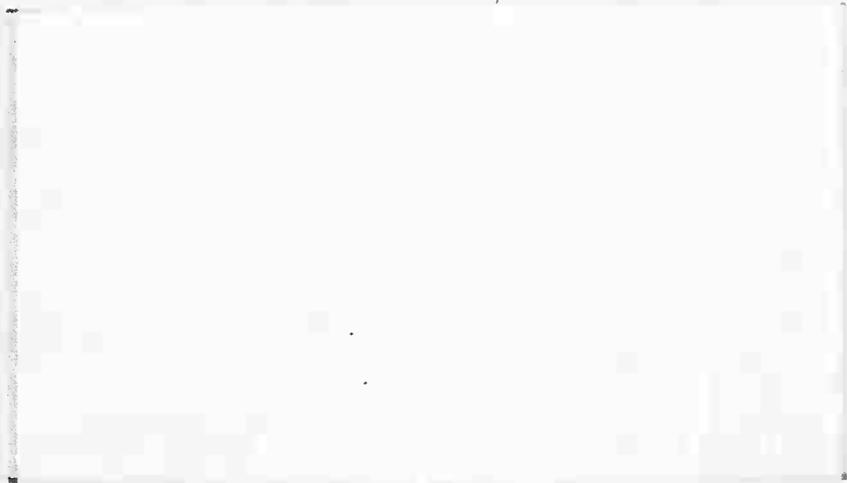


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13. ABSTRACT

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R & D Associates  
P.O. Box 3580  
Santa Monica, Calif. 90403

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**MULTIPLE THERMOMETRY IN  
PALEO CLIMATE AND HISTORIC CLIMATE**

**Leona M. Libby**

**January 1972**

**Sponsored by  
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## ABSTRACT

The principle of isotope thermometry is that isotope ratios are temperature dependent. It is proposed that isotope ratios in bio-organic material may have independent temperature coefficients, so that by measuring ratios for several elements, e.g. hydrogen, carbon and oxygen, it may be possible to show that a temperature change occurred. Assuming that cellulose is formed almost at equilibrium, temperature coefficients for C, H and O are computed and found to be of measurable size. The coefficients computed for  $C^{13}/C^{12}$  and D/H agree with measured values. Thus indications are that temperature changes in past climates may be measured in old tree rings, using this principle of multiple thermometers.

## I. INTRODUCTION

The principle of isotope thermometry is that the isotopic ratios are temperature dependent. There are two kinds of temperature dependence, kinetic and equilibrium. The theory of kinetic isotope separation is well established. For example, in the gaseous diffusion process for separation of the uranium isotopes, separation is caused by a difference in the rates with which the two species pass through holes in a barrier. In case of equilibrium, separation is caused by a difference of differences, namely the difference between separation by the forward rate and separation by the reverse rate, the two rates being equal. Distillation of liquid in a closed container is an example of separation at equilibrium, while vaporization into a vacuum is kinetic.

In distillation of a liquid containing two or more elements in the molecule, the corresponding isotope thermometers are functionally related because the corresponding vapor pressure ratios, which determine the separations on evaporation and condensation, depend on the same force constants tying them together.

In bio-organic material however, there may be at least three useful isotope thermometers, namely D/H,  $C^{13}/C^{12}$ , and  $O^{18}/O^{16}$ . The basic reaction is photosynthesis with production of cellulose, here written schematically as a basic module,  $H - \overset{\uparrow}{\underset{\downarrow}{C}} - OH$ , or  $CH_2O$ , according to  $CO_2 + H_2O \rightarrow CH_2O + O_2$ . In this reaction all three elements may yield isotope thermometers, and they may be independent of each other. That is, the ratio  $O^{18}/O^{16}$  is no longer functionally related to D/H because diatomic oxygen is being evolved and so rotational and vibrational energies of the O-O bond are involved and because in cellulose

oxygen is bound to carbon as well as hydrogen. For the same reason, the temperature coefficient of  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  may be not functionally related. And finally, the ratio  $C^{13}/C^{12}$  should be independent of D/H because carbon and hydrogen are initially in different molecules, with differing vibrational frequencies.

