

O-isotope variations in a porphyroclastic meta-anorthosite: Diffusion effects and false isotherms

Z. D. SHARP

Institut de Minéralogie et Pétrographie, Université de Lausanne, CH-1015 Lausanne, Switzerland

D. P. MOECHER

Department of Geological Sciences, University of Kentucky, Lexington, Kentucky 40506-0053, U.S.A.

ABSTRACT

A detailed O-isotope study of annealed porphyroclastic meta-anorthosite was performed to assess the degree of postpeak-metamorphic and postshearing reequilibration. Stable isotope and petrologic evidence indicate that the Whitestone anorthosite, Ontario, was infiltrated by an ^{18}O - and CO_2 -rich fluid subsequent to peak Grenville granulite facies metamorphism. Ductile shearing occurred during and following peak metamorphism. Relict igneous plagioclase phenocrysts (An_{60}) occur as coarse-grained porphyroclasts in a fine-grained recrystallized matrix of plagioclase (An_{40}) + hornblende + garnet + scapolite + epidote + ilmenite. The $\delta^{18}\text{O}$ values of mineral fragments as small as 200 μm were analyzed to assess constituents developed at different stages of the rock's history. The $\delta^{18}\text{O}_{\text{SMOW}}$ values (‰) are as follows: porphyroclastic plagioclase = 8.1–8.5 (av. 8.38 ± 0.14 , 2σ); matrix plagioclase = 8.2–9.2 (av. 8.65 ± 0.32); garnet = 6.87 ± 0.02 , $n = 2$; hornblende = 6.44 ± 0.00 , $n = 2$; ilmenite = 1.93 ± 0.18 , $n = 2$. In-situ analyses agree within error but are far more scattered (av. 8.2 ± 0.5). The plagioclase porphyroclasts are isotopically homogeneous, a result of rapid diffusion of $^{18}\text{O}/^{16}\text{O}$ at high T and slow cooling rates.

The theoretical $\delta^{18}\text{O}$ values of all minerals were calculated on the basis of O-volume diffusional considerations using diffusion rate data for both hydrous and anhydrous conditions. The Whitestone data set is in far better agreement with the diffusion data obtained in hydrothermal experiments, indicating that cooling probably occurred in the presence of a hydrous fluid. Similar calculations made for other granulite terranes are generally consistent with cooling under anhydrous conditions. The observed $\delta^{18}\text{O}$ values of all phases from the Whitestone anorthosite yield an erroneous equilibration temperature of 470 ± 30 °C that can be explained by an infinite reservoir model involving postpeak-metamorphic O-isotope exchange with an infinite reservoir of plagioclase. Comparable false isotherms are characteristic of other granulite terranes as well.

INTRODUCTION

The use of an isotherm plot for O-isotope thermometry (Javoy et al., 1970) has become a standard tool for evaluating equilibria among coexisting mineral pairs and for estimating equilibration temperatures (e.g., Javoy, 1977). The isotherm plot, a graphical representation of the $\delta^{18}\text{O}$ values of minerals vs. the temperature coefficient of fractionation, is an extension of the concept that equilibrium among three minerals is demonstrated if two independent, isotopic, temperature estimates agree within experimental error (Clayton and Epstein, 1961). Isotherm plots have also been used to estimate fractionation factors between coexisting phases for which no experimental data are available (Bottinga and Javoy, 1973, 1975). The reliability of this approach has been questioned by Deines (1977), who suggested that most terrestrial samples do not preserve isotopic equilibrium. Retrograde diffusional exchange may explain the partial resetting that can be observed in slowly cooled rocks (Giletti, 1986). If dis-

equilibrium among mineral triplets is common, then the application of the isotherm plot to thermometry and thermometric calibrations is not valid.

In the present study, we investigate the O-isotope variations in coexisting minerals in a high-grade, ductilely recrystallized, scapolite-bearing meta-anorthosite for which the history of fluid-rock interaction is well known from a petrological basis. The anorthosite has been infiltrated by an ^{18}O - and CO_2 -rich fluid at near-peak metamorphic conditions (Moecher et al., 1992). In this study, $\delta^{18}\text{O}$ values of plagioclase porphyroclasts and coexisting phases were determined on a scale of millimeters to sub-millimeters to evaluate the scale of isotopic equilibration that accompanied fluid infiltration and continued during cooling. The validity of isotherm plots is assessed in terms of isotopic variations (or lack of variations) within single crystals and the degree of isotopic equilibrium among coexisting phases. The $\delta^{18}\text{O}$ values of garnet, hornblende, ilmenite, and two generations of plagioclase yield an ap-

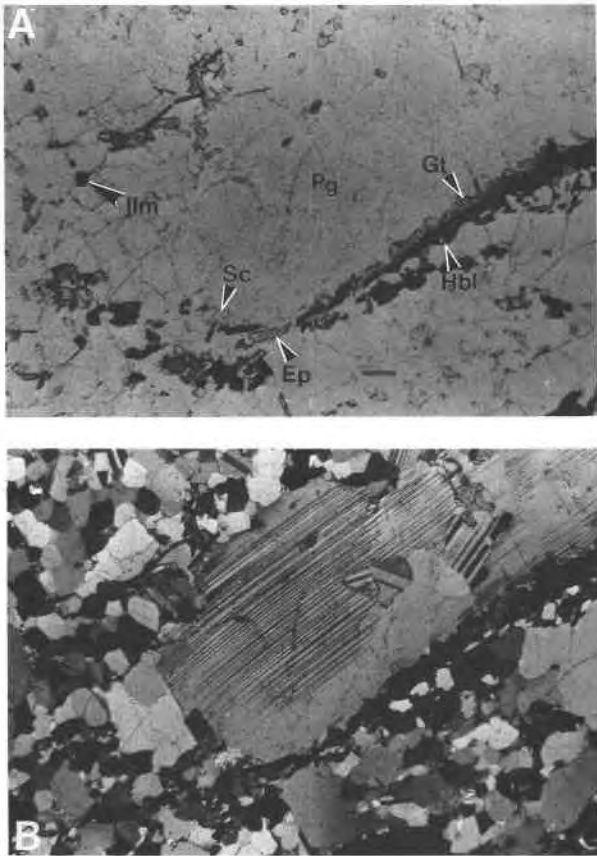


Fig. 1. Photomicrograph of the annealed porphyroclastic texture in meta-anorthosite [(A) plane light, (B) crossed polars; field of view is 6 mm]. A plagioclase porphyroblast (Pg) exhibiting internal subgrain formation is surrounded by a matrix consisting mainly of plagioclase (clear in plane light) with lesser garnet (Gt), hornblende (Hbl), scapolite (Sc), epidote (Ep), ilmenite (Ilm), and biotite (Bt).

parent equilibrium temperature that has no known geological significance but can be explained in terms of retrograde reequilibration by O-diffusional exchange.

