BIOTITE–GARNET GEOTHERMOMETRY IN GRANULITE-FACIES ROCKS: EVALUATION OF EQUILIBRIUM CRITERIA

APHRODITE INDARES AND JACQUES MARTIGNOLE

Département de géologie, Université de Montréal,
Case postale 6128, succursale A, Montréal, Québec H3C 3J7

ABSTRACT

Most commonly accepted calibrations of the biotite-garnet geothermometer have yielded inconsistent estimates of the temperature of the rocks in the granulite facies. This type of inconsistency, unrelated to the calibration, can be avoided by selecting particular minerals and specific locations for analysis within these minerals so that the calculated K_D values may be attributed to a specific stage in the evolution of the metamorphism. Garnet cores and matrix biotite isolated from garnet are not affected by late Fe–Mg exchange and are most suitable for calculating peak K_D (defined as K_{D1}) and temperature. In contrast, garnet rims and the biotite at their contact, or garnet cores near biotite inclusions and the included biotite (defining K_{D2}), have undergone Fe–Mg re-equilibration during cooling. From the new compositions, the only temperature that can be obtained corresponds to some stage of the retrograde event.

Keywords: biotite, garnet, geothermometry, granulite facies, Grenville Province, Quebec.
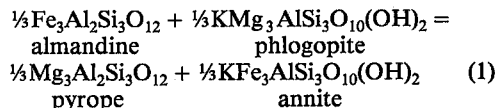
SOMMAIRE

Les différents calibrages du géothermomètre biotite-grenat couramment utilisés ont donné des estimations incohérentes de la température des roches du faciès granulite. Cette incohérence, indépendante du calibrage, peut être éliminée en sélectionnant les minéraux et, dans ces minéraux, les points à analyser de telle façon que les valeurs calculées de K_D puissent être attribuées à un stade bien déterminé de l'évolution métamorphique. Le coeur des cristaux de grenat et la biotite de la matrice, lorsque cette biotite n'est pas contiguë au grenat, ne sont pas affectés par les échanges Fe–Mg tardifs et peuvent servir à calculer le K_D et la température au maximum de métamorphisme (K_{D1}). Par contre, les bordures des grains de grenat et la biotite au contact, de même que les inclusions de biotite et la partie du grenat qui leur est contigu (qui définissent K_{D2}) ont subi une redistribution Fe–Mg pendant le refroidissement. À partir de la composition ainsi modifiée de ces minéraux, on ne peut obtenir que la température correspondant à un des stades du métamorphisme rétrograde.

Mots-clés: biotite, grenat, géothermométrie, facies granulite, province du Grenville, Québec.

INTRODUCTION

The iron–magnesium partition between coexisting biotite and garnet can be modeled in the AKFM system by the exchange reaction:

$$\tfrac{1}{3}Fe_3Al_2Si_3O_{12} + \tfrac{1}{3}KMg_3AlSi_3O_{10}(OH)_2 =$$
$$\text{almandine} \qquad \text{phlogopite}$$
$$\tfrac{1}{3}Mg_3Al_2Si_3O_{12} + \tfrac{1}{3}KFe_3AlSi_3O_{10}(OH)_2 \qquad (1)$$
$$\text{pyrope} \qquad \text{annite}$$

The corresponding equilibrium-constant K is equivalent to a distribution coefficient K_D equal to $(Fe/Mg)_{bi}/(Fe/Mg)_{ga}$ provided both solid solutions are ideal. In rocks, however, incorporation of minor elements commonly results in a departure from ideality in both biotite and garnet solid-solutions, so that K_D may significantly deviate from K. In the last ten years, several calibrations of K_D as a function of T have been used as geological thermometers, each one adopting a different model for minor-element interaction. Among these calibrations, those by Ferry & Spear (1978), Goldman & Albee (1978) and Thompson (1976) have been extensively used, but appear to give inconsistent results if applied to granulite-facies rocks (Bohlen & Essene 1980). A significant variation in K_D may occur within a single area or even a single thin-section without significant variation in concentration of minor elements (Perkins *et al.* 1982, Indares 1982). For a given calibration, these variations in K_D lead to a large span of estimated temperature.

