

Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide

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Abstract—Seventy-four mass spectrometric analyses have been made on eight isotopic standards for carbon and oxygen. The standards reported on are the National Bureau of Standards limestone, water, and graphite reference samples, the Solenhofen standard used by NIER for absolute measurements, and the carbonate standards used by the Stockholm, Basel, Wellington, and Chicago laboratories. The basic measurements are reported as δ values relative to the Chicago PDB standard and as absolute isotope ratios. The absolute ratios are based on new figures for NIER's standard, derived from a re-evaluation of his data and new measurements on atmospheric oxygen.

The correction factors for instrumental effects and for the nature of the mass spectra have been studied. Simple but precise equations for the mass spectra effects have been derived, which give the correction factors as functions of the measured differences between sample and standard. The oxygen isotopic composition of carbon dioxide produced by combustion of carbon has been studied, and the derived correction factors for carbon measurements were checked experimentally by varying the oxygen-18 content of carbon dioxide.

1. INTRODUCTION

MASS spectrometric measurement of natural isotopic variations began with the work of NIER and GULBRANSEN (1939) on carbon isotopes. In 1950, MCKINNEY *et al.* described a modification of the Nier mass spectrometer designed to increase the precision in the measurement of relative abundances by an order of magnitude; at the present writing fourteen spectrometers of this type have been constructed at various geochemical laboratories, and with these, and other instruments, a great mass of precise isotopic data has been accumulated. CRAIG and BOATO (1955) recently reviewed the present status of stable isotope geochemistry. Some thirty laboratories are or soon will be active in this field, reflecting the present-day emphasis on the quantitative aspects of geology.

This paper has been prompted by the recent availability of isotopic standards prepared and distributed by the National Bureau of Standards (MOHLER, 1955). It is based on the accumulated data and analytical experience of the past five years at the Chicago laboratory of H. C. UREY and on recent measurements on the NBS standards, and represents an attempt to obtain the most precise values possible for the various isotopic standards in use. These values should be useful in establishing the relations between the sets of data from the various different laboratories. For the most precise comparison of the various standards, a careful evaluation of the systematic errors inherent in the mass spectrometric analysis is necessary. Therefore, we first consider the mass spectrometer and the correction factors for the analysis of carbon dioxide, and then the relative and absolute isotopic values for the standards analysed in this study.

2. THE MCKINNEY-NIER MASS SPECTROMETER

The high precision of the McKinney-Nier spectrometer is chiefly the result of two factors: (1) replacing the electrometer tube and amplifier, or second feed-back amplifier, for the smaller

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ion beam in the null-reading double-collector balancing circuit devised by NIER, NEY, and INGRAM (1947) by a vibrating-reed electrometer; and (2) the introduction of a dual gas-feed system, originally designed by NEY, for rapid comparison of the voltages, tapped off from the balancing potentiometer, required to produce null readings for a sample and a standard gas. In addition, the electronic components used by NIER (1947) were redesigned for very high stability. With the introduction of the vibrating-reed electrometer, the ion-beam currents reported by MCKINNEY *et al.* (1950) were reduced by a factor of 3, and have been maintained as such ever since. In the analysis of carbon dioxide, the potential drop across the 1.5×10^{10} -ohm resistor of the mass-44 collector is maintained at 19.2 V, resulting in a mass-44 ion current of 1.3×10^{-9} amperes for both sample and standard. The second collector, for mass-45 or -46, has a 1.5×10^{11} -ohm resistor in the balancing circuit, and the observed parameters for carbon and oxygen analysis are as follows:

Mass-45	Mass-46
$i_{45} = 1.5 \times 10^{-11}$ A	$i_{46} = 5.3 \times 10^{-12}$ A
$E_{45} = 2.25$ V	$E_{46} = 0.78$ V
BP ~ 1300 ohms	BP ~ 450 ohms
$\beta = 0.117$	$\beta = 0.0405$

The currents and voltages listed are the ion-beam currents and potential drops across the small-collector resistor; BP is the balancing panel resistance tapped off from the 11,111-ohm decade resistor potentiometer, and β ($= \text{BP}/11,111$) is the ratio of the potential drops across the respective resistors for mass-45 or mass-46 to mass-44.

For the comparison of ratios on the spectrometer, the mass-44 ion-beam intensities are adjusted by means of the manifold mercury pistons to identical values for sample and standard gas. The reason for this adjustment is the effect of the squared term in the mass-44 tail contribution to the smaller ion beam, which causes a dependence of the recorded ratio on ion-beam intensity (see below). Thus the input pressures of the two gases are different, and inversely proportional to the mass-44 mole fractions. In the initial adjustment of the instrument, and at periodic intervals, the sample and standard manifolds are interconnected, and a gas sample is thoroughly mixed into both reservoirs. The two reservoirs are then closed off from each other, the gas is fed through the twin leaks, and the capillary leaks are manually adjusted to produce equal isotope ratios at equal mass-44 ion-beam intensities ($E_{44} = 19.2$ V), but generally different input pressures. This adjustment is necessary because there is a small but real fractionation in the leaks caused by back mixing, the differential effect of which must be eliminated. Mixing of the sample and standard gases in the source, due to imperfect closure of the ground-glass ball-joints in the double inlet valve, is corrected for by direct measurement of the leakage through each valve. This is done by analysing a sample gas some 3–4% different in composition from the standard, and noting the shift of the trace of the null point on the recording potentiometer when the sample and standard are alternately pumped away; from the measured difference in isotopic composition, the leakage through each valve is computed. For the instrument on which the present work was done, the correction factor for this effect has maintained a constant value of 1.007 for the past several years.

Shortly after the McKinney-Nier spectrometer was put into operation, the "pressure effect," i.e. the variation of the recorded ratio with ion-beam intensity, was discovered. Although the effect was small, it was found that it could be eliminated by setting a small potential bias on the vibrating-reed amplifier, with a polarity such as to increase the voltage drop of the smaller ion-beam current across the small-collector balancing circuit resistor, and, correspondingly, across the vibrating-reed resistor when the system is switched off balance. The biasing potential required to eliminate this effect is some 5 mV for mass-46, and 10 mV for mass-45. This procedure was followed in the Chicago laboratory for several years, but when the writer investigated the nature of the effect, the practice was then abandoned except for special circumstances. Since the voltage drop of the smaller ion current across its resistor is increased by the amount of the biasing voltage, the measured isotope ratio for a null reading is also increased, and the smaller ion-beam current is augmented by the ratio of the biasing voltage to the small-collector resistor. Thus the recorded 46/44 and 45/44 ratios are increased by an additive term in the

numerator which does not cancel when the ratio of the isotope ratios is taken. To correct for this, the measured δ value (defined below) for a sample must be multiplied by the factor $(1 + E_r/E_i)$, where E_r is the bias voltage set on the reed, and E_i is the smaller ion-beam potential drop, with values for carbon and oxygen as listed above.

