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HIGH-TEMPERATURE RETROGRADE REACTIONS IN PELITIC GNEISS, CENTRAL MASSACHUSETTS

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ABSTRACT

A coarse-grained gneiss from the highest-grade metamorphic zone of south-central Massachusetts contains the prograde minerals quartz, plagioclase, K-feldspar, garnet, cordierite, sillimanite and pyrrhotite, and displays several high-temperature retrograde metamorphic effects. Garnet–biotite and garnet–cordierite Fe–Mg K_D values indicate a peak metamorphic temperature of about 700°C at 6 kbar, and retrograde re-equilibration down to about 550°C, with pressure either remaining constant or slightly increasing. Two retrograde reactions are dealt with in this paper. The first is the growth of pale green secondary biotite on cordierite–K-feldspar grain boundaries. Although this biotite differs in composition from prograde brown biotite, its composition indicates limited extent of major element transport. Intergrowth of the pale green biotite with sillimanite and quartz suggests that all three minerals formed in a retrograde hydration reaction such as cordierite + K-feldspar + H_2O → biotite + sillimanite + quartz. The second retrograde reaction is the apparent *in situ* breakdown of cordierite within large (1 cm) grains to produce aggregates of small euhedral garnets (0.1 to 0.5 mm) with quartz and sillimanite in proportions appropriate to the reaction cordierite → garnet + sillimanite + quartz. Growth zoning in garnet grains indicates that they are coalesced smaller crystals. Host cordierite is concentrically zoned around the garnet with iron depletion close to the interface. The Fe–Mg concentration profile is interpreted as reflecting Fe–Mg interdiffusion in cordierite, and garnet growth is assumed to be diffusion-controlled. A simple moving-boundary diffusion model produces a good match to the measured concentration profile in cordierite and the size of retrograde garnets. Unfortunately, uncertainty in the Fe–Mg interdiffusion coefficient in cordierite precludes precise calculation of a cooling rate. However, the mathematical treatment given here allows for comparative constraints on cooling rate and diffusion coefficient. If a D of 7.5×10^{-18} cm^2/s is assumed, then the maximum cooling rate can be approximately 5°C/Ma, which appears to be a geologically reasonable value. Faster cooling rates would require a correspondingly higher diffusion coefficient.

Keywords: metamorphism, retrograde, diffusion, garnet, cordierite, cooling rate, Massachusetts.

SOMMAIRE

Un échantillon de gneiss à grain grossier, provenant de la zone la plus fortement métamorphisée de la partie centre-sud du Massachusetts, contient les minéraux progrades quartz, plagioclase, feldspath potassique, grenat, cordiérite, sillimanite et pyrrhotine; il montre aussi plusieurs effets d'un métamorphisme rétrograde de haute température. Les valeurs du coefficient K_D pour l'échange Fe–Mg impliquant grenat–biotite et grenat–cordiérite indiquent une température maximum d'environ 700°C à 6 kbar, et une ré-équilibration rétrograde jusqu'à environ 550°C à pression constante ou légèrement croissante. On traite ici de deux réactions rétrogrades: 1) la croissance d'une biotite secondaire vert-pâle qui chevauche les contacts inter-grains cordiérite–feldspath potassique. La différence de composition entre cette biotite et la biotite brune prograde souligne le peu d'importance du transfert d'éléments majeurs. L'intercroissance de la biotite vert-pâle avec sillimanite et quartz porte à considérer les trois phases comme produits d'une réaction d'hydratation rétrograde telle que cordiérite + feldspath potassique + H_2O = biotite + sillimanite + quartz. 2) La déstabilisation, apparemment *in situ,* de la cordiérite à l'intérieur de cristaux centimétriques, pour produire des agrégats de grenat en petits cristaux idiomorphes (0.1–0.5 mm) avec quartz + sillimanite en proportions appropriées pour la réaction cordiérite → grenat + sillimanite + quartz. Le profil de la zonation primaire de ces grains indique qu'ils se sont formés par agglomération de cristaux encore plus petits. La cordiérite-hôte est zonée de façon concentrique autour des domaines du grenat; le fer diminue près de l'interface. Le profil de concentration du couple Fe–Mg serait la réflexion de l'interdiffusion de ces éléments dans la cordiérite; on suppose la croissance du grenat gouvernée par la diffusion. Un modèle simple à interface mobile reproduit exactement le profil de concentration observé dans la cordiérite et la taille des cristaux de grenat rétrograde. Malheureusement, l'incertitude qui pèse sur le coefficient d'interdiffusion Fe–Mg dans la cordiérite entrave le calcul précis d'un taux de refroidissement. Toutefois, un traitement mathématique nous permet d'établir des limites sur ce taux et sur le coefficient de diffusion. Pour une valeur de D de 7.5×10^{-18} cm^2/s, le taux de refroidissement maximum serait d'environ 5°C/Ma, ordre de grandeur jugé raisonnable. Un refroidissement plus rapide nécessiterait un coefficient de diffusion encore plus élevé.

(Traduit par la Rédaction)

Mots-clés: métamorphisme, rétrograde, diffusion, grenat, cordiérite, taux de refroidissement, Massachusetts.

INTRODUCTION

For many years metamorphic petrologists have paid considerable attention to the changes in mineral assemblage and mineral chemistry that characterize prograde metamorphism, but have devoted much less effort to systematic analysis of retrograde features. Discussions of retrogression of pelitic rocks include papers by Grant & Weiblen (1971), Hollister (1977), Tracy *et al.* (1976) and Lasaga *et al.* (1977), among many others. A probable reason for this lack of attention is that retrograde metamorphism has been thought of as an irregular and nonpervasive process owing to limited availability of H_2O for rehydration and, therefore, considered too "random" for systematic study. Prograde metamorphism, however, occupies only a part of the P–T path taken by rocks as they are buried and then exhumed during mountain building. As pointed out by England & Richardson (1977), it is important that we obtain as much information as possible on the total path in order to understand orogenic processes. An understanding of how retrogression works and the P–T regimes in which it occurs are vital bits of information.

