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Calculation of the Reduced Partition Function Ratios of α-, β-Quartzs and Calcite

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The reduced partition function ratios (r.p.f.r.) of α, β-quartz and calcite were calculated for oxygen isotopic substitution, using the force fields. Optical vibrations are represented by factor group mode ($k=0$) and acoustic contributions were approximated by the Debye mode of vibration. The theoretical calculation predicts that the r.p.f.r. of quartz could have a discrete gap of about 0.8‰ at the α-β-transition temperature (573°C), the r.p.f.r. of α-quartz being larger in magnitude and in temperature-dependency. This implies that the isotopic fractionation factors between quartz and other materials such as water, could be significantly affected by the transition. A comparison of the calculated r.p.f.r. of quartz and calcite with the experimental fractionation factors between these minerals and water yields a fairly consistent value of the r.p.f.r. of water, supporting the force field models used for calculations. The comparison also revealed that the r.p.f.r. of water in the temperature interval 300—800°C and under a hydrostatic pressure of 2 Kb should deviate from those of ideal water vapor at the same temperatures by as much as 1‰ due to the non-ideality of the compressed water fluid.

Distribution of oxygen isotopes in nature is largely controlled by the equilibrium partitioning of the isotopes among coexisting phases. Detailed knowledge on the isotopic fractionation factors between major rock-forming minerals and water is essential in order to understand the isotopic ratios of the various substances in nature. The isotopic fractionation factors have been experimentally determined for a wide range of temperature for systems such as quartz-water, feldspar-water and calicte-water (*e.g.*, O'Neil and Clayton[1]), O'Neil and Taylor[2])). On the other hand, the theoretical calculation of the isotopic fractionation factors has been developed by Urey[3]), Bigeleisen and Mayer[4]), and Bigeleisen[5]). However, application of the theory to condenced materials has been rather limited because of the complicated nature of the calculation. The fractionation factors between calite and water were first studied by McCrea[6]), but his model was two simple to explain the experimental results. More refined calculations on the system were made by Bottinga[7]) and O'Neil *et al.*[8]) and the agreement between the experimental and theoretical values was greatly improved. The present authors calculated the reduced partition function ratios of α-quartz, β-quartz and calcite, using the force fields reported by Shiro[9,10]) and Yamaguchi.[11]) The present paper will describe the calculation in some detail and the results will be compared with the experimental fractionation factors obtained by other investigators. The effect of the non-ideality of water vapor at high temperatures and pressures on the isotopic fractination factors between water and these minerals will also be discussed.

Calculation of the Reduced Partition Function Ratios of α-, β-Quartz and Calcite. For the isotopic exchange reactions

$$1/2\,\mathrm{Si^{16}O_2} + \mathrm{H_2{}^{18}O} = 1/2\,\mathrm{Si^{18}O_2} + \mathrm{H_2{}^{16}O}, \tag{1}$$

$$1/3\,\mathrm{CaC^{16}O_3} + \mathrm{H_2{}^{18}O} = 1/3\,\mathrm{CaC^{18}O_3} + \mathrm{H_2{}^{16}O}, \tag{2}$$

the fractionation factors, α_{q-w} and α_{c-w}, are defined as follows.

$$\alpha_{q-w} = (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{quartz}}/(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{water}}, \tag{3}$$

and $$\alpha_{c-w} = (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{calcite}}/(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{water}}, \tag{4}$$

These fractionation factors can be calculated from the relations

$$\alpha_{q-w} = f_q^{1/2}/f_w, \tag{5}$$

and $$\alpha_{c-w} = f_c^{1/3}/f_w, \tag{6}$$

where f represents the reduced partition function ratios (r.p.f.r.) of the subscript substance.