Several authors (*e.g.,* Tracy *et al.* 1976) have stressed the role of local re-equilibration during cooling from peak temperatures to account for such variations in K_D. Consequently, a narrow contact-zone between adjacent minerals is usually to be avoided in electron-microprobe analysis. Nevertheless, compositional heterogeneity is not limited to mineral contacts, and several types of K_D can be calculated, probably corresponding to compositions of quenched local equilibrium. The aim of this paper is to demonstrate that a judicious selection of biotite and garnet grains, as well as the selection of targets within a given grain, provides chemical data (and thus K_D values) referring to specific temperatures attained during peak conditions or to certain stages of cooling. In a separate paper, which takes into account the conclusions of this contribution and the effects of nonideality in both biotite and garnet solid-solutions, a new biotite–garnet thermometric calibration is proposed (Indares & Martignole 1985).

SAMPLES STUDIED AND RESULTS

A systematic study of biotite and garnet grains was undertaken in seven thin sections of bi–ga–pl–Ksp–sil–qtz–ilm–gph metapelites, bi–ga–Ksp–qtz–ilm semipelites and opx–bi–ga–pl–Ksp–qtz–ilm gneisses, the latter referred to here as granulites. The samples come from an area of 750 km² located near Maniwaki, in the valley of the Gatineau River 100 km north of Ottawa (Fig. 1). This region forms part of the Central Metasedimentary Belt of the Grenville Province (Wynne-Edwards 1972) and underwent granulite-facies metamorphism. Application of bi–ga and cpx–ga thermometry and of ga–pl–sil–qtz and px–ga–pl–qtz barometry suggests that during the peak of metamorphism, temperature and pressure were in the range 760°–860°C and 6.5–8.5 kbar, respectively (Indares & Martignole 1984). The variations in P–T conditions are randomly distributed, and there is no evidence of a regional metamorphic gradient across the area. Therefore, a value of 800°C has been adopted as the peak temperature, and the area can be considered to be homogeneous in terms of temperature.

Mineral analyses were obtained with a MAC electron microprobe. Two analytical techniques were used: wavelength-dispersion spectrometry with LIF, PET and RAP spectrometers, and energy-dispersion spectrometry. Operating conditions for both were 15 kV, with a specimen current of 20 nA. Correction procedures followed the scheme of Bence & Albee (1968) for wavelength-dispersion spectrometry, and a full ZAF correction was applied to data obtained by energy-dispersion spectrometry. Differences in the results between the two methods are within the error limits for each element. A complete list of the standards (natural minerals) and of representative results and standard deviations for each element is given in Indares (1982) and is available upon request. Five to ten grains of biotite and garnet from each thin section were analyzed at 2 to 10 points within a single grain, in order to evaluate the degree of heterogeneity.