Whereas it may not be possible to make sense out of retrograde effects that occur over a large range in temperature and that are reflected by very complicated textures, there are situations where retrogression has apparently occurred over a small temperature interval and is thus represented by simple textures. The occurrence described in the present paper, an example of this type of retrogression, contains interpretable textures including secondary biotite growing on primary grain boundaries and large cordierite porphyroblasts breaking down internally to garnet–sillimanite–quartz aggregates. The intent of this paper is to demonstrate that such retrograde features may be useful to determine the physical state of the rock at, and just after, the peak of metamorphism and to attempt an estimate of initial cooling rates using kinetics of retrograde processes.

GEOLOGICAL SETTING

The sample described in this paper was collected in the Wales quadrangle, south-central Massachusetts (Fig. 1). This location lies within the highest-grade metamorphic zone in New England, characterized by the assemblage sillimanite–K-feldspar–garnet–cordierite in pelitic gneisses (Tracy & Robinson 1980, Tracy *et al.*

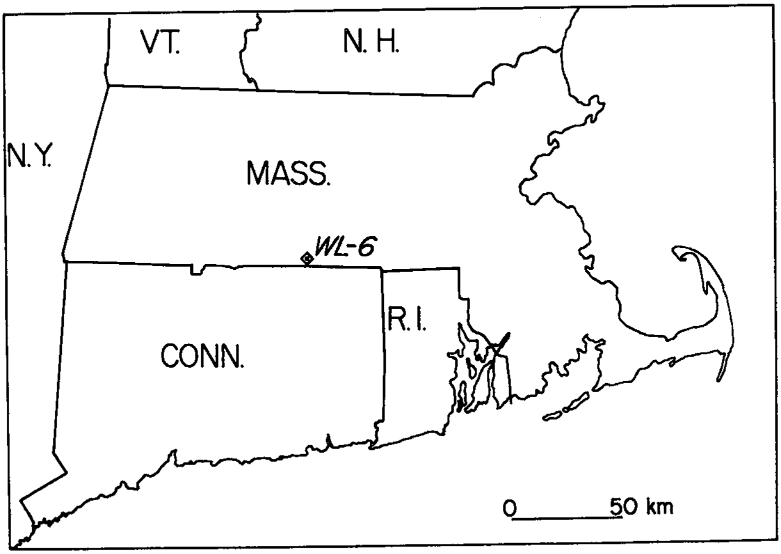

FIG. 1. Index map of southern and central New England showing the location of sample WL–6A.

1976). The stratigraphic unit that contains the sample is the Devonian Littleton Formation, and the tectonic regime is the south-central part of the Merrimack synclinorium. Details of the tectonic development of this area can be found in Robinson & Hall (1980).

Previous petrological studies of samples from central Massachusetts have shown that quite different P–T paths were taken during prograde metamorphism of different parts of the region (Tracy 1978, Tracy & Robinson 1980). In the Bronson Hill anticlinorium, the rocks apparently took a typical Barrovian path, characterized by a kyanite-to-sillimanite progression. On the other hand, rocks in the Merrimack synclinorium to the east show an andalusite-to-sillimanite progression followed by a late-stage pressure increase at and after the peak of metamorphism (Tracy & Robinson 1980). Peak metamorphic temperature in the area where the present sample was collected appears to have been about 700°C at a pressure of about 6–6.5 kbar (Tracy *et al.* 1976), but evidence suggests a pressure *increase* of up to 1.5 kbar during initial cooling (Robinson *et al.* 1977). This evidence consists of recrystallization of mylonitized cordierite gneiss to a garnet–biotite assemblage containing very magnesian garnet. Garnet composition allows an estimate of minimum pressure using the calibration of Tracy *et al.* (1976).

PETROGRAPHIC DESCRIPTION

Sample WL–6A is a coarse-grained gneissic rock that contains the primary metamorphic assemblage quartz–plagioclase–orthoclase–garnet–biotite–cordierite–sillimanite–pyrrhotite–graphite. Especially coarse are crystals of primary garnet and cordierite, which may be up to 1 cm or greater in size. In addition to the primary minerals noted above, there are several minerals that appear compositionally and texturally to be secondary, including very pale green biotite, which contrasts with the light red-brown color of primary biotite; the green biotite occurs as small flakes (up to 0.5 mm) restricted to the edge of large garnet and cordierite grains. This pale biotite is virtually restricted to cordierite–orthoclase and, to a lesser extent, garnet–orthoclase boundaries, where it is intimately intergrown with quartz and skeletal sillimanite, suggesting that biotite, quartz and sillimanite were produced in the same reaction. Mineral-composition evidence discussed below, reinforces this suggestion.

A second, apparently retrograde reaction involves the growth of small (up to 1 mm) aggregates of garnet, sillimanite and quartz in the interior of large (approximately 1 cm) cordierite grains (a typical example is shown in Fig. 3). The garnet is subhedral to euhedral, with well-developed crystal faces, whereas the associated sillimanite is semiskeletal and intergrown with quartz. Most of the cordierite in the sample shows some degree of polysynthetic twinning, but the twinning is considerably more developed in the immediate vicinity of the garnet–sillimanite–quartz aggregates. This behavior may indicate unusual strain around the aggregates, possibly due to volume change in the reaction in which cordierite breaks down; this possibility will be discussed further below.

MINERAL CHEMISTRY

Among all the minerals of variable composition in this rock, only garnet and biotite occur both as primary and secondary phases. Their primary and secondary compositions differ, as does the appearance of biotite, as noted above. Table 1 presents the chemical compositions of primary and secondary minerals in the sample. All analyses were done on the Yale University CAMECA MS–64 microprobe using a Tracor Northern TN–2000 energy-dispersion analyzer. Accelerating potential was 15 kV and sample current 5 nA measured on brass. Raw concentration data were corrected using the method of