The r.p.f.r. is generally defined by[4])

$$f = (Q^*/Q)_{\mathrm{qm}}/(Q^*/Q)_{\mathrm{cl}}, \tag{7}$$

where the numerator is the quantum mechanical partition function ratio and the denominator is the classical partition function ratio. The asterisk represents the heavy isotopic species. The partition function ratios of a crystalline solid are related to vibrational frequencies as follows.

$$(Q^*/Q)_{\mathrm{qm}} = \prod_i \frac{e^{-u_i^*/2}(1-e^{-u_i})}{e^{-u_i/2}(1-e^{-u_i^*})}, \tag{8}$$

and $$(Q^*/Q)_{\mathrm{cl}} = \prod_i \frac{u_i}{u_i^*} = \left(\frac{m^*}{m}\right)^{3n/2}, \tag{9}$$

where $u_i = h\nu_i/kT$, ν_i=vibrational frequencies, h= Planck's constant, k=Boltzman constant, m=mass of light isotope, m^*=mass of heavy isotope, n=number of atoms involved in the substitution, and T=absolute temperature.

The r.p.f.r. of quartz and calcite were calculated

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1) J. R. O'Neil and R. N. Clayton, "Isotopic and Cosmic Chemistry," edited by Craig et al, North-Holland Pub. Co., 1964, p. 157.

2) J. R. O'Neil and H. P. Taylor, Jr., *Amer. Mineralogist*, **52**, 1414 (1967).

3) H. C. Urey, *J. Chem. Soc.*, **1947**, 562.

4) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

5) J. Bigeleisen, *ibid.*, **34**, 1485 (1961).

6) J. M. McCrea, *ibid.*, **18**, 846 (1950).

7) Y. Bottinga, *ibid.*, **72**, 800 (1968).

8) J. R. O'Neil, R. N. Clayton, and T. K. Mayeda, *ibid.*, **51**, 5547 (1969).

9) Y. Shiro, *J. Sci. Hiroshima Univ.*, **A-II 32**, 69 (1968).

10) Y. Shiro, *ibid.*, **A-II 32**, 77 (1968).

11) H. Yamaguchi, *et al.*, to be submitted.

under the following assumptions: (1) all vibrations are harmonic oscillations, (2) crystal vibrations can be divided into optical and acoustic modes, and (3) the vibrational phases of all unit cells in the optical mode **are** the same, or $k=0$. The r.p.r.f. due to the optical mode are the same, or $k=0$. The r.p.f.r. due to the mode of vibration, f_{opt}, is then obtained by

$$\ln f_{\text{opt}} = \sum_{i=1}^{3N-3} \{[u_0(i) - u_0{}^*(i)]/2 + \ln[1-e^{-u_0(i)}]/[1-\mathrm{e}^{-u_0{}^*(i)}] - \ln[u_0(i)/u_0{}^*(i)]\}, \tag{10}$$

where N=number of atoms in a unit cell, $u_0 = \boldsymbol{h}\nu_0/\boldsymbol{k}T$ and ν_0=optically active vibration frequency (k=0).

The r.p.f.r. due to the acoustic vibrations can be calculated from the following equation if the Debye approximation of the acoustic vibration is valid.[12]

$$\ln f_{\text{acoust}} = \frac{3}{40}(\Theta^2 - \Theta^{*2})/T^2, \tag{11}$$

$$= \sum_{j=1}^{3} \frac{\boldsymbol{h}^2}{40\boldsymbol{k}^2 T^2}[\nu_a{}^2(j) - \nu_a{}^{*2}(j)], \tag{11$'$}$$

where Θ and ν_a represent the Debye temperature and acoustic (Debye) frequencies. Since acoustic vibration is a periodic translation of all atoms in a unit cell, acoustic frequency of the heavy isotopic crystal is assumed to be

$$\nu_a{}^*/\nu_a = \Theta^*/\Theta = (M/M^*)^{1/2} \tag{12}$$

where M denotes the mass of unit cell.