Garnet is a pyrope-rich almandine with minor grossular and spessartine components (Table 1). The composition of the core is homogeneous at the thin-section scale and is always more magnesian and poorer in iron than in a narrow zone a few micrometres wide along the rim adjacent to biotite or other ferromagnesian minerals (Fig. 2). This zoning pattern is common in high-grade metamorphic rocks (Schmid & Wood 1976, Tracy *et al.* 1976, Tracy 1978, Dahl 1979, Stephenson 1979, Lonker 1980, Grew 1981). However, zoning around biotite
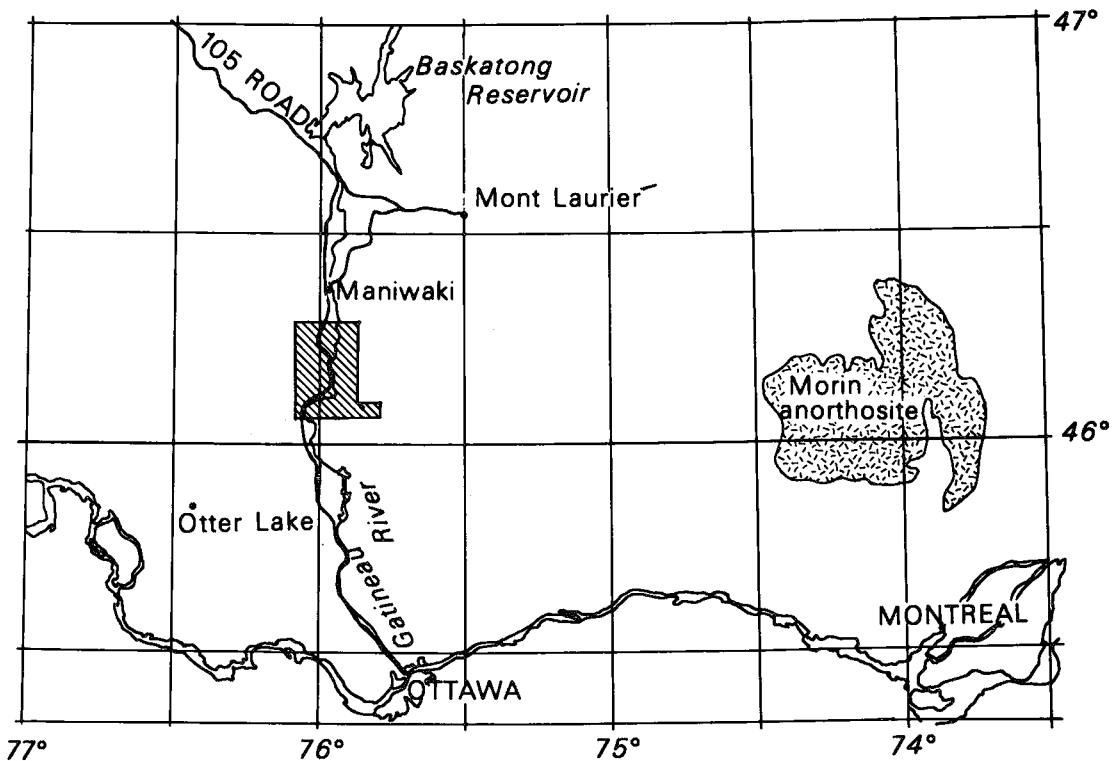

FIG. 1. Location map showing the Maniwaki area.

TABLE 1. RANGE OF GARNET COMPOSITIONS IN METAPELITES, A SEMIPELITE AND GRANULITES

	31-07-C*	31-07-R*	25-13-C	25-13-R	23-08-C	23-08-R	23-03-C	23-03-R
X_{alm}	0.55 -0.58	0.60 -0.64	0.59 -0.63	0.63 -0.64	0.60 -0.61	0.59	0.62 -0.64	0.65
X_{py}	0.35 -0.38	0.30 -0.33	0.32 -0.38	0.29 -0.30	0.33 -0.35	0.34	0.25 -0.26	0.24
X_{gr}	0.053-0.056	0.049-0.053	0.039-0.045	0.045-0.060	0.044-0.051	0.043-0.045	0.054-0.075	0.056-0.059
X_{sp}	0.013	0.015-0.016	0.010-0.011	0.012-0.013	0.014-0.015	0.042-0.049	0.04 -0.05	0.047-0.054

	31-02F-C	31-02F-R	29-02-C	29-02-R	36-04-C	36-04-R
X_{alm}	0.51 -0.54	0.56 -0.62	0.56 -0.60	0.58 -0.63	0.56 -0.57	0.60 -0.63
X_{py}	0.42 -0.45	0.39 -0.41	0.31 -0.35	0.29 -0.33	0.34 -0.35	0.28 -0.31
X_{gr}	0.033-0.035	0.031-0.034	0.072-0.090	0.048-0.070	0.056-0.067	0.059-0.064
X_{sp}	0.005-0.009	0.006-0.009	0.016-0.018	0.017-0.018	0.022-0.026	0.029-0.035

*C core, *R rim. Metapelites: 31-07, 25-13, 23-08, 23-03. Semipelite: 31-02F. Granulites: 29-02, 36-04. Abbreviations: alm almandine, py pyrope, gr grossular, sp spessartine, X mole fraction.

inclusions is less intense and of narrower width. Rims adjacent to quartz, feldspar or sillimanite show little or no Fe–Mg zoning.

