionations of multiple isotopes of the same element are proportional to differences in mass (5). A quantitative relationship between the values of ^{17}R and ^{18}R for two oxygen pools (designated by subscripts 1 and 2) linked by a single, mass-dependent process has been presented by Clayton and co-workers (6)

$$\frac{^{17}\text{R}_1}{^{17}\text{R}_2} = \left(\frac{^{18}\text{R}_1}{^{18}\text{R}_2} \right)^a \quad (15)$$

where $a = \ln(^{17}\alpha)/\ln(^{18}\alpha)$. Note, however, that variations of $^{17}\alpha$ and $^{18}\alpha$ are not linked so that a remains constant. As a result, relative fractionations of the oxygen isotopes can depend on the molecular species involved or on the mechanism of a particular reaction. In general, $0.50 \leq a \leq 0.53$ (6). It is also significant that eq 15 refers to instantaneous precursor-product relationships, not to the integrated compositions of separated or mixed isotopic pools. On the one hand, quantitative expressions describing isotopic fractionations associated with mass-dependent isotope effects are correctly cast in terms of ratios. On the other hand, accurate calculation of the compositions of mixed pools must be based on fractional abundances. As a result, eq 15 will only approximately describe isotopic relationships associated with the mixing of oxygen pools with similar isotopic compositions (i.e., natural samples of terrestrial origin). If one or more of the oxygen pools has been selectively enriched or depleted in a single isotope, serious inaccuracies can result from application of eq 15 (6).

Given these considerations, it is evident that there is no basis on which an equation *exactly* relating ^{17}R and ^{18}R in all pools of oxygen might be developed. In particular, the relationship underlying most oxygen-isotopic analytical calculations

$$\frac{^{17}\text{R}_{\text{unknown}}}{^{17}\text{R}_{\text{standard}}} = \left(\frac{^{18}\text{R}_{\text{unknown}}}{^{18}\text{R}_{\text{standard}}} \right)^{0.50} \quad (16)$$

where "unknown" and "standard" refer to a sample of unknown isotopic composition and to some primary isotopic standard, is inexact and, because 0.50 represents a minimal value for a , may not be the most satisfactory approximation.

^{17}R and ^{18}R in Natural Samples. If mass spectrometric analysis is based on O_2 instead of CO_2 , the measurement of two ion-current ratios (^{33}R and ^{34}R) allows independent calculation of ^{17}R and ^{18}R (8). Measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in lunar and terrestrial silicate minerals and samples of natural waters define a linear relationship (6, 8, 9)

$$\delta^{17}\text{O}_{\text{SMOW}} = (0.5164 \pm 0.0033)\delta^{18}\text{O}_{\text{SMOW}} \quad (17)$$

(where the indicated uncertainty is the standard error of the slope, $n = 35$). As indicated by use of the δ notation (see eq 23), this relationship is based on measurements of differences between isotopic compositions of unknown samples and isotopic standards. As such, it carries no direct information regarding absolute values of isotope ratios. Calculations of ^{17}R and ^{18}R for unknown samples—and, for that matter, accurate calculations based on eq 10 and 11—require knowledge of ^{17}R and ^{18}R for the isotopic standards. At present, the absolute value of $^{18}\text{R}_{\text{SMOW}}$ is known (10), but there have been no direct determinations of $^{17}\text{R}_{\text{SMOW}}$.

It is, therefore, of interest that the isotopic compositions of all natural terrestrial and lunar oxygen pools appear to be

related by eq 17, which is closely related to eq 15. The δ terms are identical with the first terms in the series expansions of the log terms in

$$\ln \frac{^{17}\text{R}_{\text{unknown}}}{^{17}\text{R}_{\text{SMOW}}} = a \ln \frac{^{18}\text{R}_{\text{unknown}}}{^{18}\text{R}_{\text{SMOW}}} \quad (18)$$

Higher-order terms are negligible when $^{17}\text{R}_{\text{unknown}}$ and $^{18}\text{R}_{\text{unknown}}$ are close to $^{17}\text{R}_{\text{SMOW}}$ and $^{18}\text{R}_{\text{SMOW}}$. It is evident that eq 18 is a more general form of eq 17, which can be recast as

$$^{17}\text{R} = ^{18}\text{R}^a K \quad (19)$$

where K is a constant characteristic of the relationship between ^{17}R and ^{18}R in the terrestrial oxygen pool. Because the isotopic compositions of all samples appear to be related by this equation, evaluation of K requires only that both ^{17}R and ^{18}R be known accurately in a single, representative sample.

