

## Oxygen isotope equilibration systematics between quartz and water

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### Abstract

The <sup>18</sup>O/<sup>16</sup>O fractionation accompanying the hydrothermal crystallization of quartz from silicic acid at 265°–465°C has been studied in order to assess the influences of (a) rate of quartz formation, (b) the nature of the reaction mechanism, and (c) temperature. At 360° and 465°C there are no indications of rate effects influencing isotope partitioning, but at 265°C (where fractionation factors show an unusually large scatter) the evidence is inconclusive in this respect. All reaction appears to occur through solution–precipitation processes, with the intermediate phases, cristobalite and silica K, giving identical fractionation factors (within experimental errors) to quartz samples formed at the same temperature. The temperature-dependence of fractionation in the range 265°–465°C is given by the equation

$$10^8 \ln \alpha(\text{SiO}_2\text{-H}_2\text{O}) = 3.05 \times 10^6 T^{-2} - 2.09$$

The data are in good agreement with other experimental calibrations of the quartz–water fractionation.

### Introduction

The fractionation of <sup>18</sup>O between phases containing oxygen (such as silicates and oxides) at equilibrium is temperature-dependent in response to the diminishing differences in the statistical mechanical properties of the isotopes <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O with increasing temperature (Urey, 1947; Bigeleisen and Mayer, 1947). Oxygen isotope fractionation between coexisting phases is thus the basis of both oxygen isotope geothermometry and quantitative oxygen isotope models for water–rock interaction processes (Taylor, 1977; Spooner *et al.*, 1977). Experimental calibration of the magnitude and temperature-dependence of <sup>18</sup>O fractionation is generally considered essential for precise geochemical applications, because calculation of fractionation factors is inherently difficult for solid phases and usually requires so many simplifying as-

sumptions that the results are necessarily only approximations. Published high-temperature oxygen isotope geothermometer calibrations reveal tendencies for minerals and water to concentrate <sup>18</sup>O in accord with isotopic abundances observed in natural occurrences. However, significant discrepancies exist amongst calibrations for individual mineral–water systems, particularly oxygen isotope fractionation in the quartz–water system. The experimental studies of Clayton *et al.* (1972) and Matsuhisa *et al.* (1976, 1978), utilizing complete exchange methods, gave quartz–water fractionation factors significantly lower than given by interpolation from partial exchange (*cf.* data of Clayton *et al.*, 1972) or by the theoretically based approach of Bottinga and Javoy (1973). These experimental uncertainties in calibration detract from the use of oxygen isotopic abundance studies for geothermometry and to assess equilibrium and departures from equilibrium in natural mineral assemblages. Furthermore, accurate characterization of

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equilibrium fractionations would enable more precise modelling of many geochemical processes such as water-rock interaction or retrograde metamorphic changes, in which observed isotope fractionations may be dominated by the kinetics of oxygen isotope exchange.

We present the results of an experimental investigation of the oxygen isotope fractionation accompanying the hydrothermal crystallization of quartz from silicic acid at 265°–465°C. Specifically, we aim to assess the influences of (a) rate of crystallization of quartz, (b) the nature of the reaction mechanism, and (c) temperature, *i.e.* the calibration of the temperature-dependence of the quartz-water isotopic fractionation.

### Experimental methods

The solutions were prepared by dissolving analytical-grade sodium carbonate in deionized water artificially enriched in <sup>18</sup>O (Table 1). The solid reactant was chromatographic-grade silicic acid, which gave a weight loss of approximately 15 percent on ignition at 600°C for 2 hours and a weight loss of approximately 50 percent on recrystallization to quartz. Typical experimental charges consisted of 60mg solid reactant and 500–800mg solution (depending on temperature) sealed in gold capsules. All experiments were performed in stainless-steel cold seal bombs, using conventional hydrothermal techniques.

Temperature was monitored continuously by an

Table 1. Oxygen isotopic composition of reactants

Water		Silicic Acid**	
CO <sub>2</sub> -equil.*	Guan. HCl <sup>+</sup>	Untreated	Ignited
<sup>18</sup> O ‰/‰		<sup>18</sup> O ‰/‰	
34.90(2)	34.86(2)	21.4	27.5
Mean = 34.88			

\* Isotopic analyses obtained by the CO<sub>2</sub> equilibration procedure described by Epstein and Mayeda (1953), using a value of  $\alpha_{\text{CO}_2 - \text{H}_2\text{O}}^{25^\circ\text{C}} = 1.04120$  (O'Neil *et al.* 1975).

+ Isotopic analyses obtained using guanidine hydrochloride and a modified version of the method described by Boyer *et al.* (1961).