TABLE 1. MICROPROBE ANALYSES OF MINERALS

	1	2	3	4		5	6	7
SiO_2	37.7	36.6	37.5	48.6		36.8	36.7	36.8
TiO_2	0	0	0	0		1.7	0.2	0.1
Al_2O_3	21.6	21.2	21.5	33.4		20.3	21.1	22.0
FeO	33.2	33.9	34.4	8.0		15.8	15.5	16.2
MnO	0.9	0.8	0.9	0.1		0	0	0
MgO	5.5	4.7	4.6	8.5		13.1	13.5	11.4
CaO	1.1	1.1	0.6	0		0	0	0
Na_2O	0	0	0	0.1		0.3	0.4	0.5
K_2O	0	0	0	0		8.8	8.5	9.1
Total	99.9	98.4	99.2	98.7		96.8	95.9	96.0
Oxygens	12	12	12	18		11	11	11
Si	2.99	2.97	2.99	4.99	Si	2.68	2.70	2.71
Al	2.02	2.03	2.02	4.03	Al	1.32	1.30	1.29
Fe	2.20	2.30	2.30	0.69		4.00	4.00	4.00
Mn	0.06	0.06	0.06	0.02	Al	0.42	0.53	0.62
Mg	0.65	0.57	0.57	1.29	Ti	0.10	0.01	0.01
Ca	0.09	0.10	0.05	0	Fe	0.96	0.96	1.00
Na	0	0	0	0.02	Mg	1.43	1.48	1.25
						2.91	2.98	2.88
Alm	73.4	76.0	77.1		Na	0.04	0.05	0.08
Pyr	21.6	18.9	19.1		K	0.83	0.80	0.86
Spe	2.0	1.8	2.0			0.87	0.85	0.94
Gro	3.0	3.0	1.8					
Fe/Fe+Mg	.77	.80	.80	.35		.40	.39	.44

1. Primary garnet (core). 2. Primary garent (rim). 3. Retrograde garnet. 4. Primary cordierite. 5. Primary biotite. 6. Retrograde biotite (adjacent to cordierite). 7. Retrograde biotite (adjacent to garnet.

Bence & Albee (1968) with the alpha factors of Albee & Ray (1970).

The results of analyses of garnet and cordierite given in Table 1 are intended to give the reader an idea of *typical* compositions; in fact, these minerals are generally zoned and have variable compositions. The large grains of primary garnet display zoning typical of highest-grade garnet from New England (Tracy *et al.* 1976), with compositions homogeneous except at garnet edges adjacent to cordierite or biotite. At these edges, the garnet has apparently exchanged Fe and Mg with the adjacent phase during cooling, resulting in an increased Fe/Mg ratio in the garnet.

The composition of cordierite given in Table 1 is that typical of large cordierite grains away from the garnet–sillimanite–quartz aggregates. Within about 1000 μm of these aggregates, the cordierite is zoned, with Fe/Mg dropping as an aggregate is approached. This zoning of cordierite is discussed in detail in a later section, and is assumed to represent diffusional zoning developed as the garnet aggregates grew within large grains of cordierite. The garnet in the aggregates also shows zoning. Cores of small euhedral grains have Fe/(Fe+Mg) of about 0.76, whereas rims of the same crystals have a maximum value of 0.82. The secondary garnet (that in aggregates) has a composition similar to that of the exchanged rims of the primary garnet, with one important exception: the secondary garnet always contains considerably less Ca than the primary garnet. This discrepancy is assumed to reflect the environment of growth of the later garnet. Entirely enclosed within cordierite, it is provided with a supply of Fe and Mg, and to a lesser extent Mn, from the adjacent cordierite, but does not have access to Ca. In fact, it is somewhat problematic that this garnet has as much Ca as it does.

The composition of primary red-brown biotite shows little variation except in rare instances of incipient alteration to chlorite. The TiO_2 content of the biotite is somewhat low, 1.7 wt. %, compared to a typical value of about 5% at this metamorphic grade. The low TiO_2 in biotite is apparently due to low Ti in the rock's bulk composition; notably, there is neither ilmenite nor rutile in the rock, and the biotite is therefore unlikely to be Ti-saturated (Guidotti *et al.* 1977).

Secondary biotite contrasts with the primary in several respects (see Table 1). Secondary biotite is considerably more variable in composition, and composition appears to be dependent upon local environment. In general, secondary biotite adjacent to garnet is slightly more iron-rich. These Fe–Mg relations suggest very local equilibration of mineral pairs, to be discussed in the next section. A further contrast is the low TiO_2 content of secondary biotite compared to primary biotite; this, together with higher Na/K ratio (see below), may help to explain the especially pale color of the secondary biotite. Lower TiO_2 may be due either to decreased Ti solubility in lower-temperature retrograde biotite or, more likely, to extremely restricted Ti supply in the grain-boundary environments in which this later biotite grew.

Finally, primary and secondary biotites differ in the typically higher Na/K ratio found in the latter. We believe that this also is evidence for local equilibrium. The secondary biotite is restricted to cordierite–orthoclase and, more rarely, garnet–orthoclase grain boundaries, where the alkali ratio of the local environment is dominated by the composition of the orthoclase (Or 85, Ab 15), and where unusually sodic biotites might be expected to occur.

REACTION FORMING SECONDARY BIOTITE

We have examined many high-grade pelitic rocks from central New England, and only rarely have we identified *obviously* retrograde biotite that has crystallized in rocks whose peak metamorphic grade was sillimanite–K-feldspar or higher. In these rare rocks, the typical occurrence is in recrystallized mylonite, where the fine grain-size and possible conduit for the entry of water provided favorable kinetics for recrystallization. Since the present sample is not a mylonite, there must clearly be something unusual in the post-peak metamorphic environment of sample WL-6A that allowed the secondary biotite to form. We believe that two factors combined to allow for crystallization of this retrograde phase: slow cooling at pressures near the peak metamorphic pressure and a supply of H_2O to allow progress of the rehydration reaction.

Thompson (1976) illustrated the P–T–X relations of three important dehydration reactions that occur at temperatures just above the muscovite-dehydration reaction. These three reactions are:

$$\text{Sillimanite} + \text{Biotite} + 2\ \text{Quartz} \rightarrow \text{Garnet} + \text{Orthoclase} + H_2O \quad (1)$$

$$6\ \text{Sillimanite} + 2\ \text{Biotite} + 9\ \text{Quartz} \rightarrow 3\ \text{Cordierite} + 2\ \text{Orthoclase} + 2\ H_2O \quad (2)$$

8 Sillimanite + 4 Biotite + 13 Quartz →
2 Garnet + 3 Cordierite + 4 Orthoclase
+ 4 H_2O (3)

Reactions (1) and (2) are multivariant and coupled with an $FeMg_{-1}$ exchange vector, and high-grade pelitic rocks containing either reaction-assemblage show a wide variation in compositions of biotite, garnet and cordierite. On the other hand, reaction (3) behaves as if it were univariant, with the result that the three ferromagnesian phases in this assemblage are remarkably consistent in composition in many different rocks in central New England (Hess 1971, Tracy *et al.* 1976, Thompson 1976). The mineral assemblage and the compositions of primary phases in sample WL–6A are typical of reaction (3) assemblages.

