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

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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. Reticl igneous plagioclase phenocrysts (An$_{90}$) occur as coarse-grained porphyroclasts in a fine-grained recrystallized matrix of plagioclase (An$_{90}$) + hornblende + garnet + scapolite + epidote + ilmenite. The $\delta^{18}$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 $\delta^{18}$O$_{smow}$ values (%$\delta$) 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; epidote = 7.03 ± 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 $^{18}$O/$^{16}$O at high T and slow cooling rates.

The theoretical $\delta^{18}$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 $\delta^{18}$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 $\delta^{18}$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 (Bottlinga 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 disequilibrium 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, $\delta^{18}$O values of plagioclase porphyroclasts and coexisting phases were determined on a scale of millimeters to submillimeters 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 $\delta^{18}$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 porphyroclast (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_{38} and An_{43} in composition 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 CO₂-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 CO₂ that infiltrated the anorthosite was enriched in ¹⁸O and was derived from or equilibrated with marble (Moecher et al., 1992). The infiltrating CO₂ increased the δ¹⁸O 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 BrF₃ by heating with a CO₂ laser (Sharp, 1990, 1992). O was converted to CO₂ and passed directly into the mass spectrometer.

The plagioclase porphyroclasts are isotopically homogeneous at the submillimeter scale, with a δ¹⁸O 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 δ¹⁸O relative to porphyroclasts (δ¹⁸O = 8.65 ± 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 BrF₃ 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 BrF₃; (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 CO₂-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 δ¹⁸O 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.

Original plagioclase phenocrysts should have a δ¹⁸O value of 6–7‰. Infiltration of the CO₂ fluid from the surrounding marbles has increased the average δ¹⁸O 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 (O₂ or CO₂) are orders of magnitude slower than those.
TABLE 1. O-isotope results