In case variations are measured for only one isotope ratio the relation to paleo temperature is not proven. But if ratios are measured for two, three, or more independent isotopes in the same organic material, it is possible that the relation to temperature can be firmly established and quantified, and this is the principle point of the present discussion.

Over the small temperature interval ( $0^{\circ}C < t < +30^{\circ}C$ ) within which climate could have varied without killing terrestrial life as we know it, the dependences of isotope ratios on temperature may be assumed to be linear for bio-organic material. That is, for isotope ratios  $\delta^j$ , where  $j = 2, 13, 15, 18, 34, 41, \dots$  referring to D,  $C^{13}$ ,  $N^{15}$ ,  $O^{18}$ ,  $S^{34}$ ,  $K^{41}$ ,  $\dots$  the temperature dependence may be written as

$$\delta^j = a^j t + b^j, \quad (a^j \text{ and } b^j \text{ constants})$$

where  $a^j$  is the temperature coefficient and  $t$  is temperature. Then, a change  $\Delta t$  is related to a change  $\Delta \delta^j$  by, (for a given compound),

$$\Delta t = \frac{\Delta \delta^2}{a_2} = \frac{\Delta \delta^{13}}{a_{13}} = \frac{\Delta \delta^{15}}{a_{15}} = \frac{\Delta \delta^{18}}{a_{18}} = \dots$$

The multiple over-determination of temperature by using a set of many thermometers may make it possible to show with some level of confidence that a temperature change did occur. It is also possible that new effects, not caused by temperature, will be demonstrated by the method of multiple thermometry, if some of the above ratios, but not all of them, show equality. Probably the specific relations to temperature will have to be calibrated at each geographical position to take into account local variations in water and CO<sub>2</sub>.

Finally, bio-organic data bases can be radiocarbon dated, so that if evidence for temperature changes is stored in them, the dates when the changes occurred can be evaluated.

II. EXPERIMENTAL EVIDENCE FOR TEMPERATURE DEPENDENCE OF  
ISOTOPE RATIOS IN BIO-ORGANIC MATERIAL

Although animal bio-organic material is not directly derived from photo-synthesis, nevertheless animals are largely what they eat, so that bio-organic material from both plants and animals may be useful in isotope thermometry. Some of the evidence<sup>(1)</sup> on isotope thermometers in bio-organic material is as follows.

The  $C^{13}/C^{12}$  ratio in combustible organic matter in cores from sea bottoms shows variations of as much as 6 parts per thousand with depth. These have been measured and attributed to temperature variation in the sea surface with time, by Rogers and Koons.<sup>(2)</sup> Also, in a study of marine plankton, by Sackett et al,<sup>(3)</sup> the  $C^{13}$  concentration was found depleted by 6 per mil where surface waters are near 0°C relative to samples collected where surface temperatures are about 25°C. These observations on both plant and animal plankton suggest that the temperature coefficient of  $C^{13}/C^{12}$  in bio-organic material is ~0.24 parts per thousand per degree C in the temperature range 0 - 25°C.

In further work by Degens et al,<sup>(4)</sup> the temperature coefficient of  $C^{13}/C^{12}$  in marine phytoplankton grown in laboratory cultures was measured as ~0.35 parts per thousand per degree C between 10 - 30°C.

While shell carbonate is not, strictly speaking, bio-organic material, nevertheless, for completeness we note here that variations in the  $O^{18}/O^{16}$  ratio in foraminifera shells from Caribbean Sea cores have been measured by several workers and interpreted in terms of paleo-temperature variations. (5) This in fact was the first isotope thermometer, as developed by H. C. Urey. (6)

It may be that other isotope ratios in bio-organic material are temperature dependent, such as  $N^{15}/N^{14}$  and  $S^{34}/S^{32}$ , perhaps increasing the number of independent thermometers in bio-organic data bases to five or six. This possibility should be investigated.