There has been only one set of measurements of the absolute values of both ^{17}R and ^{18}R in samples of terrestrial origin. Nier (11) determined values of the ratios $^{17}\text{O}^{16}\text{O}/^{16}\text{O}_2$ (^{33}R) and $(^{18}\text{O}^{16}\text{O} + ^{17}\text{O}_2)/^{16}\text{O}_2$ (^{34}R) for samples of air and of O_2 from a commercial gas cylinder. Discordant results were obtained for the atmospheric sample (perhaps because total air, not purified O_2 , was admitted to the ion source), but for the latter analysis, Nier reports (corrected mean and probable error) $^{33}\text{R} = (7.55 \pm 0.01) \times 10^{-4}$ and $^{34}\text{R} = (4.103 \pm 0.005) \times 10^{-3}$, which yield isotope ratios (mean and standard error of mean) of $^{17}\text{R} = (3.775 \pm 0.074) \times 10^{-4}$ and $^{18}\text{R} = (2.0514 \pm 0.0037) \times 10^{-3}$. It follows that, for $a = 0.516$, $K = (9.20 \pm 0.18) \times 10^{-3}$.

Calculation of Isotope Ratios. Combining eq 10 and 11 and substituting eq 19 for ^{17}R yields an expression for ^{18}R in terms of ion-current ratios, K , and a . Apart from uncertainties in K and a , the equation is exact.

$$-3 \cdot K^2 \cdot ^{18}\text{R}^{2a} + 2K \cdot ^{45}\text{R} \cdot ^{18}\text{R}^a + 2 \cdot ^{18}\text{R} - ^{46}\text{R} = 0 \quad (20)$$

Rearrangement of this equation to yield an explicit solution of the form $^{18}\text{R} = f(a, K, ^{45}\text{R}, ^{46}\text{R})$ is difficult except where a is exactly 0.5. An accurate value for ^{18}R can, however, be easily and rapidly obtained by using numerical techniques. A value for ^{17}R can be determined using eq 19 or, if a direct solution in terms of ion-current ratios is required, a derivation similar to that of eq 20 yields

$$-3 \cdot ^{17}\text{R}^2 + 2 \cdot ^{45}\text{R} \cdot ^{17}\text{R} + (^{17}\text{R}/K)^{1/a} - ^{46}\text{R} = 0 \quad (21)$$

The calculation of ^{13}R follows directly from ^{45}R using eq 10.

For clarity in subsequent discussions, we will refer to the following sequence of calculations as "routine":

1. ^{18}R is calculated from ^{45}R and ^{46}R (eq 20).
2. ^{17}R is calculated from ^{18}R (eq 19).
3. ^{13}R is calculated from ^{17}R and ^{14}R (eq 10).

The accuracy of calculated isotope ratios will depend on how well eq 19 actually describes the linked variations of ^{17}R and ^{18}R and on the development of representative values for a and K . Here, we will explore, by means of the application of eq 19–21 to calculation of results from analytical data, two particularly interesting cases: (i) oxygen pools derived by mixing natural-abundance material with material highly enriched in ^{18}O , and (ii) natural-abundance material with a range of oxygen-isotopic compositions wide enough that correct assignment of the values of a and K will be important.

EXPERIMENTAL SECTION

Preparation of Carbon Dioxide for Isotopic Analysis.

A series of samples of water selectively enriched in oxygen-18 was prepared by mixing varying amounts of 99% H_2^{18}O (Stohler Isotopic Chemicals) with distilled, deionized water. A second series of water samples with mass-dependent enrichment of both ^{17}O and ^{18}O was produced by fractional

distillation of tap water. For the exchange of oxygen between water and carbon dioxide, 200 μL of thoroughly degassed water and 20 μmol of carbon dioxide were placed in a sealed, evacuated Pyrex tube (6 mm, o.d.). The tubes were allowed to stand at 25 $^{\circ}\text{C}$ for 48 h to ensure that exchange of oxygen between water and carbon dioxide was complete (12). The carbon dioxide was purified by cryogenic distillation.