Zoning in terms of minor elements consists only of slight Mn enrichment toward a garnet rim adjacent to biotite (see also Ashworth & Chinner 1978, Dahl 1979, Stephenson 1979, Grew 1981, Tracy et al. 1976). Departures from compositional homogeneity among core compositions of garnet may be attributed to a "sphere effect": tangential sections of garnet might result in an apparent core with a rim composition.

There is no significant difference in garnet composition among metapelites, semipelites and granulites except that the Ca content is higher in the granulites.

Biotite is Mg-rich and has a high Ti content (Table 2). Iron is assumed to be present as Fe^{2+} only. Admittedly, like in most metamorphic rocks, biotite probably contains a certain amount of Fe^{3+}, which cannot be evaluated with the usual microprobe techniques nor by calculations of stoichiometry. In the usual procedure, according to which all Fe is taken to be Fe^{2+}, K_D is artificially increased. However, as the main point of this paper is to evaluate the meaning of K_D variations within a single specimen, only the variations in Fe^{3+} content are
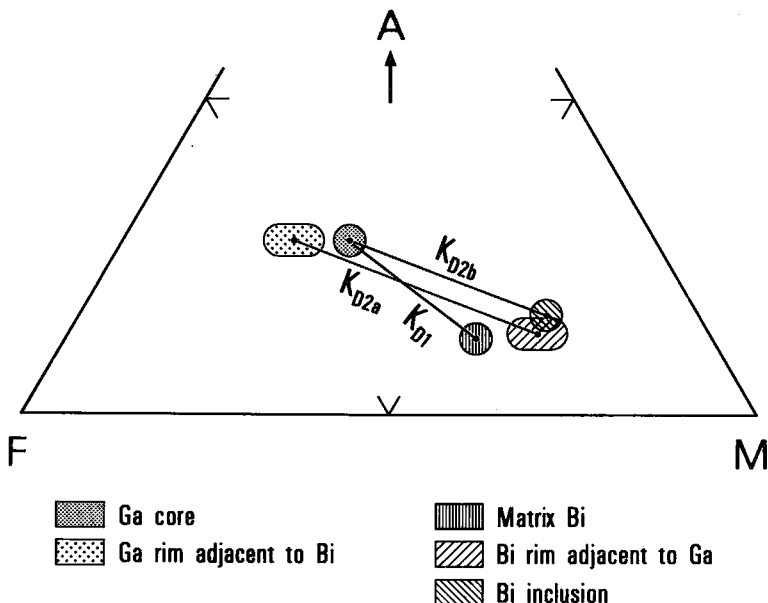

FIG. 2. Schematic AFM projection of garnet and biotite compositions from Maniwaki and tie lines corresponding to the various types of K_D.

TABLE 2. RANGE OF BIOTITE COMPOSITIONS CALCULATED ON A BASIS OF 22 OXYGEN ATOMS

	31-07-M*	31-07-C*	31-07-I*	25-13-M	25-13-C	25-13-I	23-08-M	23-08-C	23-08-I	23-03-M	23-03-C
X_{ph}	0.65	0.70-0.71	0.74-0.76	0.60-0.63	0.62-0.69	0.72-0.74	0.63	0.69	0.77	0.54-0.55	0.49
X_{Ti}	0.08	0.06	0.08-0.09	0.09-0.12	0.03-0.04	0.08-0.10	0.09-0.11	0.06	0.08-0.09	0.09-0.10	0.05
X_{viAl}	0.09-0.10	0.09-0.10	0.11-0.15	0.08-0.10	0.10-0.11	0.09-0.10	0.09-0.11	0.11	0.10-0.13	0.09-0.10	0.11