SAMPLE DESCRIPTION

The samples are from a Grenville meta-anorthosite of the Central Gneiss belt in southern Ontario, Canada. Ductile deformation and mylonitization occurred during and following the peak of granulite facies metamorphism between 1160 and 1120 Ma (van Breemen et al., 1986; Tucillo et al., 1992; Mezger et al., 1993). The sample is a porphyroclastic gabbroic meta-anorthosite, with centimeter-scale, relict, igneous plagioclase phenocrysts in a matrix of fine-grained (<1 mm in greatest dimension) plagioclase, hornblende, scapolite, epidote, garnet, ilmenite, and quartz (in order of decreasing modal abundance; Fig. 1). In general, plagioclase porphyroclasts in the meta-anorthosite are variably zoned. Porphyroclasts analyzed for this study are approximately An_{58} and An_{53} in com-

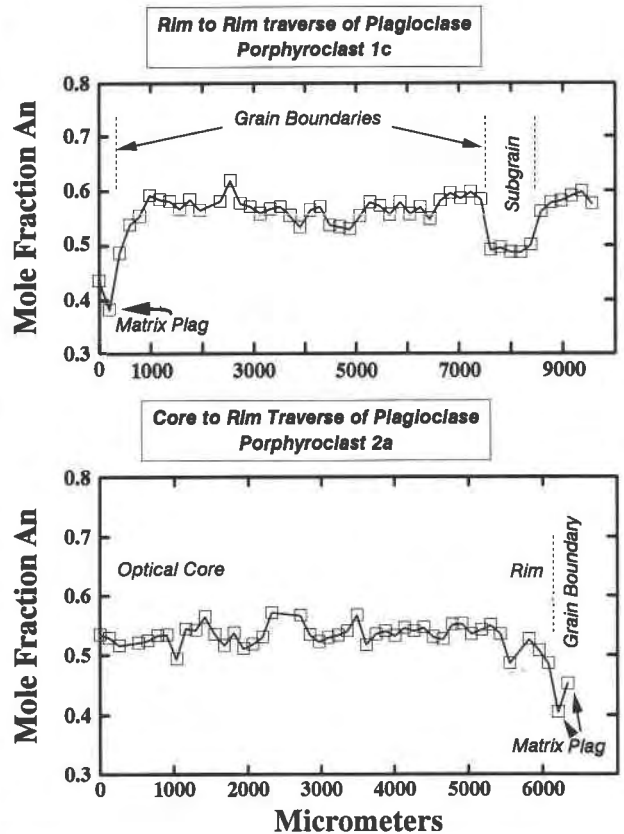


Fig. 2. The core to rim microprobe traverse across two porphyroclasts. Note the difference in composition between porphyroclastic and matrix plagioclase.

position and are homogeneous, with slight normal zoning at their margins (Fig. 2). Matrix plagioclase is typically An_{40} (Fig. 2; also see the compilation of plagioclase compositions from meta-anorthosite in Lamb and Moecher, 1992). The compositional difference resulted from the chemical reaction of calcic plagioclase porphyroclasts and clinopyroxene with an infiltrating CO_2 -rich aqueous fluid phase during recrystallization to form assemblages of calcic scapolite + plagioclase + garnet + hornblende + epidote (Moecher et al., 1992). Recrystallization occurred at 700 ± 50 °C and 10 kbar (Moecher et al., 1988).

The CO_2 that infiltrated the anorthosite was enriched in ^{18}O and was derived from or equilibrated with marble (Moecher et al., 1992). The infiltrating CO_2 increased the $\delta^{18}O$ value of the anorthosite from 6.5‰ for unaltered granulite-facies meta-anorthosite to values of 7–10‰ for variably altered meta-anorthosite. Ductile deformation of the meta-anorthosite during or subsequent to the fluid infiltration resulted in the observed mineralogical textures and compositions.

ANALYTICAL TECHNIQUES AND RESULTS

A doubly polished plate, 200 μm thick, was affixed to double-sided adhesive tape and gently cracked with an

agate pestle to produce fragments as small as 200 μm on a side (O'Neil et al., 1992). Individual fragments were removed from the tape, and their spatial positions were recorded accurately with respect to the original, unbroken plate (Fig. 3). Grains of matrix plagioclase, garnet, hornblende, and ilmenite were also sampled with this technique. Individual grains were reacted with BrF_3 by heating with a CO_2 laser (Sharp, 1990, 1992). O was converted to CO_2 and passed directly into the mass spectrometer.

The plagioclase porphyroclasts are isotopically homogeneous at the submillimeter scale, with a $\delta^{18}\text{O}$ weighted average value (given errors of 0.1‰ analytical uncertainty) of 8.38 ± 0.14 (95% confidence) (Table 1, Fig. 3a, 3b). The more sodic matrix plagioclase is, on average, slightly enriched in ^{18}O relative to porphyroclasts ($\delta^{18}\text{O} = 8.65 \pm 0.32$). Garnet averages 6.87 ± 0.02 , hornblende averages 6.44 ± 0.00 , and ilmenite averages 1.94 ± 0.13 ‰.

In-situ measurements were made by heating a plate, 200 μm thick, with a focused laser. Short, 100-ms pulses were made repeatedly until a hole ~ 200 – 300 μm in diameter was bored through the sample. Reactions were made in a BrF_3 atmosphere at 0.1 bars with a laser power of 6 W. The in-situ data are in good agreement with the mineral-separate data, but the scatter is significantly larger (av. = 8.3 ± 0.5 , 95% confidence given analytical error of 0.4‰; Table 1). The higher degree of scatter in the in-situ data is most likely due to partial reaction and isotopic fractionation in the laser pit and with the surrounding material. The in-situ method has been used successfully for some minerals (quartz: Conrad and Chamberlain, 1992; Kirschner et al., 1993; garnet: Chamberlain and Conrad, 1991), but, apparently, feldspars are too reactive with F for the in-situ technique (see also Elsenheimer and Valley, 1992). The advantages of the microsampling technique over the in-situ technique for this kind of study include (1) complete reaction of mineral phases with BrF_3 ; (2) no interaction with less reactive material near the laser beam (edge effects); (3) experimental yields may be measured; and (4) careful assessment of mineral purity by petrographic inspection can be made prior to analysis. Physical mineral separation is far more time-consuming than in-situ analyses, but it must be considered the method of choice until a more accurate method for in-situ analyses of feldspars is developed.

DISCUSSION

Infiltration by a CO_2 -rich fluid during metamorphism perturbed the isotopic equilibrium of the anorthosite (Moecher et al., 1992). The response to this perturbation was evaluated at two scales: first, by determining variations in the $\delta^{18}\text{O}$ values of single feldspar porphyroclasts, and second, by determining the isotopic fractionation that exists between coexisting phases. Isotopic variations within a single crystal is controlled only by O-volume diffusion, whereas isotopic fractionations between coexisting phases in a single hand specimen are controlled both by grain boundary and by volume diffusion.

