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Oxygen isotope fractionation between rutile and water and geothermometry of metamorphic eclogites

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SUMMARY. Oxygen isotope fractionation between rutile and water has been studied from 300 °C to 700 °C, $P_{H_2O} = 1$ kb, using aqueous oxidation of titanium metal as the equilibration reaction. The mechanism of rutile formation (which is critical to the assessment of isotopic equilibrium) is an 'armouring' reaction in which rutile grows around grains of titanium metal by solution-precipitation processes. Mean fractionation factors expressed as $10^3 \ln \alpha_{TiO_2\text{-}H_2O}$ obtained in the present study are:

-6.20 ± 0.23 ‰ at 304 ± 5 °C
-6.64 ± 0.27 ‰ at 405 ± 6 °C
-6.11 ± 0.16 ‰ at 508 ± 6 °C
-4.45 ± 0.28 ‰ at 608 ± 6 °C
-3.38 ± 0.15 ‰ at 698 ± 6 °C.

These data agree with those obtained at temperatures above 500 °C by Addy and Garlick (1974) but do not accord with theoretical predictions by Bottinga and Javoy (1973). A minimum in the calibration curve $10^3 \ln \alpha$ versus $10^6 T^{-2}$ occurs between 300 °C and 500 °C but from 500 °C to 700 °C ^{18}O fractionation between rutile and water may be expressed by the equation:

$$10^3 \ln \alpha = -(4.72 \pm 0.40) 10^6 T^{-2} + (1.62 \pm 0.53).$$

Oxygen isotope analyses of rutile and quartz from metamorphic eclogites and schists from the Tauern Window, Austria, yield isotopic temperatures at about 550 °C in agreement with results obtained on similar rocks from the Sesia Zone (Western Alps, Italy) and elsewhere by other workers. Petrologic studies indicate that the latest metamorphism of the Tauern eclogites reached about 450 °C. Thus the measured partitions of ^{18}O between rutile and quartz indicating temperatures around 550 °C have been inherited from an earlier metamorphic event.

ANATASE, brookite, and rutile, the polymorphs of TiO_2, are common accessories in igneous, metamorphic, and sedimentary mineral assemblages. Rutile, the high-temperature polymorph, is potentially very useful in oxygen isotope geothermometry because $\delta^{18}O$ determinations (Vogel and Garlick, 1970) indicate that ^{18}O fractionations between silicates, especially quartz, and rutile are relatively large. Thus experimental errors in the determination of $\delta^{18}O$ values may be small in comparison with the differences in $\delta^{18}O$ values (i.e. differences in ^{18}O contents) between phases which are directly related to temperature if the phases formed in equilibrium.

Addy and Garlick (1974) presented the following experimental calibration of the temperature dependence of ^{18}O fractionation between rutile and water from 575 to 775 °C:

$$10^3 \ln \alpha_{TiO_2\text{-}H_2O} = -4.1(10^6 T^{-2}) + 0.96$$

where T is the absolute temperature and α is the isotopic fractionation factor defined as $\alpha = (^{18}O/^{16}O)_{TiO_2}/(^{18}O/^{16}O)_{H_2O}$. Note that $\Delta_{TiO_2\text{-}H_2O} = \delta^{18}O_{TiO_2} - \delta^{18}O_{H_2O} \cong 10^3 \ln \alpha_{TiO_2\text{-}H_2O}$, and that all ^{18}O analyses are reported relative to the SMOW (Standard Mean Ocean Water) standard in δ notation in per mil (‰) where:

$$\delta^{18}O = [(^{18}O/^{16}O_{\text{sample}} - {^{18}O}/^{16}O_{\text{standard}})/(^{18}O/^{16}O_{\text{standard}})] \times 10^3.$$

However, a reappraisal of the temperature calibration of ^{18}O fractionation in rutile is necessary for two reasons. First, Addy and Garlick's calibration conflicts with theoretical predictions by Bottinga and Javoy (1973). The latter authors have calculated that minerals whose maximum vibrational frequencies do not exceed c. 1000 cm^{-1} should give ^{18}O fractionations with water from 500 to 800 °C according to the equation:

$$10^3 \ln \alpha = A(10^6 T^{-2}) - 3.70$$

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where A is a numerical constant. The maximum vibrational frequency of rutile is *c.* 826 cm^{-1} (Katiyar and Krishnan, 1967), but it is impossible to constrain the experimental data of Addy and Garlick (1974) to fit Bottinga and Javoy's equation. Secondly, Addy and Garlick (1974) used recrystallization of *amorphous* TiO_2 as the method of calibrating ^{18}O fractionations. In syntheses of this kind rapid crystallization of rutile during heating up of reaction vessels (Clayton *et al.*, 1972; Matthews, 1976*a*), formation of metastable intermediate phases (Matthews, 1976*b*), use of the partial ^{18}O exchange method, and the possibility of kinetic ^{18}O fractionations depending on the rate of crystallization (Matthews and Beckinsale, 1979) may all influence the correct determination and inference of oxygen isotope equilibrium. Addy and Garlick (1974) stated that 'It should be remembered that our starting material was amorphous TiO_2 and that we cannot be absolutely confident that this equation represents fractionation under isotopic equilibrium conditions until total exchange is achieved between water and initially crystalline rutile'.