The observed values of ν_0 (i) of α-quartz were taken from Scott and Porto[13] and Saksena[14] and are given in Table 1. Since β-quartz belongs to factor group D_3, the vibrations of B_1- and B_2-symmertry groups are infrared- and Raman-inactive and only the frequencies of vibrations belonging to A_1, A_2, E_1, and E_2 have been measured[15] (Table 1). The missing frequencies were estimated as follows. Inspection of the observed frequencies of α- and β- quartz indicates that the latter are, on the average, 0.990 of the corresponding frequencies of the former in the region above 600 cm^{-1} and 0.924 below 600 cm^{-1}. This implies that the vibrations of lower frequencies are more strongly affected by the transition than those of higher frequencies. Assuming that the frequency ratios are the same for the B_1 and B_2 vibrations, the "observed frequencies" of the missing vibrations were estimated by multiplying the corresponding freuqencies of α-quartz by the ratios mentioned above (Table 1). The optical frequencies of α- and β- ^{18}O-quartzs were calculated by using the force fields obtained by Shiro[9] and Yamaguchi.[11] The calculated frequencies $\nu_{\text{cal}}{}^*$ were then converted into the "observed values" $\nu_0{}^*$, assuming the following relationship.

$$\nu_0{}^*/\nu_0 = \nu^*{}_{\text{cal}}/\nu_{\text{cal}} \tag{13}$$

TABLE 1. OPTICAL VIBRATIONAL FREQUENCIES (cm^{-1}) AND THE DEBYE TEMPERATURES (°K) OF ^{16}O AND ^{18}O QUARTZ

α- quartz			β- quartz		
D_3	ν_0[a)]	$\nu_0{}^*$[b)]	D_6	ν_0[c)]	$\nu_0{}^*$[b)]
	464	439.9	A_1	453	427.0
	1085	1037.5		1074[f)]	1028.8
A_1	356	345.8	B_1	329[f)]	320.9
	207	196.9		191[f)]	181.6
	1080	1037.3		1072	1027.9
	495	474.9	A_2	490	468.9
A_2	778	772.0		770[f)]	769.5
	364	344.3	B_2	336[f)]	316.9
	1072	1020.3		1060	1017.3
	795	780.8		785	773.0
	475	457.7	E_1	470	454.9
	128	120.8		97	91.8
E	1162	1115.9		1154	1096.7
	696	682.8		686	676.7
	394	376.0	E_2	395	372.4
	265	251.1		250	237.0
	Θ[d)]	Θ^*[e)]		Θ[d)]	Θ^*[e)]
	204	197.5		204	197.5

a) Observed optical frequency of α-Si^{16}O$_2$, see Refs. 13, 14.
b) Hypothetical optical frequency of α-Si^{18}O$_2$, see text.
c) Observed optical frequency of β-Si^{16}O$_2$, see Ref. 15.
d) Observed Debye temperature of Si^{16}O$_2$, see Ref. 14.
e) Calculated Debye temperature of Si^{18}O$_2$, see text.
f) Hypothetical optical frequency of Si^{16}O$_2$, see text.

TABLE 2. OPTICAL AND ACOUSTIC VIBRATIONAL FREQUENCIES (cm^{-1}) OF ^{16}O AND ^{18}O CALCITE

D_{3d}	ν_0[a)]	$\nu_0{}^*$[b)]	D_{3d}	ν_0[a)]	$\nu_0{}^*$[b)]
A_{1g}	1086	1023.7	E_g	1434	1412.4
A_{1u}	1086[e)]	1023.8		712	673.7
	222	214.4		284	267.8
A_{2g}	803[e)]	795.8		156	148.8
	234[e)]	229.8	E_u	1484	1461.9
	72[e)]	68.1		706	668.1
A_{2u}	885	877.4		330	314.3
	357	347.1		182	178.6
	106	100.6		106	104.9
	ν_a[c)]	$\nu_a{}^*$[d)]		ν_a[c)]	$\nu_a{}^*$[d)]
A_{2u}	142.1	138.0	E_u	104.3	101.3

a) Observed optical frequency of CaC^{16}O$_3$, see Ref. 17.
b) Hypothetical optical frequency of CaC^{18}O$_3$, see text.
c) Calculated acoustic frequency of CaC^{16}O$_3$, see Ref. 16.
d) Calculated acoustic frequency of CaC^{18}O$_3$, see text.
e) Calculated optical frequency of CaC^{16}O$_3$, see Ref. 10.