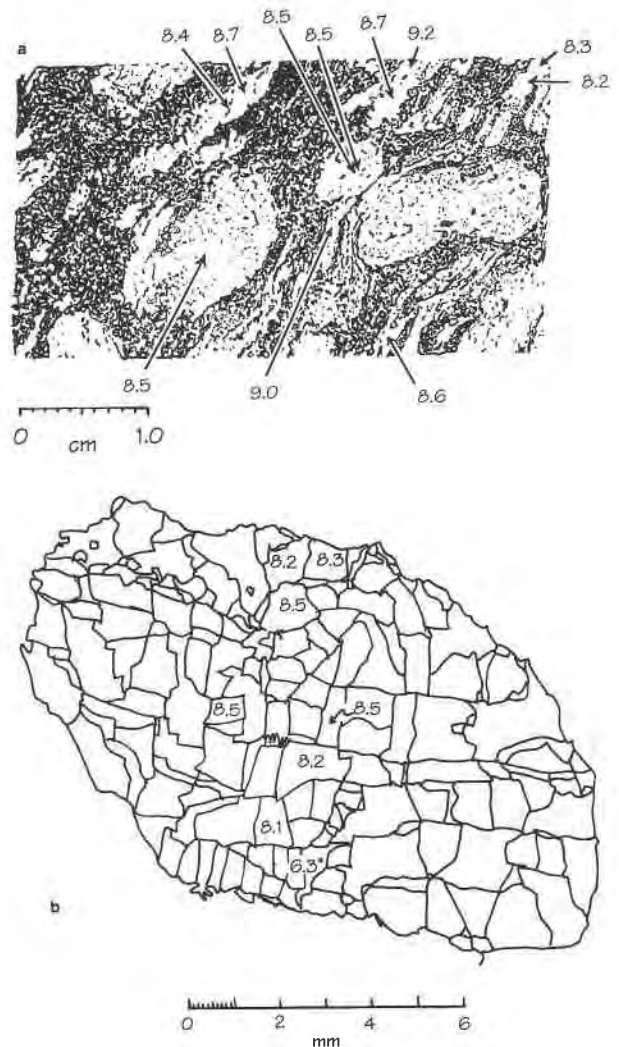


Fig. 3. (a) Illustration of a thick section and O-isotopic composition of samples extracted from the porphyroclastic meta-anorthosite (all values parts per mil, relative to SMOW). The dark areas consist of fine-grained matrix plagioclase with lesser hornblende, garnet, ilmenite, scapolite, and epidote. (b) Sketch of an individual porphyroclast, with sample locations and isotopic values. Starred value is a mixed garnet + feldspar inclusion in the porphyroclast.

Original plagioclase phenocrysts should have a $\delta^{18}\text{O}$ value of 6–7‰. Infiltration of the CO_2 fluid from the surrounding marbles has increased the average $\delta^{18}\text{O}$ value of the plagioclase porphyroclasts up to 10‰ (Moecher et al., 1992). In the absence of deformation and recrystallization, the plagioclase crystals would exchange O with the infiltrating fluid by volume diffusion. The isotopic diffusion profiles for a plagioclase porphyroclast 4 mm in diameter are calculated as a function of time (Fig. 4). O diffusion rates in feldspars are strongly dependent on the composition of the exchange fluid. Diffusion rates determined from exchange experiments with anhydrous fluids (O_2 or CO_2) are orders of magnitude slower than those

TABLE 1. O-isotope results

Sample no.	$\delta^{18}\text{O}$ (‰ vs. SMOW)	Weight (mg)	CO_2 recovered (μm)	Comments
Plagioclase porphyroclast				
8	8.48	1.02	n.d.	porphyroclast, near edge
9	8.34	1.10	n.d.	porphyroclast at edge
10	8.20	0.77	12.1	contains very small garnet inclusion
14	8.55	0.59	8.8	center of porphyroclast
15	8.22	1.56	n.d.	center of porphyroclast
18	8.07	0.79	11.9	erratic trace on mass spec. contaminated gas sample?
27	8.48	1.76	28.4	center of porphyroclast; very clean
30a	8.51	2.44	40.4	porphyroclast
30b	8.53	1.10	17.5	from same fragment as 30a
Av.	8.38 \pm 0.14			
Plagioclase groundmass				
23	9.17	1.04	n.d.	minor garnet and hornblende inclusions
25	8.69	1.16	n.d.	vein, clean
26	8.40	1.92	33.0	multiple small garnet and hornblende inclusions
28	8.96	1.47	24.1	vein, minor dusty inclusions
31	8.33	1.75	n.d.	vein
32	8.23	1.13	n.d.	vein
33	8.74	1.64	n.d.	vein, minor garnet and hornblende inclusions
Av.	8.65 \pm 0.32			
Other phases				
Garnet	6.85	1.50	19.8	
Garnet	6.89	2.07	28.6	
Hornblende	6.44	1.26	17.4	
Hornblende	6.44	1.21	15.4	
Ilmenite	2.06	1.67	16.4	
Ilmenite	1.81	2.63	n.d.	
In-situ analyses of plagioclase porphyroclast				
Expt.	$\delta^{18}\text{O}$ (‰ vs. SMOW)	Voltage* (mass 44)		Comments
S101-2	8.90	5.7		center of porphyroclast, clean hole
S101-3	6.36	3.5		1/3 distance to porphyroclast edge
S101-4	8.84	4.5		2/3 distance to edge
S101-5	4.58	n.d.		at edge, contaminated by groundmass phases?
S101-6	8.58	4.2		at center, next to S101-2
S101-7	7.90	4.2		1/3 distance to edge, next to S101-3
S101-8	7.77	3.9		2/3 distance to edge, next to S101-4
S101-9	8.25	4.3		at edge next to S101-5, clean hole
S101-10	8.50	n.d.		1/3 distance to edge, other direction
S101-11	7.68	3.0		1/2 distance to edge, next after S101-10
S101-12	8.73	2.9		3/4 distance to edge, next after S101-11
S101-13	7.92	3.8		at edge, next after S101-12, clean hole
S101-14	7.39	3.6		central portion of crystal
S101-15	6.55	3.3		next to S101-15, bad trace on mass spec.
S101-16	8.65	4.2		1/3 distance to edge
S101-17	6.12	2.8		2/3 distance to edge
S101-18	6.60	4.2		at edge
S101-19	9.19	4.2		outside of porphyroclast—groundmass plag.
Av.	8.24 \pm 0.4			

Note: locations of samples correspond to Fig. 3a and 3b; n.d. = not determined.
* One volt \sim 0.1 mol CO_2 .

obtained from exchange with hydrous fluids (Giletti et al., 1978; Elphick et al., 1988). The plagioclase porphyroclasts would completely exchange with a hydrous fluid in several thousands of years (Fig. 4), whereas the original $\delta^{18}\text{O}$ values would be retained in the cores of crystals for tens of millions of years if exchange occurred with a completely anhydrous fluid (Fig. 4). There is no observable variation in the $\delta^{18}\text{O}$ value of the plagioclase from core to rim (Fig. 3b), indicating either that the infiltrating fluid was hydrous or that deformation accompanied fluid infiltration. If a hydrous fluid is present, the preservation of feldspar zoning can only be expected as a result of low-

temperature hydrothermal events (Elsenhimer and Valley, 1993).

