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Biotite–garnet geothermometry in the granulite facies: the influence of Ti and Al in biotite

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Abstract

Temperature estimates obtained with various biotite–garnet thermometers are inconsistent in granulite facies rocks. Although the inconsistency lies partly in the lack of definition of equilibrium criteria, it still remains after rigorous selection of analyzed mineral pairs (isolated biotite and garnet cores for peak equilibrium conditions) and originate from minor element effects in garnet and biotite solid solutions. The departure from ideality due to Ca in garnet can be calculated either with the available thermodynamic data (model A), or with a combination of thermodynamic and empirical data (model B), whereas that due to Mn is probably negligible due to the low Mn content of high-grade garnets. The high Ti content of biotites seems responsible for the abnormally high temperatures obtained with an ideal $\ln K_D/T$ relation (e.g., the experimental calibration of Ferry and Spear). This deviation and that introduced by Al^{vi} substitution in biotite can be evaluated using the classical equations of regular solutions provided independent T estimates are available. Ti and Al interaction parameters have thus been evaluated as:

$$m = (W^{bi}_{FeAl} - W^{bi}_{MgAl}) = -464 \text{ or } -1590 \text{ and } n = (W^{bi}_{FeTi} - W^{bi}_{MgTi}) = -6767 \text{ or } -1451$$

(in cal per mole) depending on the model adopted for the non-ideality in garnet. Starting from the experimental ideal model of Ferry and Spear, a new calibration of the biotite–garnet geothermometer based upon the above correction for Al and Ti and the interaction of Ca in Fe–Mg garnets is proposed here:

$$T°K = \frac{12454 - 0.057P\text{ (bar)} + 3\,(m\,X^{bi}_{Al} + n\,X^{bi}_{Ti}) - (\Delta W_{Ca}X^{ga}_{Ca} + \Delta W_{Mn}X^{ga}_{Mn})}{4.662 - 5.9616\ln K_D}$$

Application of this calibration to granulite facies rocks gives results compatible with those obtained using Thompson's calibration.

Introduction

The partitioning of iron and magnesium between coexisting biotite and garnet has been extensively used in the last ten years as a geological thermometer. The exchange reaction between biotite and garnet solid solutions can be modelled in the AKFM system as:

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

and the corresponding equilibrium constant can be expressed as the distribution coefficient $K_D = (Fe/Mg)_{bi}/(Fe/Mg)_{ga}$ provided both solid solutions are ideal.

Since the first attempts of empirical calibration of K_D as a function of T (Frost, 1962; Perchuck, 1967; Saxena, 1969), one experimental (Ferry and Spear, 1978) and two empirical calibrations (Thompson, 1976; Goldman and Albee, 1977) have been used with improved confidence to evaluate temperatures in medium to high-grade pelitic and semi-pelitic rocks.

In rocks of middle amphibolite facies, the latter three calibrations give relatively consistent results. In rocks of granulite facies, however, severe inconsistencies in garnet–biotite temperatures led Bohlen and Essene (1980) to state that existing calibrations of biotite–garnet thermometry are inadequate to evaluate temperature variations in high-grade metamorphic terranes. If one tries to find reasons for such inconsistency, a discrimination should be made between reasons inherent in the calibrations and those resulting from the ambiguity in the determination of equilibrium criteria. In granulite facies rocks, ambiguity in equilibrium criteria is introduced by the presence of significant K_D differences on the scale of the thin section due to local retrograde reequilibration. This point can be resolved by

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selecting particular locations for analysis within minerals in such a way that calculated K_D can be attributed with some confidence to a specific stage of evolving metamorphic conditions (Indares and Martignole, 1985). It is recognized that in high grade rocks, a pervasive equilibrium is established between garnet and biotite. Although, during cooling, garnet rims and biotite grains adjacent to garnet are affected by late Fe–Mg exchange, garnet cores and matrix biotite isolated from garnet preserve their high grade compositions, and are suitable for calculating peak temperatures. In contrast, from the compositions of garnet rims and adjacent biotite, temperature from some stage during cooling is obtained (Indares, 1982). In the present contribution we intend to reevaluate the various bi–ga[1] geothermometers in granulite facies rocks and, from our own observations and analyses, provide an improved calibration which takes into account the affects of Ti and Al in the biotite solid-solution.

Biotite–garnet geothermometers

An experimental calibration of the biotite–garnet thermometer has been made by Ferry and Spear (1978) using pure Mg–Fe solid solutions. The linear correlation obtained between LnK_D and $1/T$ is consistent with ideal behavior of both binary solid solutions. Since natural systems also contain significant amounts of Ca, Al, Ti, and Mn, departure from this relationship should be considered in the application of this calibration.