	31-02F-M	31-02F-C	29-02-M	29-02-C	29-02-I	36-04-M	36-04-C	36-04-I
X_{ph}	0.67-0.68	0.79-0.86	0.64-0.67	0.68-0.76	0.73-0.75	0.62-0.63	0.63-0.65	0.72 0.78
X_{Ti}	0.09-0.11	0.02-0.05	0.08-0.10	0.07-0.11	0.07-0.08	0.09-0.11	0.08-0.10	0.05 0.07
X_{viAl}	0.08-0.09	0.10-0.11	0.05-0.06	0.06-0.07	0.06-0.07	0.04-0.05	0.04-0.06	0.07 0.08

*M matrix biotite, *C biotite in contact with garnet, *I biotite included in garnet, X_{ph} = Mg/(Mg + Fe), X_{Ti} = Ti/(Mg + Fe + Ti + ^{vi}Al), X_{viAl} = ^{vi}Al/(Mg + Fe + Ti + ^{vi}Al). Metapelites: 31-07, 25-13, 23-08, 23-03; semipelite: 31-02F; granulites: 29-02, 36-04.

significant. As the oxygen fugacity can be assumed to be constant throughout a single specimen, Fe^{3+} variations are uniquely controlled by ^{vi}Al variations, which are very small. Therefore, variations in Fe^{3+} can be neglected, as they will fall within the error limits of Fe determination. The H_2O, F and Cl contents of biotite have not been determined. The composition of a specific grain of biotite within a thin section is found to be a function of its distance from garnet (see also Edwards & Essene 1981, Tracy *et al.* 1976). Additional factors that may influence biotite composition are biotite–garnet modal ratios and grain dimensions. These factors have not been quantitatively evaluated. However, three categories of biotite composition characterized by sharp limits are distinguished in each sample (Fig. 2): 1) matrix biotite isolated from garnet and adjacent to quartz, feldspar or sillimanite is homogeneous at the thin-section scale and, compared to other grains, is rich in Fe and depleted in ^{vi}Al; 2) matrix biotite in contact with garnet is slightly zoned, and the rim adjacent to garnet is less magnesian than the core; 3) biotite included in garnet is the richest in Mg and ^{vi}Al. The main difference in biotite composition between the various lithologies lies in its ^{vi}Al content; ^{vi}Al is lower in biotite of granulites, whereas biotite from metapelites is richer in ^{vi}Al (Table 2).

BIOTITE–GARNET EQUILIBRIUM

The only significant ionic exchange between biotite and garnet concerns Fe and Mg and is controlled by the continuous reaction 1. Compositional heterogeneities in Fe and Mg in both biotite and garnet within analyzed samples imply the absence of pervasive, thorough equilibration between the two minerals at the scale of a thin section. However, compositional homogeneity of garnet cores and matrix biotite, which probably account for more than 90% of the mode and, thus, the major volume of these minerals, suggests that during a certain stage of metamorphism, pervasive equilibrium at the scale of the thin section, and probably the hand specimen, was established. The composition of the garnet rim and of biotite adjacent to garnet probably reflects local (retrograde) equilibrium only. Given the trend of the Fe–Mg zoning and the direction of reaction 1 (displaced to the right with increasing temperature), the equilibrium between garnet core and matrix biotite corresponds to a higher temperature than the equilibrium recorded at grain contacts.

Although garnet is very refractory in terms of ionic diffusion (Loomis 1975) and always markedly zoned in low-grade rocks, its composition tends to be homogeneous at the scale of both individual grains and a thin section during high-grade metamorphism (Woodsworth 1977). During cooling, the core of garnet tends to preserve the high-grade composition, and only a narrow rim adjacent to ferromagnesian minerals is affected by a retrograde Fe–Mg readjustment, with the garnet becoming increasingly iron-rich toward the contact.