Tracy *et al.* (1976) ascribed the concentric zoning of some high-grade garnets to the operation of a multivariant *retrograde* reaction that may be written:

Garnet + Orthoclase + H_2O →
Sillimanite + Biotite + 2 Quartz (1a)

again coupled with an $FeMg_{-1}$ exchange vector. In this case, reaction progress is marked by increasing Fe/Mg in both garnet and biotite as T drops, of course accompanied by changing proportions of garnet and biotite. This reaction appears to be common in pelites whose maximum metamorphic grade was near the lower part of the sillimanite–K-feldspar zone (*e.g.*, Tracy *et al.* 1976, Grant & Weiblen 1971) but very rare in rocks of higher grade. An obvious explanation is that the lower-grade rocks remained sufficiently hydrous that water was available for retrogression, whereas in near-granulite-grade rocks, water activity had been reduced to the point where rehydration was not possible. The production of abundant secondary biotite in WL–6A is therefore problematic, since the sample comes from this latter, near-granulite-grade environment.

It appears that reaction (2) was operating in reverse:

3 Cordierite + 2 Orthoclase + 2 H_2O →
6 Sillimanite + 2 Biotite + 3 Quartz (2a)

Reaction (2a) accounts for retrograde biotite produced on cordierite–orthoclase boundaries; the remaining secondary biotite on garnet–orthoclase boundaries formed through reaction (1a). The subtle differences in Fe/Mg ratios of primary biotite and the two types of secondary biotite are consistent with these reactions. Observed relative Fe/Mg ratios in the order secondary biotite (gar–Ksp) > primary biotite > secondary biotite (cord–Ksp) are consistent with the topologies for reactions (1a), (3) and (2a) described by Thompson (1976).

The higher Na/K ratio in secondary biotite presumably reflects the high value of Na/K in the grain-boundary environments garnet–orthoclase and cordierite–orthoclase. This, along with the very low TiO_2 of secondary biotite, suggests limited chemical communication on any scale greater than millimetres during the retrograde equilibration, and helps to explain the absence of secondary biotite except in the proximity of orthoclase. Limited mobility of components, including water, may help to explain the considerably greater development of secondary biotite on cordierite–orthoclase boundaries. Mass-balance calculations have shown that cordierite breakdown alone, both through reaction (2a) and growth of garnet aggregates at the expense of cordierite, could not liberate sufficient water to supply the growth of all the secondary biotite without introduction of externally derived water. However, the local availability of internally derived H_2O at cordierite–orthoclase boundaries, in addition to the pervasively infiltrating water, could have promoted enhanced nucleation and growth of biotite there.

The growth of secondary biotite on grain boundaries is probably not entirely a disequilibrium process, as has already been argued on the basis of biotite chemistry. An approach to equilibrium is also suggested by the patterns of Fe–Mg zoning in the outer parts of cordierite and garnet adjacent to well-developed secondary biotite. Two typical profiles for garnet and cordierite are shown in Figure 2. These demonstrate that Fe–Mg interdiffusion occurred in garnet and cordierite as these minerals attempted to maintain an equilibrium distribution of Fe and Mg at their margins with secondary biotite. The lateral extent of interdiffusion appears to have been greater in cordierite than in garnet, consistent with a predicted higher coefficient of diffusivity of Fe and Mg in cordierite (Lasaga *et al.* 1977).

REACTION FORMING AGGREGATES OF SECONDARY GARNET

Sample WL–6A is one of several high-grade rocks from central Massachusetts that have been found to contain evidence of the late-stage replacement of cordierite by garnet, presumably in response either to pressure increase at and after the peak of metamorphism or to slow cooling unaccompanied by significant decrease

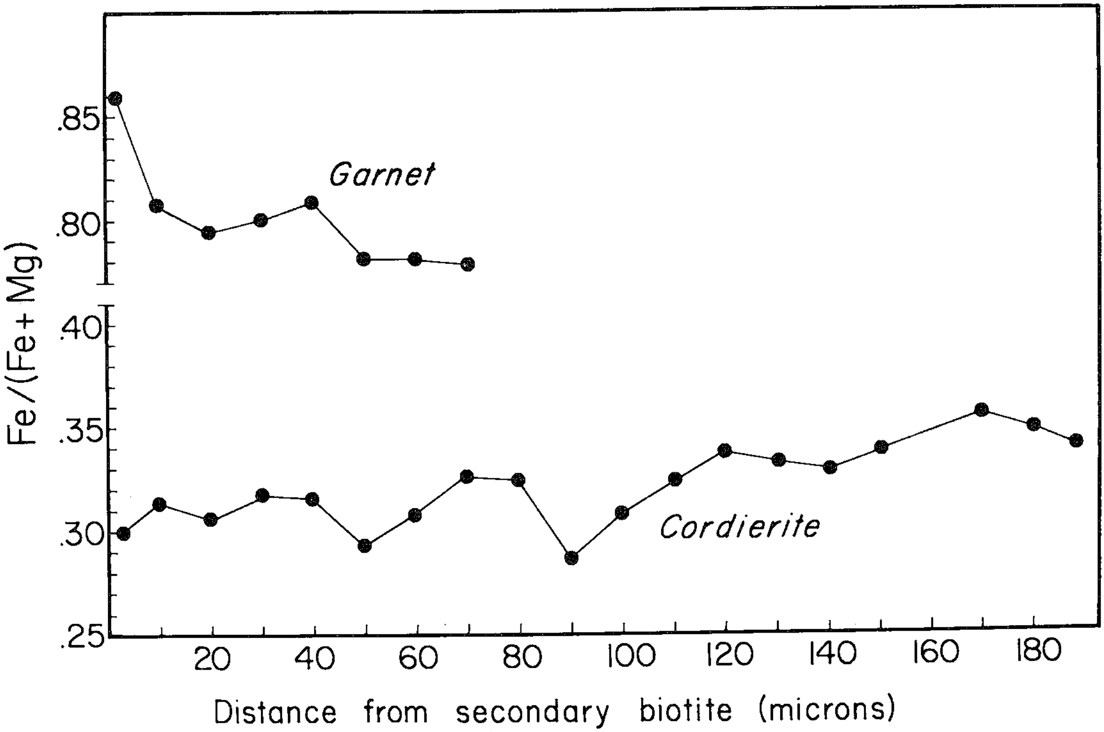

FIG. 2. Fe–Mg concentration profiles developed in garnet and cordierite adjacent to pale green secondary biotite. These concentration gradients are presumably developed through diffusion accompanying growth of secondary biotite.