Among multiple phases, the traditional approach for evaluating isotopic equilibrium is to check for equilibrium isotopic fractionations among at least three phases (Clayton and Epstein, 1958; Bottinga and Javoy, 1975; Deines, 1977). Temperatures of isotopic equilibration between any two phases i and j are related by the equation

$$1000 \ln \alpha_{ij} - b_{ij} = a_{ij} \cdot 10^6/T^2 \quad (1)$$

where $1000 \ln \alpha_{ij} \approx \Delta^{18}\text{O}(i - j) = \delta^{18}\text{O}_i - \delta^{18}\text{O}_j$, and a_{ij} and b_{ij} are the temperature coefficients of fractionation

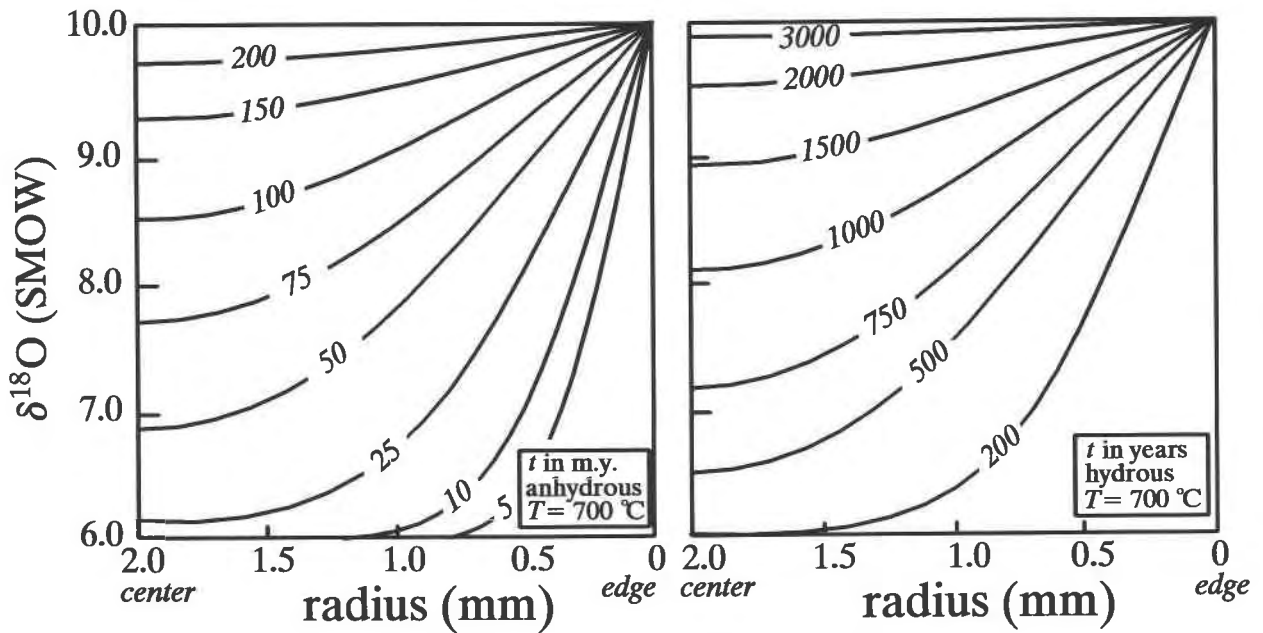


Fig. 4. Calculated O-isotope diffusion profiles for single plagioclase porphyroclasts plotted against the radius as a function of equilibration time. Calculations were made for plagioclase spheres (initial $\delta^{18}\text{O}$ value of 6‰) equilibrating with an infinite reservoir fluid ($\delta^{18}\text{O}$ value of 10‰) and were modified from Crank (1975, Fig. 6.1) using the hydrous and anhydrous diffusion coefficients in Table 2.

for the mineral pair i and j . A plot of $1000 \ln \alpha_{ij} - b_j$ vs. $a_j \cdot 10^6$ for all phases (where phase i = reference phase) defines a straight line with a slope proportional to $1/T^2$ if all phases are in equilibrium (Javoy et al., 1970). The present data define a straight line ($r^2 = 0.98$) with an equilibrium temperature of 470 °C (Fig. 5). The differences between the $\delta^{18}\text{O}$ values of the feldspar porphyroclasts (8.38‰) and groundmass (8.65‰) can be explained in terms of the different Al-Si ratio. Albite is enriched in ^{18}O relative to anorthite (O'Neil and Taylor, 1967). The equilibrium isotopic fractionation between An_{40} and An_{60} is 0.2 at 700 °C and 0.4 at 470 °C. Although chemical equilibrium has not been attained between the plagioclase porphyroclasts and groundmass, O-isotope equilibrium has been attained.

The best-fit temperature of 470 °C from the stable-isotope data has no known geological significance. There is no evidence for a postpeak-metamorphic event at ~ 500 °C. The temperature of the last metamorphism is 700 °C, and cooling below that point appears to have been gradual and continuous. Cooling rate estimates for the Grenville meta-anorthosite from thermochronological data are 1–5 °C/m.y. over the temperature range 700–<500 °C (Cosca et al., 1991; Tucillo et al., 1992). The low temperature estimates from stable-isotope thermometry may be due to either open-system fluid infiltration at some point during retrogression or retrograde O-diffusional exchange among coexisting phases (Javoy, 1977; Gilletti, 1986). There is no geologic evidence for the former process, whereas isotopic resetting during slow cooling is expected and has been shown to significantly alter the $\delta^{18}\text{O}$

of coexisting mineral phases. The importance of retrograde isotopic reequilibration among coexisting phases can be assessed following the procedure of Gilletti (1986) and more recent, quantitative, numerical models (Eiler et al., 1992; Jenkin et al., 1994).

Gilletti (1986) presented a model for interpreting the effect of isotopic reequilibration on preserved $\delta^{18}\text{O}$ values in slowly cooled rocks. The degree of isotopic exchange during cooling is a function of modal mineralogy, grain sizes and shapes, O diffusivities, temperature-dependent isotopic fractionations, and cooling rate. In the model, isotopic reequilibration between coexisting phases occurs during cooling by O intracrystalline diffusion. Each phase continues to reequilibrate with the others until its closure temperature is reached. The closure temperature is defined as the narrow temperature interval below which diffusion effectively stops (Dodson, 1973). The $\delta^{18}\text{O}$ value of each phase at the peak metamorphic conditions was calculated from the measured $\delta^{18}\text{O}_{\text{garnet}}$ value. Because of the very slow diffusion rate of O in garnet (Fortier and Gilletti, 1989), it should retain its peak $\delta^{18}\text{O}$ value during cooling. The equilibrium $\delta^{18}\text{O}$ values of the other phases at 700 °C can be calculated with Equation 1 on the basis of the measured $\delta^{18}\text{O}_{\text{garnet}}$ value. The whole rock $\delta^{18}\text{O}$ is then calculated from the relation

$$\delta^{18}\text{O}_{\text{whole rock}} = \sum x_i \delta^{18}\text{O}_i \quad (2)$$

where x_i = O mole fraction of the phase i , and $\delta^{18}\text{O}_i$ = $\delta^{18}\text{O}$ value of phase i . The $\delta^{18}\text{O}$ value was determined with Equation 2 using the actual measured $\delta^{18}\text{O}$ values of each phase and also using the $\delta^{18}\text{O}$ values of each phase