\*\* Isotopic analyses from Beckinsale and Durham (unpublished report, 1972).

automatic potentiometric recorder connected to a thermocouple located in a hole on the exterior of the bomb and adjacent to capsule position. On completion of an experimental run, bombs were quenched rapidly with cold water. After the capsule was weighed to check for leakage, the solid products were extracted, washed repeatedly with deionized water, and dried in air at 110°C. The solid products were analyzed by X-ray diffraction, using nickel-filtered CuK $\alpha$  radiation. Textural examination was made with a Cambridge Stereoscan (SEM).

The majority of isotopic analyses were made on the 30cm ratio mass spectrometer described by Beckinsale *et al.* (1973). Oxygen was extracted from the silica phases using the BrF<sub>5</sub> method of Clayton and Mayeda (1963), and subsequently converted to CO<sub>2</sub> for isotopic analysis by the carbon reduction procedure of Taylor and Epstein (1962). Several additional analyses were made on the 6cm VG micromass 602C mass spectrometer at the Hebrew University, with oxygen extractions being made with fluorine. All analyses are corrected for valve mixing, background, <sup>13</sup>C and <sup>17</sup>O contributions and are reported relative to SMOW, as defined by repeated analysis of the Caltech rose quartz standard ( $\delta$  SMOW = 8.43 per mil). The isotopic compositions of the solutions at the completion of experimental runs were calculated by material balance.

The oxygen isotope composition of the reagents is given in Table 1. Note that the solid reactant (silicic acid) was reacted in two forms, untreated and ignited for several hours at 600°C. The weight losses on ignition and quartz formation suggest that a suitable formula for the untreated reagent is approximately Si(OH)<sub>4</sub>·H<sub>2</sub>O, with the loose water molecule being lost on heating.

### Notation

Oxygen isotope analyses are reported as  $\delta$  values in per mil where:

$$\delta = \left( \frac{{}^{18}\text{O}/{}^{16}\text{O} \text{ sample}}{{}^{18}\text{O}/{}^{16}\text{O} \text{ standard}} - 1 \right) \times 10^3$$

The fractionation factor  $\alpha_{A-B}$  is defined as the <sup>18</sup>O concentration ratio between two phases

$$\alpha_{A-B} = ({}^{18}\text{O}/{}^{16}\text{O} \text{ in A}) / ({}^{18}\text{O}/{}^{16}\text{O} \text{ in B})$$

The temperature-dependence of the fractionation factor between a mineral and H<sub>2</sub>O is usually well approximated over limited temperature ranges by a straight-line equation of the form

$$10^3 \ln \alpha = A \times 10^6 T^{-2} + B$$

where  $T$  is the absolute temperature and  $A$  and  $B$  are constants.

### Results and discussion

The appearance of quartz in the hydrothermal syntheses is preceded by the formation of one or more metastable intermediate phases, as shown by the X-ray diffraction traces in Figure 1. At 265° the intermediate product is cristobalite, but at 360° and 465°C a second metastable phase—silica K—forms after cristobalite. These phase sequences parallel those observed by Campbell and Fyfe (1960) and Fyfe and McKay (1962), in which the mineralizer was sodium hydroxide, but differ from those found using sodium fluoride by Clayton *et al.* (1972), when no intermediate phase was reported. The kinetics of quartz formation in sodium carbonate solutions have been discussed by Matthews (1972), who found that the time for complete (100 percent) quartz formation,  $t_f$ , is a function of the carbonate ion concentration,  $(\text{CO}_3^{2-})$ . At 265°C,  $t_f \approx K(\text{CO}_3^{2-})^{-2}$  which varies to  $t_f \approx K(\text{CO}_3^{2-})^{-1}$  at 465°C, where the  $K$ 's are rate constants. To study the effects of variation in the rate of crystallization of quartz on oxygen isotope fractionation, a series of synthesis experiments was performed at 265°, 360° and 465°C at a pressure of 0.68 kbar (10,000 psi), using untreated silicic acid as the solid reagent. Time of quartz formation was carefully monitored and varied by at least one order of magnitude at each experimental temperature by adjusting the  $\text{CO}_3^{2-}$  ion concentration. The results are illustrated in Figures 2–4, where molar carbonate concentration is plotted against time of reaction. The curve in each diagram represents the approximate time for 100 percent quartz formation. The fractionation factors determined for selected quartz samples, expressed as  $10^3 \ln \alpha(\text{Qtz-H}_2\text{O})$ , are plotted adjacent to the solution molarity/reaction time coordinates of each analyzed quartz sample.