Experimental methods

Addy and Garlick (1974) demonstrated that direct ^{18}O exchange between crystalline rutile and water occurs too slowly at 1 kb to enable determination of accurate fractionation factors by isotopic exchange experiments. We report here studies of ^{18}O fractionation between rutile and water from 300 to 700 °C, $P_{H_2O} = 1$ kb, using synthesis of rutile by aqueous oxidation of titanium metal under controlled kinetics as the ^{18}O equilibration reaction. The reaction is:

$$\text{Ti(metal)} + 2H_2O \rightarrow TiO_2 + 2H_2.$$

All syntheses were performed in sealed Ag/Pd capsules, which allow product hydrogen to diffuse out, maintained at 1 kb pressure within conventional cold-seal hydrothermal apparatus. A typical charge consisted of 40 mg fine titanium metal powder (see Table I) and about 350 to 600 mg of solution—either pure water or dilute hydrochloric acid. Solutions enriched and depleted in ^{18}O were used to provide a test of the precision of the analytical methods. Analyses of the solutions artificially enriched in ^{18}O (Table I) have been reported by Matthews (1976*a*) and Matthews and Beckinsale (1978). The ^{18}O-depleted water was a sample of natural precipitation collected by R. D. B. from Jones Pass, Colorado. Analyses of this water by reaction with guanidine hydrochloride (Boyer *et al.*, 1961) and by the CO_2-H_2O equilibration procedure (Epstein and Mayeda, 1953) using a fractionation factor $\alpha^{25\,°C}_{CO_2-H_2O} = 1.0412$ (O'Neil *et al.*, 1975) gave average $\delta^{18}O$ values of -21.74 ‰ and -22.05 ‰, respectively. A mean value of -21.9 ‰ was adopted. The isotopic composition of acid starting solutions was calculated by material balance from an analysis of -6 ‰ for a concentrated hydrochloric acid solution and the above $\delta^{18}O$ values for enriched and depleted waters, which were used as diluents. The solid products of the synthesis were examined by reflected light and scanning electron microscopy, and analysed using X-ray diffraction and an electron microprobe. For synthesis experiments at 300 °C and 500 °C reaction progress (see Table I) was established by dissolving unreacted titanium metal from weighed aliquots of the product in 3 M sulphuric acid and analysing for titanium spectrophotometrically.

Oxygen isotope analyses were performed on a mass spectrometer described by Beckinsale *et al.* (1973), which is ideal for calibration studies of this kind because the corrections to measured $^{18}O/^{16}O$ ratios for instrumental factors are very small, and thus large differences in $^{18}O/^{16}O$ ratios may be determined without significant error magnification. Oxygen was extracted from rutile by reaction with bromine pentafluoride (Clayton and Mayeda, 1963) and quantitatively converted to carbon dioxide for mass spectrometric analysis by reaction with hot graphite using a platinum catalyst. The experimental data are summarized in Table I and figs. 1–3.

Discussion

Mechanism of rutile formation. It is evident from the data in Table I that the rate of formation of rutile by aqueous oxidation of titanium metal increases as a function of $[H^+]$ and temperature. Indeed, below 500 °C in pure water the oxidation reaction is so slow that it is impossible to synthesize rutile in reasonable experimental times. In our syntheses rutile is the only titanium dioxide phase observed. At 300 °C it is off-white in colour and with increasing temperature it becomes more yellow until a lemon-yellow coloured product is obtained at 700 °C. Electron microprobe analyses indicate that product rutile is chemically homogeneous with a composition close to stoichiometric TiO_2. Microscopic examination in reflected light of grains of products in the intermediate stages of reaction always reveals a central core of unreacted titanium metal. Thus the oxidation reaction is of an 'armouring' type in which titanium is progressively replaced and surrounded by rutile. Classical oxidation theory predicts that rutile growth results from the inward diffusion of oxygen and counter diffusion of titanium ions. However, from