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O$ (‰ vs. SMOW)</th>
<th>Weight (mg)</th>
<th>CO$_2$ recovered ($\mu$m)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>8.48</td>
<td>1.02</td>
<td>n.d.</td>
<td>Plagioclase porphyroclast, near edge</td>
</tr>
<tr>
<td>9</td>
<td>8.34</td>
<td>1.10</td>
<td>n.d.</td>
<td>Plagioclase porphyroclast at edge</td>
</tr>
<tr>
<td>10</td>
<td>8.20</td>
<td>0.77</td>
<td>12.1</td>
<td>contains very small garnet inclusion</td>
</tr>
<tr>
<td>14</td>
<td>8.55</td>
<td>0.59</td>
<td>12.1</td>
<td>center of porphyroclast</td>
</tr>
<tr>
<td>15</td>
<td>8.22</td>
<td>1.56</td>
<td>11.9</td>
<td>center of porphyroclast</td>
</tr>
<tr>
<td>18</td>
<td>8.07</td>
<td>0.79</td>
<td>28.4</td>
<td>erratic trace on mass spec.</td>
</tr>
<tr>
<td>27</td>
<td>8.48</td>
<td>1.76</td>
<td>28.4</td>
<td>center of porphyroclast; very clean</td>
</tr>
<tr>
<td>30a</td>
<td>8.51</td>
<td>2.44</td>
<td>40.4</td>
<td>from same fragment as 30a</td>
</tr>
<tr>
<td>30b</td>
<td>8.53</td>
<td>1.10</td>
<td>17.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O$ (‰ vs. SMOW)</th>
<th>Weight (mg)</th>
<th>CO$_2$ recovered ($\mu$m)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>9.17</td>
<td>1.04</td>
<td>n.d.</td>
<td>minor garnet and hornblende inclusions</td>
</tr>
<tr>
<td>25</td>
<td>8.89</td>
<td>1.16</td>
<td>n.d.</td>
<td>vein, clean</td>
</tr>
<tr>
<td>26</td>
<td>8.40</td>
<td>1.92</td>
<td>33.0</td>
<td>multiple small garnet and hornblende inclusions</td>
</tr>
<tr>
<td>28</td>
<td>8.96</td>
<td>1.47</td>
<td>24.1</td>
<td>vein, minor dusty inclusions</td>
</tr>
<tr>
<td>31</td>
<td>8.33</td>
<td>1.75</td>
<td>n.d.</td>
<td>vein</td>
</tr>
<tr>
<td>32</td>
<td>8.23</td>
<td>1.13</td>
<td>n.d.</td>
<td>vein, minor garnet and hornblende inclusions</td>
</tr>
<tr>
<td>33</td>
<td>8.74</td>
<td>1.64</td>
<td>n.d.</td>
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<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O$ (‰ vs. SMOW)</th>
<th>Weight (mg)</th>
<th>CO$_2$ recovered ($\mu$m)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av.</td>
<td>8.38 ± 0.14</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O$ (‰ vs. SMOW)</th>
<th>Weight (mg)</th>
<th>CO$_2$ recovered ($\mu$m)</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>6.85</td>
<td>1.50</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>Garnet</td>
<td>6.89</td>
<td>2.07</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>Hornblende</td>
<td>6.44</td>
<td>1.26</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>Hornblende</td>
<td>6.44</td>
<td>1.21</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>Ilimenite</td>
<td>2.06</td>
<td>1.67</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>Ilimenite</td>
<td>1.81</td>
<td>2.63</td>
<td>n.d.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O$ (‰ vs. SMOW)</th>
<th>Weight (mg)</th>
<th>CO$_2$ recovered ($\mu$m)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ analyses of plagioclase porphyroclast</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td>Voltage* (mass 44)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S101-2</td>
<td>8.90</td>
<td>5.7</td>
<td>center of porphyroclast, clean hole</td>
<td></td>
</tr>
<tr>
<td>S101-3</td>
<td>6.38</td>
<td>3.5</td>
<td>½ distance to porphyroclast edge</td>
<td></td>
</tr>
<tr>
<td>S101-4</td>
<td>8.84</td>
<td>4.5</td>
<td>½ distance to edge</td>
<td></td>
</tr>
<tr>
<td>S101-5</td>
<td>4.58</td>
<td>3.5</td>
<td>at edge, contaminated by groundmass phases?</td>
<td></td>
</tr>
<tr>
<td>S101-6</td>
<td>8.58</td>
<td>4.2</td>
<td>at center, next to S101-2</td>
<td></td>
</tr>
<tr>
<td>S101-7</td>
<td>7.90</td>
<td>3.9</td>
<td>½ distance to edge, next to S101-3</td>
<td></td>
</tr>
<tr>
<td>S101-8</td>
<td>7.77</td>
<td>4.2</td>
<td>at edge next to S101-5, clean hole</td>
<td></td>
</tr>
<tr>
<td>S101-9</td>
<td>8.25</td>
<td>4.3</td>
<td>½ distance to edge, other direction</td>
<td></td>
</tr>
<tr>
<td>S101-10</td>
<td>8.50</td>
<td>n.d.</td>
<td>½ distance to edge, next after S101-10</td>
<td></td>
</tr>
<tr>
<td>S101-11</td>
<td>7.68</td>
<td>3.0</td>
<td>¾ distance to edge, next after S101-11</td>
<td></td>
</tr>
<tr>
<td>S101-12</td>
<td>8.73</td>
<td>2.9</td>
<td>at edge, next after S101-12, clean hole</td>
<td></td>
</tr>
<tr>
<td>S101-13</td>
<td>7.92</td>
<td>3.8</td>
<td>central portion of crystal</td>
<td></td>
</tr>
<tr>
<td>S101-14</td>
<td>7.39</td>
<td>3.6</td>
<td>next to S101-15, bad trace on mass spec.</td>
<td></td>
</tr>
<tr>
<td>S101-15</td>
<td>6.55</td>
<td>3.3</td>
<td>½ distance to edge</td>
<td></td>
</tr>
<tr>
<td>S101-16</td>
<td>8.65</td>
<td>4.2</td>
<td>½ distance to edge</td>
<td></td>
</tr>
<tr>
<td>S101-17</td>
<td>6.12</td>
<td>2.8</td>
<td>at edge</td>
<td></td>
</tr>
<tr>
<td>S101-18</td>
<td>6.60</td>
<td>4.2</td>
<td>outside of porphyroclast—groundmass plag.</td>
<td></td>
</tr>
<tr>
<td>S101-19</td>
<td>9.19</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Av.</td>
<td>8.24 ± 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: locations of samples correspond to Fig. 3a and 3b; n.d. = not determined. * One volt ~ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 (Elsenhemer 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

$$1000 \ln a_{ij} - b_{ij} = a_i - a_j - 10^{6/72} T^2$$

(1)

where $1000 \ln a_{ij}$ is the temperature coefficient of fractionation.
for the mineral pair $i$ and $j$. A plot of $1000 \ln a^i - b^i$ vs. $a^i \cdot 10^6$ 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 $\delta^{18}O$ 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 $An_{90}$ and $An_{90}$ 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; Giletti, 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 $\delta^{18}O$ of coexisting mineral phases. The importance of retrograde isotopic reequilibration among coexisting phases can be assessed following the procedure of Giletti (1986) and more recent, quantitative, numerical models (Eiler et al., 1992; Jenkin et al., 1994).