Mass Spectrometric Measurement. Values of ^{45}R and ^{46}R used in analytical calculations must be numerically equivalent to the ratios of molecular species in the sample. As a first step, signals have been corrected for effects of nonzero background ion currents and offsets of amplifier base lines. Corrections for scattering of major-beam ions into minor-beam collectors, leakage of gas-switching valves, etc. (2–4) were negligibly small. "Mass discrimination" effects have been taken into account by the usual technique of differential measurement (13). In this procedure, standard and sample gases are alternately introduced to the mass spectrometer, and ion currents at m/z 44, m/z 45, and m/z 46 are measured for each gas. The true (i.e., corrected for mass-discrimination effects) ion-current ratios for the sample gas are determined using eq 22:

$$^nR_{\text{unknown}} = \frac{^{mn}R_{\text{unknown}}}{^{mn}R_{\text{standard}}} {}^nR_{\text{standard}} = {}^nQ \cdot {}^nR_{\text{standard}} \quad (22)$$

where ^{mn}R denotes a *measured* ion-current ratio, nR denotes a *true* ion-current ratio as defined in eq 10–14, and $n = 45$ or 46. Values of nR for the working standard are determined by an extension of this process to a primary standard (14).

For convenience, isotope ratios are represented in terms of the notation introduced by Urey (15) and defined by McKinney et al. (13)

$$\delta^n X_{\text{STD}} = 10^3 [({}^nR_{\text{unknown}}/{}^nR_{\text{STD}}) - 1] \quad (23)$$

where X represents the element associated with the particular value of n specified, in this case, C or O.

Mass spectrometric measurements were made with a Finnigan MAT Delta E isotope ratio mass spectrometer (Finnigan Corp.). The working standard was calibrated with carbon dioxide produced by phosphorolysis of the primary standards K-2 and TKL-1 (16).

RESULTS AND DISCUSSION

Mixed Samples Enriched in ^{18}O . If a sample has been selectively enriched in ^{18}O , inaccuracies will result from use of the routine sequence of calculations. Because ^{46}R is primarily dependent on ^{18}R , solution of eq 20 will yield a roughly correct value for ^{18}R . The value of ^{17}R will, however, be overestimated by eq 19. Insertion of that overestimate in eq 10 will lead to an incorrectly low value for ^{13}R . Further, use of eq 19 in the derivation of eq 20 causes the initially calculated value of ^{18}R (termed "roughly correct" above) to be low. Because the relative contribution of the term $\{2 \cdot {}^{17}\text{R}\}$ to ^{45}R is greater than that of $\{2 \cdot {}^{13}\text{R} \cdot {}^{17}\text{R} + {}^{17}\text{R}^2\}$ to ^{46}R , the error in ^{13}R will be greater than the error in ^{18}R .

Clearly, this cascade of errors can be most appropriately prevented by "uncoupling" ^{17}R and ^{18}R (that is, by not using eq 19 to express the relationship between ^{17}R and ^{18}R). Two approaches are possible. If ^{13}R is known independently, the sequence of calculations that we will term " ^{13}C known" can be employed:

1. ^{17}R is calculated from ^{45}R and ^{13}R (eq 10).
2. ^{18}R is calculated from ^{46}R , ^{13}R , and ^{17}R (eq 11).