TABLE I

Run no.‡	Time (hrs.)	Solutions		Titanium grain size (μm)	Solid products		δ^{18}O‰‡ rutile	$10^3 \ln \alpha_{TiO_2\text{-}H_2O}$ $\pm 2 \times$ SE
		Molar* strength	δ^{18}O‰ (initial)		Mineralogy†	Mole fraction rutile		
$T = 304 \pm 5$ °C								
114	1.5	0.5	33.6	42-58	Ti, Ru	0.10		
105	4.5	0.5	33.6	42-58	Ti, Ru	0.20		
75	40	0.5	33.6	42-58	Ti, Ru	0.40		
93	211	0.5	33.6	42-58	Ru, Ti	0.60	28.0	−5.7
99	670	0.5	33.6	42-58	Ru, Ti	0.90	27.9	−5.8
112	1008	0.5	33.6	42-58	Ru		27.7(3)	−6.1
63	504	0.5	32.2	30-42	Ru, Ti?		25.9	−6.5
100	670	0.5	−21.3	42-58	Ru, Ti		−27.2(2)	−6.3
113	1008	0.5	−21.3	42-58	Ru		−27.5(3)	−6.7
95	211	0.5	33.6	58-112	Ru, Ti		27.4	−6.3
123	1.5	1.0	32.3	58-112	Ti, Ru(S)			
94	211	1.0	32.3	58-112	Ru		25.9	−6.5
1008	1008	1.0	−20.8	52-112	Ru		−26.3	−5.9
							Mean =	−6.20 ± 0.23
$T = 405 \pm 6$ °C								
124	1.5	0.25		42-58	Ti, Ru(S)			
90	692	0.25	34.2	42-58	Ru, Ti		28.0(2)	−6.4
83	1800	0.25	34.2	42-58	Ru, Ti(S)		27.7(2)	−6.7
104	672	0.25	−21.6	42-58	Ru, Ti(S)		−28.4	−7.3
70	238	0.4	32.5	42-58	Ru, Ti(S)		25.8	−6.8
125	1.5	0.5		42-58	Ti, Ru(S)			
58	551	0.5	32.2	30-42	Ru, Ti(S)		26.1	−6.3
103	672	0.5	33.6	42-58	Ru		27.4(2)	−6.3
102	672	0.5	−21.3	42-58	Ru		−27.6	−6.7
							Mean =	−6.64 ± 0.27
$T = 508 \pm 6$ °C								
156	1.5	W		42-58	Ti, Ru	0.05		
79	40	W		42-58	Ti, Ru	0.40		
71	190	W	33.5	42-58	Ru, Ti	0.75	27.4	−6.3
85	410	W	34.9	42-58	Ru, Ti	0.90	28.9	−6.1
12	619	W	33.5	42-58	Ru, Ti	0.95	27.8	−5.8
11	619	W	33.5	42-58	Ru, Ti(S)		27.6(2)	−6.1
13	619	W	33.5	42-58	Ru, Ti(S)		27.4	−6.3
109	1056	W	34.9	58-112	Ru		29.2(2)	−5.8
87	410	W	−21.9	58-112	Ru, Ti		−27.5	−6.1
110	1056	W	−21.9	58-112	Ru		−27.8	−6.4
							Mean =	−6.11 ± 0.16
$T = 608 \pm 6$ °C								
163	1.5	W		42-58	Ti, Ru(S)			
31	145	W	33.5	42-58	Ru		29.1	−4.6
30	145	W	33.5	58-112	Ru		29.4(3)	−4.2
72	185	W	33.5	58-112	Ru		29.2	−4.5
98	212	W	34.9	58-112	Ru		30.3(2)	−4.7
135	306	W	34.9	58-112	Ru		30.2	−4.8
136	306	W	−21.9	58-112	Ru		−25.4	−3.9
							Mean =	−4.45 ± 0.28
$T = 698 \pm 6$ °C								
115	168	W	34.9	210-325	Ru		31.6	−3.5
117	168	W	34.9	210-325	Ru		31.7	−3.3
116	145	W	−21.9	210-325	Ru		−24.8(3)	−3.2
118	168	W	−21.9	210-325	Ru		−25.0	−3.5
							Mean =	−3.38 ± 0.15

Rutile standard (Australian detrital concentrate)

yield %	99	103	102	100	100	99	96	96	99		
δ^{18}O	7.00	6.78	6.82	7.21	6.88	7.13	6.74	6.75	6.57	Mean =	6.88 ± 0.14

* Molar strength of HCl solution. W refers to water.

† Phases identified by X-ray diffraction, scanning electron microscope, and fluorination yields. (S) indicates a phase to be present in small quantities ($\leqslant 20\%$).

‡ Number of replicates given in parentheses.

a knowledge of the diffusion coefficient of oxygen in rutile $D = 0.017 \exp(-66 \text{ kcal}/RT)$ (Lees *et al.*, 1971) and the Einstein equation which relates the mean penetration distance (Px) of a diffusing particle to its diffusion coefficient (D) and time (t), i.e. $Px = (2Dt)^{\frac{1}{2}}$, it is clear that such a growth mechanism is at least four orders of magnitude too slow to account for the rate of formation of rutile observed in our experiments.

Scanning electron microscopy reveals that the first-formed rutile consists of small euhedral to subhedral crystals embedded in a matrix of extremely fine crystals on the surfaces of grains of titanium. As the reaction progresses the surface crystals grow until the final rutile product consists of crystals larger than those formed initially, and a matrix of small anhedral crystals (fig. 1A, B). Product rutile crystals formed at 304 °C and 405 °C have pyramidal habits (fig. 1A) but at temperatures of 508 °C and above crystals with tabular habits are formed (fig. 1B). The sequence of morphological features during crystal growth must result from solution-precipitation processes. However, it is not clear whether the large rutile crystals grow from dissolution and reprecipitation of the smaller rutile crystals or by transport of titanium ions from the titanium-solution interface within grain interiors. The method of Martin and Fyfe (1970) can be used to discriminate between reaction kinetics controlled by interfacial processes, such as dissolution of titanium metal and reaction kinetics controlled by a diffusion process, such as transport of solution ions through an armouring oxide layer. The rates of reaction in these two general cases are described by the following equations:

$$K_{\text{I}}t = (1-(1-f)^{\frac{1}{3}}) = 0.206(t/t_{0.5})$$

for interfacial process control where f is the fractional extent of rutile formation, t is time, $t_{0.5}$ is the time for 50 % rutile formation and K_{I} is a constant; and