Biotite is less refractory; although at the peak of metamorphism biotite grains were probably homogeneous both within samples and within single grains, chemical readjustments during cooling affected biotite adjacent to garnet. This effect reached a maximum at the contact. Therefore, during cooling, isolated grains of biotite are most susceptible to retain a composition close to that of peak metamorphism.

Textural evidence suggests that re-equilibration of garnet and biotite during cooling was essentially controlled by a continuous reaction. Slight Mn-enrichment in the rim of garnet grains adjacent to biotite corresponds to garnet consumption, and demonstrates the coupling of reaction 1 with a discontinuous reaction such as:

$$py + Ksp + H_2O = phl + sil + qtz \qquad (2)$$
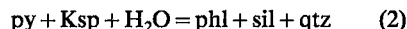
between the garnet rim and adjacent biotite.

DISCRIMINATION BETWEEN
THE VARIOUS TYPES OF K_D

In each thin section we can thus distinguish more than one type of K_D depending on the location of material analyzed.

Limiting cases (Fig. 2, Table 3) are:

$$K_{D1} = K_{D_{Fe-Mg}}{}^{\text{isolated matrix bi-ga core}}$$

$$K_{D2} = K_{D_{Fe-Mg}}{}^{\text{contact bi-ga}}$$

K_{D1} reflects equilibrium at or near the peak temperature, whereas K_{D2} reflects equilibrium at the approximate temperature at which diffusion between the two minerals ceased.

K_{D2} may be determined by using two different kinds of mineral contact: 1) garnet rim + rim of adjacent matrix biotite (K_{D2a}) and 2) garnet rim around biotite inclusion + biotite inclusion (K_{D2b}). In Table 3, it is shown that K_{D2a} and K_{D2b} are equivalent.

As in the selected samples, biotite inclusions in garnet are small in comparison with the garnet host, their composition is more thoroughly re-equilibrated (more Mg-rich) than the composition of biotite adjacent to garnet rim. On the contrary, garnet around biotite inclusions is less re-equilibrated (less Fe-rich) than the external rims, which are in exchange with a larger volume of biotite. The extreme steepness of the zoning profiles precludes accurate analysis by microprobe of grain-boundary compositions. It thus follows that no pair of compositions at a grain boundary can be construed to represent accurately equilibrium at the end of diffusion. However, despite the foregoing, we can still consider that K_{D2} gives some information about cooling.

CONCLUSIONS

Comparison of the two groups of K_D values among metapelites, semipelites and granulites (Fig. 3) leads to the following conclusions:

1. There is no significant difference in K_{D1} between metapelites and granulites. The difference in K_D between semipelites and granulites could be due to an effect of the grossular component, the garnet of the semipelites having the lower grossular content. K_{D1} intervals are invariably narrow, which is
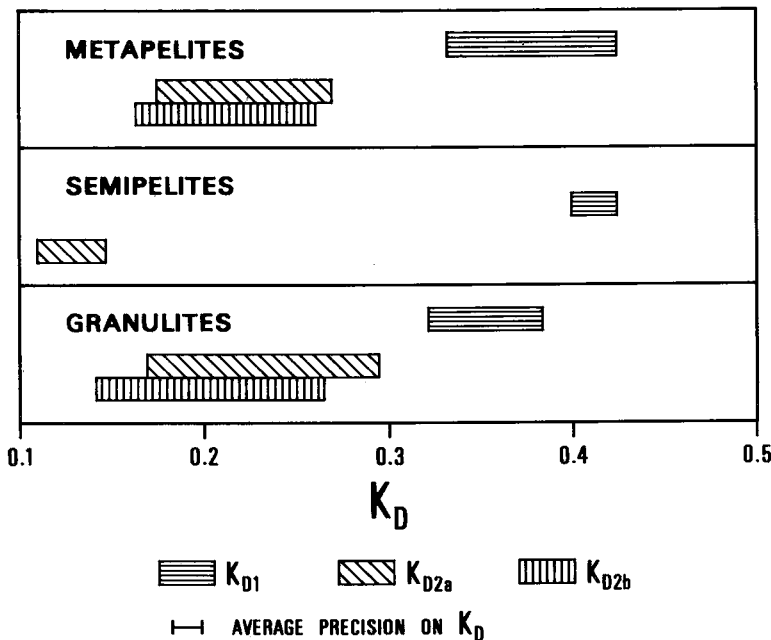
TABLE 3. RANGE OF VALUES OF DISTRIBUTION COEFFICIENTS K_{D1}, K_{D2a} AND K_{D2b} FOR SAMPLES FROM THE MANIWAKI AREA