The "pressure effect" cited above appears to be due to a squared dependence of the mass-44 tail contribution to the less abundant ion beams, since the isotope ratio would not increase with ion-beam intensity, nor with the applied reed bias, as is observed, unless the dependence were higher than first-order. The 44 tail contribution most probably goes as the square of the 44 ion-beam intensity, representing a coulombic effect. Thus we write the current added to the less abundant ion-beam current by the spreading of the mass-44 beam, as $i_t = k_1 I^2 + k_2 I$, where I is the mass-44 ion current. If i_{46} and i_r are then respectively the normal mass-46 ion current, reflecting only the mass-46 abundance, and the current across the small-collector resistor produced by the vibrating-reed bias voltage, the measured ratio will be $(i_{46} + i_r + i_t)/I$, or:

$$R_m = (R + k_2) + (i_r/I) + k_1 I$$

where we have written $R = i_{46}/I$ = the mass ratio in the impinging ion beams. Thus we see that the squared-term assumption predicts the elimination of the "pressure effect" by means of the reed-bias voltage, because of the addition of a term which goes as $1/I$ in the measured ratio. This expression predicts that, for small I , R_m should decrease with increasing I with a slope of $-i_r/I^2$, then go through a minimum, and finally increase linearly with a slope of k_1 . For a reed bias of opposite polarity, R_m should increase continuously before attaining a linear dependence. After derivation of the above expression, measurements were made on R_m as a function of I , and these predictions were verified completely except that at very high values of I ($E_{44} > 25$ V), R_m again begins to increase rapidly because of saturation of the D.C. amplifier.

Setting $dR_m/dI = 0$ for the minimum where the ratio does not vary with I , we have: $i_r/I_{\min} = k_1 I_{\min}$, the I dependent terms are equal in the above expression, and their variation with I is equal and of opposite sign, explaining the minimum. The constant k_1 , evaluated from the data for the minima as E_r was varied from -1.5 to $+6$ mV, and from the slope of the linear dependence, was found to be $25,000 \text{ A}^{-1}$, with an error of about 20%. However, k_2 cannot be determined from these data, because, although R can be estimated by applying a square-root-of-mass correction for source fractionation to the absolute value, derived in a later section, for the standard gas, its value, so estimated, differs from R_m by much less than the uncertainty imposed by the tolerances assigned to the values of the resistors used in the balancing circuit. Since the sign of k_2 is not known, we make no correction for the tail effect as such, but data taken before the use of the reed-bias voltage was eliminated have been corrected for the applied voltage (which was recorded), because of the fact that it was variable from time to time and caused significant departures from our estimated analytical precision for samples quite different in composition from the standard.

However, the most interesting result of this effect is the quick and easy method it offers for evaluating the contribution of the H_3^+ ion to the HD beam in the mass spectrometric analysis of hydrogen. For, since the H_3^+ ion abundance varies with the square of the H_2 ion-beam abundance, and since with the use of double collectors there is no tail effect because of the wide beam separation, at the minimum ratio dependence on I produced at the working H_2 beam intensity by an empirically determined reed voltage, the equivalent reed current i_r is equal to the ion current contributed by the H_3^+ ions. k_1 above then becomes the proportionality constant for the H_3^+ dependence on I^2 , and k_2 will be 0

Notation and Symbols

We continue to report our data as δ values relative to our standard. The Chicago carbon dioxide standard is CO_2 produced from PDB calcium carbonate by reaction with 100% H_3PO_4 at 25.2°C . PDB is a Cretaceous belemnite, *Belemnitella americana*, from the Peedee formation of South Carolina; the carbonate has undergone no treatment prior to the acid reaction other than crushing

and grinding. δ is the per mil isotopic ratio enrichment in a sample relative to the standard, i.e.:

$$\delta(\text{‰}) = \left[\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right] \times 1000$$

Throughout this paper we shall distinguish two δ functions, both of which refer always to the PDB standard, as follows:

δ_m = measured enrichment, calculated from the recorded ratios of the molecular masses collected. It is corrected for instrumental effects, i.e. for gas leakage through the inlet valves and vibrating-reed bias (if used), but for nothing else.

δ_c = the true enrichment of the sample relative to the standard, i.e. the measured δ corrected by the factors derived in section 4.

We have considered publishing data in the future as δ values relative to the new NBS standard, but after consultation with other laboratories have decided to continue using the Chicago standard as a reference. The paleotemperature scale is defined in terms of this standard, and a great deal of data on carbon and oxygen variations has been published relative to it; it is currently used as a reference standard by four laboratories. In addition, its oxygen value is very close to the average value for ocean water (as measured by the equilibration technique), and its carbon value is close to that of average limestone, which makes it a convenient reference standard for geochemical calculations.

In the following sections we derive the absolute and relative abundance values of the various standards, and the correction factors to be applied to the raw mass spectrometric data. The symbol R is used throughout both for isotope ratios and for the molecular mass ratios measured in the mass spectrometer. Oxygen isotope ratios are uniformly molecular, i.e. R refers always to $\text{O}^{16}\text{O}^{18}/\text{O}^{16}\text{O}^{16}$ rather than to $\text{O}^{18}/\text{O}^{16}$. With R we associate two sets of subscripts, denoting first the particular ratio, and second the material to which the ratio refers. The ratio denoting subscripts are:

$$R_{13} = \text{C}^{13}/\text{C}^{12}$$

$$R_{17} = \text{O}^{16}\text{O}^{17}/\text{O}^{16}\text{O}^{16}$$

$$R_{18} = \text{O}^{16}\text{O}^{18}/\text{O}^{16}\text{O}^{16}$$

$$R_{46} = \frac{\text{Number of mass-45 ions collected}}{\text{Number of mass-44 ions collected}}$$

$$R_{46} = \frac{\text{Number of mass-46 ions collected}}{\text{Number of mass-44} + \text{mass-45 ions collected}}$$

As material-denoting subscripts we shall use (std) for the Chicago PDB carbon dioxide standard described above, (air) for atmospheric oxygen, and (x) for any sample of carbon dioxide being analysed. In addition, we distinguish the following:

(Solen) = carbon dioxide from the Solenhofen Jurassic limestone, Bavaria, analysed for carbon and oxygen isotopic ratios by NIER (1950). CO_2 was produced by treatment with an unspecified acid. This subscript refers specifically to NIER's values for his sample of CO_2 .