in pressure. Textural evidence in WL–6A suggests that the garnet was produced through the virtually isochemical breakdown of cordierite in the following reaction:

$$3 \text{ Cordierite} \rightarrow 2 \text{ Garnet} + 4 \text{ Sillimanite} + 5 \text{ Quartz} \quad (4)$$

The process cannot have been strictly isochemical locally because of the quite different Fe/Mg ratios of coexisting garnet and cordierite, because of minor Ca in garnet that could not have been derived from the original cordierite, and because of the evidence, discussed in detail below, of fairly long-range Fe and Mg interdiffusion in cordierite (up to 1000 μm). On a millimetre scale, however, it does appear to have been isochemical with respect to all major components except possibly H_2O and CaO. The localized character of this retrograde equilibration is consistent with the local biotite reaction discussed above.

Further evidence for the isochemical and *in situ* production of the garnet aggregates is provided by the proportions of each phase in the aggregates. Several point-counts have yielded the following approximate volume proportions: garnet 55, sillimanite 30 and quartz 15%. Operation of reaction (4) at 700°C and 6 kbar should produce the following proportions of phases: garnet 43, sillimanite 36 and quartz 21%. These numbers are based upon the stoichiometry of reaction (4), molar volume data from Robie *et al.* (1978) and thermal expansion and compressibility corrections from Clark (1966). The agreement between predicted and observed proportions is surprisingly good, especially considering the difficulty of obtaining a truly representative three-dimensional approximation of proportions through the point-counting of thin sections. An interesting by-product of the above calculations is an estimate that the reaction produced a volume reduction of about 20%. Since the aggregates make up only a tiny fraction of the whole rock, this amounts to very little volume-reduction on a whole-rock scale, but the local effect should be important. It seems likely that the exaggerated cordierite twinning in the vicinity of the garnet aggregates may be the expression through local strain of this reduction in volume.

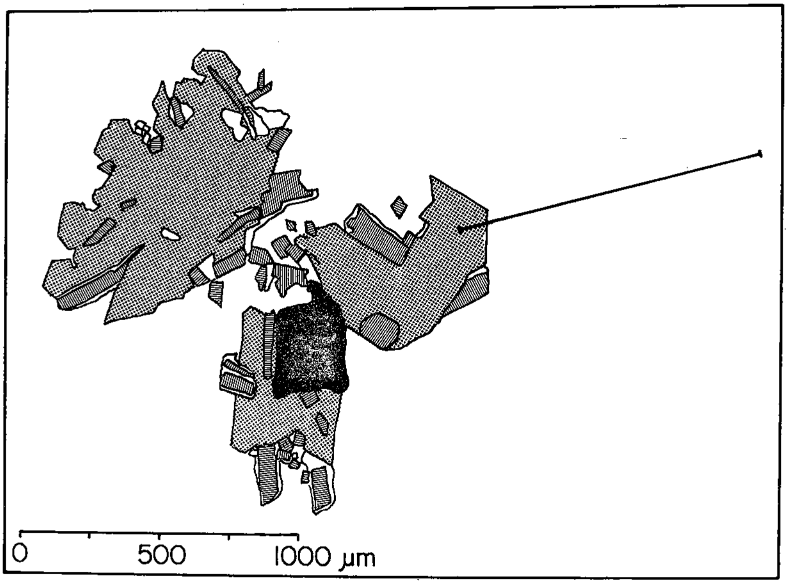

FIG. 3. Map of the garnet–sillimanite–quartz aggregate that was analyzed. Unpatterned: cordierite host; stippled: garnet; lined: sillimanite; unpatterned rims on sillimanite: quartz; black: pyrrhotite. The heavy line shown is the line of profile in Figure 4.

Many microprobe analyses were done of garnet grains in the aggregates and of adjacent cordierite in order to determine the areal distribution of compositions in both minerals. The aggregate studied in most detail is shown in Figure 3. A high density of probe analyses was made in the garnet to map its zoning, and a very carefully measured linear profile was determined from garnet interior to cordierite 1000 μm from the contact (shown by the line in Figure 3). Compositional mapping of the garnet shown in Figure 3 indicates that the grains in the aggregates are actually aggregates themselves: their interior zoning delineates a number of nuclei that apparently coalesced as they grew larger. The cores of individual nuclei are the most magnesian, in fact very similar in composition to the homogeneous interiors of the large grains of primary garnet. The outer zones of the small nuclei become progressively more iron-rich, but Fe/Mg ratios at "triple junctions" of coalescence are never quite as high as those at the outer margin of the coalesced grain adjacent to cordierite. This zoning is interpreted to be growth zoning due to maintenance of roughly equilibrium distribution of Fe and Mg between garnet and cordierite at their interface. If it is assumed that the two phases did maintain equilibrium and that this equilibrium was temperature-dependent, then relative K_D values for garnet–cordierite from beginning to end of garnet growth indicate that this growth occurred while temperature decreased.