If ^{17}R is known independently, or if it is expedient to adopt an estimated value in order to reduce systematic errors in the analysis of samples for which neither ^{13}R nor ^{18}R is known, but in which ^{18}O has been enriched well above natural abundance, a sequence of calculations that might be termed

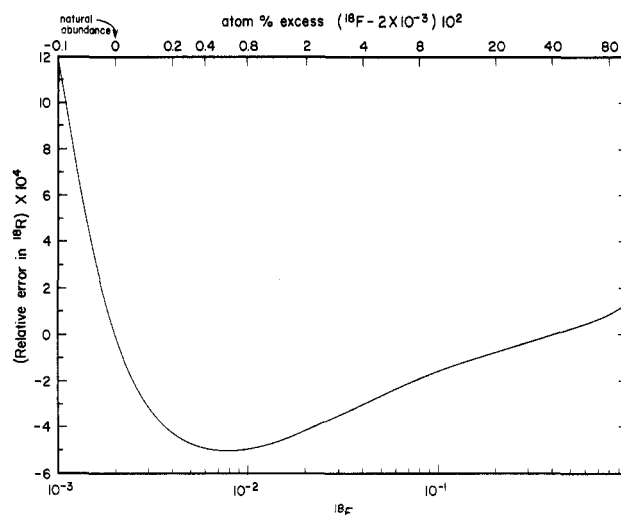


Figure 1. Relative error in ^{18}R (from step 1 of the routine sequence of calculations) as a function of oxygen-18 enrichment.

" ^{17}O known" can be employed:

1. ^{13}R is calculated from ^{45}R and ^{17}R (eq 10).
2. ^{18}R is calculated from ^{46}R , ^{13}R , and ^{17}R (eq 11).

To explore these problems and possibilities, we have prepared and analyzed mass spectrometrically a series of carbon dioxide samples enriched in the heavy isotopes of oxygen. Oxygen in these samples was derived by exchange with waters prepared by mixing 99% ^{18}O water with distilled tap water. Because only oxygen-isotopic compositions could be affected by exchange, the true carbon-12/carbon-13 ratio in all samples was identical.

Results of the mass spectrometric analyses are summarized in Table I, which includes normalized ion-current ratios as well as two different sets of calculated isotopic compositions. The columns headed " R " tabulate *apparent* isotopic compositions derived from the routine sequence of calculations. Samples bearing higher numbers have higher abundances of ^{18}O , and it can be seen that, as the oxygen-18 content of the samples increases, the apparent value of $\delta^{13}\text{C}_{\text{PDB}}$ does not remain constant, but, instead, decreases systematically. For samples enriched in ^{18}O by approximately 300‰, the error amounts to almost -10‰ (see sample 20: the routine calculation yields -19.11‰ even though the correct result must still be -10.17‰).

Inasmuch as it is known that all samples must, in this case, have carbon-isotopic abundances equal to that of the initial, unexchanged CO_2 , use of the " ^{13}C known" sequence of calculations is appropriate. Columns headed "CK" in Table II tabulate results. Because routine analysis of the unexchanged material indicated a carbon-isotopic composition of -10.17‰ vs. PDB, this value was assigned to all samples in which ^{18}O had been enriched by exchange. Comparison of oxygen-isotopic compositions reported for each sample in the " R " and "CK" columns shows (i) that differences in the abundance of ^{18}O determined by the routine sequence and the " ^{13}C known" sequence of calculations are, indeed, small and (ii) that much larger changes in the calculated abundance of ^{17}O result from uncoupling its abundance from that of ^{18}O .

To generalize these observations, the difference between the solution to eq 20 and the true value of ^{18}R was determined for all possible values of ^{18}F (^{17}O and ^{13}C were assumed to be at natural abundance). Results are summarized in Figure 1. In this example, it was assumed that the abundances of ^{13}C and ^{17}O were near natural levels ($^{13}\text{R} = 0.0112372$, $^{17}\text{R} = 3.73 \times 10^{-4}$) but that abundance of ^{18}O had been increased by admixture of pure ^{18}O . The error depicted arises because the derivation of eq 20 incorporates an assumption, incorrect in mixtures of this kind, that the abundances of ^{17}O and ^{18}O are

