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Constraint on the time scale of biotite-grade metamorphism during Acadian orogeny from a natural garnet-garnet diffusion couple

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ABSTRACT

We have determined the concentration profiles across the interface of a natural garnet-garnet couple in a biotite-grade rock from eastern Vermont. The couple consists of a grossular-spessartine garnet that had formed during regional metamorphism associated with the Acadian orogeny on an almandine core, which had crystallized during an earlier episode of metamorphism related to the intrusion of Fairlee granite at 411 ± 5 Ma. The concentration profiles were measured by both electron microprobe and analytical transmission electron microscope, and they were modeled to retrieve the value of $\int D(t)\mathrm{d}t$ through the time that diffusion was effective but without recourse to any diffusion data. The length of the concentration profiles measured in microprobe is barely resolvable from that resulting from a convolution effect from the spatial averaging in the spot analyses. Deconvolution of the microprobe profiles yields a value of $\int D(t)\mathrm{d}t = 0\text{–}3.4 \times 10^{-11}$ cm^2, suggesting very little or no diffusion. TEM analyses of the concentration profiles, which are not subject to any significant convolution effect, show a very small but definitive diffusion zone across the interface of the garnet-garnet couple, which yields a value of $\int D(t)\mathrm{d}t = 7.6 \times 10^{-12}$ cm^2. Because D is a function of time through its dependence on temperature, this value of $\int D(t)\mathrm{d}t$ provides an important constraint on the thermal history during the regional metamorphism. As an example, we used it in conjunction with the available diffusion data for garnet to derive ~40–50 Ma as the probable time scale for the biotite-grade metamorphism, taking into account the effects of the off-diagonal terms and thermodynamic nonideality on the diffusion process.

INTRODUCTION

Overgrowth of a mineral on itself is a well-documented petrographic feature in rock samples. Specifically for garnets, there are many reported instances in which a second metamorphic event led to overgrowth of garnet of different composition on another garnet crystal that had formed during an earlier metamorphic episode (e.g., Albee 1968; Brown 1969; Rosenfeld 1970; Edmunds and Atherton 1971; Rumble and Finnerty 1974; Erembert and Austrheim 1993). Although little work has been conducted in this area, the diffusion-induced compositional zoning across the interface of an overgrowth of a mineral on itself can be used to extract important constraints on the time scale of geologic or planetary processes (e.g., Ganguly et al. 1994).

Rumble and Finnerty (1974) described an overgrowth of grossular-spessartine garnet on an almandine core from eastern Vermont. From field and petrographic relations, they concluded that the almandine core had crystallized during contact metamorphism caused by the intrusion of Fairlee granite, whereas the overgrowth had formed during biotite-grade regional metamorphism associated with the Acadian orogeny. From U-Pb data of zircon grains abraded from the intrusion, the Fairlee granite has been dated to have intruded at 411 ± 5 Ma (Moench and Aleinikoff 1991). Rumble and Finnerty (1974) presented preliminary data on the concentration change of divalent cations, as determined by step scanning in an electron microprobe, across the interface of one of these natural garnet-garnet diffusion couples. Although not of the quality required for quantitative modeling, the scale of these reported concentration changes was sufficiently long, in comparison with the spatial averaging effect of the probe beam (Ganguly et al. 1988), to make us believe that a more careful determination of the compositional zoning by electron microprobe would yield unambiguous data for modeling the time scale of its development. Thus, we selected a pair of rock samples from the same thin-section block used by Rumble and Finnerty (1974) and prepared polished thin sections for electron microprobe analysis of concentration profiles. However, our expectation was not fulfilled because the spatial extent of compositional change across the interface was much smaller than we had ex-

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Figure 1. Backscattered electron image of the overgrowth of spessartine-grossular garnet on an almandine core. The thickness of the overgrowth is ~200 μm.

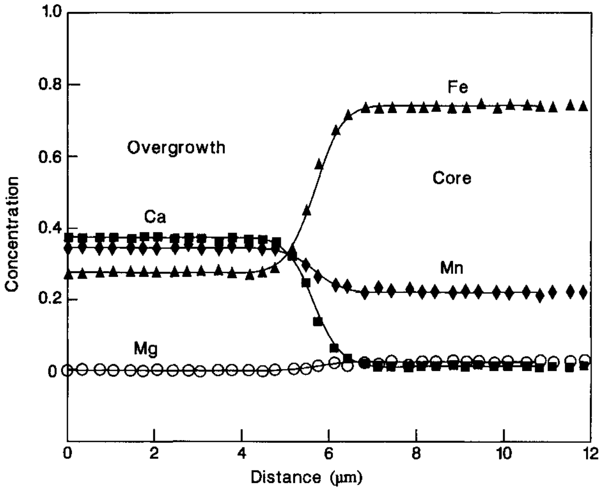

Figure 2. Concentration (i.e., atomic fraction) profiles across the core-overgrowth interface of garnet, as determined by spot analyses made with an electron microprobe at ⅓ μm steps, and simulation of these data (solid lines) with $Dt = 1.16 \times 10^{-9}$ cm^2. The analyzed data are represented by symbols.

pected from the preliminary data of Rumble and Finnerty (1974). In fact, it was almost too small to be resolved beyond the expected length of compositional change simply because of the spatial averaging effect of the microprobe beam as it spreads across the core-overgrowth interface. This failure led us to conduct an analytical transmission electron microscopic (ATEM) study of the concentration profiles across the interface to establish more clearly the extent of diffusion-induced compositional zoning that occurred during the regional metamorphism. In this work we report on the measurement of concentration profiles across the core-overgrowth interface of a garnet-garnet diffusion couple and the results of the modeling of these data to help determine the time scale of biotite-grade metamorphism during the Acadian orogeny.