The acoustic frequencies of calcite can be calculated by means of the Giulotto-Loinger model[7,16], since carbonate ions are relativaly independent of each other in calcite crystals. However, the structure of quartz is too complicated to apply thier method. Thus,

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[13] J. F. Scott and S. P. S. Porto, *Phys. Rev.*, **161**, 903 (1966).

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[15] a) I. Shimon and H. O. McMahon, *J. Chem. Phys.*, **21**, 23 (1953); b) P. K. Narayanaswamy, *Proc. Ind. Acad. Sci.*, **A28**, 417 (1948).

[16] L. Giulotto and A. Loinger, *Nuovo Cimento*, **8**, 475 (1951).

the Debye temperature obtained by specific heat measurement of α-quartz[14] was used to calculate the acoustic portion of the r.p.f.r. of both α- and β-quartz (Table 1). Contribution of the acoustic vibrations to the total reduced partition function ratios is less than 0.5% and the assumption made above will not seriously affect the results.

The observed optical frequencies of calcite were taken from Ramdas results.[17] The optically inactive frequencies of A_{1u}- and A_{2g}-symmetry groups were calculated by Shiro.[10] The "observed frequencies" of ^{18}O-calcite were obtained as described above by using the force field given by Shiro.[10] The Debye temperatures of ^{16}O-calcite were taken from the calculation of Giulotto and Loinger.[16] The values are given in Table 2.

Results

The r.p.f.r. of α-, β-quartz and calcite are given in Table 3. The r.p.f.r. of calcite were obtained by using the same frequencies of the free carbonate ion and the lattice vibrations as used by Bottinga.[7] Our "Bottinga's values" are approximately 1.5‰ larger than his at all temperatures. The reason for this is not clear at present. The values quoted as "Bottinga's values" are those we re-calculated using the vibrational frequencies presented by Bottinga[7], and the value of 3/2 $\ln(m^*/m) = 3/2 \ln\dfrac{17.999167}{15.99491} = 0.17708$.

Table 3. Reduced partition function ratios of quartz and calcite

Temp (°C)	$1/2 \ln f_q$		$1/3 \ln f_c$	
	α-quartz	β-quartz	Ours	Bottinga's
0	123.04	(118.95)	112.50	115.47
25	106.99	(103.41)	97.96	100.54
50	93.83	(90.67)	86.03	88.29
75	82.92	(80.11)	76.12	78.11
100	73.77	(71.24)	67.80	69.56
150	59.42	(57.34)	54.71	56.11
200	48.82	(47.07)	45.02	46.15
250	40.78	(39.27)	37.64	38.56
300	34.55	(33.23)	31.89	32.66
350	29.63	(28.45)	27.35	27.98
400	25.69	(24.62)	23.70	24.22
500	19.84	(18.95)	18.26	18.62
600	15.78	15.01	14.47	14.72
700	12.85	12.17	11.74	11.91
800	10.68	10.05	9.69	9.81
900	9.01	8.44	8.14	8.20
1000	7.72	7.18	6.92	6.94

Discussion

The oxygen isotopic fractionation factors between calcite and water have been experimentally studied by McCrea[6] and Epstein *et al.*[8] at higher temperatures. The observed fractionation factors were found to be well approximated by an equation of the form $10^3 \ln \alpha_{c-w} = a/T^2 + b$, for a wide range of temperature, although the deviation from the linear equation becomes large at temperatures above 800°C. The experimental fractionation factors employed in this paper for calcite-water system is that given by O'Neil *et al.*[8]:

$$10^3 \ln \alpha_{c-w} = 2.78 \times 10^6/T^2 - 3.39 \qquad (14)$$

The experimental range of temperature was 0—500°C for equation (14). The calculation was extended to 800°C for the purpose of comparison with the fractionation factors between quartz and water. A slightly different equation, $10^3 \ln \alpha_{c-w} = 2.71 \times 10^6/T^2 - 1.84$, was also given by the same authors[1] for a temperature rage 0–750°C. The former equation gives a value about 0.6‰ higher at room temeprature and about 1.5‰ higher at 1000°C than that given by the latter equation.