### III. THE QUESTION OF EQUILIBRIUM

In the following paper an attempt is made to estimate the magnitudes of the temperature coefficients of the several isotope thermometers in bio-organic data bases. This can be done using thermodynamic considerations, if one assumes that the organic material is manufactured in equilibrium with its surroundings. This is of course a major assumption, but one which does not seem too unlikely. For example, in experiments in the laboratory the isotopic composition of  $CaCO_3$  slowly formed from aqueous solution, was found to be the same as in the shells produced by aquatic organisms at the same temperature. (7) In any case, this assumption can be tested for plants and animals grown in laboratory conditions.

In the wild state, in coastal waters and estuaries, the carbon and oxygen isotopic composition of shell carbonate has been shown to be in isotopic equilibrium with bicarbonate dissolved in the water.<sup>(8)</sup> The life span of the shell fish is about one year, so it would seem equilibration in self-manufacture might take place rapidly, say in less than or about a day. Equilibration between CO<sub>2</sub> gas and sea water is known to occur in less than 48 hours,<sup>(9)</sup> and between CO<sub>2</sub> gas, water and precipitated CaCO<sub>3</sub> in less than 6 days.<sup>(10,11)</sup> In living animals, tritiated water is known to equilibrate with blood serum of rats in 6 days or less.<sup>(12)</sup> Thus the evidence, although meager, is that equilibration takes place rapidly compared with the relevant life spans.

It should be pointed out that in shells the carbon and oxygen are not independent thermometers because they are tied by the same vibrations in the C-O bond. But there is also organic material in the shell matrix which could provide a set of multiple thermometers, and furthermore could be radiocarbon dated.

The question of the degree to which equilibrium obtains in formation of cellulose is interesting in itself. If equilibrium seems to apply, the assumption could be extended to computations of production of other substances. If equilibrium does not obtain, and instead the processes of isotope fractionation are kinetic, then the temperature coefficients should be even larger than those estimated by assuming equilibrium.

CALCULATION OF PARTITION FUNCTION FOR CELLULOSE

For a reaction in which there is isotope exchange, the equilibrium constant  $K_{eq}$  can be expressed in terms of the total partition functions  $Q^*$  and  $Q$ , for molecules containing the heavy and light isotopes respectively, as follows. We define  $Q$  as the product of rotational, vibrational and translational parts, neglecting vibrational-rotational coupling:

$$Q = Q_{rot} Q_{vib} Q_{tr} \quad (1)$$

For solids and liquids,  $Q_{tr} = 1$ , and  $Q_{vib}$  is given by

$$Q_{vib}(T) = \sum_j \sum_n g_j \exp \left( -\nu_j n \frac{h}{kt} \right) \exp(-\Delta\epsilon_j/kT) \quad (2)$$

$$(n = 0, 1, 2, \dots)$$

which may be written as,

$$Q_{vib}(T) = \prod_j g_j [1 - \exp(-h\nu_j/kT)]^{-1} \exp(-\Delta\epsilon_j/kT) \quad (3)$$

We shall be computing partition functions at  $\sim 300^\circ\text{K}$  so that the harmonic oscillator approximation, is reasonably good. Here  $k$  is the Boltzman constant,  $t$  is the absolute temperature,  $\nu_j$  is the frequency of the  $j^{\text{th}}$  appropriate vibration of degeneracy  $g_j$  and  $n$  is the vibrational quantum number and  $\Delta\epsilon_j$  is the difference in zero point energy between the isotopes. In cellulose the barriers preventing free internal rotation are high, so that rotations deteriorate into torsional oscillations or bending vibrations. In the present treatment these will be included in  $Q_{\text{vib}}$  as part of the vibrational partition function.

The stretching and bending vibrations appropriate to cellulose, which is a chain molecule of module (H - C - OH), are listed in Tables I and II. Their frequencies differ slightly for molecules containing different isotopes because the isotopic mass enters into the reduced mass,  $\mu$ , of the appropriate oscillator from which the particular frequency is computed, according to:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad (4)$$

where  $K$  is the force constant of the particular vibration. Substituting in (3) the frequencies from Table I, and noting that the torsional frequency,  $920 \text{ cm}^{-1}$ , is 3-fold degenerate, one computes  $Q(273^\circ\text{K}) = 1.2302$  and  $Q(298^\circ\text{K}) = 1.2981$  for the module {H - C - OH}. In principle, the D-H isotope effect in cellulose involves two possible substitutions: namely substitution of a deuteron for the hydrogen linked to the carbon atom and

secondly substitution of the hydrogen attached to oxygen. In the case of R and R' attached to the pivotal carbon, the appropriate reduced mass is insensitive to substitution of H by D because the masses of R and R' are almost infinitely large relative to H or D. The partition functions computed for the various isotopic substitutions of the cellulose module are given in Table III.