(Solen- H_3PO_4) = carbon dioxide produced from NIER's Solenhofen limestone sample by reaction with 100% H_3PO_4 at 25.2°C in our laboratory. The limestone sample has undergone no treatment other than crushing and grinding.

It should be noted that, for the case of oxygen ratios, the (std) and the two Solenhofen subscripts refer specifically to the carbon dioxide rather than to the carbonate, since it is known that in the production of carbon dioxide by acid treatment of carbonate, the oxygen isotopes are fractionated. The two Solenhofen subscripts, referring to the same carbonate sample treated with different acids, are distinguished because it is also known that the oxygen ratio in the carbon dioxide varies with the acid used, and probably also with the isotopic composition of the water, if water is present. (See McCREA, 1950, for data on the variation with type of acid.) According to NIER (personal communication), the acid used on his sample was probably HCl.

3. DERIVATION OF THE ABSOLUTE ABUNDANCE RATIOS

Eleven isotopic abundance ratios are needed for the derivation of the mass spectrometric correction factors discussed in the next section; the three basic data are NIER's measurements of R_{18} and R_{17} in atmospheric oxygen and R_{13} in the Solenhofen limestone. In this section we discuss NIER's data, from which we obtain six ratios, and then derive the remaining five ratios from our relative abundance data.

Evaluation of NIER's data on atmospheric oxygen and Solenhofen limestone

NIER (1950) obtained the most precise isotopic abundance ratios for carbon and oxygen, by using synthetic mixtures of argon isotopes for calibration of the mass discrimination effects in his spectrometers. The analyses were made on two mass spectrometers, and after correction for mass discrimination effects, a weighted grand mean of data was obtained from six measurements of each isotopic ratio. NIER's absolute ratios for atmospheric and tank oxygen are shown in Table 1, which gives the 34/32 and 33/32 ratios (R_{18} and R_{17} respectively) obtained on each spectrometer. Each figure is the average of three measurements, and the bottom row gives NIER's weighted average from the two sets of data.

Table 1. Mass spectrometric analyses of atmospheric and tank oxygen
A. O. NIER (1950)

	$34/32 \times 10^5$			$33/32 \times 10^6$		
	Tank	Air	$\Delta(\%)$ tank/air	Tank	Air	$\Delta(\%)$ tank/air
MS-2	410.7	408.2	6.1	752.8	757.5	-6.2
MS-1	410.3	408.8	3.7	755.1	741.1	+18.9
Weighted average	410.3	408.8	3.7	755	749*	+8.0

* Unweighted value, as data from two instruments were assumed to be inconsistent.

The values of R_{18} for tank and air oxygen are in very good internal agreement, and we adopt immediately from NIER's data

$$R_{18(\text{air})} = 408.8 \times 10^{-5} \quad (1)$$

In Table 1 we have also calculated the per mil enrichment in O^{18} and O^{17} of tank oxygen with respect to atmospheric oxygen, termed Δ . TUDGE's data (Table 2) show that tank oxygen

is enriched from 4–6‰ in O^{18} with respect to atmospheric oxygen, in exact agreement with NIER's measurements; this agreement, though probably fortuitous in its exactitude, nevertheless testifies to the precision of NIER's data.* (Probable errors are given in NIER's original paper.)

NIER chose the unweighted average value of 749×10^{-6} for $R_{17(\text{air})}$, noting that the two sets of data were inconsistent. Comparison of the enrichment factors for O^{17} in tank oxygen compared with air oxygen (Table 1) shows that the data are also inconsistent with the enrichment factors expected from consideration of the O^{18} enrichment in tank oxygen over air oxygen, for which the data are quite consistent. For systems in thermodynamic equilibrium, consideration of the vibrational frequency decrease for the addition of one and of two neutrons to a nucleus indicates that the fractionation factor for the distribution of O^{18} between two compounds should be the square of the fractionation factor for O^{17} (cf. CRAIG, 1954, p. 133). (Since these factors are close to 1, the enrichments should differ by about a factor of 2.) BIGEISEN's reaction-rate theory predicts the same relationship for kinetic effects (BIGEISEN, 1952). Such a relationship has been observed for sulphur in natural compounds and experimental systems (THODE *et al.*, 1949, p. 368–369), and in numerous instances for carbon (e.g. YANKWICH *et al.*, 1954). NIER's data for R_{17} in air oxygen are thus not only internally inconsistent, but are also inconsistent with the expected enrichment with respect to tank oxygen, based on the O^{18} data. The two sets of data give O^{17} enrichments which differ in both sign and magnitude, and there is thus no indication of a systematic deviation from the expected relationship. The measurements on atmospheric oxygen were made on air without removal of the nitrogen, which may account for the large deviations in the 33/32 ratios.

Since the R_{17} values for tank oxygen are quite consistent, we here assume that the 33/32 ratio in air oxygen is 2‰ less than in tank oxygen (based on the O^{18} difference.) Then, using NIER's value of 755×10^{-6} for R_{17} of tank oxygen, we obtain and adopt the value:

$$R_{17(\text{air})} = 753.5 \times 10^{-6} \quad (2)$$

We need next the ratio C^{13}/C^{12} in NIER's Solenhofen limestone sample. NIER's measured value of the 45/44 ratio is $R_{45} = 1199 \pm 2 \times 10^{-5}$. Now, since the measured ratio $R_{45} = R_{13} + R_{17}$, the value of R_{17} in the carbon dioxide which was analysed for the carbon ratio must be known in order to obtain the C^{13}/C^{12} ratio. NIER used his value of $R_{17(\text{air})}$ for this figure and thus obtained $R_{13(\text{Solen})} = 1124 \times 10^{-5}$. However, the value of $R_{17(\text{Solen})}$ may be obtained from comparison of his data on $R_{18(\text{Solen})}$ and $R_{18(\text{air})}$, by assuming the relationship:

$$\left[\frac{R_{18(\text{Solen})}}{R_{18(\text{air})}} \right]^{\frac{1}{2}} = \frac{R_{17(\text{Solen})}}{R_{17(\text{air})}}$$

(cf. discussion on $R_{17(\text{air})}$ above). Then, using NIER's value $R_{18(\text{Solen})} = 415 \times 10^{-3}$, and the values of $R_{18(\text{air})}$ and $R_{17(\text{air})}$ given in (1) and (2) above, we obtain:

$$R_{17(\text{Solen})} = 759.2 \times 10^{-6} \quad (3)$$

this value referring to the O^{17} content of the CO_2 sample analysed by NIER. Then, from NIER's value for R_{45} given above, we obtain by direct subtraction:

$$R_{13(\text{Solen})} = 1123 \times 10^{-5} \quad (4)$$

From NIER's final probable-error assignment we have an uncertainty corresponding to $1123 \pm 3 \times 10^{-5}$. Now, for much of the relative abundance work currently being done we are working one decimal beyond NIER's figure. We thus adopt arbitrarily the value $R_{13(\text{Solen})} = 1123.00 \times 10^{-5}$ as the C^{13}/C^{12} ratio in NIER's Solenhofen limestone sample, in order to present absolute ratios for other standards with the precision corresponding to that obtainable when relative, rather than absolute, measurements are being made. This corresponds to a C^{12}/C^{13} ratio of 89.05.