The experimental fractionation factors in the system quartz-water have been subjected to significant revision since the first experimental work of O'Neil and Clayton.[1] The value of $\ln \alpha_{q-w}$=used in the following discussion was taken from Fig.1 of Epstein and Taylor[19] and approximated by the least square fit equation[20],

$$10^3 \ln \alpha_{q-w} = 3.57 \times 10^6/T^2 - 2.71 \qquad (15)$$

The applicable temperature range of equation (15) would be 300–800°C. However, the equation gives about 2‰ larger fractionation factors in the temperature range 500–800°C than those reported by O'Neil and Clayton.[1] These discrepancies are apparently due to experimental difficulty in determination of the fractionation factors, suggesting that a comparison of theory and experimental rseults can not be free from uncertainty arising not only from the theory, but also from the experimental estimation of the fractionation factors.

The difference between the calculated r.p.f.r. of quartz and the observed values of $\ln \alpha_{q-w}$ is shown in Table 4. Similar values for calcite-water system are also shown. The differences (denoted as $f_{lw(q)}$ and $f_{lw(c)}$), should be equal to the r.p.f.r. of water and can be compared to the r.p.f.r. of water obtained independently by other methods.

The r.p.f.r. of liquid water may be obtained from the theoretically calculated r.p.f.r. of gaseous water and the observed isotopic vapor pressure ratios of water by means of the relationship

$$\ln f_{lw} = \ln f_{vw} + \ln \alpha_{lw-vw}, \qquad (16)$$

where subscripts lw and vw stand for liquid and vapor water, respectively. The latest values of $\ln f_{vw}$ (Table 4) were claculated by Bottinga[7] who took into account the anharmonicity of the vibrations of water molecules. The values of $\ln \alpha_{lw-vw}$ have been mesaured by several

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[17] A. K. Ramdas, *Proc. Ind. Acad. Sci.*, **37A**, 441 (1953).

[18] S. Epstein, R. Buchsbaum, A. Lowenstam and H. C. Urey, *Bull. Geol. Soc. Amer.*, **64**, 1315 (1953).

[19] S. Epstein and H. P. Taylor, Jr., "Researches in Geochemistry" II, New York, John Wiley, P. H. Abelson ed., (1966) p. 32 Fig. 1.

[20] H. P. Taylor, Jr., Personal communication (1971).

TABLE 4. REDUCED PARTITION FUNCTION RATIOS OF WATER

Temp °C	$\ln f_{\mathrm{vw}}$ ‰	$\ln \alpha_{\mathrm{1w-vw}}$ ‰	$\ln f_{\mathrm{1w}}$ ‰			
			$\ln \alpha_{\mathrm{vw-1w}} + \ln f_{\mathrm{vw}}$	$\ln f_{\mathrm{CO_2}} - \ln \alpha_{\mathrm{CO_2-1w}}$	$1/2 \ln f_{\mathrm{q}} - \ln \alpha_{\mathrm{q-w}}$	$1/3 \ln f_{\mathrm{c}} - \ln \alpha_{\mathrm{c-w}}$
0	68.22	11.19	79.41	80.20	(77.18)	(78.59)
25	61.64	8.86	70.50	71.25	(68.96)	70.05
50	56.08	6.88	62.96	63.68	(61.89)	62.77
75	51.33	5.19	56.52	57.20	(55.80)	56.55
100	47.21	3.73	50.94	51.58	(50.53)	51.21
150	40.46	1.32	41.78	(42.35)	(41.98)	42.56
200	35.16	−0.58	34.58	(35.07)	(35.44)	35.98
250	30.90	(−2.11)	(28.79)	(29.18)	(30.36)	30.87
300	27.40	(−3.38)	(24.02)	(24.32)	(26.34)	26.81
350	24.49				23.13	23.58
400	22.03				20.53	20.95
500	18.11				16.61	17.00
600	15.15				13.10	14.21
700	12.86				11.19	12.19
800	11.04				9.75	10.67