Thompson (1976) proposed an empirical linear relationship between LnK_D and $1/T$. This calibration is based on natural metapelitic assemblages of low and medium grade and on independent temperature estimates obtained from various metamorphic reactions. Although it implicitly integrates minor elements substituting for Fe and Mg, the reliability of this calibration could decrease considerably in the case where the analyzed samples depart markedly in terms of minor constituents from the samples used in the calibration. Moreover, the nature of the calibration precludes the introduction of correction factors for such departures.

Natural assemblages were also used in the calibration of Goldman and Albee (1977), and a relationship between K_D and oxygen isotope fractionation between quartz and magnetite was established. In order to take into account compositional effects, a relationship between K_D and the Ca and Mn content of garnet and the Fe, Ti and Al content of biotite was derived, in which X_{Fe}^{bi} and X_{Ca}^{ga} are the most important factors.[2] The solution of Fe and Mg in biotite was considered as non-ideal, and there were uncertainties in the K_D *vs.* composition relationship. The $^{16}O/^{18}O$ *vs.* T dependence was determined at temperatures below 600°C and the extrapolation to higher temperatures may not be valid.

Note added in proof: Perchuk and Lavrent'eva (1983, Experimental investigation of exchange equilibria in the system cordierite–garnet–biotite, in Kinetics and Equilibrium in Mineral Reactions. Ed Saxena, Springer-Verlag, 199–239) have experimentally derived a new K_D vs $1/T$ relationship which yields temperature estimates slightly lower than those given by Thompson's calibration.

Biotite–garnet geothermometry in the Maniwaki area

Samples used to test and refine available bi–ga geothermometers are from an area of 750 km^2 near Maniwaki in the Gatineau valley, 100 km north of Ottawa. This region belongs to the Central Metasedimentary Belt of the Grenville Province (Wynne-Edwards, 1972). Typical lithologies are marbles, quartzites and metapelites interlayered with ortho-amphibolites (Gauthier, 1981). In the metapelites, sillimanite is the only Al_2SiO_5 polymorph, while cordierite occasionally forms rims around garnet or biotite. The ubiguitous presence of orthopyroxene in quartzofeldspathic rocks of suitable composition suggests that the whole area underwent granulite facies metamorphism. Maximum metamorphic temperatures (Indares and Martignole, 1984) calculated with the clinopyroxene–garnet geothermometer range from 740° to 820°C (Ellis and Green, 1981; Ganguly, 1979). Maximum pressures of 6.5–8.5 Kbar are obtained with the plagioclase–garnet–sillimanite–quartz and pyroxene–plagioclase–garnet–quartz barometers (Newton and Haselton, 1981; Perkins and Newton, 1981).

Application of biotite–garnet thermometers on the Maniwaki area samples has been carried out with garnet core and matrix biotite compositions (Tables 1 and 2) considered as representing peak equilibrium (Indares, 1982). Temperatures range between 760–860°C when evaluated with Thompson's equation, and are less dispersed than those obtained from the two other calibrations (Table 3). Moreover these values are consistent with independent estimates (Indares and Martignole, 1984). Temperatures estimated according to Goldman and Albee's calibration vary between 800°–980°C; the highest values, in the range 900–1065°C, are obtained using Ferry and Spear's calibration. Nowhere in the Maniwaki area do other mineral assemblages reflect such high temperatures (Indares and Mar-

Table 1. Average garnet-core compositions

	METAPELITES			SEMIPELITE	GRANULITES	
SAMPLE	31-07	25-13	23-03	31-02F	29-02	36-04
Xalm	0.55-0.58	0.59-0.63	0.62-0.64	0.51-0.54	0.56-0.60	0.56-0.57
Xpy	0.35-0.38	0.32-0.38	0.25-0.26	0.42-0.45	0.31-0.35	0.34-0.35
Xgr	0.05	0.04	0.07	0.03	0.07-0.09	0.06-0.07
Xsp	0.01	0.01	0.04-0.05	0.01	0.02	0.02

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[1] Abbreviations are as follows: bi—biotite; phl—phlogopite; ga—garnet; py—pyrope; pl—plagioclase; Ksp—potash feldspar; sil—sillimanite; qtz—quartz; ilm—ilmenite; gph—graphite.