MEASUREMENT OF DIFFUSION PROFILES ACROSS THE CORE-OVERGROWTH INTERFACE

Electron microprobe analyses

Garnet grains with cores and overgrowth of contrasting compositions were clearly identifiable in thin sections as grains with a "spongy" outer segment. Backscattered imaging (Fig. 1) allowed identification of regions of good contact between the core and overgrowth garnet. Because of the spongy nature of the overgrowth resulting from holes and inclusions, it was necessary to search for clean garnet-garnet contacts where the profiles could be measured across the entire diffusion zone without any interference from inclusions. Concentration profiles across an interface of one of these natural diffusion couples were measured by beam scanning, that is, by electronically stepping the microprobe beam at ⅓ μm steps in a Cameca SX-50 electron microprobe (for further details, see Chakraborty and Ganguly 1992). Standards used were andradite for Si, Al, and Ca, synthetic hematite or metallic iron for Fe, forsterite for Mg, and $MnTiO_3$ for Mn. Counting times varied between 30 and 60 s for each element at each point. The oxide totals in the accepted analyses were always within 99–101 wt%.

Measured profiles of the divalent cations (Fe, Mg, Mn, and Ca) are illustrated in Figure 2. Because the spatial scale of concentration changes is very small, ~3 μm, we tested for the spatial averaging effect by measuring the concentration profiles, under the same operating conditions, across the interface of a garnet-aluminum couple that did not experience any perceptible diffusion. This couple, which is henceforth referred to as the "standard couple," was prepared by inserting a garnet crystal with polished surfaces into molten aluminum and was used by Ganguly et al. (1988) in their study of the convolution effect in microprobe analyses of diffusion profiles. (They found that the spatial averaging effect in the garnet-aluminum couple was essentially the same as that in a garnet-garnet couple that was prepared in the laboratory and that did not experience any significant diffusion.) The concentration profiles with spatial gradients across the garnet-aluminum interface, which were solely due to the spatial averaging effect of the microprobe beam, were found to be approximately of the same length (~3 μm) as those in the natural garnet-garnet couple.

Transmission electron microscopic analyses

At present only Auger probe and ATEM provide the spatial resolution necessary to resolve the diffusion-induced compositional zoning that may be present in the natural garnet-garnet couple from Vermont. However, each of these techniques has been utilized only once before (Hochella et al. 1986; Eisenhouer et al. 1993) owing

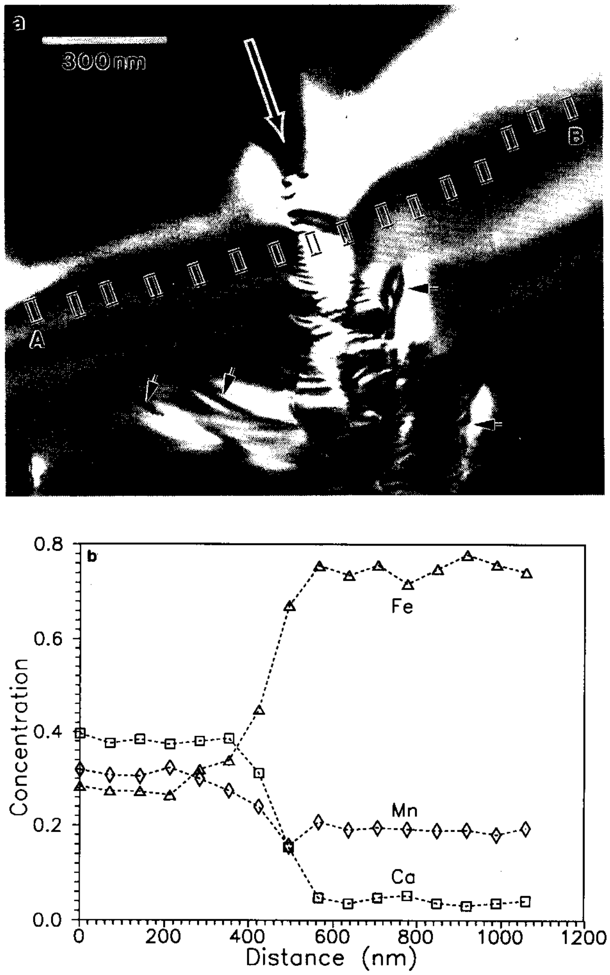

Figure 3. (**a**) Dark-field TEM image across the core-overgrowth interface of garnet with the analyzed areas marked by rectangles, and (**b**) the corresponding concentration profiles of the divalent cations. The analyzed concentrations (i.e., atomic fraction) of each cation are connected by a dashed line. The image obtained using the 242 reflection shows thickness contours (light and bright fringes) parallel to the thin edge. The concentration profiles were measured between A and B in **a** as an array of small scanned rectangles (30 × 70 nm) along the first dark thickness contour in both spessartine-grossular overgrowth (left side) and almandine core (right side). The interface is marked by moiré contrast and misfit dislocations, with additional dislocations extending outward from the interface (small arrows in **a**).

to the extraordinary technical difficulties associated with these procedures. Charging of the electron beam for analysis of nonconducting materials, coupled with the instability of commercially available epoxy at the extremely evacuated operating conditions, poses a special problem for Auger probe analysis. ATEM, on the other hand, presents the problem of the potential loss of the interface as a result of preferential thinning while the sample is being ion milled to electron transparency. Additional problems in the ATEM result from the variability of sample thickness and the need to standardize the energy-dispersive counting system. A brief description of sample preparation and analytical technique for the ATEM study of the natural garnet-garnet couple follows.