Evaluation of the abundance ratios in PDB standard

Having obtained the values of $R_{18(\text{air})}$, $R_{17(\text{air})}$, and $R_{13(\text{Solen})}$ from NIER's data, we next proceed to derive $R_{18(\text{std})}$, $R_{17(\text{std})}$, $R_{13(\text{std})}$, and $R_{45(\text{std})}$ from direct measurement of the isotopic

* According to NIER (*op. cit.*), THODE has also found a difference of almost exactly the same magnitude.

differences between PDB standard carbon dioxide, atmospheric oxygen, and NIER's sample of Solenhofen limestone with which he kindly supplied the writer.

The measurements on atmospheric oxygen were made by A. TUDGE in the course of his work on the phosphate paleotemperature scale. Table 2 shows TUDGE's data on two brands of tank oxygen and air oxygen, given as δ values relative to PDB standard. The tank-oxygen samples were measured relative to each other as molecular oxygen. Atmospheric and Linde tank oxygen were then converted quantitatively to CO_2 by heating over spectroscopic graphite and condensing the CO_2 in liquid nitrogen. Details of the procedure will be published by TUDGE; the error in the present data is less than $\pm 0.2\%$. The values in the table are corrected by the factors given in section 4; δC^{13} of the carbon dioxide was taken as -28% , based on analyses of other samples of such graphite.

Table 2. Mass spectrometric analyses of oxygen from various sources (A. TUDGE)

Source	$\delta_c (\text{O}^{18})\%$
Tank—National Cylinder oxygen	-10.8
Tank—Linde oxygen	-12.7
Air	-16.73

From NIER's value of $R_{18(\text{air})}$ and TUDGE's analysis, we obtain:

$$R_{18(\text{std})} = 415.8 \pm 0.5 \times 10^{-5} \quad (5)$$

the uncertainty being that assigned by NIER to his value for $R_{18(\text{air})}$.

An independent check on TUDGE's analysis of atmospheric oxygen is obtained from analyses in our laboratory on samples of water produced from atmospheric oxygen which were given to us by M. DOLE. Analyses of two of these samples are as follows:

1. Dole sample No. 4, analysis published by EPSTEIN and MAYEDA (1953).^{*}
Analysed May 1952. $\delta_c (\text{O}^{18}) = +22.66\%$
2. Dole sample No. 1.
Analysed February 1953. $\delta_c (\text{O}^{18}) = +22.81\%$

$$\text{Average} \quad +22.73\%$$

The δ value of $+22.73\%$ is the analysis of CO_2 equilibrated with the water at 25.2°C , measured vs. the PDB standard. Taking the fractionation factor for O^{18} exchange between water and carbon dioxide as 1.039 at 25°C , the direct value for atmospheric oxygen vs. PDB standard is $\delta = -15.66\%$, to be compared with TUDGE's value of -16.73% . Considering the possibility of some fractionation in the conversion of oxygen to water, the fact that the water samples were stored for years in small flasks sealed with rubber stoppers, and the considerable uncertainty in the fractionation factor between water and carbon dioxide, the agreement is considered excellent. Using the value obtained from DOLE's water samples, we would obtain $R_{18(\text{std})} = 415.3 \times 10^{-5}$, which is within the uncertainty assigned in (5) above.

In order to obtain the value of $R_{17(\text{std})}$ we assume a similar relationship to that given above (3), namely:

$$\left[\frac{R_{18(\text{air})}}{R_{18(\text{std})}} \right]^{\frac{1}{2}} = \frac{R_{17(\text{air})}}{R_{17(\text{std})}}$$

and using the values given above by (1), (2), and (5), we obtain:

$$R_{17(\text{std})} = 759.9 \times 10^{-6} \quad (6)$$

^{*} This value differs from their published value of $+22.10$ in having been here corrected for instrumental effects, C^{13} and O^{17} effects, and a 20 ml-size sample, using the factors derived in this paper. See footnote in Section 4.

We now need the value of $R_{17}(\text{Solen-H}_3\text{PO}_4)$ which differs from R_{17} in NIER's sample because of the different acid used in our analytical technique. NIER's Solenhofen limestone gives an analysis of $\delta_c(\text{O}^{18}) = -4.40\%$ relative to PDB (see section 5). We therefore take the O^{17} enrichment (of the CO_2 produced by reaction with H_3PO_4) relative to PDB as -2.2% , and from (6) we obtain $R_{17}(\text{Solen-H}_3\text{PO}_4) = 758.2 \times 10^{-6}$.

We may now derive $R_{13}(\text{std})$ from the following relationship:

$$\frac{R_{13}(\text{Solen}) + R_{17}(\text{Solen-H}_3\text{PO}_4)}{R_{13}(\text{std}) + R_{17}(\text{std})} = 1 + \Delta \left(\frac{45}{44} \right)$$

where $\Delta(45/44)$ is the measured difference in mass 45/44 ratio between Solenhofen limestone and PDB standard carbon dioxide, both produced by reaction with H_3PO_4 , the value being corrected only for valve leakage in the spectrometer. The value of Δ is -0.74% (see section 5), and using the ratio values given in (4), (6), and above, we calculate:

$$R_{13}(\text{std}) = 1123.72 \times 10^{-5} \quad (7)$$

based on the adopted value of 1123.00×10^{-5} for the $\text{C}^{13}/\text{C}^{12}$ ratio of NIER's Solenhofen limestone. By direct addition, $R_{45}(\text{std}) = R_{13}(\text{std}) + R_{17}(\text{std}) = 1199.71 \times 10^{-5}$ for carbon dioxide prepared with H_3PO_4 .

The basic isotopic ratios adopted in this paper for the two standards and for atmospheric oxygen are given in Table 3.