Giletti (1986) presented a model for interpreting the effect of isotopic reequilibration on preserved $\delta^{18}O$ 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 $\delta^{18}O$ value of each phase at the peak metamorphic conditions was calculated from the measured $\delta^{18}O_{garnet}$ value. Because of the very slow diffusion rate of O in garnet (Fortier and Giletti, 1989), it should retain its peak $\delta^{18}O$ value during cooling. The equilibrium $\delta^{18}O$ values of the other phases at 700 °C can be calculated with Equation 1 on the basis of the measured $\delta^{18}O_{garnet}$ value. The whole rock $\delta^{18}O$ is then calculated from the relation

$$\delta^{18}O_{\text{whole rock}} = \sum x_i \delta^{18}O_i,$$  

where $x_i$ = O mole fraction of the phase $i$, and $\delta^{18}O_i = \delta^{18}O$ value of phase $i$. The $\delta^{18}O$ value was determined with Equation 2 using the actual measured $\delta^{18}O$ values of each phase and also using the $\delta^{18}O$ values of each phase.
assumed to be independent of fluid composition. The diffusion rate of O in hornblende was presented the experimental and theoretical basis for this assumption. The $\delta^{18}O$ values calculated with both anhydrous and hydrous 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 (isostuctural 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $CO_2$-$H_2O$ fluid phase was present at peak metamorphic conditions (Moecher and Essene, 1991) and persisted down to lower temperatures.

The infinite reservoir model (Giletti, 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 (Giletti 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.

### Table 2. Diffusion data used in calculations

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Hydrous/ anhydrous</th>
<th>Preexponential factor $D_0$ (cm$^2$/s)</th>
<th>Activation energy $Q$ (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ quartz</td>
<td>hydrous</td>
<td>190</td>
<td>284</td>
<td>1</td>
</tr>
<tr>
<td>$\beta$ quartz</td>
<td>hydrous</td>
<td>$4 \times 10^{-7}$</td>
<td>142</td>
<td>1</td>
</tr>
<tr>
<td>Anorthite</td>
<td>hydrous</td>
<td>$2.1 \times 10^{-8}$</td>
<td>159</td>
<td>2</td>
</tr>
<tr>
<td>Pyroxene</td>
<td>hydrous</td>
<td>$1.4 \times 10^{-7}$</td>
<td>110</td>
<td>3</td>
</tr>
<tr>
<td>Hornblende</td>
<td>hydrous</td>
<td>$1.5 \times 10^{-8}$</td>
<td>236</td>
<td>4</td>
</tr>
<tr>
<td>Magnetite</td>
<td>hydrous</td>
<td>$2.7 \times 10^{-7}$</td>
<td>107</td>
<td>5</td>
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<tr>
<td>Hematite</td>
<td>hydrous</td>
<td>$4.3 \times 10^{-7}$</td>
<td>226</td>
<td>6</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>hydrous</td>
<td>$6.3 \times 10^{-3}$</td>
<td>405</td>
<td>7</td>
</tr>
<tr>
<td>Garnet</td>
<td>hydrous</td>
<td>$630$</td>
<td>405</td>
<td>8</td>
</tr>
<tr>
<td>Garnet</td>
<td>anhydrous</td>
<td>assumed equal to hydrous value</td>
<td>203</td>
<td>9</td>
</tr>
<tr>
<td>Garnet</td>
<td>anhydrous</td>
<td>assumed equal to hematite</td>
<td>211</td>
<td>10</td>
</tr>
<tr>
<td>Garnet</td>
<td>anhydrous</td>
<td>assumed equal to hydrous value</td>
<td>405</td>
<td>11</td>
</tr>
<tr>
<td>Garnet</td>
<td>anhydrous</td>
<td>assumed equal to hydrous value</td>
<td>405</td>
<td>12</td>
</tr>
<tr>
<td>Garnet</td>
<td>anhydrous</td>
<td>assumed equal to hydrous value</td>
<td>280</td>
<td>13</td>
</tr>
</tbody>
</table>

References: (1) Giletti and Yund, 1984; (2) Sharp et al., 1991; (3) Giletti et al., 1978; (4) Elphick et al., 1988; (5) assumed equal to anorthite; (6) Elphick and Giletti, 1989; (7) Connolly and Meuhlenbachs, 1988; (8) Farver and Giletti, 1985; (9) Giletti and Hess, 1988; (10) Sharp, 1991; (11) equal to the anhydrous values of Reddy and Cooper (1983) with $D_0 = D_{anhydrous} \times 100$; (12) Reddy and Cooper, 1983; (13) Fortier and Giletti, 1989.
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 δ18O 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 δ18O values are best fit by hydro or anhydrous diffusion data. Three additional granulite-facies samples were evaluated—a banded iron formation, a mafic granulate, and an orthogneiss (Table 3, Fig. 3, 6A–6C). The iron formation cooled under anhydrous conditions (Sharp et al., 1988). The measured δ18O 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 δ18O values for the mafic granulate are very similar for both the hydro 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 δ18O values. The granulate probably cooled under anhy-