Copper rings with 600 μm central holes were glued to the samples with epoxy such that the core-overgrowth interface was ~150 μm from the center. The samples were mechanically thinned from ~30 to ~10 μm with a Gatan dimple grinder before being ion milled with 5 kV Ar^+ ions incident to the sample at a grazing angle of 15°. The milling was performed nearly perpendicular to the interface by using the sector–speed control option of a Gatan Duomill. With this technique, the sample rotation was modulated such that most of the thinning occurred where the beam was within a 20° angle from the interface normal. The milling was terminated after the sample was perforated and several small holes were produced. In the first sample investigated, the interface was found to pass through one of these small holes.

The sample was analyzed using a Philips CM20 FEG transmission electron microscope in the scanning (STEM) mode with 200 kV electrons. Amplitude-contrast images (conventional TEM) of the interface region were also obtained to investigate interface structure. The concentration profiles were measured by scanning a sequence of small rectangular areas spaced approximately 74 nm apart along a path that followed the thin edge of the sample (Fig. 3a). Analyses were performed by rastering 30 × 70 nm areas to minimize beam damage, which would otherwise be severe, with the use of the sharply focused beam in the STEM mode. Analyses lasted 60 s each, with an X-ray count rate of approximately 1000 counts per second. The sample thickness was held approximately constant along the profile by using a constant beam current and positioning the analyzed regions such that the count rate remained constant.

The ATEM profiles (Fig. 3b) show that the extent of compositional zoning ranges from 210 nm (0.21 μm) for Ca to 350 nm (0.35 μm) for Fe. The dark-field image in Figure 3a was obtained with the specimen tilted such that there was strong diffraction from 242 planes and passing of the 242 reflection through the objective aperture. When the diffraction condition for imaging was used, dislocations near the core-overgrowth interface produced strong contrast and the thickness of the sample was reflected by light and dark thickness contours parallel to the thin edge of the sample. The problem of differential X-ray absorption due to variation of thickness along a line of analyses was avoided by locating the successive steps along the first dark thickness contour. The analytical spots along the chosen thickness contour are shown by small rectangles. The interface itself was somewhat inclined toward the electron beam and therefore produced a wedgelike array of moiré fringes and dislocations that accommodate the misfit between the structures of the almandine-rich core and grossular- and spessartine-rich overgrowth garnet crystals. Also present are several dislocations that extend away from the interface and may represent free dislocations that were pinned at the interface. The fact that the interface was somewhat inclined relative to the profile line means that the measured lengths of compositional zoning are somewhat larger than their actual lengths, which should be measured normal to the interface.

MODELING OF THE DIFFUSION PROFILES

Multicomponent diffusion in a semi-infinite diffusion couple can be treated in terms of an effective binary diffusion model (Cooper 1968; Chakraborty and Ganguly 1992). Assuming that the effective binary diffusion coefficient of a component [EBDC or $D_{i(\mathrm{EB})}$] is independent of the distance (X) within the diffusion zone, the transient concentration profile of a component (i) at constant P-T in a semi-infinite couple with the interface at $X = 0$, and with no initial concentration gradient on either side of the interface, is given by the following solution of the diffusion equation (cf. Crank 1975, Eq. 2.14):

$$C_i(t,X) = C_i(0) + \frac{C_i^0}{2}\left\{1 - \mathrm{erf}\frac{X}{\sqrt{4[D_{i(\mathrm{EB})}]t}}\right\}. \quad (1)$$

Here C_i^0 represents the initial concentration difference between the two sides of the couple, and $C_i(0)$ is the lower of the two initial values of C_i. In principle, $D_{i(\mathrm{EB})}$ is different for each component in multicomponent diffusion in a semi-infinite diffusion couple. However, the EBDCs of the various components may be sufficiently similar in special circumstances such that all concentration profiles can be effectively modeled by a single diffusion coefficient (e.g., Chakraborty and Ganguly 1992).

Because the diffusion coefficient is a function of temperature, variation of temperature during a geologic process makes the diffusion coefficient a function of time, the exact form of which depends on the relationship between temperature and time (see, e.g., Dodson 1973; Ganguly et al. 1994). Following the method of the solution of the diffusion equation involving time-dependent diffusion coefficients (e.g., Crank 1975, Eq. 7.4), it can be easily shown that for nonisothermal diffusion, Dt represents the integral $\int D(t)\mathrm{d}t$ through the period of effective diffusion. The multicomponent diffusion profiles measured in the microprobe were modeled according to Equation 1 and a nonlinear least-squares–fitting technique developed by Ross and Chakraborty (unpublished data). A single value of Dt [or $\int D(t)\mathrm{d}t$] = 1.16 (±0.31) × 10^{-9} cm^2, where the uncertainty represents one standard deviation (1σ), was found to model adequately the microprobe profiles of all components (Fig. 2).