Table 3. Isotopic ratios adopted in this paper

	$R_{18} \times 10^5$	$R_{17} \times 10^6$	$R_{45} \times 10^5$	$R_{13} \times 10^5$
Atmospheric oxygen	408.8	753.5	—	—
Solenhofen carbon dioxide as analysed by NIER	415	759.2	1199	1123.00
PDB standard carbon dioxide prepared with H_3PO_4	415.8	759.9	1199.71	1123.72

4. CORRECTION FACTORS FOR MASS SPECTROMETRIC ANALYSIS OF CO_2

In this section we derive the correction factors to be applied to δ_m in order to convert the molecular mass ratio differences to specific isotope ratio differences (δ_c). It is assumed that δ_m is the recorded δ value, corrected for the instrumental effects described in section 2. Finally, we give the correction factor for the isotopic analysis of water by means of equilibration with carbon dioxide.

Carbon-13 analysis

In the analysis of carbon we collect simultaneously masses 44 and 45, and the ratio is given by:

$$R_{45} = \frac{\text{C}^{13}\text{O}^{16}\text{O}^{16} + \text{C}^{12}\text{O}^{16}\text{O}^{17}}{\text{C}^{12}\text{O}^{16}\text{O}^{16}}$$

The $\text{C}^{12}\text{O}^{16}\text{O}^{17}$ component constitutes about 7% of $\text{C}^{13}\text{O}^{16}\text{O}^{16}$ and about 6.5% of the total mass-45 beam. The delta functions are:

$$1 + \delta_m = R_{45(x)}/R_{45}(\text{std})$$

$$1 + \delta_c = R_{13(x)}/R_{13}(\text{std})$$

where (x) denotes, as always, the ratio in the sample gas. From the relationship $R_{45} = R_{13} - R_{17}$, we substitute for $R_{13(x)}$ in the second delta function, and after manipulation obtain:

$$\delta_c = \frac{R_{45(\text{std})}\delta_m + R_{17(\text{std})} - R_{17(x)}}{R_{13(\text{std})}}$$

The unknown term is $R_{17(x)}$, which we obtain from measurement of the O^{18} enrichment of the sample gas with respect to the standard gas. From the considerations discussed in section 3, equation (2), we write:

$$\frac{R_{17(x)}}{R_{17(\text{std})}} = \left[\frac{R_{18(x)}}{R_{18(\text{std})}} \right]^{\frac{1}{2}} = (1 + \delta \text{O}^{18})^{\frac{1}{2}} \sim 1 + \frac{\delta \text{O}^{18}}{2}$$

where δO^{18} is the (corrected) oxygen-18 enrichment. Substituting for $R_{17(x)}$ in the previous expression gives:

$$\delta_c C^{13} = \delta_m \left[\frac{R_{45(\text{std})}}{R_{13(\text{std})}} \right] - \left[\frac{R_{17(\text{std})}}{2R_{13(\text{std})}} \right] \delta \text{O}^{18} \quad (1)$$

in which all the ratio terms are known from section 3. Substitution of numerical values for the ratio terms gives:

$$\delta_c C^{13} = 1.0676\delta_m - 0.0338 \delta \text{O}^{18} \quad (2)$$

which is the correction factor to be applied to analyses made against the PDB standard. Equation (1) is, of course, perfectly general, and the ratio terms for any standard may be found by comparison of the standard with PDB (see Section 5).

The correction factor for carbon analyses thus contains a constant term, reflecting the O^{17} content of the standard, and a variable term, reflecting the difference in the O^{17} content of the sample and the standard. The latter correction is obtainable directly from an oxygen-18 analysis of the gas being analysed for C^{13} .

In previous papers (CRAIG, 1953, 1954a,b) it was assumed that the difference in O^{17} content of sample and standard was negligible, and only the first term of the correction factor given above was applied (δ_m was multiplied by 1.067). Since then the oxygen-18 content of carbon dioxide produced by combustion of carbon with tank oxygen and copper oxide (CRAIG, 1953) has been investigated. As might be expected, the oxygen-18 content of the CO_2 fluctuates between the general limits of tank and air oxygen (see Table 2), varying probably as a function of the degree of exchange between the hot CuO and atmospheric oxygen during the time the combustion tube is open, and also as a function of the proportions of oxygen in CuO to tank oxygen bled into the line for the combustion. Oxygen-18 analyses of CO_2 resulting from the combustion procedure range from $\delta = -11.4$ to -18.4% , averaging about -15% relative to PDB. (The lightest values probably reflect a dominance of an isotopic effect in distillation of oxygen from liquid oxygen in the guard trap of the oxygen purification system.)

Using a value of $-15 \pm 3.5\%$ for the O^{18} content of combusted gas samples, the second term in equation (2) is $+0.5\% \pm 0.1$, the uncertainty here being about the same as the analytical precision. We use this value for general correction of combusted samples except where high precision is desired, in which case the samples are analysed for O^{18} as well as for C^{13} . Thus, all the analyses of combusted carbonaceous material given in the papers cited above should be corrected further by the addition of $+0.5\%$; the differences between such samples remain the same, but their differences from carbonate samples will be altered. Corrected values for noncombusted samples will be published in a future paper dealing with the isotopic geochemistry of carbon and oxygen in carbonates and the carbon paleotemperature scale.

A direct check on the derived correction factor was made by cycling CO_2 , extracted from carbonates by phosphoric acid, over hot copper oxide with oxygen gas in the system, thus duplicating the combustion technique using samples of known C^{13} content. From equation (2), equating the δ_c values before and after the experiment, since they must be the same, we may write the change in δ_m as a function of the O^{18} content before and after the experiment, and compare the measured and calculated change. A sample of PDB gas was "combusted" in this fashion, and on measuring the new C^{13} and O^{18} concentrations, the measured and calculated change in δ_m differed by only 0.02‰.

At this point fourteen more CO_2 samples, derived from carbonates of varying known composition, were run through the mock combustion procedure. These samples ranged in C^{13} content from $\delta = +3$ to -30 ‰, and in original O^{18} content from $\delta = 0$ to -25 ‰, relative to PDB. The samples were run under varying conditions, such as presence or absence of oxygen, and using different times and temperatures. The change in $\delta_m \text{C}^{13}$ was then calculated, assuming an O^{18} content, after "combustion," of -15 ‰, and compared with the measured change. The calculated changes in δ_m ranged from $+0.33$ to -0.46 ‰, a spread of about eight times the precision of an individual analysis. For the total series of fifteen samples, the differences between the measured and calculated changes in δ_m ranged from $+0.16$ to -0.17 ‰, with only four differences exceeding 0.10‰. The average difference, taken by algebraic summation, was just zero, i.e. there was no systematic direction of difference. The average deviation, taken without regard to sign, was 0.07‰, and the experiments thus gave a decided confirmation to the derived correction factor. Nine of these "combusted" gases were then put through the mock combustion procedure a second time, which should not have produced any change in C^{13} content; for this series the algebraic average change in δ_m was $+0.04$ ‰, and the average change, taken without regard to sign was 0.06‰.