Table I. Carbon Dioxide Oxygen Derived from Mixed Waters

sample	$^{45}Q^a$	$^{46}Q^b$	$\delta^{13}C_{PDB}, \text{‰}$		$\delta^{17}O_{SMOW}, \text{‰}$		$\delta^{18}O_{SMOW}, \text{‰}$	
			R^c	CK^d	R^c	CK^d	R^c	CK^d
0 ^e	0.999 857	1.001 108	-10.17		16.95		32.56	
1	0.999 835	1.004 370	-10.24	-10.17	18.68	17.65	35.92	35.93
2	0.999 900	1.018 367	-10.66	-10.17	20.06	18.70	50.38	50.40
3	0.999 952	1.036 724	-11.19	-10.17	34.58	18.64	69.72	69.77
4	0.999 913	1.045 923	-11.66	-10.17	40.44	19.82	78.84	78.90
5	0.999 982	1.061 658	-12.06	-10.17	48.57	20.00	95.08	95.14
6	0.999 935	1.074 606	-12.56	-10.17	55.22	20.38	108.46	108.52
7	1.000 006	1.090 567	-13.02	-10.17	63.36	19.25	124.93	125.02
8	0.999 960	1.102 645	-13.48	-10.17	69.48	19.65	137.40	137.50
9	0.999 973	1.116 238	-13.92	-10.17	76.34	19.84	151.44	151.55
10	1.000 012	1.131 351	-14.38	-10.17	83.91	20.48	167.04	167.17
11	0.999 940	1.140 809	-14.77	-10.17	88.63	19.33	176.81	176.95
12	1.000 060	1.159 847	-15.27	-10.17	98.06	21.25	196.47	196.62
13	1.000 009	1.174 993	-15.81	-10.17	105.48	20.51	212.03	213.39
14	0.999 982	1.187 568	-16.25	-10.17	111.67	20.00	225.09	225.28
15	1.000 003	1.201 021	-16.67	-10.17	118.21	20.32	238.98	239.18
16	1.000 048	1.215 488	-17.08	-10.17	125.21	21.05	253.92	254.13
17	1.000 046	1.229 741	-17.54	-10.17	132.07	21.02	268.64	268.86
18	1.000 050	1.242 293	-17.94	-10.17	138.08	21.09	281.60	281.84
19	1.000 078	1.258 186	-18.41	-10.17	145.65	21.53	298.01	298.26
20	1.000 106	1.270 707	-18.77	-10.17	151.58	21.97	310.94	311.20
21	1.000 184	1.284 294	-19.11	-10.17	157.98	23.22	324.97	325.24

^a $^{45}Q = m^{45}R_{\text{unknown}}/m^{45}R_{\text{standard}}$. $^{45}R_{\text{standard}} = 0.011\,881\,58$. ^b $^{46}Q = m^{46}R_{\text{unknown}}/m^{46}R_{\text{standard}}$. $^{46}R_{\text{standard}} = 0.004\,149\,577$. ^c R indicates routine sequence of calculations, $a = 0.52$, $K = 0.009\,433\,02$. ^d CK indicates " ^{13}C known" sequence of calculations. ^e Sample 0 was initial, unexchanged CO_2 .

Table II. Carbon Dioxide Oxygen Derived from Distilled Waters

sample	$^{45}Q^a$	$^{46}Q^b$	$\delta^{18}O_{SMOW}, \text{‰}$	$\delta^{13}C_{PDB}, \text{‰}$		
				c	d	e
0 ^f	0.999 857	1.001 108	+35.56	-10.36	-10.35	-10.15
1	0.996 008	0.888 515	-82.31	-10.20	-10.28	-10.03
2	0.996 375	0.897 943	-72.56	-10.16	-10.23	-10.02
3	0.996 499	0.900 305	-70.11	-10.11	-10.19	-9.98
4	0.996 168	0.900 698	-69.71	-10.48	-10.55	-10.35
5	0.996 495	0.901 266	-69.12	-10.15	-10.22	-10.02
6	0.996 647	0.906 725	-63.48	-10.19	-10.26	-10.08
7	0.996 855	0.912 028	-57.99	-10.16	-10.23	-10.07
8	0.997 078	0.915 067	-53.92	-10.07	-10.13	-9.98
9	0.997 128	0.916 327	-53.55	-10.03	-10.09	-9.95
10	0.997 114	0.916 420	-53.45	-10.05	-10.11	-9.96
11	0.997 289	0.919 115	-50.67	-10.13	-10.19	-10.05
12	0.997 242	0.919 410	-50.36	-10.02	-10.08	-9.94
13	1.000 050	0.999 867	+32.83	-9.92	-9.88	-10.05
14	1.000 953	1.026 080	+59.93	-9.87	-9.81	-10.07