		K_{D1}	K_{D2a}	K_{D2b}
Metapelite	31–07	0.383–0.386	0.190–0.224	0.202–0.223
	25–13	0.388–0.433	0.209–0.276	0.226–0.259
	23–08	0.336–0.339	0.202	
	23–03	0.345–0.362	0.272	
Semipelite	31–02F	0.405–0.426	0.112–0.148	
Granulite	29–02	0.327–0.333	0.171–0.221	0.183–0.252
	36–04	0.389–0.369	0.196–0.294	0.142–0.240

FIG. 3. Comparison between K_{D1}, K_{D2a} and K_{D2b} for the Maniwaki samples.

additional evidence of large-scale equilibrium during high-grade conditions. However, minor but significant differences in K_{D1} within a given lithology may be attributed (a) to the "sphere effect" on garnet composition, and (b) to uncertainties inherent in the choice of matrix biotite isolated from garnet. Apparently isolated biotite in a thin section may have been very close to a garnet grain in the third dimension. Owing to the lack of systematic distribution of K_{D1} differences in the area studied, we do not consider variation in the peak temperature as a reasonable explanation for these minor variations in K_D.

2. K_{D2} intervals are large, and there is only a partial overlap among the three lithologies, the semipelites yielding the lowest K_{D2} values. The difficulty in bracketing K_{D2} within a narrow range of values results from 1) the imprecision in the location of analyzed points at grain boundaries in a steep gradient, 2) the possibility of local differences in retrograde equilibrium obtained at diffferent temperatures, and 3) the likely existence of frozen-in compositions due to incomplete diffusion in the path toward equilibrium. An increasing influence of minor elements at low temperatures could also be an additional factor. However, despite all these restrictions, and even though the calculated values of K_{D2} do not represent equilibrium, their overall consistency supports their use for an approximate estimation of retrograde conditions.

The main point from Figure 3 is the marked difference between K_{D1} and K_{D2} within each lithology. This difference might in itself explain the apparently erratic distribution of temperatures obtained with a given calibration over a limited area (e.g., Bohlen & Essene 1978, Perkins et al. 1982). Assuming that the mineral rims underwent late Fe–Mg re-equilibration, several investigators have accepted that in high-grade metapelites, the cores of adjacent garnet and biotite preserve peak-temperature compositions (Stephenson 1979, Schmid & Wood 1976). According to our observations, this is not the case because iron–magnesium redistribution during retrograde events occurs throughout the biotite grain. Consequently, the use of distribution coefficients in biotite–garnet thermometry necessitates a systematic determination of the various K_D values according to the information desired.

In a separate paper (Indares & Martignole 1985), we suggest that reasonable estimates of temperature are obtained if the above equilibrium criteria are used, in conjunction with Thompson's (1976) biotite–garnet thermometer, or better, with our own calibration, which evaluates the influence of Al and Ti substitution in biotite and that of Ca in garnet.

REFERENCES

ASHWORTH, J.R. & CHINNER, C.A. (1978): Coexisting garnet and cordierite in migmatites from the Scottish Caledonides. Contr. Mineral. Petrology 65, 379-395.