$$K_{\text{D}}t = (1-(1-f)^{\frac{1}{3}})^2 = 0.0426(t/t_{0.5})$$

for diffusion process control where K_{D} is a constant and the other symbols are defined above. Both equations neglect nucleation phenomena which is justified in relation to the present studies because no induction times for rutile growth are observed and the initial stages of reaction show very large numbers of small rutile crystals growing on titanium surfaces. The data for the kinetics of rutile formation at both 304 °C and 508 °C are plotted as f versus ($t/t_{0.5}$) in fig. 2. Both sets of data plot close to the curve representing the second equation above, indicating that diffusion-related processes dominate the reaction rate controlling mechanism. Most probably, since solid state diffusion has been shown to be too slow to account for the observed growth rate of rutile, the diffusion process in the present case is a solution transport process such as ionic diffusion.

Oxygen isotope fractionation. The oxygen isotope fractionation data have been summarized as mean fractionation factors at each experimental temperature in Table I and $10^3 \ln \alpha_{\text{TiO}_2\text{-H}_2\text{O}}$ is plotted

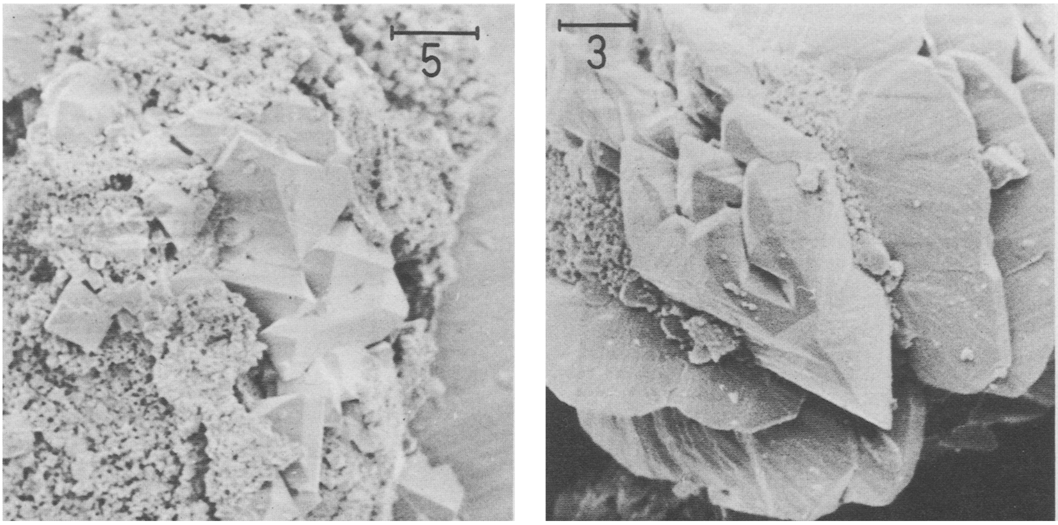
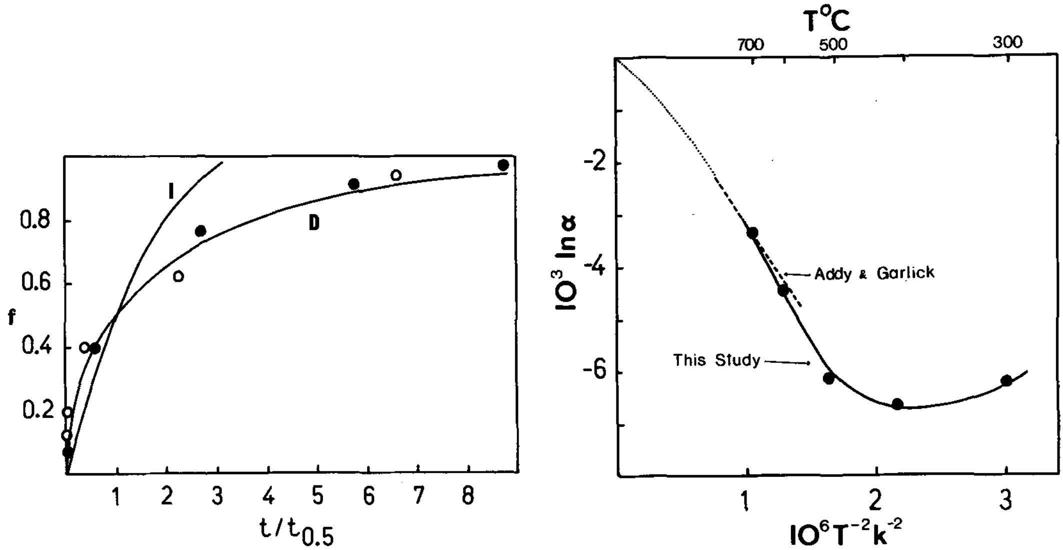


FIG. 1. Scanning electron micrographs of rutile grains. (A, *left*). Grain at 304 °C, showing euhedral crystals embedded within a matrix of extremely fine crystals. (B, *right*). Portion of a grain at 508 °C, showing larger tabular crystals with re-entrant angles prominent. Lines indicate scale in microns.