Ganguly et al. (1988) conducted a detailed mathematical and experimental investigation of the convolution effect in the determination of compositional profiles by microprobe step scans. Assuming that the excitation intensity of the sample volume had a Gaussian distribution with radial symmetry about the beam axis, they showed (Ganguly et al. 1988, Eq. 20) that the true value of Dt is related to the value calculated [$(Dt)_C$] from the measured concentration profile as

$$Dt = (Dt)_C - \frac{\epsilon^2}{2} \quad (2)$$

where ϵ represents the error standard deviation of the intensity distribution of X-rays resulting from the spatial averaging effect of the microprobe beam. Following Ganguly et al. (1988), we estimated $\epsilon = 0.536$ μm from the concentration profiles across the interface of the "standard couple" of garnet and aluminum, which were measured under operating conditions that were essentially identical to those used for the garnet-garnet couple. Thus, imposing the restriction that Dt cannot be negative, we obtain a corrected Dt = 0–3.4 × 10^{-11} cm^2 from the above values of ϵ and $(Dt)_C$ obtained by least-squares fitting of the microprobe data. The microprobe data, therefore, fail to show unambiguously a true diffusion profile between the natural garnet-garnet couple.

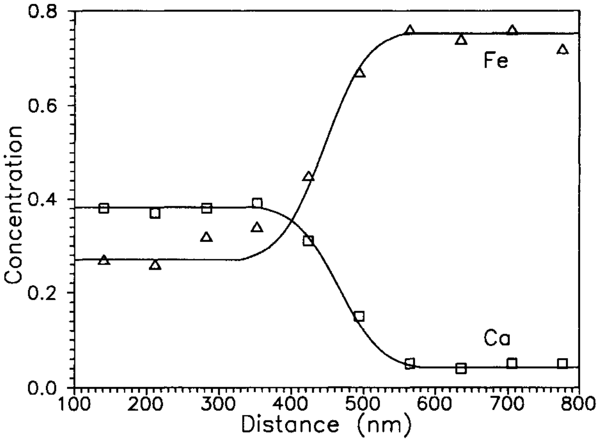

FIGURE 4. Fits of the measured concentration profiles in ATEM of Ca (squares) and Fe (triangles) across the core-overgrowth interface of garnet with $Dt = 7.5 \times 10^{-12}$ cm^2.

The presence of a diffusion zone between the garnet-garnet couple is clearly borne out by the ATEM data (Fig. 3). However, the data points on the Fe- and Mn-diffusion zones near the Fe-poor end are irregular and seem to have complementary errors. Overall, the analyzed data points for the Mn-diffusion profile are too irregular to be amenable to unambiguous modeling. Therefore, we selected only the Fe- and Ca-diffusion profiles to obtain Dt. The best fit to the Ca-concentration data across the interface of the garnet-garnet couple is given by $Dt = 7.5 \times 10^{-12}$ cm^2 (Fig. 4). This value falls within the range of Dt (0–3.4 × 10^{-11} cm^2) inferred from the deconvolution of the concentration profiles determined by electron microprobe. The convolution effect in the TEM analyses was vanishingly small because of the very small size of the excited analytical volume in comparison with the profile length (Ganguly et al. 1988), which was due not only to

TABLE 1. Representative analyses of ilmenite inclusions within the overgrowth garnet, adjacent overgrowth garnet, and core garnet

	Ilmenite	Ilmenite	Overgrowth garnet	Core garnet
FeO	43.02	42.34	11.37	36.80
MgO	0.01	0.04	0.03	1.44
CaO	0.21	0.18	14.99	1.01
MnO	3.99	4.14	15.50	3.73
Cr_2O_3	0.00	0.01	0.02	0.02
Al_2O_3	0.00	0.00	20.19	20.62
TiO_2	50.92	51.43	0.24	0.04
SiO_2	0.03	0.05	37.09	36.16
Total	98.19	98.21	99.45	99.86
Fe	18.52	18.20	3.82	12.62
Mg	0.01	0.03	0.02	0.88
Ca	0.12	0.10	6.45	0.44
Mn	1.74	1.80	5.28	1.30
Cr	0.00	0.003	0.01	0.01
Al	0.00	0.00	9.56	9.97
Ti	19.71	19.88	0.07	0.01
Si	0.02	0.03	14.91	14.83
K_D	14.71	13.98		

Note: K_D is defined as the ratio $(Fe/Mn)^{Ilmenite}/(Fe/Mn)^{Overgrowth\ garnet}$. All analyses are from areas outside the diffusion zone across the core-overgrowth interface.

the small beam size and rastering area, but also to the thinness of the sample (to electron transparency).

The *Dt* values for the best fit of the Ca- and Fe-concentration profiles need not be the same, because the EBDC for Fe can, in principle be different from that of Ca. However, we found that the same *Dt* value that yields the best match of the calculated profile with the measured Ca-concentration data in ATEM also leads to a satisfactory fit of the Fe-concentration data except for the two obviously anomalous data points near the Fe-poor end (Fig. 4). This is consistent with the results of our ongoing experimental diffusion studies using natural grossular-almandine diffusion couples, in which we have found the EBDCs of Fe and Ca to be essentially the same. Thus, we accept a value of *Dt* [or $\int D(t)dt$] of 7.5×10^{-12} cm^2 for both the Ca and Fe profiles in the following analysis.