BENCE, A.E. & ALBEE, A.L. (1968): Empirical correction factors for the electron microanalysis of silicates and oxides. J. Geol. 76, 382-403.

BOHLEN, S.R. & ESSENE, E.J. (1980): Evaluation of coexisting garnet–biotite, garnet–clinopyroxene, and other Mg–Fe exchange thermometers in Adirondack granulites: summary. Geol. Soc. Amer. Bull. 91, 107-109.

DAHL, P.S. (1979): Comparative geothermometry based on major-element and oxygen isotope distributions in Precambrian metamorphic rocks from southwestern Montana. Amer. Mineral. 64, 1280-1293.

EDWARDS, R.L. & ESSENE, E.J. (1981): Zoning patterns and their effect on biotite-garnet K_D thermometry. Amer. Geophys. Union Trans. 62, 411 (abstr.).

FERRY, J.M. & SPEAR, F.S. (1978): Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. Contr. Mineral. Petrology 66, 113-117.

GOLDMAN, D.S. & ALBEE, A.L. (1977): Correlation of Mg/Fe partitioning between garnet and biotite with $^{18}O/^{16}O$ partitioning between quartz and magnetite. Amer. J. Sci. 277, 750-767.

GREW, E.S. (1981): Granulite-facies metamorphism of Molodezhnaya station, east Antarctica. J. Petrology 22, 297-336.

INDARES, A. (1982): L'évolution des Conditions de Température et de Pression pendant le Métamorphisme Catazonal dans la Région de Maniwaki, Province de Grenville, Bouclier Canadien. Thèse de maîtrise, Université de Montréal, Québec.

_____ & MARTIGNOLE, J. (1984): Evolution of P-T conditions during a high-grade metamorphic event in the Maniwaki area (Grenville Province). Can. J. Earth Sci. 21, 853-863.

_____ & _____ (1985): Biotite–garnet geothermometry in the granulite facies: the influence of Ti and Al in biotite. Amer. Mineral. 70, 272-278.

LONKER, S. (1980): Conditions of metamorphism in

high-grade pelitic gneisses from the Frontenac Axis, Ontario, Canada. *Can. J. Earth Sci.* **17**, 1666-1684.

LOOMIS, T.P. (1975): Reaction zoning of garnet. *Contr. Mineral. Petrology* **52**, 285-305.

PERKINS, D., III, ESSENE, E.J. & MARCOTTY, L.A. (1982): Thermometry and barometry of some amphibolite–granulite facies rocks from the Otter Lake area, southern Quebec. *Can. J. Earth Sci.* **19**, 1759-1774.

SCHMID, R. & WOOD, B.J. (1976): Phase relationships in granulitic metapelite from the Ivrea–Verbano Zone (northern Italy). *Contr. Mineral. Petrology* **54**, 255-279.

STEPHENSON, N.C.N. (1979): Coexisting garnets and biotites from Precambrian gneisses of the south coast of Western Australia. *Lithos* **12**, 73-87.

THOMPSON, A.B. (1976): Mineral reactions in pelitic rocks. II. Calculation of some P–T–X(Fe–Mg) phase relations. *Amer. J. Sci.* **276**, 425-454.

TRACY, R.J. (1978): High grade metamorphic reactions and partial melting in pelitic schist, west-central Massachusetts. *Amer. J. Sci.* **278**, 150-178.

_____, ROBINSON, P. & THOMPSON, A.B. (1976): Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. *Amer. Mineral.* **61**, 762-775.

WOODSWORTH, G.J. (1977): Homogenization of zoned garnets from pelitic schists. *Can. Mineral.* **15**, 230-242.

WYNNE-EDWARDS, H.R. (1972): The Grenville Province. *In* Variations in Tectonic Styles in Canada (R.A. Price & R.J.W. Douglas, eds.). *Geol. Assoc. Can. Spec. Pap.* **11**, 263-334.