It can be shown (see appendix) that crystal-growth isotopic rate effects, in which diffusion across a boundary solution layer adjacent to the growing crystal surface is the rate-determining effect, can be defined by the steady-state equation

$$\alpha_m = \alpha_e / [\alpha'_e + (1 - \alpha'_e) \cdot \exp(Vl/D)]$$

in which  $\alpha_m$ ,  $\alpha_e$  and  $\alpha'_e$  are the measured, equilibrium and solid-aqueous ion fractionation factors, respectively.  $V$  is the linear crystal growth rate,  $D$  is the diffusion coefficient of aqueous solute ions and  $l$  the dimension of the 'Nernst' solution layer. This equation shows that if solution boundary layers surround-

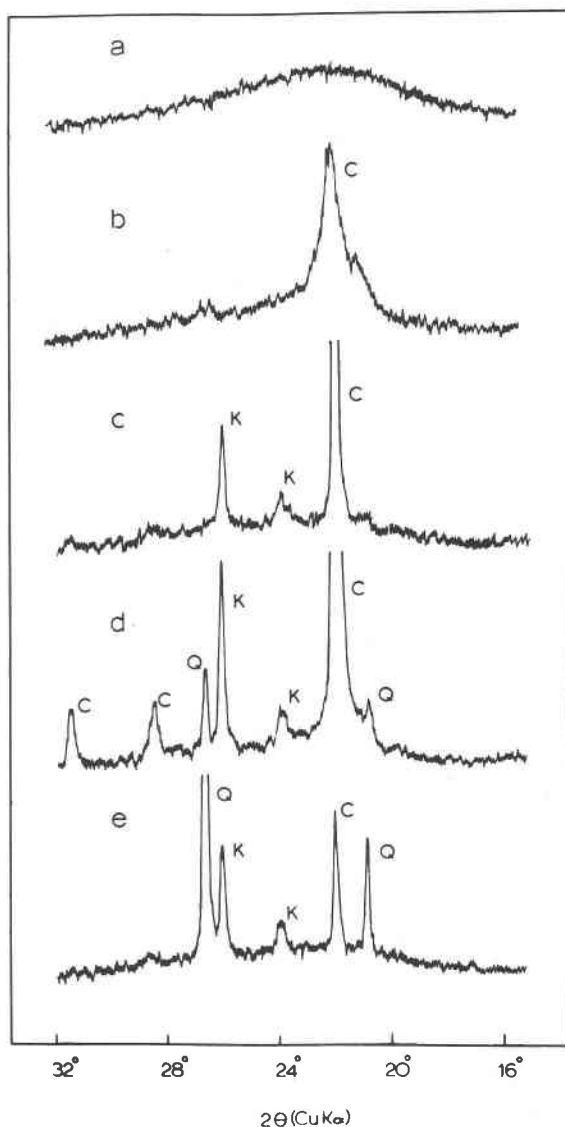


Fig. 1. X-ray diffraction patterns indicating the development of phases at 360° and 465°C. (a) Largely unreacted silicic acid; (b) cristobalite developing; (c) cristobalite major phase with silica K forming; (d) cristobalite and silica K, with quartz forming; (e) quartz major phase, cristobalite and silica K disappearing. Legend: C = cristobalite; K = silica K; Q = quartz. At 265°C, the only intermediate phase to form is cristobalite.

ing the growing crystals are influencing oxygen isotope fractionation, the fractionation factors would be expected to decrease from an equilibrium value with increase in the rate of formation of quartz. No such trend is evident (Figs. 3 and 4) in the data at 465° and 360°, but at 265°C the measured fractionation factors do appear to increase with the time for quartz formation as predicted by the equation (Fig. 2). However, the range in the results at 465° and 360° is

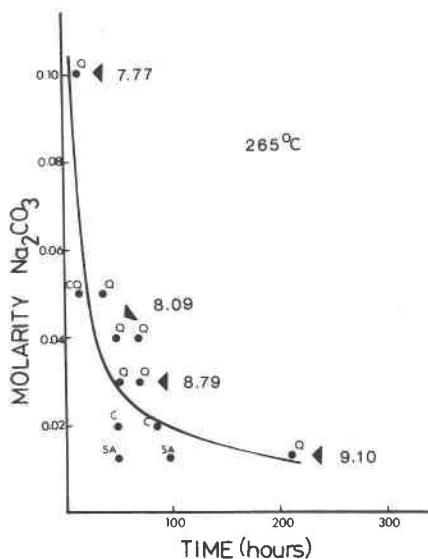


Fig. 2. Experimental results from hydrothermal synthesis experiments at 0.68 kbar. Experiments at 265°C. Legend: SA = unreacted silicic acid; C = cristobalite; K = silica K; Q = quartz.