APPLICATION TO THE TIME SCALE OF BIOTITE-GRADE METAMORPHISM DURING THE ACADIAN OROGENY

Because D is a function of time through its dependence on temperature, the value of the integral $\int D(t)dt$ provides an important constraint on the temperature-time relation of the host rock. We discuss below an application of the value of $\int D(t)dt$ to determine the time scale over which diffusion was effective during the biotite-grade regional metamorphism. For this exercise, we first need to determine the peak temperature of regional metamorphism responsible for the formation of the garnet overgrowth. As discussed below, no significant error is introduced into our calculation by neglecting the effect of growth during diffusion. Because diffusion processes characterized by a high activation energy (Q), such as in garnet, are very sensitive to temperature ($D \propto e^{-Q/RT}$), and diffusion is therefore effective only within a narrow temperature interval, we suggest that the period of effective cation diffusion in garnet closely approximates the period that the rock had spent near the peak temperature. We thus propose the duration of diffusion in garnet as the time scale of biotite-grade regional metamorphism during the Acadian orogeny.

Temperature of formation of garnet overgrowth

From petrographic evidence, Rumble and Finnerty (1974) concluded that the garnet overgrowth formed during biotite-grade regional metamorphism according to the reaction 0.47 biotite + 304 plagioclase + 10.2 ilmenite + 9.43 H_2O + 3.87 Fe_2O_3 + 20.3 Na_2O + 100 quartz → 302 albite + 2.78 sphene + 16 epidote + 12.6 garnet + 0.46 muscovite. It is not possible at present to define clearly the temperature of this reaction, especially in the absence of any knowledge of the chemical composition of white mica and reactant biotite. However, the garnet overgrowth contains inclusions of relict ilmenite (which reacted to form the overgrowth), so that the temperature-composition dependence of Fe-Mn fractionation between garnet and ilmenite (Pownceby et al. 1991) may be used to estimate the temperature of metamorphism. It should be noted that the thermometric formulation given by Pownceby et al. (1991) has an error resulting from wrong input in the regression analysis. The corrected formulation (Hugh O'Neill, personal communication) is

$$T\,(\mathrm{K}) = \frac{14642(\pm 375) - 2200(\pm 300)(2X_{Mn} - 1) + 539(\pm 109)(X_{Mn} - X_{Fe})^{Gt}}{\mathrm{R} \ln K_D + 4.203\ (\pm 0.347)} \tag{3}$$

where R is the gas constant in joules per mole-kelvin.

Table 1 summarizes the compositions of two ilmenite inclusions, that of enclosing overgrowth garnet close to the inclusions, and that of core garnet, as determined by microprobe spot analyses. All ilmenite inclusions are rimmed by thin layers of sphene that accompanied the formation of garnet according to the above reaction. If we assume that the ilmenite inclusions and the adjacent domains of overgrowth garnet were in cation-exchange equilibrium through the grain boundaries of the thin layers of intervening sphene, then we obtain temperatures of ~349 ± 20 and 358 ± 20 °C from the two K_D(Fe-Mn) values between garnet and ilmenite (Table 1). Unfortunately, there are at present no additional thermometric constraints for the biotite-grade rocks from which the present sample was collected that can be used to check the temperature estimated from the garnet-ilmenite cation-exchange thermometer. Because of the small concentration of Mg in the minerals (Table 1), and the analytical error associated with the determination of small concentrations of elements, the Fe-Mg fractionation between garnet and coexisting biotite, which constitutes one of the most widely used geothermometers (e.g., Ferry and Spear 1978; Ganguly and Saxena 1984), cannot be used to obtain a reliable temperature for our sample. Thus, we accept the mean of the two temperature estimates from garnet-ilmenite geothermometry, 353 ± 15 °C, as the peak temperature for the biotite-grade metamorphism.

Time scale of regional metamorphism

A nonisothermal diffusion problem can be reduced to a problem of isothermal diffusion by finding the temperature, which we refer to as the characteristic temperature, T_{Ch}, such that

$$\int_{t_0}^{t'} D(t)\mathrm{d}t = D(T_{\mathrm{Ch}})(t' - t_0) \tag{4}$$

(Shewmon 1963; Chakraborty and Ganguly 1991). Using the value of $\int D(t)\mathrm{d}t \approx 7.5 \times 10^{-12}$ cm², as deduced above from the ATEM data, we obtain

$$\Delta t = \frac{7.5 \times 10^{-12}\ \mathrm{cm}^2}{D_{i(\mathrm{EB})}(T_{\mathrm{Ch}})} \tag{5}$$

where $\Delta t = t' - t_0$ and $D_{i(\mathrm{EB})}(T_{\mathrm{Ch}})$ is the effective binary diffusion coefficient at the characteristic temperature (T_{Ch}). Chakraborty and Ganguly (1991) explored the relationship between peak temperature, T_{Peak}, and T_{Ch} for simple metamorphic T-t cycles characterized by one thermal maximum and concluded that in these cases Equation 4 is satisfied for $T_{\mathrm{Ch}} \approx 0.97T_{\mathrm{Peak}}$. Thus, we obtain $T_{\mathrm{Ch}} = 343 \pm 15$ °C, using the estimated peak temperature for the biotite-grade regional metamorphism.