FIGS. 2 and 3: FIG. 2 (*left*). Plot of experimental *f*, the K_It and K_Dt functions, against the reduced time scale ($t/t_{0.5}$). The solid circles represent experimental runs at 305 °C, using 0.5M HCl and the open circles runs at 508 °C using water. FIG. 3 (*right*). Plot of mean fractionation factors against 10^6T^{-2}. Plotted for comparison is the rutile-water curve of Addy and Garlick (1974). The fine dotted line (*top left*) represents a schematic high-temperature extrapolation of our curve according to the model of Stern *et al.* (1968), fig. 2D.

against 10^6T^{-2} in fig. 3. With the possible exception of the 'triple isotope' method recently developed (Matsuhisa *et al.*, 1978) it is extremely difficult to provide proof of attainment of equilibrium in any calibration of oxygen isotope fractionation versus temperature. The only really convincing argument in demonstrating that isotopic equilibrium had been attained would be that several investigators in different laboratories using different experimental or theoretical approaches had produced the same calibration of oxygen isotope fractionation versus temperature. Moreover, the inference of equilibrium on even this basis could not be regarded as formal proof that equilibrium had been attained. The following observations do favour inference of equilibrium in the present experiments: initial reaction during the heating up stage is minimal; the slow rates of formation of rutile make it unlikely that any kinetic isotope fractionation would be significant; and, most important, as demonstrated above rutile growth occurs through solution-precipitation processes. Despite these observations the mean fractionation data at 304, 405, and 608 °C have associated errors (two standard errors) up to a factor of two larger than that obtained (± 0.14 ‰) for a rutile standard analysed nine times during the course of these studies (Table I). At present we cannot offer a satisfactory explanation for the increased scatter in the fractionation data at these temperatures, especially since the errors associated with the data at 508 and 698 °C are comparable to that associated with $\delta^{18}O$ determinations on the rutile standard, but it is not surprising that the errors associated with determination of water-rutile fractionations involving $\delta^{18}O$ determinations of both fluid and crystalline products and the process of synthesis should be larger than those associated with only $\delta^{18}O$ determination on a rutile standard.

The mean fractionation data from 508 °C to 698 °C reported here agree reasonably well with those obtained by Addy and Garlick (1974) between 575 and 775 °C. Addy and Garlick (1974) derived the calibration equation $10^3 \ln \alpha_{TiO_2\text{-}H_2O} = -4.1(10^6T^{-2})+0.96$ whereas least squares regression of the data from 508 °C to 698 °C in Table I allowing for the quoted errors in both axes (Williamson, 1968) yields the equation $10^3 \ln \alpha_{TiO_2\text{-}H_2O} = -(4.72 \pm 0.40)10^6T^{-2} + (1.62 \pm 0.53)$. A minimum in the fractionation curve (fig. 3) must occur somewhere between 304 and 508 °C. Such minima have been predicted (Stern *et al.*, 1968) and shown to occur in several calculated fractionation curves (e.g. Onuma *et al.*, 1972; Becker and Clayton, 1976) where the temperature derivatives of the isotopic partition function ratios for the two phases (rutile and water) become equal. Magnetite, which is one of the few minerals naturally more depleted in ^{18}O than rutile, has a maximum ^{18}O fractionation with water at a minimum in the calibration curve $10^3 \ln \alpha$ versus $10^6 T^{-2}$ at about 220 °C (Becker and Clayton, 1976) but for ^{18}O fractionation between most silicates and water the minima in the calibrations occur at temperatures above 800 °C.

Despite uncertainties in the experimental calibration of ^{18}O fractionation between rutile and water versus temperature both the data we present here and those of Addy and Garlick (1974) do not accord with the theoretical prediction of Bottinga and Javoy (1973) that between 500 °C and 800 °C ^{18}O fractionations may be expressed by equations with a constant intercept of the form $10^3 \ln \alpha = A(10^6 T^{-2}) - 3.70$ (as noted above). Although the theoretical basis of Bottinga and Javoy's equation appears to be a reasonable approximation, the systematics of isotopic fractionation are extremely complex and we suggest that the experimental calibration of the temperature dependence of ^{18}O fractionation is a more reliable approach. One widely used experimental technique for calibration of isotopic geothermometers is the so-called 'two directional approach' method in which isotopic exchange occurs between crystalline material (such as rutile) and solutions enriched and depleted in ^{18}O relative to the starting composition of the crystalline solid. The systematics of this approach have been discussed by Northrop and Clayton (1966) and Matthews and Beckinsale (1979). However Addy and Garlick's studies, discussed above, clearly indicate that at 1 kb the rate of ^{18}O exchange between crystalline rutile and water is far too slow to allow this approach to be used as a method of calibration.

Geothermometry of some metamorphic eclogites

Few oxygen isotope data are available for natural mineral assemblages containing rutile; the only extensive studies being those of Vogel and Garlick (1970) and Desmons and O'Neil (1978) on metamorphic eclogites. In order to use the calibration curve for the temperature dependence of ^{18}O fractionation between rutile and water (derived above) to determine isotopic 'temperatures' it must be combined with other mineral-water calibration curves. As noted above ^{18}O fractionations between quartz and rutile in equilibrium are relatively large and are thus also sensitive to small temperature differences within the limits provided by the experimental errors in determining these fractionations. Equations describing approximately linear segments of experimental calibration curves in some mineral-water systems and the derived mineral-mineral calibration equations are set out in Table II.