so large, about 0.7 per mil, that the trend in the data at 265°C is possibly fortuitous. The reproducibility of  $\delta^{18}\text{O}$  values determined for a quartz standard during the course of this work was about  $\pm 0.08$  per mil (one standard deviation). Thus for a large number of analyses the total range of  $\delta^{18}\text{O}$  values would be expected to be about  $\pm 0.24$  per mil, and occasional 'wild' values (normally excluded because of poor oxygen yields) would extend this range. Nevertheless, for standards very few (<5 percent) of the results fall outside  $\pm 0.2$  per mil of the mean, and we are convinced that at least part of the range of  $\delta^{18}\text{O}$  values obtained for synthesized quartz samples reflects experimental problems in the syntheses. Matsuhisa *et al.* (1978) also found low  $^{18}\text{O}/^{16}\text{O}$  (and  $^{17}\text{O}/^{16}\text{O}$ ) fractionations associated with an extremely rapid cristobalite-quartz transformation at 250°C. They related these low fractionations to isotopic zoning in quartz caused by variation in the isotopic composition of the water, itself brought about by high mineral/solution ratios in experimental charges. However, using their model, it is not possible to determine if the instantaneous fractionation between precipitated quartz and solution is equilibrium or involves a kinetic effect of the type discussed here.

Table 2 lists the results of a series of synthesis experiments at  $P_{\text{H}_2\text{O}} = 1.02$  kbar (15,000 psi) in which relatively long reaction times were used and the sodium carbonate solution concentration was varied. Selected intermediate products as well as

quartz were analyzed for  $\delta^{18}\text{O}$  values. Textural examination of the synthesis products with a scanning electron microscope reveals distinct morphological differences between quartz and cristobalite. The cristobalite texture consists of small, approximately equidimensional particles packed together into a form which resembles that of the silicic acid reactant (Fig. 5a,b,c). The quartz, in contrast, consists largely of bipyramidal crystals (Fig. 5d) which clearly have crystallized from solution. These textural differences are similar to those observed by Matthews (1976) for the amorphous titanium dioxide  $\rightarrow$  anatase (intermediate)  $\rightarrow$  rutile transformation under hydrothermal conditions. It was suggested there that the texture of the intermediate phase represented rearrangement of the amorphous reagent structure with possible participation of small-scale solution-precipitation processes. The data in Table 2 show that the intermediate phases give fractionation factors identical within errors to those given by quartz at the same temperature. This suggests that the mechanism of cristobalite growth also involves solution-precipitation processes but with smaller-scale transport of solution species than in the case of quartz. Shiro and Sakai (1972) calculated that an oxygen isotope fractionation of 0.8 per mil should accompany the  $\alpha/\beta$  quartz inversion, but our study provides no evidence that such a large fractionation should occur between silica polymorphs at elevated temperatures.

As noted above for the earlier series of experi-

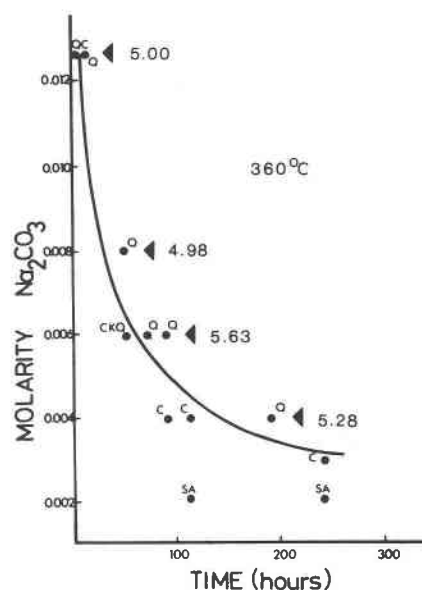


Fig. 3. Experimental results from hydrothermal synthesis experiments at 0.68 kbar. Experiments at 360°C. Legend as Fig. 2.