It was found that for combustion temperatures from 800–1000°C, there was no relationship between temperature and oxygen isotopic composition of the product CO_2 ; however, at a temperature of 550°C, the product CO_2 has a δO^{18} of only -9 ‰. Assuming the oxygen to have $\delta \text{O}^{18} = -15$ ‰, the CO_2 is thus about 6‰ heavier than the oxygen at the lower temperature, the difference vanishing at about 800°. This relationship is in good agreement with the calculations of UREY (1947), which indicate that CO_2 should be 11‰ heavier than oxygen at 327°C, with a fractionation factor approaching unity with increasing temperature.*

It should be noted that δO^{18} may vary over a range of 30‰ in carbonates alone; this variation would give a false spread in δC^{13} of 1‰ if the variable correction term were not applied, corresponding to about ten times the analytical error of the McKinney-Nier spectrometer. Alternatively, the samples and standard could all be equilibrated against a common water, but this is not practical, as, except for combusted samples, we wish to have the O^{18} analysis of the material also, and it is easier to make an oxygen-18 analysis directly after the carbon analysis, than to remove the sample, equilibrate it, and rerun it.

Oxygen-18 analysis

For the analysis of oxygen we measure the mass-46 ion beam vs. the combined mass-44 + mass-45 ion beam, and the ratio in terms of isotopic molecules is thus:

$$R_{46} = \frac{\text{C}^{12}\text{O}^{16}\text{O}^{18} + \text{C}^{13}\text{O}^{16}\text{O}^{17} + \text{C}^{12}\text{O}^{17}\text{O}^{17}}{\text{C}^{12}\text{O}^{16}\text{O}^{16} + \text{C}^{13}\text{O}^{16}\text{O}^{16} + \text{C}^{12}\text{O}^{16}\text{O}^{17}}$$

whereas the desired ratio, assuming the distribution to be purely statistical, is:

$$R_{18} = \frac{\text{C}^{12}\text{O}^{16}\text{O}^{18} + \text{C}^{13}\text{O}^{16}\text{O}^{18}}{\text{C}^{12}\text{O}^{16}\text{O}^{16} + \text{C}^{13}\text{O}^{16}\text{O}^{16}} = \frac{\text{C}^{12}\text{O}^{16}\text{O}^{18}}{\text{C}^{12}\text{O}^{16}\text{O}^{16}}$$

* In one experiment it was found that CO_2 exchanges directly with CuO at 550°C, with no oxygen having been put into the system. It thus appears that the technique used by KERR *et al.* (1950, 1952) of oxidizing CO over CuO at 455°C, in order to measure the $\text{O}^{18}/\text{O}^{16}$ ratio in quartz, cannot give correct results. These authors state that the reaction involves a 50% dilution of the oxygen from the quartz sample, but since the original oxygen in the CO can exchange with the CuO , the oxygen isotopic record is lost completely. TITANI, NAKATA, and KANOME (1942) have shown that the isotopic exchange reaction between CO_2 and CuO begins at about 400°C.

In the expression for R_{46} , reading from left to right, the isotopic species have the following relative abundances (McCREA, 1950): (numerator) 0.004 , 9×10^{-6} , and 1.5×10^{-7} ; (denominator) 0.984 , 0.011 , and 8×10^{-4} . The species $C^{12}O^{17}O^{17}$ is thus two orders of magnitude lower than the next most abundant molecule and of no importance; it is neglected in the following derivation. The delta functions are:

$$1 + \delta_m = R_{46(x)} / R_{46(std)}$$

$$1 + \delta_c = R_{18(x)} / R_{18(std)}$$

Taking the first delta function (for δ_m), and substituting for each R_{46} the isotopic ratio given above, we now divide the numerator and denominator of $R_{46(x)}$ by $(C^{12}O^{16}O^{16})_{(x)}$, and the numerator and denominator of $R_{46(std)}$ by $(C^{12}O^{16}O^{16})_{(std)}$ and then write:

$$1 + \delta_m = \frac{\frac{R_{18(x)} + [C^{13}O^{16}O^{17}/C^{12}O^{16}O^{16}]_{(x)}}{1 + (1 + \delta C^{13}) R_{13(std)} + \left(1 + \frac{\delta_c}{2}\right) R_{17(std)}}}{\frac{R_{18(std)} + [C^{13}O^{16}O^{17}/C^{12}O^{16}O^{16}]_{(std)}}{1 + R_{13(std)} + R_{17(std)}}}$$

In this expression we have made the obvious substitutions of R_{18} , R_{17} , and R_{13} for their isotopic equivalents, and in addition, have substituted in the denominator of $R_{46(x)}$ the following:

$$R_{13(x)} = (1 + \delta C^{13}) R_{13(std)}$$

$$R_{17(x)} = \left(1 + \frac{\delta_c}{2}\right) R_{17(std)}$$

the latter equation having been derived for equation (1) of this section (see above), where δ_c is the oxygen delta.

We next perform the substitution:

$$\left[\frac{C^{13}O^{16}O^{17}}{C^{12}O^{16}O^{16}}\right] = R_{13}R_{17}$$

for both sample and standard terms, substituting again for $R_{13(x)}$ and $R_{17(x)}$ the expressions just given, and finally divide the entire numerator and entire denominator by $R_{18(std)}$, substituting $(1 + \delta_c)$ for $R_{18(x)}/R_{18(std)}$, and after rearranging, we have:

$$1 + \delta_m = \frac{\left[(1 + \delta_c) + \frac{(1 + \delta C^{13}) R_{13(std)} \left(1 + \frac{\delta_c}{2}\right) R_{17(std)}}{R_{18(std)}} \right]}{\left[1 + \frac{R_{13(std)} R_{17(std)}}{R_{18(std)}} \right]} \quad (3)$$

$$\times \frac{[1 + R_{13(std)} + R_{17(std)}]}{\left[1 + (1 + \delta C^{13}) R_{13(std)} + \left(1 + \frac{\delta_c}{2}\right) R_{17(std)} \right]}$$

which is the general expression relating δ_r and δ_m in terms of known ratios evaluated for the PDB standard in section 3, and the difference in C^{13} content of the sample and standard, δC^{13} . As with equation (1), the ratio terms for any standard may be found by analysis of the standard vs. PDB.