Calculation of the EBDC of a component requires knowledge of the self-diffusion coefficients of all the diffusing components along with concentration gradients of all but one component, which is chosen as a dependent component. Because the Mn-concentration profile within the diffusion zone is relatively poorly defined, Mn is selected as the dependent component so that the Mn-concentration gradient does not enter into the calculation. Further, because Mg concentration in both core- and overgrowth-garnet is very dilute ($X_{\mathrm{Mg}} \approx 0.004$: Table 1 and Fig. 2), we treat the diffusion problem in garnet as one of ternary diffusion. Following the method of calculation of EBDC outlined in Chakraborty and Ganguly (1992) for diffusion within a semi-infinite couple, we have

$$D_{\mathrm{Fe(EB)}} = D_{\mathrm{FeFe}} + D_{\mathrm{FeCa}}\frac{\partial C_{\mathrm{Ca}}}{\partial C_{\mathrm{Fe}}} \tag{6.1}$$

and

$$D_{\mathrm{Ca(EB)}} = D_{\mathrm{CaCa}} + D_{\mathrm{CaFe}}\frac{\partial C_{\mathrm{Fe}}}{\partial C_{\mathrm{Ca}}}. \tag{6.2}$$

Here D_{ij} is an element of the **D** matrix, which can be calculated for a thermodynamically ideal solution according to (Lasaga 1979):

$$D_{ij} = D_i^*\delta_{ij} - \frac{(X_iD_i^*)(D_j^* - D_n^*)}{\sum\limits_i X_iD_i^*} \tag{7}$$

where D_i^* is the self-diffusion coefficient of the component i, δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ when $i = j$, and $\delta_{ij} = 0$ when $i \neq j$), and n represents the dependent component. Even though $D_{i(\mathrm{EB})}$ is, in principle, a function of composition, the diffusion profile of either Ca or Fe can be modeled quite well by using a constant $D_{i(\mathrm{EB})}$ (Fig. 4). We thus calculate $D_{\mathrm{Ca(EB)}}$ and $D_{\mathrm{Fe(EB)}}$ at the middle of the diffusion zone ($X_{\mathrm{Fe}} = 0.56$, $X_{\mathrm{Mn}} = 0.20$, $X_{\mathrm{Ca}} = 0.24$) to approximate the average EBDC of either component within the diffusion zone.

For nonideal solution, $D_{i(\mathrm{EB})}$ may be corrected according to an effective binary model suggested by Chakraborty and Ganguly (1992). However, inasmuch as Ca and Fe interact with Mn very similarly (Pownceby et al. 1991), the calcium iron manganese garnet can be treated effectively as a quasi-binary solid solution of Ca and Fe + Mn components. Thus, the EBDCs of Fe and Ca, calculated according to Equation 6, may be corrected by multiplying by the following factor, which is strictly valid for a binary solution (Darken 1948; Brady 1975) and is the same for both components:

$$D_i(\mathrm{thermo}) = 1 + \frac{\partial \ln \gamma_i}{\partial \ln X_i} \tag{8}$$

where γ_i is the activity coefficient of the component i. Using the optimized thermodynamic mixing property data for Ca and Fe in garnet from Berman (1990) and Ganguly and Saxena (1984), we obtain $D_{\mathrm{Ca(EB)}}(\mathrm{thermo}) = D_{\mathrm{Fe(EB)}}(\mathrm{thermo}) = 1.13$ and 1.9, respectively, at the median composition within the diffusion zone.

To calculate the ideal part of $D_{\mathrm{Fe(EB)}}$ and $D_{\mathrm{Ca(EB)}}$, the high-temperature self-diffusion data for Fe and Mn in garnet were extrapolated to the characteristic temperature of 343 °C according to the Arrhenian relations given by Chakraborty and Ganguly (1992). These relations were derived from experiments that used spessartine-almandine diffusion couples encased in graphite containers under dry conditions. There are, however, virtually no published data on D_{Ca}^* in garnet, especially in Ca-Fe-Mn–rich and Mg-poor garnet compositions such as encompassed by the natural garnet-garnet couple. Loomis et al. (1985) tentatively suggested on the basis of a single experiment at 40 kbar, 1440 °C, using a pyrope-almandine diffusion couple, that $D_{\mathrm{Ca}}^* \approx 0.5D_{\mathrm{Fe}}^*$. Our ongoing experimental investigation suggests that D_{Ca}^* increases with the enrichment of Ca component, possibly because of the expansion of the lattice, so that D_{Ca}^* in the present garnet-garnet couple might have been somewhat larger than that suggested by Loomis et al. (1985) for the pyrope-almandine couple.

For the purpose of calculating the EBDCs of Ca and Fe, we treated D_{Ca}^* as an unknown and varied it until we obtained the same values of $D_{\mathrm{Fe(EB)}}$ and $D_{\mathrm{Ca(EB)}}$ from Equations 6.1 and 6.2, respectively, because otherwise different time scales of the diffusion process would be obtained from the concentration profiles of Fe and Ca, both of which can be modeled adequately by the same value of Dt [or $\int D(t)\mathrm{d}t$] (Fig. 4). The changes in the calculated values of Δt as functions of $D_{\mathrm{Fe(EB)}}$ and $D_{\mathrm{Ca(EB)}}$, which were derived from the assumed values of D_{Ca}^* according to Equations 6 and 7, are illustrated in Figure 5. In these