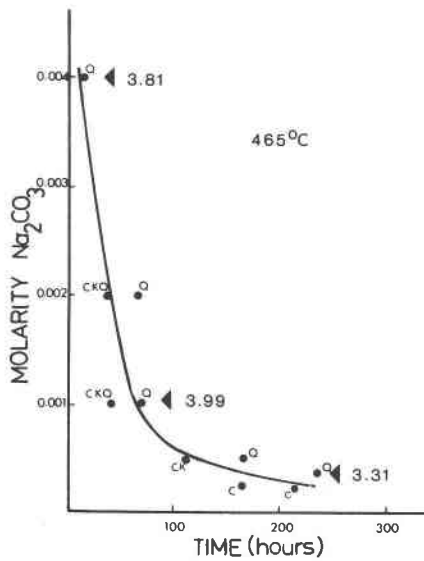


Fig. 4. Experimental results from hydrothermal synthesis experiments at 0.68 kbar. Experiments at 465°C. Legend as Fig. 2.

ments, there is a very large range of measured oxygen isotope fractionation factors between quartz and water at 265°C. The range of values in all our experiments ( $7.8 < 10^3 \ln \alpha < 9.3$ ) is virtually identical to that found by Clayton *et al.* (1972) in their synthesis experiments at 250°C (approximately  $8.8 < 10^3 \ln \alpha < 9.9^2$ ). We cannot provide an adequate explanation for this range of fractionation factors. If this problem is an effect of the rate of crystal growth, the solutions with greatest concentrations of sodium carbonate might be expected to give the smallest fractionations. The data in Table 2, however, indicate that the reverse situation tends to occur, with the more dilute solutions yielding lower fractionation factors. Since rate of quartz formation was not monitored in these experiments, this argument does not preclude kinetic effects, but it does indicate that additional mechanisms must be operating to produce the spread of results. We conclude that the evidence for the effects of solution boundary layers indicated in Figure 2 is inconclusive.

Other possible explanations for the range of values for  $10^3 \ln \alpha$  (Qtz-H<sub>2</sub>O) are (1) fluid inclusions within the solids analyzed for  $\delta^{18}\text{O}$ , (2) O activity effects in solutions at elevated temperatures of the type discussed by Truesdell (1974), or (3) retrograde precipitation of quartz during quenching of the hydrothermal bombs. None of these possibilities provides a feasible explanation. Infrared absorption spectra in-

<sup>2</sup> Recalculated for a CO<sub>2</sub>-H<sub>2</sub>O fractionation factor of  $\alpha$  (25°C) = 1.0412.

dicate that minimal amounts of water are present in the synthetic quartz crystals, solution concentrations are so low that the activity of <sup>18</sup>O would not be affected by dissolved ions, and scanning electron microscope examination shows no evidence of fine-grained precipitate characteristic of quench phases.

One final mechanism which may be considered is the isotopic zoning model of Matsuhisa *et al.* (1978). The isotopic composition of solutions in this study decreases during quartz precipitation to a maximum of ~1.0 per mil less than initial in runs at 265°C. However, since the intermediate phases evidently crystallize at or near equilibrium with solution, the variation in isotopic composition of the water occurs prior to the formation of quartz, whose growth consequently occurs under constant isotopic conditions. We are therefore unable to resolve the problem of the scatter of results at 265°C in terms of kinetics, mechanisms, isotopic heterogeneity, or analytical errors. The correspondence of our data with those of Clayton *et al.* (1972) suggests that the results at least span the equilibrium value. Possibly the preferred determination of an equilibrium fractionation in this temperature range is  $10^3 \ln \alpha = 9.0$  by Matsuhisa *et al.*

Table 2. Hydrothermal synthesis experiments at 1.02 kbar

Run No.	Time (hrs)	Reactants		Final	Solid	$10^3 \ln \alpha$
		Solid*	Solutions <sup>+</sup>	Products**	$\delta^{18}\text{O}$ o/oo	
<b>T=265°C</b>						
119	240	SA	0.020	Q	42.33	9.31
136	267	"	0.012	Q	42.18(2)	8.17
102	166	"	0.008	C	43.16	9.15
114	335	ISA	0.010	Q	42.88	8.46
120	240	"	0.008	Q	42.39	7.98
<b>T=360°C</b>						
115	335	SA	0.004	Q,K,C	39.39	5.41
121	479	"	"	Q	39.70(2)	5.72
131	484	"	"	Q	38.84	4.87
110	281	"	0.003	C	39.66	5.68
116	335	ISA	0.004	Q	39.54	5.14
122	479	"	0.003	Q	39.68	5.29
132	484	"	"	Q	39.66(2)	5.26
<b>T=465°C</b>						
105	165	SA	0.0005	Q,K	37.30	3.34
111	238	"	"	Q	37.61(2)	3.65
112	238	"	0.0003	Q	37.79(2)	3.83
155	268	"	"	Q	37.82	3.86
129	468	"	0.0002	C,K	37.62	3.66
124	263	ISA	0.0001	C	37.59	3.30

\* SA = untreated silicic acid; ISA = ignited silicic acid

+ sodium carbonate solution molar concentration

\*\* Q = quartz, C = cristobalite and K = silica K

Major phases quoted first.