Equation (3) is evaluated numerically by substituting for the known ratios and neglecting all products of deltas, and yields:

$$\delta_c O^{18} = 1.0014\delta_m + 0.009\delta C^{13} \quad (4)$$

which is the correction factor for oxygen analysis made against the PDB standard. Thus 1% of the C^{13} difference enters into the oxygen correction factor; since natural carbonates show a range in C^{13} content of some 60‰, the C^{13} difference can cause a false spread in δO^{18} of 0.6‰, or six times the analytical error, unless corrected for.

Correction of oxygen-18 analyses on water samples

The analysis of water for oxygen-18 content is commonly done by equilibrating CO_2 against the water samples and then analysing the CO_2 samples (e.g. EPSTEIN and MAYEDA, 1953). In this case the data must also be corrected for the amount and isotopic composition of the oxygen in the CO_2 used for the equilibration. From an equation derived in a previous paper (CRAIG, 1953, p. 87) for the material balance in a two-component isotopic system, we write out the material balance expressions before and after the equilibration and readily obtain:

$$\delta = \delta' \frac{(\rho + \alpha)}{\rho} - \frac{\alpha}{\rho} (\delta O^{18})_{(tank\ CO_2)} \quad (5)$$

In this expression α is the fractionation factor $R_{18(CO_2)}/R_{18(H_2O)}$, here taken as 1.039 at 25°C; δ' is the measured enrichment of the equilibrated CO_2 relative to the standard, this CO_2 being in equilibrium with a water whose O^{18} content has been slightly changed by the added CO_2 ; while δ is the corrected value, namely the delta of CO_2 in equilibrium with the original water. $\delta (O^{18})_{(tank\ CO_2)}$ is the oxygen-18 analysis of the tank CO_2 used for the equilibration, and ρ is the ratio of gram atoms of oxygen in the water sample to gram atoms of oxygen in the CO_2 introduced into the flask.

The correction factor thus consists of two terms, the first being a function only of the relative proportions of H_2O and CO_2 , while the second term reflects the O^{18} content of the tank CO_2 . In our case (EPSTEIN and MAYEDA, 1953; CRAIG and MAYEDA, in press) with 25 ml of water in a 200 cm³ flask filled to a CO_2 pressure of 74 cm, ρ is about 90, ranging from 83 to 92 for distilled water depending on the amount of CO_2 which dissolves in the water before the flask is cut off from the gas. The uncertainty in ρ is negligible. The composition of the tank carbon dioxide (Liquid Carbonic Corporation, Chicago) is very constant, δO^{18} having ranged from -12.8 to -15.9‰ for three large tanks used over a period of two years, with an average value of -14.9‰. (δC^{13} averages -29.2‰ having shown a total variation of only 0.3‰ during the same period.) Thus the correction factor for the Epstein-Mayeda technique becomes:

$$\delta = 1.0113\delta' + 0.17\text{‰} \quad (6)$$

Combining this expression with the correction factor for O^{18} analyses given by equation (4), putting in the C^{13} value for the tank CO_2 , we obtain:

$$\delta_c = 1.013\delta_m - 0.09\% \quad (7)$$

which is the total correction to be applied to oxygen-18 analyses of water samples relative to PDB, using the Chicago technique, assuming that the instrumental corrections mentioned in section 2 have already been made. §

Table 4. Isotopic analyses of National Bureau of Standards reference samples relative to PDB standard (Chicago)

	$\delta_c (C^{13}) \%$	$\delta_c (O^{18}) \%$
Isotope reference sample No. 20: CaCO ₃ (Solenhofen limestone) *	-1.05 -1.11 -1.01	-4.14 -4.24 -4.03
Average	-1.06	-4.14
Isotope reference sample No. 21: Spectroscopic graphite †	-27.80 -27.76 -27.80	
Average	-27.79	
Isotope reference sample No. 1: Water (steam condensate from Potomac River water) ‡		-8.05 -8.09
Average		-8.07

* No treatment other than reaction with 100% H_3PO_4 at 25-2°C to produce CO_2 ; analytical procedure described by McCREA J. M. (1950) *J. Chem. Phys.* **18**, 849.

† Combusted at 1000°C; procedure described by CRAIG H. (1953) *Geochim. et Cosmochim. Acta* **3**, 53. The oxygen-18 analyses of the CO_2 produced by combustion were respectively: $\delta_c O^{18} = -15.58$, -11.39 , and -17.25% .

‡ Analyses of CO_2 equilibrated with the water at 25-2°C as described by EPSTEIN S. and MAYEDA T. (1953) *Geochim. et Cosmochim. Acta* **4**, 213. Each figure represents an individual equilibration in which two aliquots of equilibrated CO_2 were analysed and found to differ by less than 0.2%. The oxygen-18 content of the CO_2 used for the equilibration was $\delta = -15.74\%$.

5. COMPARISON OF ISOTOPIC STANDARDS

The isotopic reference sample programme of the National Bureau of Standards has been described by MOHLER (1955). Since publication of that list of reference samples, a new carbon standard has been added to the list; the addition is a sample of spectroscopic graphite, some 3% lower in C^{13} than the limestone

§ The O^{18} analyses of natural waters given by EPSTEIN and MAYEDA (1953) are raw data uncorrected for any of the effects discussed in this paper. Including valve leakage and reed bias, their values should be corrected by $\delta_c = 1.025 \delta_{(EM)} - 0.09\%$, where $\delta_{(EM)}$ signifies their published data. Most of their data are for ocean waters with small δ values, and the multiplying factor is negligible except for their nonmarine samples; however, all values should also be 0.1% lighter, and thus their value for average ocean water, relative to PDB standard, becomes -0.1% rather than 0.

standard, adopted in order to permit intercalibration on a *difference* between two samples and thus allow comparative estimates of systematic errors in measurement. It should be noted that the Bureau of Standards is not analysing these reference samples, but is distributing them together with the analytical data provided by workers in the field.

In Table 4 we give the results of the mass spectrometric analyses of the NBS isotope reference samples relative to the PDB standard. Table 5 then shows

Table 5. Isotopic composition of various carbon and oxygen isotope standards. Carbonates untreated except for H_3PO_4 reaction.