authors in a temperature range below 100°C.[21-24] Unfortunately, agreement between the values reported by these authors was rather poor, the maximum discrepancy being as much as 1‰. Values were obtained from the least square fit equation of the form $\ln p/p^* = a/T + b$ to the data given by Uvarov *et al.*[23] Theoretical verification of the equation was given by Bigeleisen.[5] We selected the data of Uvarov *et al.*[23] because only their measurements were extended to temperatures above 100°C, but in the least square fit calculation, the three highest temperature points were excluded for the reason that their data show a significantly different temperature dependency as compared to the lower temperature data. O'Neil and Adami[25] computed the values of $\ln f_{\mathrm{1w}}$ from the observed isotopic fractionation factor between carbon dioxide and water and the calculated reduced partition function ratios of carbon dioxide. Their results are represented by the least square fit equation, $10^3 \ln f_{\mathrm{1w}} = 29.14 \times 10^3/T - 26.54$ as shown in Table 4. The values of $\ln \alpha_{\mathrm{1w-vw}}$ reported by Uvarov *et al.*[23] are essentially the lowest among those reported by other investigators, while the values of O'Neil and Adami[25] would rather represent a highest estimation of this kind. Hence, the two sets of data could define a possible range of values of $\ln f_{\mathrm{1w}}$. We see from Table 4 that in spite of many uncertainties involved in the experimental and theoretical estimations, the values of $\ln f_{\mathrm{1w(c)}}$ and $\ln f_{\mathrm{1w(q)}}$ at a temperature range below 600°C are fairy close to each other, especially those of $\ln f_{\mathrm{1w(c)}}$ being within a possible range of the values presented above.

Above the α-β transition point of quartz (573°C) the values of $\ln f_{\mathrm{1w(q)}}$ deviate significantly from those of $\ln f_{\mathrm{1w(c)}}$, because the r.p.f.r. of β-quartz is about 0.8‰ smaller at the transition point. The temperature dependency is also smaller than for α-quartz. This is a reflection of the fact that β-quartz is characterized by a less dense crystal structure than α-quartz: the unit cell of the former being appeoximately 0.1Å

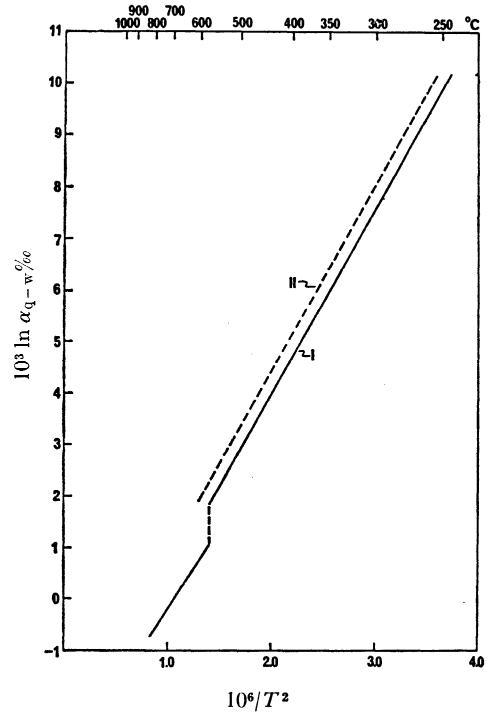

Fig. 1. Isotopic fractionation factors between quartz and water.
I: Theoretical values obtained by the calculated values of $1/2 \ln f_{\mathrm{q}}$ and those of $\ln f_{\mathrm{1w(c)}}$.
II: Experimental values by equation (18).