Brackets indicate duplicate analyses.

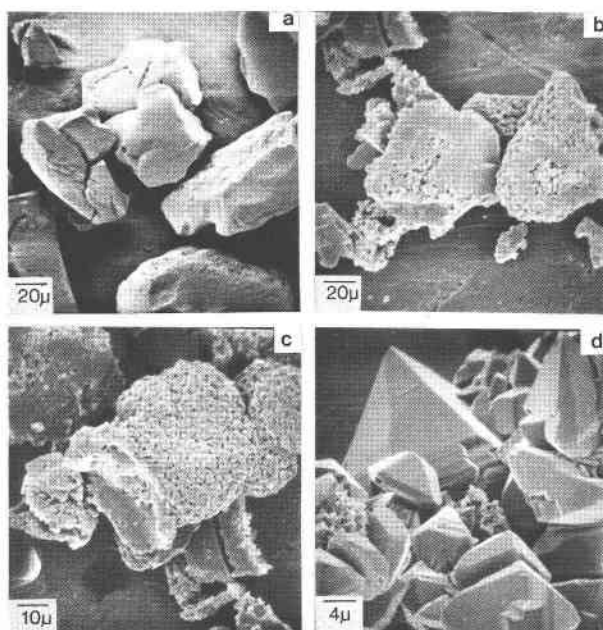


Fig. 5. Scanning electron micrographs illustrating the growths of cristobalite and quartz. (a) Silicic acid reagent; (b) cristobalite crystals packed together in a grain whose morphology resembles the reagent; (c) as B; (d) bipyramidal quartz crystals, characterized by striations parallel to the basal section.

(1978). Their use of high-pressure equilibration techniques, a two-directional approach to equilibrium using  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  partitioning, and direct analysis of water samples has contributed toward a highly sophisticated study of this intriguing problem.

#### Temperature-dependence of $^{18}\text{O}$ partition between quartz and water

The mean fractionation factors at each temperature (from all experiments—including intermediates) are plotted in Figure 6. The points show a slight concave upward curvature with respect to the  $10^6 \times T^{-2}$  axis, but may be approximated by the linear equation defined by least-squares regression:

$$10^3 \ln \alpha (\text{SiO}_2\text{-H}_2\text{O}) = 3.05 \times 10^6 T^{-2} - 2.09$$

At  $360^\circ$  and  $465^\circ\text{C}$  there is good evidence that the mean data points represent at least a close approach to isotopic equilibrium, but some question remains as to the validity of this proposal at  $265^\circ\text{C}$ . This curve may be compared with two other calibrations obtained at temperatures less than  $500^\circ\text{C}$  (Clayton *et al.*, 1972; Matsuhisa *et al.*, 1976, 1978). For the purpose of comparison, the former calibration has been recalculated for water analysis using a  $\text{CO}_2\text{-H}_2\text{O}$  fractionation factor of  $\alpha (25^\circ\text{C}) = 1.0412$  (rather than

1.0407). The studies of Matsuhisa *et al.* (1976, 1978) used direct fluorination in water analyses. The  $200^\circ\text{-}500^\circ\text{C}$  fractionation data of Clayton *et al.* (1972) give the line

$$10^3 \ln \alpha = 3.38 \times 10^6 T^{-2} - 2.90$$

and the three data points of Matsuhisa *et al.* (1976) at  $300^\circ$ ,  $400^\circ$  and  $500^\circ\text{C}$  together with their point  $10^3 \ln \alpha = 9.0$  at  $250^\circ\text{C}$  (Matsuhisa *et al.*, 1978) define the line

$$10^3 \ln \alpha = 3.31 \times 10^6 T^{-2} - 3.26$$

All three curves are plotted in Figure 6. Within the temperature range of this study, all curves give reasonably similar fractionation factors. Although a  $\text{CO}_2\text{-H}_2\text{O}$  fractionation factor of  $\alpha (25^\circ\text{C}) = 1.0412$  has been used in water analyses (according to the suggestion of Friedman and O'Neil, 1977), it can be noted that use of a factor of 1.0407 would significantly improve the correspondence between the vari-