As the composition of the interface garnet changed while the garnet grew, the composition of cordierite also changed. The compositional changes of both phases are best seen in the profile shown in Figure 4. The inception of crystallization of nuclei of garnet (+ sillimanite + quartz), a rather iron-rich phase, in the middle of cordierite, a magnesian one, produced strong depletion of iron in cordierite in the vicinity of the nuclei. Further growth of garnet that maintained Fe–Mg equilibrium at the interface with cordierite required diffusion of Fe through cordierite toward the garnet interface and diffusion of Mg away from the interface. Garnet growth must, therefore, have been a diffusion-controlled process whose rate was dependent upon the rate of Fe and Mg interdiffusion in cordierite. As the profile in Figure 4 indicates, the "diffusion aureole" around the garnet aggregate of Figure 3 extends up to 1000 μm from the interface. The profile in cordierite composition shown in Figure 4 is a function both of the interdiffusion process and of the increasingly magnesian composition of cordierite in equilibrium with garnet at the inter-

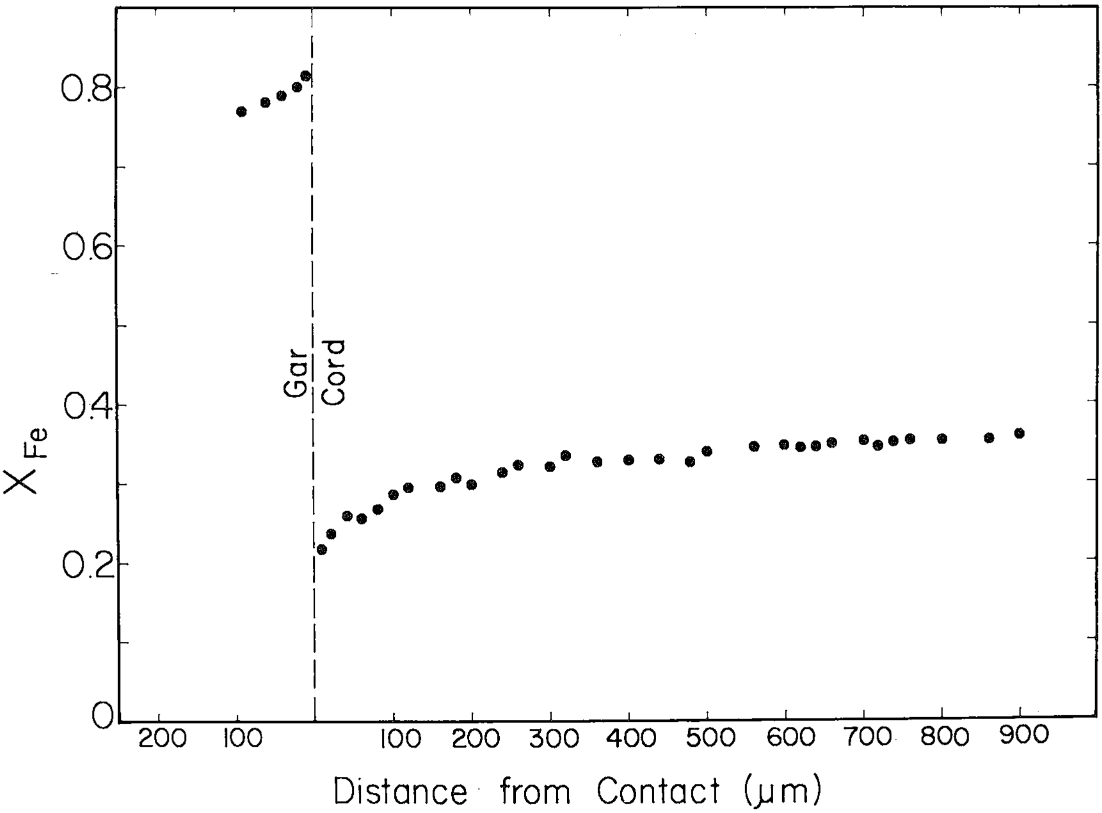

FIG. 4. Plot of concentration profile in garnet and cordierite along the 1000 μm line shown in Figure 3. The composition parameter shown, Fe/(Fe+Mg), is proportional to the mole fraction Fe in octahedral sites in both garnet and cordierite. The filled circles represent the sites of individual microprobe analyses.

face as T fell. The garnet–cordierite Fe–Mg K_D inferred at the beginning of garnet growth, based upon compositions of the most magnesian nuclei of garnet and unaltered cordierite far from the garnet interface, is 6.2, which yields a temperature estimate of 700°C (Thompson 1976). The K_D for garnet and cordierite at the present interface is about 16.0, giving a temperature of about 450–500°C. Interestingly, the latter temperature is in close accord with the 500°C obtained from the Fe–Mg distribution between secondary biotite and the retrograded edge of the primary garnet adjacent to this biotite (calibration of Ferry & Spear 1978); this may represent an approximate "closure temperature" for major element re-equilibration in silicates in this type of retrograde P–T trajectory. It must be noted, however, that these lower-temperature estimates are somewhat speculative, since they are based upon mineral pairs whose compositions may not reflect complete equilibration owing to slow kinetics.

A MODEL FOR RETROGRADE DIFFUSION IN CORDIERITE

Documentation of the Fe–Mg concentration profile in cordierite (Fig. 4), along with the assumption that growth of retrograde garnet as described above is a diffusion-controlled process, presents us with an opportunity for making some kinetic estimates regarding cooling phenomena. There is a special benefit in making estimates for this terrane because of a previous estimate based upon a different process made by Lasaga *et al.* (1977) for the same area.

Whereas the geometry of the garnet aggregates is complicated by the presence of sillimanite and quartz grains, the relatively systematic concentric zoning of both garnet and cordierite suggests that a fairly simple geometric diffusion model may be appropriate, provided that it is a moving boundary model to account for garnet growth and movement of the garnet–cordierite interface. Frank (1950) developed an analytical solution for the problem of radially and spherically symmetrical diffusion-controlled growth of a new phase within a second phase from an initial condition of negligible volume of the new phase. Though the problem is effectively spherical and three-dimensional, it can be reduced to one dimension by treating a radial profile.

Two assumptions must be made in order to apply the Frank treatment to the present garnet–cordierite occurrence. The first involves the nature of the diffusing species. Frank's model is mathematically appropriate for the diffusion of a single species, but we may define the interdiffusion of Fe and Mg in this way because of the stoichiometric constraint of the medium (cordierite) through which diffusion occurred. Since cordierite may be considered as an aluminosilicate matrix that contains only Mg and Fe as additional cations, and that must maintain a constant sum of 2 (Mg + Fe) per 18 oxygen atoms, the diffusing species may be defined as MgFe_{-1}. Cordierite is an unusually appropriate diffusional matrix because of this stoichiometric constraint. The second assumption involves the constancy of composition of the two phases at the interface as implied by the Frank model. As noted earlier in this paper, $K_{D\mathrm{Fe-Mg}}^{\mathrm{Ga-Cord}}$ apparently changed significantly from the inception of garnet growth to its conclusion. This K_D change over an interval of about 150°C has been ignored in the treatment below because its inclusion in the calculations through a numerical approximation did not appear to cause more than insignificant shift in the calculated profiles.