[2]

$$X_i^{bi} = \frac{i}{Fe + Mg + Mn + Al^{vi} + Ti} \quad \text{where i: Fe, Mg, Mn, Al}^{vi}\text{, Ti}$$

$$X_j^{ga} = \frac{j}{Fe + Mg + Mn + Ca} \quad \text{where j: Fe, Mg, Mn, Ca}$$

Table 2. Average compositions of biotite isolated from garnet

	METAPELITES			SEMIPELITES	GRANULITES	
	31-07	25-13	23-03	31-02F	29-02	36-04
Xph	0.65	0.60-0.63	0.54-0.55	0.67-0.68	0.64-0.67	0.62-0.63
XTi	0.08	0.09-0.12	0.09-0.10	0.09-0.11	0.08-0.10	0.09-0.11
XAl^{vi}*	0.09-0.10	0.08-0.10	0.09-0.10	0.08-0.09	0.05-0.06	0.04-0.05
XAl^{vi}**	0.07-0.08	0.06-0.07	0.08-0.09	0.06	0.02-0.03	0.01-0.02

$X_{ph} = Mg/(Mg + Fe)$

* calculated on a 22(O) basis
** calculated on a $\sum$ cations + Ti - (K + Na) = 14 basis

tignole, 1984). Temperatures obtained using Thompson's calibration thus seem to be the most reasonable.

The role of minor elements substitution in garnet and biotite

The major difference between the three tested calibrations lies in the importance attributed to minor constituents substituting for Fe and Mg in biotite and garnet. Therefore, a better understanding of the differences between these calibrations in terms of minor elements and their effect on the K_D *vs.* T relationship is needed.

We have already noted that in Goldman and Albee's calibration there are uncertainties on both K_D–T and K_D–composition correlations. We cannot test the $^{16}O/^{18}O$ partitioning between magnetite and quartz *vs.* T relationship in the range of temperature considered here, but we can evaluate their compositional parameter affecting T, which we call here SumX.

$$\text{SumX} = -1.22\ X^{ga}_{Mn} - 2.14\ X^{ga}_{Ca} + 1.40\ X^{bi}_{Fe} + 0.942\ X^{bi}_{Ti} - 1.59\ X^{bi}_{Al^{vi}} \qquad (2)$$

Given the apparent lack of a regional T gradient in the Maniwaki area, a SumX *vs.* K_D plot of our data should define a linear relationship if SumX adequately accounts for the compositional dependence of K_D. This is not the case and the irregularity in the distribution of points in Figure 1 suggests that empirical correction (2) is not applicable to our samples.

A $\ln K_D$ *vs.* $1/T$ plot of Ferry and Spear's experimental and Thompson's empirical equations gives two straight lines (Fig. 5). In the high temperature range, Ferry and Spear's equation corresponds to higher temperature for a specific K_D than Thompson's. This is well illustrated by the results obtained from Maniwaki samples. Neglecting experimental error and error inherent to the empirical calibration, such differences are most likely the result of minor components.

The role of Ca and Mn substitution in garnet

In a quaternary garnet solid solution using a simple mixture model (Gugenheim, 1967) and neglecting multicomponent interactions, the nonideality may be expressed as (Ganguly and Kennedy, 1974):

$$RT\ln(\gamma^{ga}_{Fe}/\gamma^{ga}_{Mg}) = W^{ga}_{FeMg}(X^{ga}_{Mg} - X^{ga}_{Fe}) + (W^{ga}_{FeCa} - W^{ga}_{MgCa})X^{ga}_{Ca} + (W^{ga}_{FeMn} - W^{ga}_{MgMn})X^{ga}_{Mn} \qquad (3)$$

and the distribution coefficient K_D can be replaced by an equilibrium constant K' where:

$$\ln K' = \ln K_D + \ln(\gamma^{ga}_{Fe^{2+}}/\gamma^{ga}_{Mg}) \qquad (4)$$

Based upon thermodynamic data, Newton and Haselton (1981) considered W_{MgCa} as the only significant parameter in equation (3):

$$W^{ga}_{MgCa} = 3300 - 1.5T\ (\text{K}) \quad \text{cal/mole of cation} \qquad (5)$$

Interactions due to Mn were neglected due to the lack of thermodynamic data. Thus, according to Haselton and Newton (1981):

$$\ln(\gamma^{ga}_{Fe}/\gamma^{ga}_{Mg}) = -(3300 - 1.5T)X^{ga}_{Ca}/RT \qquad (6)$$

More recently, thermodynamic and statistical treatment of natural data allowed Ganguly and Saxena (1984) to suggest the following values expressing the nonideality of garnet in the temperature range 500–700°.

$$\Delta W_{Ca} = W_{MgCa} - W_{FeCa} = 3000 \pm 500 \text{ cal/mole of cation} \qquad (7)$$
$$\Delta W_{Mn} = W_{MgMn} - W_{FeMn} = 3000 \pm 500 \text{ cal/mole of cation}$$