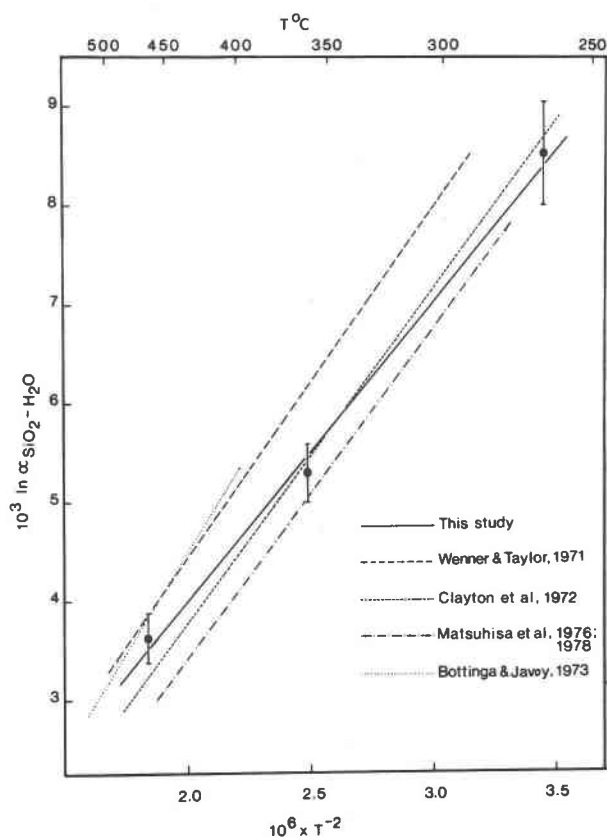


Fig. 6. Oxygen isotope fractionation curves between  $\text{SiO}_2$  and  $\text{H}_2\text{O}$  in the temperature range  $250\text{-}500^\circ\text{C}$ . For details of curves see text. Data points and error bars represent mean fractionation factors and standard deviations, respectively. Standard errors of the mean are approximately one half of the indicated error bars.

ous sets of data. Extrapolation of our line to 0°C gives a fractionation factor of 38.8. This compares reasonably well with a factor of 39.0 deduced by Knauth and Epstein (1975) and a factor of 39.9 deduced from the data of Labeyrie (1974). We do not consider that our equation supersedes the two earlier calibrations; rather it confirms their general validity.

In Figure 6 we have plotted a curve given in Wenner and Taylor (1971), obtained from partial exchange data, and a limited extrapolation of the Bottinga and Javoy (1973) quartz–water equation. The significant differences between the fractionation factors given by these two curves and the three lower curves is evident. The tendency for partial exchange methods to give high fractionation factors relative to complete exchange techniques has been established in several studies (O'Neil *et al.*, 1969; Clayton *et al.*, 1972; Matthews and Katz, 1977). Because of the errors inherent in the partial exchange procedures, obvious weight should be given to results obtained from complete (*i.e.* 100 percent) exchange experiments. This does not resolve the discrepancy with Bottinga and Javoy's (1973) interpretation, though we may note that a similar disagreement has been found between their theoretical approach and experimental data for the rutile–water system (Matthews *et al.*, in preparation).

Though our data provide no conclusive resolution of the differences among quartz–water calibrations, they do provide positive support for previous experimental complete exchange studies. We may finally return to the fundamental question of whether isotopic equilibrium is established and preserved between minerals in igneous and metamorphic rocks, or if retrograde kinetically-controlled re-equilibration of isotopes commonly occurs. Bottinga and Javoy (1975) and Deines (1977) have made extensive analyses of oxygen isotope distributions amongst mineral triplets in igneous and metamorphic rocks. However, whereas the former used their theoretically-based equations in the analysis, Deines employed experimentally-calibrated fractionations. Their conclusions correspondingly differ. Bottinga and Javoy (1975) concluded that a great majority of igneous and metamorphic rocks, for which three or more minerals were analyzed, preserved a state of isotopic equilibrium. In contrast, Deines (1977), although observing regularities in  $^{18}\text{O}$  fractionations suggesting frequent approach to equilibrium, concluded that only in a small fraction of mineral triplets were the fractionations compatible with isotopic equilibrium. Our data support this latter conclusion.

## Appendix

### Oxygen isotope exchange during crystal growth—the problem of solution boundary layers

Crystal growth is described using the sequential model: (1) diffusion of solute molecules through a supersaturated solution to the growth surface; (2) adsorption of solute molecules on the surface; (3) diffusion of solute across the crystal surface; and (4) incorporation of adsorbed molecules at kink sites. Processes (1)–(4) are accompanied by desolution. Volume diffusion of ions to the crystal surface is assumed to be the critical rate process.