TABLE 2. Diffusion data used in calculations

Mineral	Hydrous/ anhydrous	Preexponential factor D_0 (cm ² /s)	Activation energy (Q) (kJ/mol)	Reference
α quartz	hydrous	190	284	1
β quartz	hydrous	4×10^{-7}	142	1
	anhydrous	2.1×10^{-8}	159	2
Anorthite	hydrous	1.4×10^{-7}	110	3
	anhydrous	1×10^{-5}	236	4
Potassium feldspar	hydrous	4.5×10^{-8}	107	3
	anhydrous	1×10^{-5}	236	5
Pyroxene	hydrous	1.5×10^{-6}	226	6
	anhydrous	6.3	405	7
Hornblende	hydrous	1.0×10^{-7}	171	8
	anhydrous	assumed equal to hydrous value		
Magnetite	hydrous	2.7×10^{-5}	203	9
	anhydrous	4.3×10^{-7}	211	10
Hematite	hydrous	6.3×10^4	405	11
	anhydrous	630	405	12
Ilmenite		assumed equal to hematite		
Garnet	hydrous	2×10^{-8}	280	13
Garnet	anhydrous	assumed equal to hydrous value		

References: (1) Gilletti and Yund, 1984; (2) Sharp et al., 1991; (3) Gilletti et al., 1978; (4) Elphick et al., 1988; (5) assumed equal to anorthite; (6) Farver, 1989; (7) Connolly and Meuhlenbachs, 1988; (8) Farver and Gilletti, 1985; (9) Gilletti and Hess, 1988; (10) Sharp, 1991; (11) equal to the anhydrous values of Reddy and Cooper (1983) with $D_0 = D_{0(\text{meas})} \times 100$; (12) Reddy and Cooper, 1983; (13) Fortier and Gilletti, 1989.

calculated to be in equilibrium with garnet at 700 °C. Both methods give identical values of $\delta^{18}\text{O}_{\text{whole rock}}$, indicating that the rock behaved as a closed system following peak metamorphism.

The final $\delta^{18}\text{O}$ values of each phase were calculated following the procedures of Gilletti (1986) and of Jenkin et al. (1994). In the Gilletti model, the closure temperature is based on two assumptions: (1) that there is an infinite O reservoir with which all phases can exchange and (2) that cooling begins from above the closure temperature of all minerals. The model of Jenkin et al. (1994) incorporates the effects of a finite reservoir and the condition that peak temperature may equal the closure temperature of any phase. The calculations for the Gilletti model were made with the computer program Cool (Jenkin et al., 1991), and the more complex modeling following Jenkin et al. (1994) was carried out by G.R.T. Jenkin at the Scottish Universities Research and Reactor Centre, Scotland. The $\delta^{18}\text{O}$ value of each phase calculated by each method, agrees to within 0.1‰.

The degree of retrograde diffusional exchange was calculated with both anhydrous and hydrous diffusion-rate data. Of the phases considered in this study, anhydrous and hydrous experimental diffusion data have been obtained only for anorthite (Table 2). For the phases quartz and magnetite, the preexponential factor for O diffusion is two orders of magnitude larger under hydrous conditions (Table 2), and it was assumed that a similar effect exists for hematite (isostructural with ilmenite). Castle and Surman (1969) and Schmalzried and Wagner (1962) presented the experimental and theoretical basis for this assumption. The diffusion rate of O in hornblende was assumed to be independent of fluid composition. The closure temperature for garnet is above 700 °C, regardless of the composition of the fluid. The $\delta^{18}\text{O}$ values calculated

with the hydrous diffusion data are in excellent agreement with the measured values (Table 3). Only the plagioclase matrix value differs from the measured value. The calculated matrix value is 9.15‰, compared with the average measured value of 8.65‰. Several $\delta^{18}\text{O}$ values of the matrix plagioclase are high (no. 23, 9.2‰; no. 28, 9‰), and these may be more representative of the true matrix values; the lower measurements could be a mélange of porphyroclasts and matrix. The agreement between the calculated and measured $\delta^{18}\text{O}$ values for the dry system is not nearly as good (Fig. 5), suggesting that cooling occurred in the presence of a hydrous fluid. This conclusion is supported by the lack of isotopic zoning in the feldspar porphyroclasts. If the diffusion rate of O in feldspar was as slow as predicted by dry diffusion experiments (Elphick et al., 1988), then isotopic zoning acquired during retrogression should be preserved in the feldspar porphyroclasts. The agreement between the diffusion calculations using hydrous diffusion data and the measured values supports the conclusion that a mixed $\text{CO}_2\text{-H}_2\text{O}$ fluid phase was present at peak metamorphic conditions (Moecher and Essene, 1991) and persisted down to lower temperatures.

The infinite reservoir model (Gilletti, 1986) is particularly well suited to the present rock type if the rapid wet diffusion data for feldspar are applicable. Plagioclase makes up 70 modal% of the rock and has a very rapid O diffusivity under H_2O -rich conditions (Gilletti et al., 1978). For a cooling rate of 1–10 °C/m.y. and time scales of 0.1–10 m.y., the scale of O diffusion at 700 °C is on the order of tens of centimeters, easily allowing the plagioclase to homogenize isotopically. The assumption that plagioclase served as an infinite reservoir is therefore appropriate for this sample. The more rigorous treatment of Jenkin et al. (1994) involves none of the assumptions

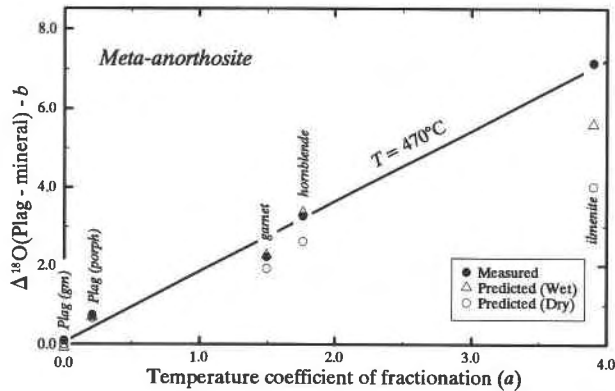


Fig. 5. Isotherm plot for the Grenville meta-anorthosite. Measured and predicted $[\Delta^{18}\text{O}_{\text{plag-mineral}}] - b$ values vs. the temperature coefficient of fractionation, a . The relationship is given by Eq. 1. The line defined by the locus of points should be proportional to T^{-2} (Javoy et al., 1970). The best-fit line to the measured data corresponds to 470 °C, far lower than the peak temperatures of metamorphism. The low isotherm temperature can be explained by retrograde diffusional exchange. The predicted ($\Delta^{18}\text{O} - b$) values for the slowly cooled rock (3 °C/m.y.) were calculated using the method outlined by Giletti (1986) based on the closure temperature concept of Dodson (1973). Calculated $\delta^{18}\text{O}$ values were determined with both the hydrous (wet) and anhydrous (dry) diffusion coefficients (Table 2). The measured and hydrous calculated $\delta^{18}\text{O}$ values agree well except for ilmenite. Values for the a and b coefficients for all calculations are from Bottinga and Javoy (1975).