^a $^{45}Q = m^{45}R_{\text{unknown}}/m^{45}R_{\text{standard}}$. $^{45}R_{\text{standard}} = 0.011\,881\,58$. ^b $^{46}Q = m^{46}R_{\text{unknown}}/m^{46}R_{\text{standard}}$. $^{46}R_{\text{standard}} = 0.004\,149\,577$. ^c Routine sequence of calculations, $a = 0.516$, $K = 0.009\,202\,36$. ^d Routine sequence of calculations, $a = 0.500$, $K = 0.008\,335$. ^e Routine sequence of calculations, $a = 0.516$, $K = 0.009\,923\,5$. ^f Sample 0 was initial, unexchanged CO_2 .

related by eq 19. More important in tracer studies, the relative difference between the calculated and true values of ^{18}F under the same conditions was also determined and is shown in Figure 2. Isotope ratios were determined by using the routine sequence of calculations, and the fractional abundance of ^{18}O was derived by substitution in $^{18}F = ^{18}R/(1 + ^{17}R + ^{18}R)$.

A slight increase in $\delta^{17}O_{SMOW}$ is reflected in the results of the "CK" calculations. This increase appears to be genuine. It corresponds exactly to the increase expected from the admixture of a small, excess- ^{17}O component accompanying the excess ^{18}O . The expected magnitude of this contribution was calculated by substitution in eq 19 of the observed value of ^{18}R for the "99% ^{18}O " water, followed by calculation of ^{17}R , given $a = 0.516$ and $K = 0.009\,20$.

^{17}R and ^{18}R in Natural Samples. To examine relationships between ^{17}R and ^{18}R typical of those found in natural

systems, a series of water samples was produced by fractional distillation. Subsequent exchange of oxygen between these samples and carbon dioxide yielded a series of samples of CO_2 with widely varying ^{18}O content. Because the same stock of CO_2 was used to prepare all samples, the carbon-isotopic compositions of all samples were identical.

Results of mass spectrometric analyses of these samples are summarized in the second and third columns of Table II. The fourth column, based on routine calculations with $a = 0.516$ and $K = 0.009\,203\,6$ (although the number of significant figures exceeds the precision with which K can presently be estimated, the value specified exactly reflects the mean isotopic abundances reported in ref 13 and was employed in these calculations), indicates the range of oxygen-isotopic compositions. The fifth column tabulates carbon-isotopic abundances as determined in the same set of calculations. Inspection of the

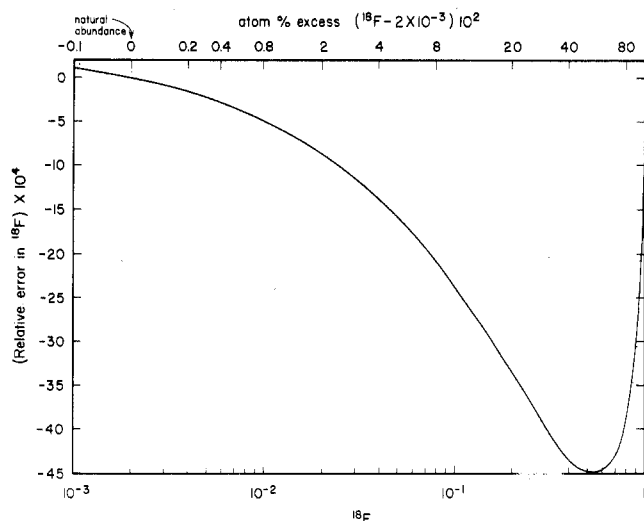


Figure 2. Relative error in ^{18}F as a function of oxygen-18 abundance. Conditions are the same as those given for Figure 1.

latter results shows that the calculated carbon-isotopic composition is not independent of the oxygen-18 abundance, as it should be. In fact, regression of $\delta^{13}\text{C}$ on $\delta^{18}\text{O}$ indicates a slope of 0.0025 C/O, a result which differs significantly ($p < 0.008$) from zero.