The calibration equation for the quartz-rutile oxygen isotope geothermometer derived in Table II is slightly different from that given by Addy and Garlick (1974) which is $10^3 \ln \alpha_{SiO_2\text{-}TiO_2} = -2.4 + 6.6(10^6 T^{-2})$. Note that we have corrected this equation so that both the component quartz-water and quartz-rutile calibrations are based on $\alpha^{25\,°C}_{CO_2\text{-}H_2O} = 1.0412$. Application of the equation derived in Table II to the mean ^{18}O fractionation of 6.45 ± 0.05 ‰ between quartz and rutile (Vogel and Garlick, 1970; Addy and Garlick, 1974) from B-type eclogites (i.e. bands and lenses within migmatite gneiss terrains, Coleman *et al.*, 1965) yields an equilibration temperature of 598 ± 2 °C whereas Addy and Garlick's equation yields 590 ± 2 °C. Both temperatures are reasonable from a petrological point of view. Desmons and O'Neil (1978) report oxygen isotope data for minerals separated from C-type eclogites (i.e. lenses within alpine-type metamorphic eclogites) from the Sesia Zone, Western Alps, Italy. The average ^{18}O fractionation between quartz and rutile was determined at 7.00 ± 0.37 ‰ (error one standard deviation after omitting one clearly anomalous result), which corresponds to an isotopic temperature of 574 ± 14 °C using the calibration equation in Table II. The temperature represented by this ^{18}O fractionation was accepted by Desmons and O'Neil (1978) as reflecting at least a close approach to equilibrium for three main reasons: First, it is consistent with the mineral phase relations and the generally accepted view that C-type eclogites form at lower temperatures than B-type eclogites (about 600 °C, see above). Secondly, the range in measured ^{18}O

TABLE II

Quartz-water	$10^3 \ln \alpha = -1.46 + 2.51(10^6 T^{-2})$ from 500–750 °C*
Muscovite-water	$10^3 \ln \alpha = -3.89 + 2.38(10^6 T^{-2})$ from 400–650 °C†
Rutile-water	$10^3 \ln \alpha = +1.62 - 4.72(10^6 T^{-2})$ from 500–700 °C‡
Quartz-rutile	$10^3 \ln \alpha = -3.08 + 7.23(10^6 T^{-2})$ from 500–700 °C
Quartz-muscovite	$10^3 \ln \alpha = +2.43 + 0.13(10^6 T^{-2})$ from 500–650

* Clayton *et al.* (1972) recalculated using $\alpha^{25\,°C}_{CO_2\text{-}H_2O} = 1.0412$.

† O'Neil and Taylor (1969).

‡ This work.

fractionations between quartz and rutile is less than 1 ‰ despite a range in $\delta^{18}O$ values for the mineral separates of about 2 ‰ and there is no correlation between $\delta^{18}O$ values and $\Delta_{SiO_2\text{-}TiO_2}$. In other words the ^{18}O fractionations are essentially constant within a range of host rock compositions. Thirdly, ^{18}O fractionations between quartz and phengite yield an average isotopic temperature of 540 ± 20 °C using the quartz–muscovite calibration of Bottinga and Javoy (1973). These quartz–rutile and quartz-phengite isotopic temperatures are concordant within the limits of error (quoted above at one sigma). The problem of whether this calibration of the temperature dependance of ^{18}O fractionation between quartz and phengite is appropriate will be discussed below.

During the course of the present calibration studies we have determined $\delta^{18}O$ values for mineral separates from C-type eclogites from the Tauern Window, Austria. The data are averaged and listed in Table II. The samples were provided by Dr C. Miller who has discussed their metamorphic petrology and chemistry in detail (Miller, 1974). She demonstrated that the rocks have experienced two metamorphic events: First, a high-pressure event to produce eclogite from pre-existing (probably igneous) rocks. The *P*–*T* conditions during this early metamorphism are uncertain because the constraints placed on them by phase relations are not very rigid, but high pressure and a temperature greater than 400 °C are most likely. Secondly, the eclogites and associated rocks were involved in the main Alpine metamorphism for which phase relations indicate a temperature of about 430–70 °C and a pressure, P_{H_2O} = about 4 kb. With the exception of the result for sample number T145, the isotopic temperatures which average 555 ± 14 °C (one standard deviation) derived from the quartz–rutile fractionations in Table III are concordant with those established by Desmons and O'Neil (1978) for C-type eclogites from the Sesia Zone and Vogel and Garlick (1970) for a C-type (? transitional B–C-type) eclogite from Venezuela. This leads us to suggest that these ^{18}O fractionations reflect isotopic equilibrium, or at least a close approach to it, and that they must have been established at some stage during the high-pressure metamorphic event which lead to eclogite formation. It follows that in the Tauern eclogites these ^{18}O fractionations have survived the subsequent Alpine metamorphism without isotopic exchange processes re-establishing equilibrium at the lower temperature of the second metamorphism. A corollary of this conclusion is that the Alpine metamorphism probably did not sustain high water pressures for its entire duration.