Most relevant to the present discussion are the existence of  $^{18}\text{O}$  concentration gradients existing in the solution layer adjacent to the growing crystal, as illustrated in Figure A1. The layer is bounded on one side by the crystal surface and on the other by the condition  $(^{18}\text{O})^{\text{B}} = (^{18}\text{O})^{\text{L}}$ , in which the superscripts B and L refer to the boundary layer and bulk solution respectively and the brackets indicate concentrations. If diffusion in the boundary layer is rapid compared with oxygen isotope exchange between solute ions and solvent, the equilibrium situation is:

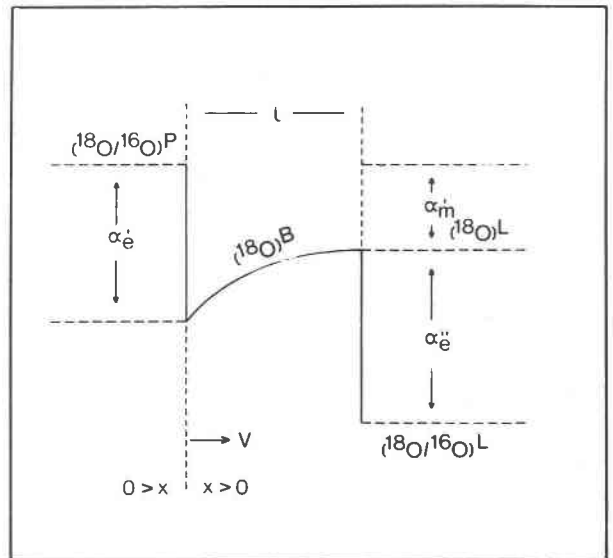


Fig. A1. Steady-state solution boundary layer model defining  $^{18}\text{O}$  concentration gradients adjacent to a growing crystal surface assuming  $\alpha_e > \alpha_e' > 1$ . For definition of  $\alpha_e$ ,  $\alpha_m$ ,  $\alpha_e'$ ,  $V$ ,  $(^{18}\text{O})^{\text{B}}$ ,  $(^{18}\text{O})^{\text{L}}$  and  $l$ , see text. The positional coordinates move with crystal–solution interface (all solid is at  $x < 0$ ; all solution at  $x > 0$ ).  $\alpha_e''$  is the equilibrium fractionation factor between solute ions and solvent ( $\alpha_e' \cdot \alpha_e'' = \alpha_e$ ) and  $\alpha_m'$  is the real (measured) fractionation factor between the precipitating solid and solute ions in the bulk solution ( $\alpha_m' \cdot \alpha_e'' = \alpha_m$ ). Full steady-state conditions for the model are detailed in Delves (1975).

$$\alpha_e = ({}^{18}\text{O}/{}^{16}\text{O})^{\text{P}}/({}^{18}\text{O}/{}^{16}\text{O})^{\text{I}} \quad (\text{A1})$$

where superscript I refers to the solute ions at the crystal-boundary layer interface and P refers to the precipitating solid. If  $({}^{18}\text{O})^{\text{L}}$  is taken to be time-independent, a steady-state differential equation can be written for the diffusion of  ${}^{18}\text{O}$  species to the crystal surface:

$$D \cdot d^2({}^{18}\text{O})/dx^2 - V \cdot d({}^{18}\text{O})/dx = 0 \quad (\text{A2})$$

where D is the diffusion coefficient of  ${}^{18}\text{O}$  species in solution and V is the velocity of the coordinate system which can be equated with a linear rate of crystal growth. If bulk flow in the solution is sufficient to keep  $({}^{18}\text{O})^{\text{B}} = ({}^{18}\text{O})^{\text{L}}$  at  $x = \iota$  where  $\iota$  is the width of the boundary layer (Nernst approximation, cf. Delves, 1975) the solution to equation (A2) can be written

$$\alpha_m = \alpha_e / [\alpha_e' + (1 - \alpha_e') \cdot \exp(-V\iota/D)] \quad (\text{A3})$$

in which  $\alpha_m$  is the measured fractionation factor

$$\alpha_m = ({}^{18}\text{O}/{}^{16}\text{O})^{\text{P}}/({}^{18}\text{O}/{}^{16}\text{O})^{\text{L}}$$

Theory indicates that  $\alpha_e' > 1$ . The precursor solute ions lack the particular lattice vibrations of the solid which will contribute positively to the isotope partition function ratio (O'Neil *et al.*, 1969; McCrea, 1950; Bottinga, 1968), and experimental studies support this conclusion (McCrea, 1950; Lloyd, 1968). If  $\alpha_e' > 1$  then  $\alpha_e > \alpha_m$ . As the crystal growth rate increases,  $\alpha_m$  approaches the fractionation between the solute ions and solvent in the bulk solution ( $\alpha_e'/\alpha_e'$ ); with decrease in the crystal growth rate,  $\alpha_m \rightarrow \alpha_e$ .

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