inherent in the closure temperature concept (Dodson, 1973) as used by Giletti (1986). Even so, the calculated $\delta^{18}\text{O}$ values by Jenkin are within 0.1‰ of the values obtained with the Giletti model, illustrating that the far simpler Giletti model may be valid as long as appropriate rock types are chosen. Rock types in which the modally dominant phase has a very rapid diffusion rate, such as feldspar (this study) or calcite (Sharp and Jenkin, 1994), can be modeled accurately with the simple approach of Giletti (1986).

Although the isotherm derived from a best fit of all the data has no geologic meaning, peak temperatures of metamorphism can still be extracted from this data set when diffusional effects are considered. The calculated change in the $\delta^{18}\text{O}$ value of the modally abundant feldspar porphyroclasts is only 0.1‰ during cooling, and the $\delta^{18}\text{O}$ value of the garnet did not change during retrogression. Therefore, this mineral pair should yield nearly peak-metamorphic temperatures. The $\Delta^{18}\text{O}_{\text{plagioclase-garnet}}$ value of 1.7‰ corresponds to a temperature of 660 °C, indistinguishable from peak temperatures within error. The conclusion that most mineral triplets have no meaning (Deines, 1977) must be reviewed in light of known diffusional effects—when appropriate mineral pairs are chosen, peak temperatures can be extracted. When measured stable isotope data are evaluated in terms of expected, retrograde, diffusional-exchange effects, apparent disequilibrium effects can be explained and information such

TABLE 3. Calculated and measured $\delta^{18}\text{O}$ values from high-grade metamorphic terranes

Mineral	Mode	Grain diam. (mm)	Calculated final $\delta^{18}\text{O}$ value/closure temperature (°C)		$\delta^{18}\text{O}$ value measured		
			Hydrous	Anhydrous			
Grenville meta-anorthosite (present study)							
PI porph An ₈₀	0.5	4.0	8.4	265	8.2	695	8.4
PI gm An ₄₀	0.2	0.3	9.1	175	8.8	560	9.1*
Garnet	0.05	0.2	6.9	>700	6.9	>700	6.9
Hornblende	0.2	0.3	6.0	470	6.5	470	6.1
Ilmenite	0.05	0.3	3.4	595	4.1	665	1.9
Wind River iron formation—T2-h (Sharp et al., 1988)							
Quartz	0.26	0.5	11.2	455	9.9	500	9.9
Garnet	0.03	0.5	6.8	775	6.6	775	6.7
Opx	0.60	0.5	6.8	660	6.8	>800	6.9
Magnetite	0.11	0.5	0.7	455	2.3	585	1.9
Mafic granulite—EO11 (McNaughton and Wilson, 1980); diameters approx.							
Quartz	0.01	0.8	8.9	465	8.5	525	8.4
PI An ₈₀	0.35	0.8	5.5	215	5.4	620	5.4
Cpx	0.10	0.8	4.3	690	4.3	>730	4.1
Opx	0.18	0.8	4.3	690	4.3	>730	4.4
Hornblende	0.34	0.8	3.8	535	4.0	535	4.2
Orthogneiss, Sri Lanka—BSL-88-46-4 (Hoffbauer et al., 1993)							
Quartz	0.24	0.4	12.9	445	13.0	525	12.8
Kspar	0.33	0.4	11.4	200	11.1	585	10.3
PI An ₅₀	0.10	0.2	8.9	170	10.5	550	n.d.
Garnet	0.07	0.4	9.0	760	9.0	760	9.0
Hornblende	0.27	0.4	7.8	500	8.4	500	8.0
Ilmenite	0.001	0.2	5.1	590	6.0	660	4.9

Note: abbreviations are defined as follows: porph = porphyroclasts; gm = groundmass; Cpx = clinopyroxene; Kspar = potassium feldspar; Opx = orthopyroxene; PI = plagioclase; n.d. = not determined.

* Assumed equal to the upper range of measured values.

as the presence or absence of a fluid can be deduced (e.g., Eiler et al., 1993; Farquhar et al., 1993).

The apparent temperature of 470 °C obtained with the graphical method (Javoy et al., 1970) can be explained in terms of retrograde diffusional exchange. To determine whether the near-linear locus of points is unique to the Whitestone anorthosite or is expected for most slowly cooled granulite terranes, calculated and measured $\delta^{18}\text{O}$ values were compared from other granulite-facies terranes. With these data, we were able to evaluate (1) whether the false isotherm generated with the present data set is a common feature in other rock types and (2) whether the calculated and measured $\delta^{18}\text{O}$ values are best fit by hydrous or anhydrous diffusion data. Three additional granulite-facies samples were evaluated—a banded iron formation, a mafic granulite, and an orthogneiss (Table 3, Fig. 6A–6C). The iron formation cooled under anhydrous conditions (Sharp et al., 1988). The measured $\delta^{18}\text{O}$ values for this sample agree very well with the dry diffusion data, and all phases plotted on an apparent or false isotherm of ~600 °C, which is not geologically significant. The calculated $\delta^{18}\text{O}$ values for the mafic granulite are very similar for both the hydrous and anhydrous calculations. The similarity can be explained in terms of the bulk composition and relative insensitivity to fluid composition for the phases pyroxene and hornblende. The anhydrous calculations most closely match the measured $\delta^{18}\text{O}$ values. The granulite probably cooled under anhy-