A very similar situation has been described by Frey *et al.* (1976) from the Monte Rosa granite on the border of Italy and Switzerland where certain ^{18}O fractionations in optically distinct mineral assemblages of Permian age have survived a mid-Tertiary metamorphism during which other distinct mineral assemblages have developed. There is clearly considerable scope for research into the application of such ^{18}O abundance studies to trace the reaction pathways by which the different components of a metamorphic mineral assemblage have formed (see also O'Neil, 1977).

However the ^{18}O fractionations between quartz and phengite from the Tauern eclogites and associated rocks (Table III) yield isotopic temperatures which are grossly discordant from those derived from quartz-rutile fractionations. It is important to note that in the Tauern eclogites this

TABLE III

Rock type	Sample no.	$\delta^{18}O$ ‰ (SMOW)			Δ_{QR}†	T°C	Δ_{QP}†	T_1 °C	T_2 °C
		Quartz	Rutile	Phengite					
Eclogite	312	8.71	1.74	—	6.97	575	—	—	—
Eclogite	T145	9.33	5.71	6.93	3.62	766	2.40	583	*
Garnet mica schist	T141	12.17	4.78	8.94	7.39	558	3.23	485	130
Eclogite	T235	13.49	5.79	11.04	7.70	546	2.45	576	*
Eclogite	T174	14.92	7.08	—	7.84	541	—	—	—
Mica schist	Ph N	14.97	—	11.90	—	—	3.07	501	178
Mica schist	NN	26.47	—	24.95	—	—	1.52	746	*

† Based on simple subtraction for conformity with the literature.

T_1 °C based on the calibration equation of Bottinga and Javoy (1973).

T_2 °C based on the experimental calibration equation derived in Table II.

* Impossible or absurd isotopic temperature.

discordance occurs whether the quartz-phengite isotopic temperatures are derived from the experimental calibration equation indicated in Table II or from the theoretical calibration of Bottinga and Javoy (1973), in marked contrast to the situation described by Desmons and O'Neil (1978, see above). This strongly suggests that in the Tauern samples phengite has formed or recrystallized during the Alpine metamorphism and in the case of sample T145 which gives an anomalous quartz-rutile fractionation it is possible that quartz and/or rutile have recrystallized as well.

In view of the discordant isotopic temperatures discussed above it is pertinent to consider whether we are using an appropriate calibration equation for fractionations involving phengite. First, there is little or no ^{18}O fractionation between phengite and muscovite and it is justifiable to use a muscovite calibration. Secondly, it should be noted that whereas natural ^{18}O fractionations between rutile and quartz are so large that the choice of numerical constants in the quartz-water calibration equation is not very critical to the derived quartz-rutile calibration equation, in the case of quartz-muscovite the ^{18}O fractionations are so small that the choice of numerical constants in the calibration equations is very critical. Furthermore any small perturbation of ^{18}O fractionations between quartz and muscovite subsequent to equilibration would have a very dramatic effect on calculated isotopic temperatures. All theoretical calibration equations tend to be subject to very large errors (e.g. Kawabe, 1978) because of the complexity of the calculations and the need to make simplifying assumptions. Nevertheless the calibration equations for the quartz-water and muscovite-water systems derived by Bottinga and Javoy (1973) using a theoretical approach do often yield quartz-muscovite isotopic temperatures which are sensible from a petrological point of view. Desmons and O'Neils's (1978) results for the eclogites of the Sesia Zone provide a good example. The data show a small range of quartz-muscovite fractionations, about 0.6‰, despite a range in $\delta^{18}O$ values for quartz of about 3.7‰ which implies that these fractionations reflect some equilibration temperature, and, as noted above, Bottinga and Javoys calibration equation yields isotopic temperatures that are essentially concordant with those derived from quartz-rutile fractionations.

Finally an interesting feature of the data in Table III is the large range of $\delta^{18}O$ values for each mineral phase. In general terms this probably results from isotopic exchange with carbonates, which are abundant constituents of the successions containing the eclogites and associated schists. Sample number NN, for example, is in contact with carbonates. Excluding the data for sample T145 there appears to be a correlation between increasing $\delta^{18}O$ values for quartz and increasing ^{18}O fractionations between quartz and rutile. Although more data are clearly needed to confirm this correlation beyond reasonable doubt it is possible that it is genuine and reflects progressive lowering of the temperature of eclogite formation with increasing P_{CO_2} derived from local ^{18}O-enriched carbonate sequences. The possibility that the fluid phase present during the high-pressure event leading to eclogite formation was rich in CO_2 has been discussed on other grounds by Miller (1974).

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REFERENCES

Addy (S. K.) and Garlick (G. D.), 1974. Oxygen isotope fractionation between rutile and water. *Contr. Mineral. Petrol.* **45**, 119-21.

Becker (R. H.) and Clayton (R. N.), 1976. Oxygen isotope study of a Precambrian banded iron-formation, Hamersly Range, Western Australia. *Geochim. Cosmochim. Acta*, **40**, 1153-63.

Beckinsale (R. D.), Freeman (N. J.), Jackson (M. C.), Powell (R. E.), and Young (W. A. P.), 1973. A 30 cm radius 90° sector double collecting mass spectrometer with a capacitor integrating detector for high precision isotopic analyses of carbon dioxide. *Int. J. Mass Spectrom. Ion Physics*, **12**, 299-308.