The model begins with definition of a dimensionless "reduced radius" defined as:

$$s = r/\sqrt{D}t \qquad (6)$$

where r is the radial distance from the point of nucleation of the new phase, D is the diffusivity of the diffusing component, and t is time. The reader is referred to Frank (1950) for details of the derivation that follows, which is only summarized here.

The diffusion equation for dependence of concentration on s becomes:

$$\frac{\partial C}{\partial s} = -A\, s^{-2} \exp\left(-\tfrac{1}{4} s^2\right), \qquad (7)$$

where C is concentration and A is a constant. We then have

$$C_S = A \int_s^{\infty} s^{-2} \exp\left(-\tfrac{1}{4} s^2\right) ds + C_\infty \qquad (8)$$

After integrating by parts, Frank arrived at the expression

$$C_S - C_\infty = A\left[s^{-1} \exp\left(-\tfrac{1}{4} s^2\right) - \tfrac{1}{2}\pi^{1/2} \left\{ 1 - \mathrm{erf}\left(\tfrac{1}{2} s\right) \right\} \right] \qquad (9)$$

or

$$\frac{C_S - C_\infty}{A} = F(s) \qquad (10)$$

where A is a constant of integration that depends upon the value of the net flux of material across the interface (see Frank 1950). The maximum possible absolute value of $(C_s - C_\infty)/A$ is obtained when $F(s) = 1$, owing to the constraint that $C_s - C_\infty$ at any particular time is greatest at the interface between the two phases. It is also the case that the value of r when $F(s) = 1$ is the distance from the point of initial nucleation of the new phase to the interface after any time t, that is, the radius of the new phase. The solution thus provides a means of calculating both a predicted size of the new phase, in our case garnet, and a predicted concentration profile in the host phase, cordierite.

The Frank treatment is isothermal and its only implicit temperature-dependence is in the variation of D with temperature. An explicit solution for time-dependent variation of D (and therefore temperature-dependent) can be arrived at by substituting a new variable t′ for t in equation (6). This new variable is defined by

$$dt' = d(t)dt \qquad (11)$$

and

$$t' = \int_0^t d(t)dt \qquad (12)$$

Lasaga *et al.* (1977) suggested the following form for d(t):

$$d(t) = e^{-\gamma t}, \qquad (13)$$

where

$$\gamma = \frac{\Delta\overline{H}_D\alpha}{RT_0^2}; \qquad (14)$$

ΔH_D is the activation energy of Fe–Mg interdiffusion in cordierite, α is the cooling rate (in °C/Ma), and T_0 is the temperature at which diffusion is initiated (taken to be 973 K in this case). Integration of d(t) yields:

$$\int_0^t d(t)dt = \frac{1}{\gamma}[1 - e^{-\gamma t}] = t' \qquad (15)$$

which gives us the relation between t and t′.

The profiles calculated in Figure 5 for a variety of times ranging from 10^5 to 20 x 10^6 years are actually calculated from equation (10) but with the time values being values of t′ rather than t; the value of D that was used in the calculations is 7.5 x 10^{-18} cm²/s, a value that is not very well constrained but was suggested by Lasaga *et al.* (1977) as a reasonable estimate. In order to convert the values of t′ shown in Figure 5 to values for absolute time, we need to make estimates for the parameters in equation (14) that are needed to calculate γ. Some constraint on these values is already provided by equation (15), which shows that the upper limit of t′ is the value of $1/\gamma$. Figure 5b compares the concentration-profile data from Figure 4 with calculated profiles, and shows that the best match of the calculated profiles with the data is for t′ ranging between 5x10^6 and 10x10^6 years. According to equation (15), we cannot have a profile for 10x10^6 years unless γ is less than or equal to 0.10.

Therefore, in order to evaluate γ we must calculate it using appropriate values for the parameters in equation (14). The only parameter in which there is much latitude for variation is α, the cooling rate; $\Delta\overline{H}_D$ (Cord) is a constant with an estimated value of 46 kcal/mole (Lasaga *et al.* 1977) and T_0 is 700°C. If we set an approximate upper bound on γ of 0.10, as discussed above, then the upper bound on cooling rate, α, is 4°C/Ma.

Unfortunately, almost all calculations of diffusion are very sensitive to uncertainties in the value of the diffusion coefficient D, since they involve the term $\sqrt{D}t$. Because of this identical functional relationship of D and t, an uncertainty of plus or minus one order of magnitude in D will mean an inverse change of one order of magnitude in calculated time. This is effectively a scaling problem and indicates equal scaling of D and t, or t′ in the present case.

If one accepts the goodness of fit between the data points and the calculated t′ profile for 10 x 10^6 years in Figure 5b, then some limits can be placed on cooling rate and diffusion coefficient. The D that we used in the calculations for Figure 5 was 7.5 x 10^{-18} cm²/s, a value suggested by Lasaga *et al.* (1977). If this diffusion coefficient is assumed, then the maximum cooling rate allowable is about 5°C/Ma. In order to raise the cooling rate to 25°C/Ma, it is necessary to assume a value for D that is five times higher than the D suggested by Lasaga *et al.* (1977). The model we have presented here, therefore, allows the placing of some comparative limits on D and cooling rate. It does appear from our model that there is a potential inconsistency between the minimum rate of cooling suggested by Lasaga *et al.* of 100°C/Ma and the D that they suggest. A cooling rate as high 100°C/Ma would require a minimum D twenty times higher than the recommended value.

A test of the applicability of the Frank model is also provided by its prediction of the size of newly grown grains of garnet. As can be seen on Figure 5a, for a t′ of 5–10 x 10^6 years, the range of radii should be 200–300 μm, which is entirely consistent with the size of garnet observed in thin section.