**Table 3.** Calculated and measured δ18O values from high-grade metamorphic terranes

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mode</th>
<th>Grain diam. (mm)</th>
<th>Hydrous</th>
<th>Anhydrous</th>
<th>Calculated final δ18O value/closure temperature (°C)</th>
<th>δ18O measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grenville meta-anorthosite (present study)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pl porph An80</td>
<td>0.5</td>
<td>4.0</td>
<td>8.4</td>
<td>265</td>
<td>8.5</td>
<td>695</td>
</tr>
<tr>
<td>Pl gm An70</td>
<td>0.2</td>
<td>0.3</td>
<td>9.1</td>
<td>175</td>
<td>8.8</td>
<td>580</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.05</td>
<td>0.2</td>
<td>6.9</td>
<td>&gt;700</td>
<td>6.9</td>
<td>&gt;700</td>
</tr>
<tr>
<td>Hornblende</td>
<td>0.27</td>
<td>0.3</td>
<td>6.0</td>
<td>470</td>
<td>6.5</td>
<td>470</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.05</td>
<td>0.3</td>
<td>3.4</td>
<td>595</td>
<td>4.1</td>
<td>665</td>
</tr>
<tr>
<td>Wind River iron formation—T2-h (Sharp et al., 1988)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.26</td>
<td>0.5</td>
<td>11.2</td>
<td>455</td>
<td>9.9</td>
<td>500</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.03</td>
<td>0.5</td>
<td>6.8</td>
<td>775</td>
<td>6.6</td>
<td>775</td>
</tr>
<tr>
<td>Opx</td>
<td>0.60</td>
<td>0.5</td>
<td>6.8</td>
<td>680</td>
<td>6.8</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.11</td>
<td>0.5</td>
<td>0.7</td>
<td>455</td>
<td>2.3</td>
<td>585</td>
</tr>
<tr>
<td>Mafic granite—EO11 (McNaughton and Wilson, 1980); diameters approx.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.01</td>
<td>0.6</td>
<td>8.9</td>
<td>485</td>
<td>8.5</td>
<td>525</td>
</tr>
<tr>
<td>Pl An80</td>
<td>0.35</td>
<td>0.8</td>
<td>5.5</td>
<td>215</td>
<td>5.4</td>
<td>620</td>
</tr>
<tr>
<td>Cpx</td>
<td>0.10</td>
<td>0.8</td>
<td>4.3</td>
<td>690</td>
<td>4.3</td>
<td>&gt;700</td>
</tr>
<tr>
<td>Opx</td>
<td>0.18</td>
<td>0.8</td>
<td>4.3</td>
<td>690</td>
<td>4.3</td>
<td>&gt;700</td>
</tr>
<tr>
<td>Hornblende</td>
<td>0.34</td>
<td>0.8</td>
<td>3.8</td>
<td>535</td>
<td>4.0</td>
<td>535</td>
</tr>
<tr>
<td>Orthogneiss, Sri Lanka—BSSL-88-48-4 (Hoffbauer et al., 1993)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.24</td>
<td>0.4</td>
<td>12.9</td>
<td>445</td>
<td>13.0</td>
<td>625</td>
</tr>
<tr>
<td>Kspar</td>
<td>0.33</td>
<td>0.4</td>
<td>11.2</td>
<td>201</td>
<td>11.1</td>
<td>585</td>
</tr>
<tr>
<td>Pl An80</td>
<td>0.10</td>
<td>0.2</td>
<td>8.9</td>
<td>170</td>
<td>10.5</td>
<td>550</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.07</td>
<td>0.4</td>
<td>9.0</td>
<td>760</td>
<td>9.0</td>
<td>760</td>
</tr>
<tr>
<td>Hornblende</td>
<td>0.27</td>
<td>0.4</td>
<td>7.8</td>
<td>500</td>
<td>8.4</td>
<td>500</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>0.001</td>
<td>0.2</td>
<td>5.1</td>
<td>590</td>
<td>6.0</td>
<td>690</td>
</tr>
</tbody>
</table>

* Assumed equal to the upper range of measured values.

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

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Fig. 5. Isotherm plot for the Grenville meta-anorthosite. Measured and predicted [(Δ18O unpl – 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 (Δ18O – 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 δ18O values were determined with both the hydro (wet) and anhydrous (dry) diffusion coefficients (Table 2). The measured and hydro values calculated δ18O 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 δ18O 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 δ18O value of the modally abundant feldspar porphyroclasts is only 0.1‰ during cooling, and the δ18O value of the garnet did not change during retrogression. Therefore, this mineral pair should yield nearly peak-metamorphic temperatures. The Δ18O unpl–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 as the presence or absence of a fluid can be deduced (e.g., Eiler et al., 1993; Farquhar et al., 1993).
The calculated hydrous samples fit the measured $\delta^{18}O$ 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 $\delta^{18}O$ values define a false isotherm.

$\delta^{18}O$ 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**

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**References Cited**


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