Small variations in assigned values of a and/or K have almost no effect on calculated values of $\delta^{18}\text{O}$ but can substantially affect the apparent variations in $\delta^{13}\text{C}$. As an example, the sixth column in Table II summarizes apparent carbon-isotopic compositions determined by use of the routine sequence of calculations with $a = 0.50$ and $K = 0.008335$. This corresponds to the present conventional approach (e.g., ref 4). Regression of $\delta^{13}\text{C}$ on $\delta^{18}\text{O}$ in this case yields a slope of 0.0036 C/O, a systematic error even greater than that encountered in the preceding calculation. The seventh column in Table II reports apparent carbon-isotopic compositions determined by use of the routine sequence of calculations with $a = 0.516$ and $K = 0.0099235$. In this case, K was adjusted to eliminate covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Routine calculations based on the mass spectrometric data summarized in Table II show that, to a good approximation, this condition will be met by any pair of a , K values fulfilling the criterion

$$K = 0.04103a - 0.011387 \quad (25)$$

That is, eq 25 defines the locus of a , K , pairs that yield $\delta^{13}\text{C}$ independent of $\delta^{18}\text{O}$ when the routine sequence of calculations is applied to the observed ratios summarized in Table II. It is evident that a "correct" value cannot be chosen for K without first specifying a , or vice versa.

Evidence favoring assignment of $a = 0.516$ is relatively strong: (i) Many different samples, analyzed over a considerable period of time, have been found to fit the relationship of eq 17. (ii) Use of the conventional alternative ($a = 0.500$, column 6, Table II) leads to obvious systematic errors in $\delta^{13}\text{C}$. (iii) $a = 0.516$ is at the center of the expected range of values for a (6).

A value for K can then be chosen either by reference to eq 25 or by inserting the results of Nier's analysis of tank oxygen in eq 19 with $a = 0.516$. Neither of these criteria seems as strong as that used to choose $a = 0.516$, and it is unfortunate that they yield different results. If the single absolute abundance measurement is relied upon (Table II, column 5)

results are obtained that are clearly in error in that $\delta^{13}\text{C}$ is found to depend on $\delta^{18}\text{O}$. If the single series of distilled water samples is used (Table II, column 7), a systematic error is avoided but one is choosing—in essence—to base the absolute abundance of ^{17}O on a very indirect measurement.

The contrasting results can be illustrated in terms of the calculated abundance of ^{17}O in Standard Mean Ocean Water. It is known that $^{18}\text{R}_{\text{SMOW}} = 2.0052 \times 10^{-3}$ (10). Adopting $a = 0.516$ and $K = 0.00920235$ (tank O_2 based value), one obtains $^{17}\text{R}_{\text{SMOW}} = (3.73 \pm 0.07) \times 10^{-4}$ (standard error based on mass spectrometric uncertainty reported in ref 13). Adopting $a = 0.516$ and $K = 0.0099235$ in order to eliminate covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, one obtains $^{17}\text{R}_{\text{SMOW}} = (4.02 \pm 0.08) \times 10^{-4}$ (standard error based on standard deviation of slope for the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ relationship). These values differ by nearly 8%, a disagreement which is probably significant.

CONCLUSIONS

The method (termed "routine" in the preceding discussion) outlined here for resolution of isotopic contributions in the mass spectrum of carbon dioxide is superior to approaches incorporating eq 17 in that it is more exact mathematically and more realistic in its approach to natural variations of carbon and oxygen isotopic abundances.

Significant systematic errors can arise if calculations incorporating eq 17 are applied to analyses of ^{13}C or ^{17}O in samples enriched in ^{18}O . In these cases, the procedures here termed " ^{13}C known" or " ^{17}O known" are advantageous.

The absolute value of $^{17}\text{R}_{\text{SMOW}}$ should be measured directly, and a value for K that avoids systematic errors should be adopted as a temporary expedient.

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Registry No. CO_2 , 124-38-9; H_2O , 7732-18-5; ^{17}O , 13968-48-4; ^{18}O , 14797-71-8; ^{13}C , 14762-74-4.

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