CONCLUSION

In this paper we have tried to deal quantitatively with two retrograde phenomena in a near-granulite-grade gneiss in central Massachusetts. Both processes appear to involve equilibration on a very local level, with most transport of material operating on a scale of a millimetre or less. The first retrograde feature, crystallization of secondary biotite, sillimanite and quartz, occurs only along grain boundaries of cordierite or garnet with orthoclase. This pale green biotite is quite different in composition from primary biotite in the rock and has a chemical composition that is strongly constrained by the immediate environment. Most of the material for growth of this biotite was apparently supplied by the adjacent primary phases, as demonstrated by measured profiles of concentration developed through diffusion in garnet and cordierite. Water must have been introduced from farther away, but the abundance of biotite on cordierite–orthoclase boundaries suggests that some water may have been locally derived through cordierite breakdown.

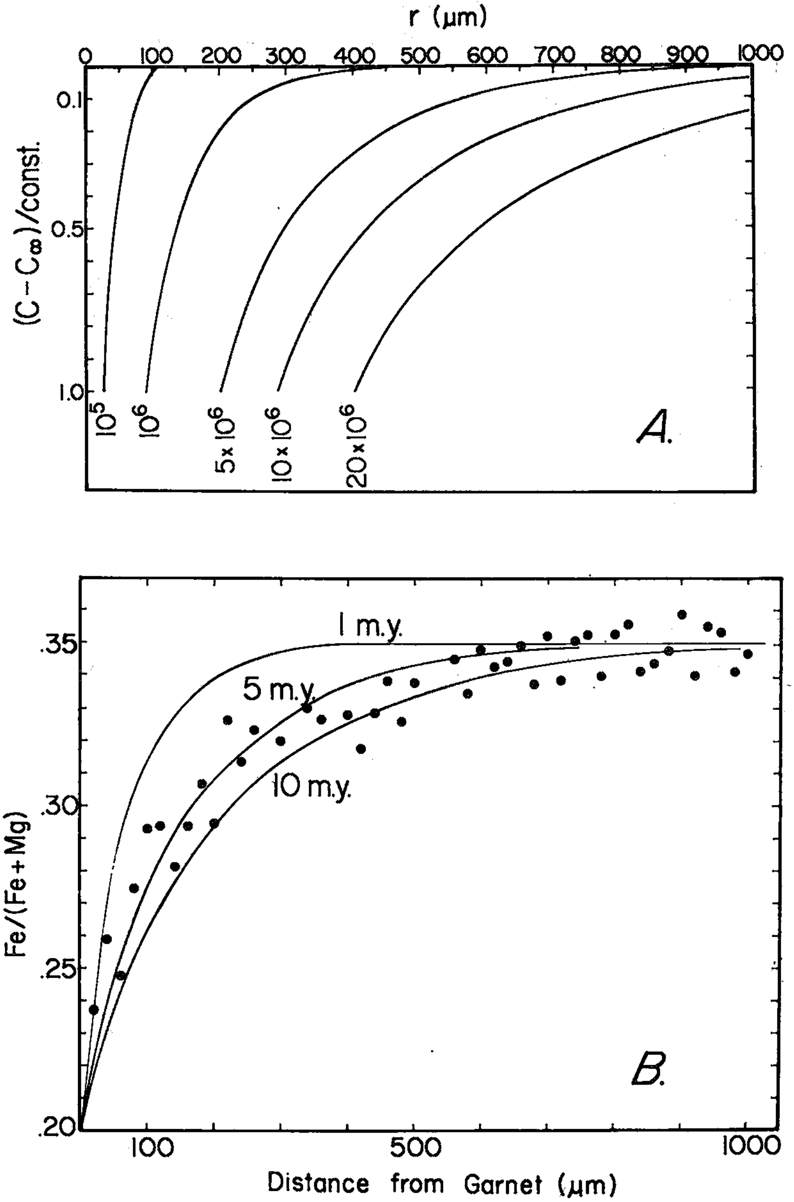

FIG. 5. a) Profiles calculated by the method described in the text for values of t' ranging from 100 thousand to 20 million years. These profiles show the evolution of the concentration profile of cordierite as well as the movement of the garnet–cordierite interface. b) Measured profile of concentration in cordierite (same data as in Figure 4) compared to several of the calculated profiles. The position of the abscissa of the calculated profiles has been adjusted so that they originate at the *present* garnet–cordierite interface.

The second retrograde feature, formation of garnet–sillimanite–quartz aggregates within large crystals of cordierite, appears to involve the *in situ* breakdown of cordierite in response to slow cooling at constant or increasing pressures. Garnet is growth-zoned consistent with falling temperature during the growth process, and adjacent cordierite is also zoned up to 1000 μm from the garnet–cordierite interface. This cordierite zoning is interpreted to be developed through interdiffusion of Fe and Mg in the cordierite in order to supply the growing retrograde garnet, whose growth is therefore a diffusion-controlled process.

A diffusion model that takes into account the slowing of diffusion with time and with dropping temperature, when applied to the growth of secondary garnet, yields calculated profiles of concentration in cordierite and estimates of size of garnet that agree well with those measured in the sample. Unfortunately, there are considerable uncertainties in some of the input parameters needed for the calculations, especially the Fe–Mg interdiffusion coefficient and the cooling rate. The model, however, provides some useful constraints on the relative values of these two parameters. For the diffusion coefficient of 7.5×10^{-18} cm^2/s suggested by Lasaga *et al.* (1977), a maximum cooling rate of 5°C/Ma is possible. For cooling rates any more rapid than this, the diffusion coefficient must be considerably greater.

There is substantial reason to believe that a very low cooling rate of 5°C/Ma or lower is appropriate for this terrane. Rates as rapid as 20°C/Ma, such as those suggested by Jäger *et al.* (1967) for the Alps, apply to terranes in which rapid uplift and erosion, and therefore rapid cooling, have been demonstrated. Evidence cited earlier in this paper, both petrological and tectonic, indicates that the central Massachusetts terrane did not suffer rapid uplift, but in fact cooled very slowly at elevated pressures. It can be argued, therefore, that the consistency of our model with a very slow rate of cooling gives support to the estimate by Lasaga *et al.* (1977) of the diffusion coefficient for cordierite. We very much hope that future kinetic treatments, such as the one presented here, may be improved by the measurement of more precise coefficients of diffusion in rock-forming minerals.

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