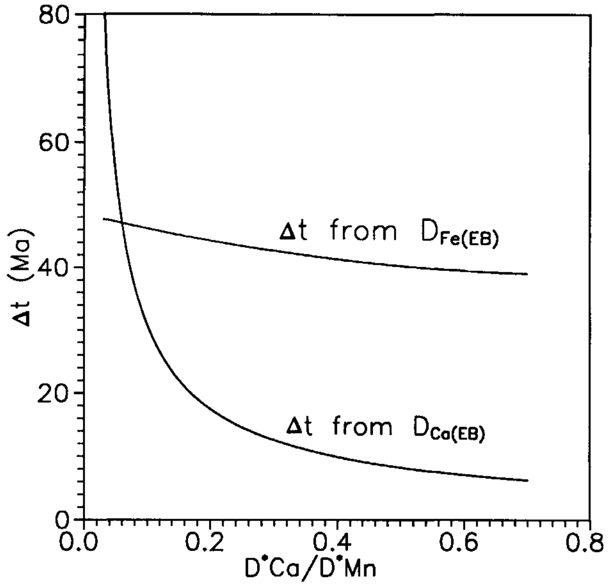

Figure 5. Variations of the calculated time scales (Δt) of biotite-grade metamorphism ($T_{\text{Ch}} = \sim 343$ °C) as functions $D_{\text{Fe(EB)}}$ and $D_{\text{Ca(EB)}}$, which are derived from assumed values of D^*_{Ca}. The latter were normalized to D^*_{Mn}. Convergence of values of Δt was obtained at $D^*_{\text{Ca}}/D^*_{\text{Mn}} = 0.06$ (i.e., $D^*_{\text{Ca}} = 9.72 \times 10^{-27}$ cm^2/s).

calculations, no correction was made for pressure and f_{O_2} effects on the diffusion coefficients. The calculated (ideal) EBDCs of Ca and Fe converge to a value of 5.1×10^{-27} cm^2/s, and the corresponding values of Δt converge to 47 Ma, when $D^*_{\text{Ca}} = 9.7 \times 10^{-27}$ cm^2/s. At this condition (1 bar, 343 °C), $D^*_{\text{Fe}} = 2.8 \times 10^{-27}$ cm^2/s and $D^*_{\text{Mn}} = 1.62 \times 10^{-25}$ cm^2/s.

Using now the thermodynamic factor calculated from the Ca-Fe mixing property in Berman (1990), we have, for the above value of D^*_{Ca}, $D_{\text{Fe(EB)}} = D_{\text{Ca(EB)}} = 5.7 \times 10^{-27}$ cm^2/s and a corresponding $\Delta t = 41.6$ Ma, whereas the thermodynamic factor calculated from that in Ganguly and Saxena (1984) yields $D_{\text{Fe(EB)}} = D_{\text{Ca(EB)}} = 9.6 \times 10^{-27}$ cm^2/s and a corresponding $\Delta t = 25$ Ma. However, we prefer the result obtained from the Berman model because it incorporates, in addition to the experimental data used by Ganguly and Saxena (1984), all careful experimental data that have become available since the latter work. The **D** matrix calculated from the above self-diffusion data and Equation 7 is as follows (Mn is treated as the dependent component, and the unit of the matrix elements is squared centimeters per second):

$$\mathbf{D} = \begin{pmatrix} D_{\text{FeFe}} & D_{\text{FeCa}} \\ D_{\text{CaFe}} & D_{\text{CaCa}} \end{pmatrix} = \begin{pmatrix} 9.75 \times 10^{-27} & 6.63 \times 10^{-27} \\ 1.02 \times 10^{-26} & 1.95 \times 10^{-26} \end{pmatrix}. \quad (9)$$

In retrieving Δt, we assumed that the time scale of formation of the garnet overgrowth through the thickness of the diffusion zone was instantaneous in comparison with that of diffusion. This assumption can be justified as follows. Christensen et al. (1989) determined the growth rate of garnet crystal from radial variation of the ^{87}Sr/^{86}Sr ratio in a single garnet crystal separated from a metapelitic schist in southeast Vermont, which consists of paragonite, muscovite, chlorite, quartz, and plagioclase. Their measured rate of crystal growth is ~1.4 mm/Ma (according to the data of Christensen et al. 1994, a growth rate of ~1 mm/Ma may be typical for garnet during regional metamorphism). This yields 1214 yr as the time required to produce a garnet overgrowth equal to the half-thickness of the diffusion zone (i.e., approximately the thickness of the diffusion zone within the overgrowth), which is negligible in comparison with the time scale of the diffusion process. Thus, no significant error is introduced into our calculation by assuming that the effective thickness of the overgrowth "seen" by diffusion (which is about one-half the thickness of the diffusion zone) was plated on the almandine core instantaneously.

Uncertainties in the estimated time scale of metamorphism

Because the diffusion coefficients in garnet have activation energies (Q) on the order of 60 kcal/mol (Chakraborty and Ganguly 1992), these are very sensitive to temperature changes ($D \propto e^{-Q/RT}$), and consequently a small error in the determination of T results in a large error in the calculated value of D and, hence, that of Δt. The estimated error of the mean temperature of ±15 °C results in an uncertainty factor of ~3 in the value of Δt, which highlights a general problem associated with the retrieval of time scales of geologic processes from diffusion-controlled properties characterized by large activation energies (e.g., Dodson 1973; Ganguly et al. 1994).

Potential problems with the above estimate of Δt also stem from the fact that we neglected the possibility of the change of diffusion mechanism within the domain of low-temperature extrapolation of the experimental diffusion data, and the possible effect of H_2O or H-related species. However, as discussed elsewhere (Chakraborty and Ganguly 1991), the lower temperature data (750–900 °C) on ^{27}Mg tracer diffusion in garnet by Cygan and Lasaga (1985) are in excellent agreement with the Arrhenian extrapolation of the higher temperature data of Chakraborty and Ganguly (1991, 1992) when both sets of data are normalized to the same pressure and f_{O_2} conditions. Chakraborty and Ganguly (1991) thus concluded that there is no change of diffusion mechanism in garnet within the temperature range of 750–1400 °C. This conclusion is reinforced by the recent data of Chakraborty and Rubie (1996) on ^{26}Mg tracer diffusion at 750–900 °C in pyropic garnet crystals, which were selected from the same stock of material used by Chakraborty and Ganguly (1991, 1992) in their high-P-T studies. The Mg tracer-diffusion data of Chakraborty and Rubie (1996) are in excellent agreement with the low-temperature Arrhenian extrapolation of that of Chakraborty and Ganguly (1991, 1992) when both data sets are normalized to the same pressure and f_{O_2} conditions.