Standard	Isotopic composition		Number of analyses and std. deviation			
	$\delta_c (\text{C}^{13}) \text{ ‰}$	$\delta_c (\text{O}^{18}) \text{ ‰}$	Carbon N σ		Oxygen N σ	
PDB-Chicago	0	0	—	—	—	—
Nier-Solenhofen limestone [<i>Phys. Rev.</i> 77 , 789(1950)]	-0.64	-4.40	13	0.10	8	0.14
NBS-Solenhofen limestone Reference sample No. 20	-1.06	-4.14	3	0.04	3	0.09
Basel (BAERTSCHI) Ticino marble	+2.77	-1.62	9	0.03	21	0.07
Wellington (RAFTER) Te Kuiti limestone	-1.67	-4.17	3	0.04	3	0.02
Stockholm (WICKMAN) BaCO_3	-10.32	-15.38	3	0.02	3	0.03
NBS-Graphite Reference sample No. 21	-27.79	—	3	0.02	—	—
NBS-Water Reference sample No. 1	—	-8.07	—	—	2	0.02

the analyses of the various standards for carbon and oxygen, together with the number of samples analysed and the standard deviations; a total of seventy-four analyses of these standards was made. The Nier, Basel, and Stockholm standard analyses were made at intervals during the past several years, the NBS and Wellington standard (RAFTER, 1955) carbonate analyses were spaced fairly equally over a three-month period in 1955, during which some five-hundred mass spectrometric analyses were made, and the two water analyses were spaced six weeks apart.

It should be noted that the Nier and NBS Solenhofen standards represent different samples of this limestone; the NBS sample was recently acquired from the U.S. Geological Survey. The values required for the derivations in section 3 were the $\delta_m(\text{C}^{13})$ (which was -0.74‰) and $\delta_c(\text{O}^{18})$ of NIER's Solenhofen standard. The calculation of the correction factors was done by successive approximation, beginning with the raw data and running until no values changed. The figures given in Tables 4 and 5 are the final delta values, corrected according to the procedure described in the previous sections of this paper; the δ_m values may be

derived from the equations relating δ_m and δ_c and the values in the tables. Footnote 1 of Table 4 applies also to all carbonates in Table 5.*

Isotopic analyses reported relative to the various standards other than PDB may be converted to δ values relative to PDB by the equation:

$$\delta_{(x-PDB)} = \delta_{(x-B)} + \delta_{(B-PDB)} + 10^{-3} \delta_{(x-B)} \delta_{(B-PDB)}$$

in which $(x-B)$ and $(x-PDB)$ refer to analyses of a sample (x) relative to some standard (B) and relative to PDB, and $(B-PDB)$ is the analysis of the standard (B) relative to PDB, these values being given in Table 5. All δ 's in this equation are expressed directly in per mil. In this form, which is exact, comparisons are easily made, and the relationship of course simplifies to the direct algebraic sum when the delta values are small.

The standard deviations shown in Table 5 are well in accord with the limit of error of $\pm 0.1\%$ for both carbon and oxygen, generally given by the Chicago laboratory. In general, the precision for carbon is better than for oxygen because of the three-times-larger ion beam, and is probably about $\pm 0.05\%$ for samples ranging up to about 10% different from the standard; at differences of the order of 30% the reproducibility for both carbon and oxygen drops off to about $\pm 0.2\%$, all factors considered. The Nier standard analyses showed a spread of 0.3% for both carbon and oxygen and were thus considerably less reproducible than analyses of the other standards; this material was finely ground and there was some indication that isotopic exchange with atmospheric CO_2 and water over several years might account for the deviations, but this was not certain. On the other hand, the Basel standard, which was the coarsest of the carbonates, gave highly reproducible analyses over three years; in fact, the reproducibility was so high that this sample was used as a check on oxygen-18 fractionation of the standard in the machine with time. Thus the oxygen variance shown in Table 5 includes analyses in which the standard was slightly off, and the real reproducibility of this sample was much better than shown. The desirability of storing finely powdered carbonate samples under vacuum or in a dry gas should be emphasized. The Basel standard also shows no change of C^{13} and O^{18} composition upon roasting in helium to char organic matter, as described by EPSTEIN *et al.* (1953); carbon and oxygen analyses made on two roasted samples were identical with analyses of the untreated material.

Table 6 gives the absolute $\text{C}^{13}/\text{C}^{12}$ and the R_{18} ratios deduced for the various standards. The $\text{C}^{13}/\text{C}^{12}$ ratios are based on the value 1123.00×10^{-5} for the Nier Solenhofen standard, adopted in (4) of section 3, the other ratios being derived from the PDB ratio and the delta measurements. The oxygen ratios for carbonate standards refer specifically to CO_2 derived by reaction of 100% H_3PO_4 at 25°C with the untreated (i.e. unroasted) carbonate material. The standard ratio is based on NIER'S value of 408.8×10^{-5} for $R_{18(\text{air})}$ and TUDGE'S analysis of CO_2

* DANSGAARD (1953) reported analyses of the Nier, Stockholm, and Chicago standards. His values, stated in terms of δ relative to PDB, are $\delta \text{C}^{13} = -1.42\%$, and -10.22% , $\delta \text{O}^{18} = -5.33\%$ and -22.47% , for the Nier and Stockholm standards respectively. With the exception of the C^{13} value for the Stockholm standard, these values do not agree at all with those given in Table 5. The reason for the discrepancy is not known. He records his values as absolute ratio differences, i.e. $R - R_{\text{std}}$, rather than percentage differences, and thus the systematic errors, which cancel when ratios of the recorded ratios are made, are not eliminated from his data.

prepared from atmospheric oxygen, as described in section 3; the other ratios are derived directly from the measured deltas. The relative and absolute values for the NBS water standard refer of course to CO_2 in isotopic equilibrium with the water at 25.2°C . The direct values for water are obtained by dividing by

Table 6. $\text{C}^{13}/\text{C}^{12}$ and oxygen ratios in isotopic standards for carbon and oxygen. Oxygen values for carbonates refer to CO_2 produced by reaction with 100% H_3PO_4 , for water to CO_2 in equilibrium with the water at 25°C . All carbon ratios are based on the adopted value for the Nier Solenhofen limestone standard

Standard	$\text{C}^{13}/\text{C}^{12} \times 10^5$	$\text{O}^{18}\text{O}^{18}/\text{O}^{16}\text{O}^{16} \times 10^5$
PDB-Chicago	1123.72	415.80
Nier-Solenhofen l.s.	1123.00	413.97
NBS-Solenhofen l.s. (No. 20)	1122.53	414.08
Basel (BAERTSCHI)	1126.83	415.13
Wellington (RAFTER)	1121.84	414.07
Stockholm (WICKMAN)	1112.12	409.40
NBS-Graphite (No. 21)	1092.49	—
NBS-Water (No. 1)	—	412.44

the fractionation factor, which is approximately 1.039 for O^{18} concentration in CO_2 with respect to liquid water; this value has not as yet been measured precisely.

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