Because of the crudeness inherent in assuming bond frequencies for cellulose to be equal to those known in rather small organic molecules, we neglect anharmonic corrections, and complications such as hydration in solution, effect of hydrogen bond formation, etc.

The fractionation ratios may be written as follows. For the oxygen isotopes, there are three equilibria corresponding to isotopic exchange between cellulose and each of the three oxygen-containing molecules involved in the reaction:

$$K^{18}(\text{O}_2) = \frac{Q^*(\text{CH}_2\text{O}^{18})}{Q(\text{CH}_2\text{O}^{16})} \frac{Q(\text{O}_2^{16})}{Q^*(\text{O}^{16}\text{O}^{18})} \quad (5a)$$

$$K^{18}(\text{CO}_2) = \frac{Q^*(\text{CH}_2\text{O}^{18})}{Q(\text{CH}_2\text{O}^{16})} \frac{Q(\text{CO}_2^{16})}{Q^*(\text{CO}^{16}\text{O}^{18})} \quad (5b)$$

$$K^{18}(\text{H}_2\text{O}) = \frac{Q^*(\text{CH}_2\text{O}^{18})}{Q(\text{CH}_2\text{O}^{16})} \frac{Q(\text{H}_2\text{O}^{16})}{Q^*(\text{H}_2\text{O}^{18})} \quad (5c)$$

where  $Q^*$  is the partition function for the heavier isotope.

For the hydrogen isotopes, two equilibria enter so that

$$K(\text{HCO}) = \frac{Q^*(\text{HCO})}{Q(\text{CH}_2\text{O})} \cdot \frac{Q(\text{H}_2\text{O})}{Q^*(\text{HDO})}; \quad K(\text{DCO}) = \frac{Q^*(\text{DCO})}{Q(\text{CH}_2\text{O})} \cdot \frac{Q(\text{H}_2\text{O})}{Q^*(\text{HDO})} \quad (6)$$

and for the carbon isotopes, only one equilibrium enters, that with  $\text{CO}_2$ , so,

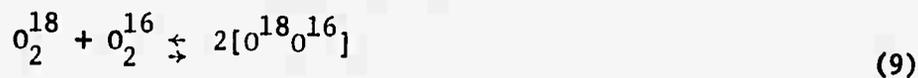
$$K^{13} = \frac{Q^*(\text{C}^{13}\text{H}_2\text{O})}{Q(\text{C}^{12}\text{H}_2\text{O})} \cdot \frac{Q(\text{C}^{12}\text{O}_2)}{Q^*(\text{C}^{13}\text{O}_2)} \quad (7)$$

but what the chemist actually measures<sup>(6)</sup> is an isotopic fractionation,  $a$ .

For example for oxygen the fractionation factor corresponding to equation 5a is:

$$\frac{\{2[\text{O}_2^{18}] + [\text{O}^{18}\text{O}^{16}]\}}{\{[\text{O}^{18}\text{O}^{16}] + 2[\text{O}_2^{16}]\}} \cdot \frac{[\text{CH}_2\text{O}^{16}]}{[\text{CH}_2\text{O}^{18}]} = a^{-1} \quad (8)$$

Considering the reaction,



the equilibrium constant is 4, neglecting a tiny correction for isotope effect:<sup>(6)</sup>

$$4 = \frac{[\text{O}^{18}\text{O}^{16}]^2}{[\text{O}_2^{18}][\text{O}_2^{16}]} \quad (10)$$

because  $O_2^{18}$  and  $O_2^{16}$ , being symmetrical, have only half as many rotational states as the asymmetrical molecule  $O^{16}O^{18}$ . Substituting (10) into (8), the fractionation factor reduces to:

$$a^{18}(O_2) = \frac{Q(O_2^{16})^{1/2}}{Q^*(O_2^{18})^{1/2}} \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \quad (11)$$