The issue of whether the diffusion mechanism in garnet changes between 750 and 350 °C cannot be resolved at present and is probably not even resolvable because of the extreme sluggishness of the diffusion process at these temperatures in comparison with any practical time scale of laboratory experiments. However, if there were indeed a change of cation-diffusion mechanism in garnet below 750 °C, then the diffusion process would be enhanced. This would also be true if H_2O or H-related species had an effect on the cation-diffusion process in garnet analogous to their effect on Al-Si order-disorder kinetics and interdiffusion in feldspars (Yund and Tullis 1980; Graham and Elphick 1991; Goldsmith 1991). Thus, both the possible change of diffusion mechanism and the potential effect of H_2O (or H-related species) would contribute to a compression of the estimated time scale of metamorphism from that derived above. Further reduction of the calculated Δt would result if we were able to correct for the sectioning effect, which artificially extended the length of the diffusion profile, as discussed above. This, however, may be a relatively small effect because the true length of the profile (L) normal to the couple-interface is $L'\cos\theta$, where L' is the measured length and θ is the angle between the normal to the interface and the plane of the section (for example, if $\theta = 20°$, then $L = 0.94L'$). Thus, it seems that the potential errors introduced by the extrapolation of diffusion data from the laboratory (high temperature, dry) to natural conditions (low temperature, hydrous) and by the sectioning effect would lead to an overestimation of Δt.

We also recall that in calculating Δt from Dt, we neglected the effects of f_{O_2} and pressure on the diffusion coefficient. As noted above, the experimental diffusion data were for f_{O_2} defined by graphite. Unfortunately, the mineral assemblage of the rock does not permit meaningful determination of f_{O_2}. However, inasmuch as the cation-diffusion coefficient in garnet is expected to vary as $(f_{O_2})^{1/6}$ (Chakraborty and Ganguly 1991), and the systematic mineralogic changes during progressive metamorphism were usually due to the buffering of f_{O_2} by graphite (Miyashiro 1964; Ganguly 1977), the diffusion data used in this work are unlikely to be significantly in error as a result of neglecting the effect of f_{O_2}.

If the activation volumes given by Chakraborty and Ganguly (1992) are used, the diffusion coefficient changes by a factor of $\sim\exp(-0.11P)$, where P is in kilobars, and consequently Δt changes by the inverse of the same factor. This increases Δt by ~3.3 m.y./kbar increase of pressure up to a few kilobars. Considering, however, the metamorphic grade of these rocks, the pressure was probably on the order of a few kilobars. Thus, by neglecting the effect of pressure, we somewhat underestimated Δt, which is partly compensated by the fact that the diffusion profile used in retrieving Δt is larger than the true profile because of the sectioning effect, and the fact that the true diffusion coefficient might have been greater because of the possible change of diffusion mechanism and potential effect of H_2O or H-related species.

In summary, there are several sources of uncertainty in the calculation of Δt, some of which are compensating in nature. Perhaps the largest source of uncertainty is the estimate of the temperature of the rock. At this point, we feel that $\Delta t \approx 40$–50 Ma is the probable time scale of the biotite-grade metamorphism reflected by the diffusion zoning across the core-overgrowth interface of garnet.

DISCUSSION

The results reported in this work show good agreement between the length of the diffusion profile determined by ATEM and the range of its deconvolved length determined by electron microprobe, even though the latter by itself was not sufficiently accurate to permit reliable calculation of thermal history. This is a consequence of the extremely short diffusion zoning across the core-overgrowth interface of the garnet sample, so that the lengths measured in the microprobe were barely distinguishable from the convolution effect. This is the second study demonstrating the feasibility of TEM analysis across grain boundaries of natural samples, and the potential importance of the results obtained in this work should encourage more ATEM analysis across the contact of mineral grains of the same or different phases to detect incipient compositional zoning that is not resolvable under an electron microprobe.

On the basis of geochronologic data, Naylor (1971) suggested a maximum time scale of Acadian orogeny of 30 Ma and argued that "the actual span was probably considerably shorter." Our best estimate of the time scale of biotite-grade metamorphism (~40–50 Ma) is longer than this geochronologic limit but is not incompatible with the latter considering the uncertainties in our calculation, and it reinforces the notion (Naylor 1971) that the Acadian orogeny involved a collision between two sialic plates and the closing of an ocean basin.

One result of major importance in the present work is the retrieval of the quantity $\int D(t)dt$, which formally relates temperature and time and is independent of any uncertainty of the geothermometric estimate or of the diffusion kinetic data. A more definitive time scale of Acadian orogeny can be deduced when additional geothermometric estimates of peak temperature become available for the same rocks (e.g., from O-isotope fractionation data). Further, the validity of a T-t relation inferred from geochronologic or other evidence can be tested, when such data become available, by transforming the relation into a D vs. t relation and comparing the value of the integral $\int D(t)dt$ with that deduced above.

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