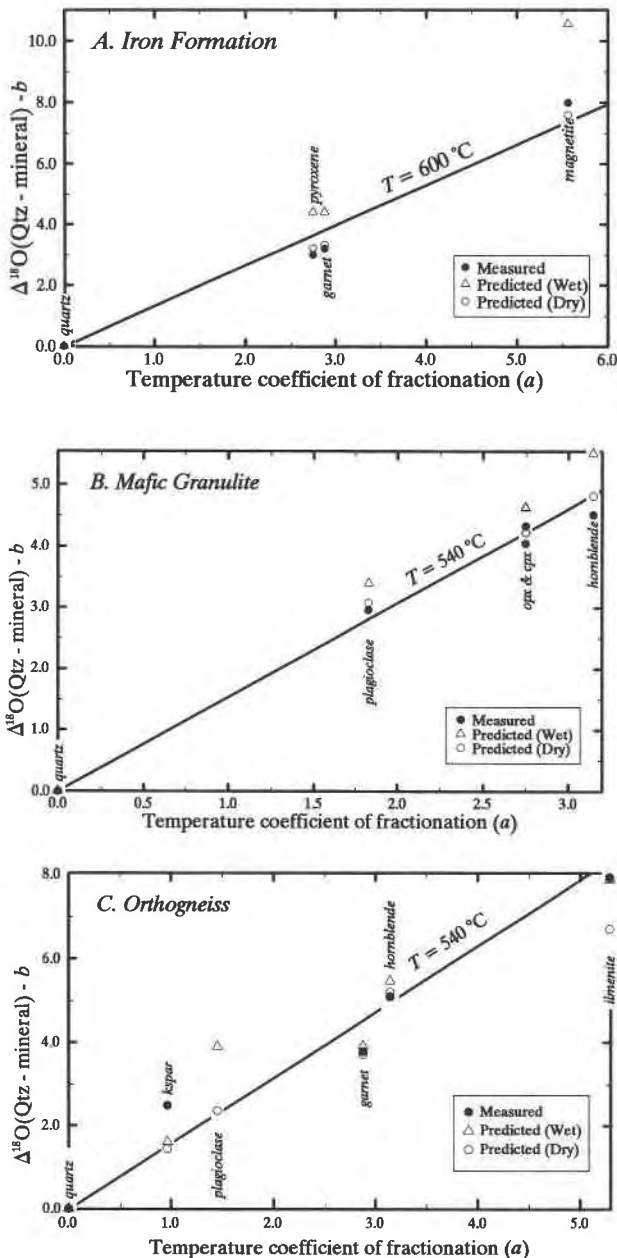


Fig. 6. Isotherm plot illustrating measured and predicted $\delta^{18}\text{O}$ values for a granulite-facies banded iron formation (A) (Sharp et al., 1988), a granulite-facies mafic rock (B) (McNaughton and Wilson, 1980), and a granulite-facies orthogneiss (C) (Hoffbauer et al., 1993). Calculated $\delta^{18}\text{O}$ values for anhydrous and hydrous diffusion coefficients for a cooling rate of $5^\circ\text{C}/\text{m.y.}$ The best-fit line to the measured data is given, along with the corresponding temperatures. Although the locus of points may closely define a line, the temperature derived from the slope does not have any geologic significance.

drous conditions, or the pyroxenes would have retrogressed to amphiboles. Similar to the meta-anorthosite and iron formation, the data define a false isotherm—one that has no geological significance. The orthogneiss sam-

ple is the most ambiguous. The calculated hydrous samples fit the measured $\delta^{18}\text{O}$ values except for the potassium feldspar. The discrepancy can be explained if the analyzed feldspars were a mixture of potassium feldspar and plagioclase (Fig. 6C). This sample may have undergone open-system retrograde exchange (Hoffbauer et al., 1993), explaining the poor fit between calculated and measured values for feldspar. Except for the feldspar data, the measured and predicted $\delta^{18}\text{O}$ values define a false isotherm.

O isotope temperature estimates are often below the peak temperatures of metamorphism. The isotherm method based on three or more minerals is equivocal for establishing equilibrium. As illustrated in Figures 5 and 6, apparent isotherms can develop from diffusional exchange and are not related to a recognized geological event. Only in cases where the mineral samples are extremely refractory and coarse-grained, or have cooled very rapidly, will isotherms provide peak temperatures. Carefully selected mineral pairs, such as plagioclase + garnet in the present study, may provide peak temperatures, and the overall isotopic compositions of a mineral suite may be used to constrain the fluid composition of a rock during cooling.

ACKNOWLEDGMENTS

We thank G.R.T. Jenkin (S.U.R.R.C.) for his computational assistance and advice. The reviews of B. Giletti, R. Joesten, and especially D. Henry improved the quality of this manuscript. J.C. Hunziker is thanked for his continued advice and support at the University of Lausanne Stable Isotope Laboratory.

REFERENCES CITED

- Bottinga, Y., and Javoy, M. (1973) Comments on oxygen isotopic geothermometry. *Earth and Planetary Science Letters*, 20, 250–265.
- (1975) Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. *Reviews of Geophysics and Space Physics*, 13, 401–418.
- Castle, J.E., and Surman, P.L. (1969) The self-diffusion of oxygen in magnetite. The effect of anion vacancy concentrations and cation-distribution. *Journal of Physical Chemistry*, 73, 632–634.
- Chamberlain, C.P., and Conrad, M.E. (1991) Oxygen isotope zoning in garnet. *Science*, 254, 403–406.
- Clayton, R.N., and Epstein, S. (1958) The relationship between $^{18}\text{O}/^{16}\text{O}$ ratios in coexisting quartz, carbonate, and iron oxides from various geological deposits. *Journal of Geology*, 66, 352–371.
- (1961) The use of oxygen isotopes in high-temperature geological thermometry. *Journal of Geology*, 68, 447–452.
- Connolly, C., and Muehlenbachs, K. (1988) Contrasting oxygen diffusion in nepheline, diopside and other silicates and their relevance to isotopic systematics in meteorites. *Geochimica et Cosmochimica Acta*, 52, 1585–1591.
- Conrad, M.E., and Chamberlain, C.P. (1992) Laser-based in situ measurements of fine-scale variations in the $\delta^{18}\text{O}$ values of hydrothermal quartz. *Geology*, 20, 812–816.
- Cosca, M.A., Sutter, J.F., and Essene, E.J. (1991) Cooling and inferred uplift/erosion history of the Grenville Orogen, Ontario: Constraints from $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology. *Tectonics*, 10, 959–977.
- Crank, J. (1975) *The mathematics of diffusion* (2nd edition), 414 p. Clarendon, Oxford, U.K.
- Deines, P. (1977) On the oxygen isotope distribution among mineral triplets in igneous rocks. *Geochimica et Cosmochimica Acta*, 41, 1709–1730.
- Dodson, M.H. (1973) Closure temperature in cooling geochronological and petrologic systems. *Contributions to Mineralogy and Petrology*, 40, 259–274.