Correspondingly  $CO_2^{18}$  and  $CO_2^{16}$ , being symmetric, have only half the rotational states as  $CO^{18}O^{16}$ , so that

$$a^{18}(CO_2) = \frac{Q(CO_2^{16})^{1/2}}{Q^*(CO_2^{18})^{1/2}} \frac{Q^*(CH_2O^{18})}{Q(CH_2O^{16})} \quad (12)$$

but for  $a(HCOD)$  and  $a(DCOH)$  the isotope effect is large so,

$$a(HCOD) = \frac{Q^*(HCOD)}{Q(CH_2O)} \left\{ \frac{[2Q(H_2O) + Q(HDO)]}{[Q(HDO) + 2Q(D_2O)]} \right\} \quad (13)$$

$$a(DCOH) = \frac{Q^*(DCOH)}{Q(CH_2O)} \left\{ \frac{2Q(H_2O) + Q(HDO)}{Q(HDO) + 2Q(D_2O)} \right\}$$

Here, while  $H_2O$  and  $D_2O$  are symmetric, none of the deuterated or hydrogenated cellulose modules are. Finally because  $C^{13}O_2$  and  $C^{12}O_2$  have the same number of rotational states, also  $H_2O^{16}$  and  $H_2O^{18}$ , the fractionation factors are

$$a^{18}(\text{H}_2\text{O}) = \frac{Q(\text{H}_2\text{O}^{16})}{Q^*(\text{H}_2\text{O}^{18})} \frac{Q^*(\text{CH}_2\text{O}^{18})}{Q(\text{CH}_2\text{O}^{16})} \quad (14)$$

$$a^{13} = \frac{Q(\text{C}^{12}\text{O}_2)}{Q^*(\text{C}^{13}\text{O}_2)} \frac{Q^*(\text{C}^{13}\text{H}_2\text{O})}{Q(\text{C}^{12}\text{H}_2\text{O})} \quad (15)$$

For the isotope ratios D/H,  $\text{C}^{13}/\text{C}^{12}$ , and  $\text{O}^{18}/\text{O}^{16}$ , we may now compute the partition function ratios  $(Q^*/Q)_{\text{CH}_2\text{O}}$ . The partition function ratios for  $(Q^*/Q)_{\text{oxygen}}$  are taken from Grey (Ref. 6), those for  $(\text{H}_2\text{O})_{\text{liq.}}$  are taken from computations of Bottlinga<sup>(13)</sup> and those for  $(\text{CO}_2)_{\text{gas}}$  from Bottlinga<sup>(13)</sup> and for HDO and D<sub>2</sub>O from Grey.<sup>(6)</sup>

The ratios appropriate for each isotope exchange are listed in Tables IV, V and VI. By substituting these in equations (11) through (15) the fractionation factors have been calculated for 273°K and 298°K. The corresponding temperature coefficients are listed in Table VII.

The temperature coefficient so calculated for  $\text{C}^{13}/\text{C}^{12}$  of 0.36 ppt/°C. agrees with the coefficient measured for  $\text{C}^{13}/\text{C}^{12}$  in plant and animal material by Sackett and his co-workers,<sup>(3, 4)</sup> so that the assumption of equilibrium appears to be more or less valid and one can hope that the like calculations for oxygen and hydrogen may be meaningful.

From Ref. 6, at equilibrium the temperature coefficient of HDO/H<sub>2</sub>O is -312‰ per degree C, namely much larger than that of the (D/H) ratio calculated for cellulose, so that measuring it in a geographical distribution of the same kind of trees would measure the

distribution in D/H ratios of rain water, and measuring it in a chronological sequence would measure time dependence of the rain water.