Bottinga (Y.) and Javoy (M.), 1973. Comments on oxygen isotopic geothermometry. *Earth Planet. Sci. Lett.* **20**, 250-65.

——— 1975. Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. *Rev. Geophys.* **13**, 401-18.

Boyer (P. D.), Graves (D. J.), Suelter (G. J.), and Dempsey (M. E.), 1961. Simple procedure for the conversion of oxygen of orthophosphate or water to carbon dioxide for oxygen-18 determination. *Anal. Chem.* **33**, 1906-9.

Clayton (R. N.) and Mayeda (T. K.), 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta*, **27**, 43-52.

——O'Neil (J. R.), and Mayeda (T. K.), 1972. Oxygen isotope exchange between quartz and water. *J. Geophys. Res.* **77**, 3057-67.

Coleman (R. G.), Lee (D. E.), Beatty (L. B.), and Brennock (W. W.), 1965. Eclogites and eclogites: their differences and similarities. *Geol. Soc. Am. Bull.* **76**, 483-508.

Desmons (J.) and O'Neil (J. R.), 1978. Oxygen and hydrogen isotope compositions of eclogites and associated rocks from the eastern Sesia zone (Western Alps, Italy. *Contr. Mineral. Petrol.* **67,** 79–85.

Epstein (S.) and Mayeda (T. K.), 1953. The variations in O^{18} content of water from natural sources. *Geochim. Cosmochim. Acta,* **4,** 213–24.

Frey (M.), Hunziker (J. C.), O'Neil (J. R.), and Schwander (H. W.), 1976. Equilibrium-Disequilibrium relations in the Monte Rosa Granite, Western Alps: Petrological, Rb–Sr and Stable Isotope Data. *Contrib. Mineral. Petrol.* **55,** 147–79.

Katiyar (R. S.) and Krishnan (R. S.), 1967. The vibrational spectrum of rutile. *Phys. Lett.* A, **25,** 525–6.

Kawabe (I.), 1978. Calculation of oxygen isotope fractionation in quartz–water system with special reference to the low temperature fractionation. *Geochim. Cosmochim. Acta,* **42,** 613–21.

Lees (D. G.), Calvert (J. M.), and Derry (D. J.), 1971. A technique using resonance capture of protons to study oxygen diffusion in titanium dioxide. In Sherwood (J. N.), Chadwick (A. V.), Muir (W. M.), and Swinton (F. L.) (eds.), *Diffusion Processes.* Gordon and Breach, London, 429–36.

Martin (B.) and Fyfe (W. S.), 1970. Some experimental and theoretical observations on the kinetics of hydration reactions with particular reference to serpentinization. *Chem. Geol.* **6,** 185–202.

Matsuhisa (Y.), Goldsmith (J. R.), and Clayton (R. N.), 1978. Mechanisms of hydrothermal crystallisation of quartz at 250 °C and 15 kilobars. *Geochim. Cosmochim. Acta,* **42,** in press.

Matthews (A.), 1976*a*. Magnetite formation by the reduction of hematite with iron under hydrothermal conditions. *Am. Mineral.* **61,** 927–32.

—— 1976*b*. The crystallisation of anatase and rutile from amorphous titanium dioxide under hydrothermal conditions. Ibid. 419–32.

—— and Beckinsale (R. D.), 1979. Oxygen isotope equilibration systematics between quartz and water. Ibid. **64,** 232–40.

Miller (C.), 1974. On the metamorphism of the eclogites and high-grade blueschists from the Penninic Terrane of the Tauern Window, Austria. *Schweiz. Mineral. Petrogr. Mitt.*, Band 54, 2/3, 371–84.

O'Neil (J. R.), 1977. Stable Isotopes in Mineralogy. *Phys. Chem. Minerals,* **2,** 105–23.

—— and Taylor, Jr. (H. P.), 1967. The oxygen isotope and cation exchange chemistry of feldspars. *Am. Mineral.* **52,** 1414–37.

—— —— 1969. Oxygen isotope equilibrium between muscovite and water. *J. Geophys. Res.* **74,** 6012–22.

—— —— Clayton (R. N.), and Mayeda (T. K.), 1969. Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.* **51,** 5547–58.

—— Adami (L. H.), and Epstein (S.), 1975. Revised value of the O^{18} fractionation between CO_2 and water at 25 °C. *J. Res. US Geol. Surv.* **3,** 623–4.

Onuma (N.), Clayton (R. N.), and Mayeda (T. K.), 1972. Oxygen isotope cosmothermometer. *Geochim. Cosmochim. Acta,* **36,** 169–88.

Stern (M. J.), Spindel (W.), and Monse (E. U.), 1968. Temperature dependence of Isotope Effects. *J. Chem. Phys.* **48,** 2908–19.

Truesdell (A. H.), 1974. Oxygen isotope activities and concentrations in aqueous salt solutions at elevated temperatures—consequences for isotope geochemistry. *Earth Planet Sci. Lett.* **23,** 387–96.

Vogel (E. D.) and Garlick (G. D.), 1970. Oxygen isotope ratios in metamorphic eclogites. *Contrib. Mineral. Petrol.* **28,** 183–91.

Williamson (J. H.), 1968. Least Squares Fitting of a Straight Line. *Canad. J. Phys.* **46,** 1845–7.

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