- Eiler, J.M., Baumgartner, L.P., and Valley, J.W. (1992) Intercrystalline stable isotope diffusion: A fast grain boundary model. *Contributions to Mineralogy and Petrology*, 112, 543–557.
- Eiler, J.M., Valley, J.W., and Baumgartner, L.P. (1993) A new look at stable isotope thermometry. *Geochimica et Cosmochimica Acta*, 57, 2571–2583.
- Elphick, S.C., Graham, C.M., and Dennis, P.F. (1988) An ion microprobe study of anhydrous oxygen diffusion in anorthite: A comparison with hydrothermal data and some geological implications. *Contributions to Mineralogy and Petrology*, 100, 490–495.
- Elsenhaimer, D., and Valley, J.W. (1992) In situ oxygen isotope analysis of feldspar and quartz by Nd:YAG laser microprobe. *Chemical Geology*, 101, 21–42.
- (1993) Submillimeter scale zonation of $\delta^{18}\text{O}$ in quartz and feldspar, Isle of Skye, Scotland. *Geochimica et Cosmochimica Acta*, 57, 3669–3676.
- Farquhar, J., Chacko, T., and Frost, B.R. (1993) Strategies for high-temperature oxygen isotope thermometry: A worked example from the Laramie Anorthosite complex, Wyoming, USA. *Earth and Planetary Science Letters*, 117, 407–222.
- Farver, J.R. (1989) Oxygen self-diffusion rates in diopside with application to cooling rate determinations. *Earth and Planetary Science Letters*, 92, 386–396.
- Farver, J.R., and Giletti, B.J. (1985) Oxygen diffusion in amphiboles. *Geochimica et Cosmochimica Acta*, 49, 1403–1411.
- Fortier, S.M., and Giletti, B.J. (1989) An empirical model for predicting diffusion coefficients in silicate minerals. *Science*, 245, 1481–1484.
- Giletti, B.J. (1986) Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks. *Earth and Planetary Science Letters*, 77, 218–228.
- Giletti, B.J., and Hess, K.C. (1988) Oxygen diffusion in magnetite. *Earth and Planetary Science Letters*, 89, 115–122.
- Giletti, B.J., and Yund, R.A. (1984) Oxygen diffusion in quartz. *Journal of Geophysical Research*, 89, 4039–4046.
- Giletti, B.J., Semet, M.P., and Yund, R.A. (1978) Studies in diffusion. III. Oxygen in feldspars, an ion microprobe determination. *Geochimica et Cosmochimica Acta*, 42, 45–57.
- Hoffbauer, R., Hoernes, S., and Fiorentini, E. (1993) Oxygen isotope thermometry based on a refined increment method and its application to granulite-grade rocks from Sri Lanka. *Precambrian Research*, 66, 199–220.
- Javoy, M. (1977) Stable isotopes and geothermometry. *Journal of the Geological Society of London*, 133, 609–636.
- Javoy, M., Fourcade, S., and Allegre, C.J. (1970) Graphical method of examination of $^{18}\text{O}/^{16}\text{O}$ fractionations in silicate rocks. *Earth and Planetary Science Letters*, 10, 12–16.
- Jenkin, G.R.T., Fallic, A.E., Farrow, C.M., and Bowes, G.E. (1991) COOL: A Fortran-77 computer program for modeling stable isotopes in cooling closed systems. *Computers and Geoscience*, 17, 391–412.
- Jenkin, G.R.T., Farrow, C.M., Fallic, A.E., and Higgins, D. (1994) Oxygen isotope exchange and closure temperatures in cooling rocks. *Journal of Metamorphic Petrology*, 12, 221–235.
- Kirschner, D.L., Sharp, Z.D., and Teyssier, C. (1993) Vein growth mechanisms and fluid sources revealed by oxygen isotope laser microprobe. *Geology*, 21, 85–88.
- Lamb, W.M., and Moecher, D.P. (1992) CO_2 -rich fluid inclusions in the Whitestone anorthosite: Implications for the retrograde history of the Parry Sound Shear Zone, Grenville Province, Canada. *Journal of Metamorphic Petrology*, 10, 763–776.
- McNaughton, N.J., and Wilson, A.F. (1980) Problems in oxygen isotope geothermometry in mafic granulite facies rocks from near Einsaleigh, northern Queensland. *Precambrian Research*, 13, 77–86.
- Mezger, K., Essene, E.J., van der Pluijm, B.S., Halliday, A.N. (1993) U-Pb geochronology of the Grenville Orogen of Ontario and New York: Constraints on ancient crustal tectonics. *Contributions to Mineralogy and Petrology*, 114, 13–26.
- Moecher, D.P., and Essene, E.J. (1991) Calculation of CO_2 activities using scapolite equilibria: Constraints on the presence and composition of a fluid phase during high grade metamorphism. *Contributions to Mineralogy and Petrology*, 108, 219–240.
- Moecher, D.P., Anovitz, L.M., and Essene, E.J. (1988) Calculation and application of clinopyroxene-plagioclase-garnet-quartz geobarometers. *Contributions to Mineralogy and Petrology*, 100, 92–106.
- Moecher, D.P., Essene, E.J., and Valley, J.W. (1992) Stable isotope and petrological constraints on scapolitization of the Whitestone meta-anorthosite, Grenville Province, Ontario. *Journal of Metamorphic Petrology*, 10, 745–762.
- O'Neil, J.R., and Taylor, H.P., Jr. (1967) The oxygen isotope and cation exchange chemistry of feldspars. *American Mineralogist*, 52, 1414–1437.
- O'Neil, J.R., Masuda, H., and Sharp, Z.D. (1992) Oxygen isotope analyses of microsamples of silicates and oxides. Program and Abstracts, V.M. Goldschmidt Conference May 8–10, 1992, A-79.
- Reddy, K.P.R., and Cooper, A.R. (1983) Oxygen diffusion in MgO and $\alpha\text{-Fe}_2\text{O}_3$. *Journal of the American Ceramic Society*, 66, 664–666.
- Schmalzried, H., and Wagner, C. (1962) Fehlordnung in ternären Ionenkristallen. *Zeitschrift für physikalische Chemie neue Folge*, 31, 198–221.
- Sharp, Z.D. (1990) A laser based microanalytical method for the in situ determination of oxygen isotope ratios in silicates and oxides. *Geochimica et Cosmochimica Acta*, 54, 1353–1357.
- (1991) Determination of oxygen diffusion rates in magnetite from natural isotopic variations. *Geology*, 19, 653–656.
- (1992) In situ laser microprobe techniques for stable isotope analyses. *Isotope Geoscience*, 101, 3–19.
- Sharp, Z.D., and Jenkin, G.R.T. (1994) An empirical estimate of the diffusion rate of oxygen in diopside. *Journal of Metamorphic Geology*, 12, 89–97.
- Sharp, Z.D., O'Neil, J.R., and Essene, E.J. (1988) Oxygen isotope variations in a granulite-grade iron formation: Constraints on oxygen diffusion and retrograde isotopic exchange. *Contributions to Mineralogy and Petrology*, 98, 490–501.
- Sharp, Z.D., Giletti, B.J., and Yoder, H.S., Jr. (1991) Oxygen diffusion rates in quartz exchanged with CO_2 . *Earth and Planetary Science Letters*, 107, 339–348.
- Tucillo, M.E., Mezger, K., Essene, E.J., and van der Pluijm, B.A. (1992) Thermobarometry, geochronology, and the interpretation of P - T - t data in the Britt Domain, Ontario Grenville Orogen, Canada. *Journal of Petrology*, 33, 1225–1259.
- van Breemen, O., Davidson, A., Loveridge, W.D., and Sullivan, R.W. (1986) U-Pb geochronology of Grenville tectonites, granulites and igneous precursors, Parry Sound, Ontario. In J.M. Moore, A. Davidson, and A.J. Baer, Eds., *The Grenville Province. Geological Association of Canada Special Paper*, 31, 191–207.

MANUSCRIPT RECEIVED JULY 22, 1993

MANUSCRIPT ACCEPTED MAY 27, 1994