Our naive assumptions are mainly as follows. We have assumed that cellulose is formed in solution, that in cellulose rotations have degenerated into torsional vibration, that its vibrations are like those in small organic molecules, and that manufacture of cellulose in plants is an almost equilibrium process.<sup>(14)</sup>

The intent of the present computation is to show that all three of the isotope ratios D/H,  $C^{13}/C^{12}$ , and  $O^{18}/O^{16}$  may well be thermometers, and that their temperature coefficients may have measurable magnitudes in bio-organic plant residues, and so may give information about climate variation in the past.

For example, we may measure these ratios in a chronological sequence of tree rings. The results of Parker<sup>(15)</sup> are that (1) different plant species growing side by side in a marine estuary can have different percentages of  $C^{13}$  in total carbon content, and (2) individuals of the same species have about the same percentage of  $C^{13}$ . So in evaluating past climates from isotope thermometers we should measure changes in a single species of tree and we should measure a chronological sequence consisting of several individuals, of the same kind of tree, having overlapping life spans. By measuring trees of overlapping life spans, and trees that grow in sparse environments such as mountain slopes, one may avoid spurious effects caused by the relatively greater removal of  $CO_2$  from air near the ground by abundant low growing plants.

From Ref. 6, the temperature coefficient of oxygen in rain water could be as large as  $-0.36\%$  per degree C. Also important is the fact that  $\text{CO}_2$  mixes rapidly through the entire global atmosphere in a time of  $\sim 5$  years, and with the oceans<sup>(16-19)</sup> in about 15 years, so that at any time the atmospheric carbon isotope ratios reflect the temperature-dependent isotope separation in the sea, which has a coefficient of  $-0.21 \text{ ppt}/^\circ\text{C}$  for oxygen (Ref. 10), and  $-0.11 \text{ ppt}/^\circ\text{C}$  for carbon (Ref. 11).

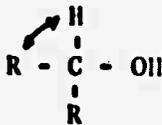
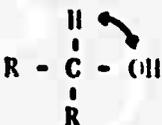
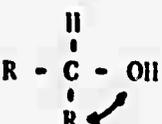
One may ask whether there is isotope exchange between the hydrogens bound in old cellulose and in new sap. As shown in Table I, both hydrogens are bound very tightly, even more so than the C-C bonds, so that, knowing that radio-carbon dates in tree cellulose mainly agree with the tree ring dates, meaning that in heart wood carbon does not exchange, we can hope the same to be true of hydrogen in heart wood. But this point should be tested. When cellulose is prepared in a thin layer or finely ground, and repeatedly wetted and dried, there is some exchange,<sup>(21)</sup> but these conditions are quite different from cellulose in sound heart wood.

Table I

Bond	Stretching Vibration
$\begin{array}{c}   \\ - C - H \\   \end{array}$	2960 $\text{cm}^{-1}$
$\begin{array}{c}   \quad   \\ - C - C - \\   \quad   \end{array}$	900 $\text{cm}^{-1}$
- O - H	3680 $\text{cm}^{-1}$
$\begin{array}{c}   \\ - C - (OH) \\   \end{array}$	(1200 $\text{cm}^{-1}$ )*
$O^{16} - O^{16}$	1580 $\text{cm}^{-1}$ $B = 1.44560 \text{ cm}^{-1}$

\* Calculated from a force constant taken as 1/2 of force constant for C = O, see G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand & Co., Inc., New York, 1945, Table 51, pg. 196, and see also Table 89.

Table II

Bending Vibration	Bending Frequency
	920 cm <sup>-1</sup>
	920 cm <sup>-1</sup>
	920 cm <sup>-1</sup>
	(700 cm <sup>-1</sup> )*
	(375 cm <sup>-1</sup> )**

\* See Herzberg, Infrared and Raman Spectra, op. cit., page 196, and Tables 51 and 89.

\*\* See Herzberg, Infrared and Raman Spectra, op. cit., Tables 118 and 119.