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25) J. R. O'Neil and L. H. Adami, *J. Phys. Chem.*, **73**, 1553 (1969).

longer than the latter in both the *a* and *c* axes.[26]) Yamaguchi[11]) also demonstrated that the streething force constant of Si-O bond in β-quartz is about 0.2 mdyn/Å smaller than that in α-quartz on normal coordinate treatment. The "theoretical" values of $\ln \alpha_{q-w}$, calculated by the relationship $\ln \alpha_{q-w}=1/2 \ln f_q - \ln f_{lw(c)}$, are plotted against $10^6/T^2$ in Fig. 1. The experimental values represented by equation (15) are also shown for comparison (dotted line). It is seen that the α-β transition of quartz should have a significant effect on the isotopic fractionation factors between quartz and water, although the experimental results so far obtained do not support the prediction. The calculated discontinuity at the transition point may be made smaller by adjusting the vibrational frequencies of α-quartz, while the uncertainty in the experimental determinations of the fractionation factor may also be large. Thus we feel that an exact comparison between theory and experiments is rather difficult at present.

The experimental data of quartz-water and calcite-water system at higher temperatures were determined under a hydrostatic pressure of 2 Kbar.[1]) The values of $f_{lw(q)}$ and $f_{lw(c)}$ in Table 4 are, therefore, those of supercritical water at 2 Kbar. A good agreement between $f_{lw(q)}$ and $f_{lw(c)}$ below the α-β transition temperature of quartz allows us to say with some confidence that the difference between $f_{lw(c)}$ and the r.p.f.r. of gaseous water calculated by Bottinga above the critical temperature of water is ascribed to the non-ideality of water fluid under the experimental conditions. The non-ideality in the r.p.f.r. is about 1‰ at temperatures around 600°C and then decreases rapidly above 700°C. It should be noted that the compressed supercritical water fluid is "isotopically lighter" than the freely expanded water vapor at the same temperature. The cross-over point of the liquid-vapor water system lies somewhere around 150–200°C.[23]) Above this temperature the heavy water ($H_2{}^{18}O$) possesses a higher vapor pressure than that of $H_2{}^{16}O$. The cross-over phenomena are qualitatively ascribed to the difference between $H_2{}^{16}O$ and $H_2{}^{18}O$ of the zero-point energy change by condensation of water.[5]) The non-ideality in the r.p.f.r. of the compressed supercritical water fluid would also be due to the same effect, although a quantitative explanation is not possible at the present time.

Table 3 indicates that "Bottinga's values" of the r.p.f.r. of calcite ($1/3 \ln f_c$) are about 3% larger than our values. In our model, the carbonate ions in calcite crystals are not independent of each other, while in Bottinga's model, they vibrate freely without interaction.[7]) As a result of mutual interaction of carbonate ions in our model, the ν_3 vibration at 1467 cm^{-1} a free carbonate ion[27]) splits into two broad lines at 1434 and 1484 cm^{-1}. In general, the vibration of higher frequency makes more contribution to the r.p.f.r., hence the neglect of this unsymmetric splitting in Bottinga's model could be a cause of the discrepancy mentioned above.

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Added in Proof: The experimental equation of high temperature liquid-vapor fractionation factor for $H_2{}^{16}O$-$H_2{}^{18}O$ by Y. Bottinga and H. Craig (*Amer. Geophys. Union Trans.* **49**, 356 (1968)) is $\ln \alpha_{lw-vw} = -7.174 + 4.716 \times 10^3/T - 0.058 \times 10^6/T^2$. Due to their values, our obtained values $\ln \alpha_{q-w}$ become 6.3‰, 11.1‰, and 21.1‰, at 300°C, 200°C, and 100°C, respectively. The values are *ca.* 2‰ smaller than the Talor's results.[20])

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