Table III

	Partition Functions for the Module of Cellulose ( $\text{H} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{OH}$ ) and Its Isotopic Modifications				
	$Q(\text{HCOH})$	$Q^*(\text{DCOH})$	$Q^*(\text{HCOH})$	$Q^*(\text{C}^{13}\text{H}_2\text{O})$	$Q^*(\text{CH}_2\text{O}^{18})$
273°K	1.2302	40.850	35.014	1.4240	1.5620
298°K	1.2981	32.695	28.086	1.4844	1.6659

Table IV

Partition Function	273°K	298°K	Comment
$Q^*(\text{DCOII})/Q(\text{HCOII})$	33.206	25.187	Table III
$Q^*(\text{HCOI})/Q(\text{HCOII})$	28.462	21.636	
$(Q^*(\text{D}_2\text{O})_{\text{gas}}/Q(\text{H}_2\text{O})_{\text{gas}})^{1/2}$	16.503	12.543	H. C. Urey (Ref. 6)*
$Q^*(\text{HDO})_{\text{gas}}/Q(\text{H}_2\text{O})_{\text{gas}}$	32.7400	24.9460	

\* The partition function ratio for liquid is obtained by multiplying the partition function ratio for gas by the D/H ratio in liquid divided by that for gas. It is taken here as 1.10% at 273°K, and as 1.074 at 298°K, where the numbers in parentheses refer to partition of tritium, see Ref. 22.

Table V

Partition Function	273°K	298°K	Comment
$Q^*(\text{C}^{13}\text{H}_2\text{O})/Q(\text{C}^{12}\text{H}_2\text{O})$	1.1575	1.1435	Table III
$\ln Q^*(\text{C}^{13}\text{O}_2)/Q(\text{C}^{12}\text{O}_2)$ (gas)	0.19732	0.17558	Y. Bottinga <sup>9</sup>
$Q^*(\text{C}^{13}\text{O}_2)/Q(\text{C}^{12}\text{O}_2)$ (gas)	1.2181	1.1919	

Table VI

Partition Function	273°K	298°K	Source
$Q^*(\text{H}_2\text{O}^{18})/Q(\text{H}_2\text{O})^{16}$	1.2697	1.2833	This paper
$[Q^{**}(\text{O}_2^{18})/Q(\text{O}_2^{16})]_{\text{gas}}^{1/2}$	1.0923	1.0818	Brey (Ref. 6)
$1/2 \ln(Q^*(\text{CO}_2^{18})_{\text{gas}}/Q(\text{CO}_2^{16})_{\text{gas}})$	0.12530	0.11108	Bottlinga, (Ref. 13)
$(Q^*(\text{CO}_2^{18})/Q(\text{CO}_2^{16}))^{1/2}_{\text{gas}}$	1.1336	1.1175	
$\ln(Q^*(\text{H}_2\text{O}^{18})_{\text{gas}}/Q(\text{H}_2\text{O}^{16})_{\text{gas}})$	0.06822	0.06164	
$Q^*(\text{H}_2\text{O}^{18})/Q(\text{H}_2\text{O}^{16})_{\text{gas}}$	1.0706	1.0635	Bottlinga, (Ref. 13) See comment below

**Comment:** The partition function ratio for liquid water is obtained by multiplying the partition function ratio for water vapor with the  $\text{O}^{18}/\text{O}^{16}$  ratio in liquid water divided by the ratio in the vapor. This correction is taken as 1.01150 at 273° and as 1.00930 at 298°K; (Ref. 13, page 806)

Table VII

	273°K	298°K	Temperature Coefficient	
$\alpha^{18}(\text{O}_2)$	1.1624	1.1863	+0.96	‰ per °C
$\alpha^{18}(\text{CO}_2)$	1.1200	1.1484	+1.14	‰ per °C
$\alpha^{18}(\text{H}_2\text{O})$	1.1725	1.1956	+0.92	‰ per °C
$\alpha^{13}$	0.9503	0.9594	+0.36	‰ per °C
$\alpha(\text{HCOH})$	1.5881	1.5983	+0.4	‰ per °C
$\alpha(\text{DCOH})$	1.8095	1.8606	+2.0	‰ per °C

The computed temperature coefficients listed above agree very well with the value 0.35 ppt per °C measured for C13/C12 by Degens et. al., Ref. 4, and with the value 3.0 ppt per °C measured for D/H by W. E. Schiegl, Science 175, 512-513, (1972), "Deuterium Content of Peat as a Paleo-Climatic Recorder."

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