The nonideality of the Fe-Mg solution is also considered, but the proposed parameters may not be valid for an alm/py ratio lower than 3. In the samples used for our investigation, this ratio is much smaller than 3, and W_{FeMg} was thus neglected in the calculations. Combining (7) and (3) yields:

$$RT\ln(\gamma^{ga}_{Fe}/\gamma^{ga}_{Mg}) = -3000\ (X^{ga}_{Ca} + X^{ga}_{Mn}) \qquad (8)$$

From equations (6) and (8), it can be seen that disregarding the effect of grossular and spessartine in bi–ga thermometry would result in an underestimation of temperatures. Equation (8) allows a greater effect of X_{Ca} upon K_D than equation (6) and this effect is temperature independent. These corrections are not obviously applicable to Thomp-

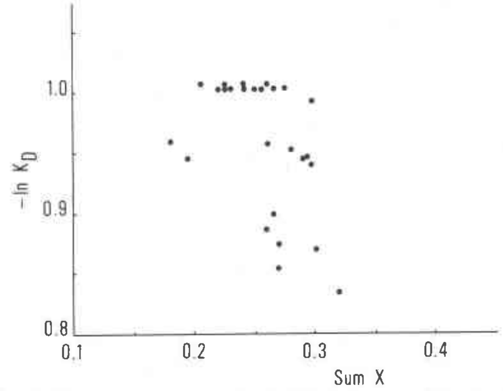

Fig. 1. LnK_D *vs.* Goldman and Albee's compositional effect on K_D, SumX $= 1.22\ X^{ga}_{Mn} - 2.14\ X^{ga}_{Ca} + 1.40\ X^{bi}_{Fe} + 0.942\ X^{bi}_{Ti} - 1.59\ X^{bi}_{Al^{vi}}$ for the Maniwaki garnet-biotite pairs.

son's thermometer which implicitly takes into account the grossular and spessartine component, but K' instead of K_D should be preferred when using the calibration of Ferry and Spear.

In the following treatment both expressions (6) and (8) will be used and will be referred to as model A and model B respectively. The absence of a ΔW_{Mn} in model A does not significantly alter the results due to the very low Mn-content of high-grade garnets: $(0.01 < X_{Mn} < 0.04)$.

Maniwaki garnets also have a low grossular content $(X^{ga}_{Ca} < 0.10)$ and temperatures obtained from K' instead of K_D using Ferry and Spear's calibration are shifted by less than 40°C towards higher temperatures if K' is calculated according to model A, or 80° if model B is used.

In conclusion, correction for affects of grossular and spessartine contents in Maniwaki garnets increases the discrepancy between temperatures obtained from Thompson's and Ferry and Spear's calibration.

The role of Ti and Al substitution in biotite

In natural biotites, Fe and Mg are partially replaced by Al and Ti. There is a positive correlation between Ti in biotite and metamorphic grade (Dallmeyer, 1974; Dymek, 1983), whereas Al^{vi} in biotite is more directly a function of rock chemistry (Indares and Martignole, 1984).

Several substitution mechanisms allow the incorporation of Al and Ti in the octahedral layer of biotite (Dymek, 1983). These are, with the sense of volume change indicated:

Ti substitutional reactions

$$(R^{2+})^{vi} + 2(Si^{4+})^{iv} = (Ti^{4+})^{vi} + 2(Al^{3+})^{iv} \qquad (9) \qquad \Delta V < 0$$

$$(Al^{3+})^{vi} + (Si^{4+})^{iv} = (Ti^{4+})^{vi} + (Al^{3+})^{iv} \qquad (10) \qquad \Delta V > 0$$

$$2(Al^{3+})^{vi} = (Ti^{4+})^{vi} + (R^{2+})^{vi} \qquad (11) \qquad \Delta V > 0$$

$$2(R^{2+})^{vi} = (Ti^{4+})^{vi} + (\quad)^{vi\,3} \qquad (12) \qquad \Delta V < 0$$

$$(R^{2+})^{vi} + 2(OH)^{+} = (Ti^{4+})^{vi} + 2(O^{2-}) + H_2 \qquad (13) \qquad \Delta V < 0$$

Al substitutional reactions

$$(M^{2+})^{vi} + (Si^{4+})^{iv} = (Al^{3+})^{vi} + (Al^{3+})^{iv} \qquad (14) \qquad \Delta V < 0$$

$$3(M^{2+})^{vi} = 2(Al^{3+})^{vi} + (\quad)^{vi} \qquad (15) \qquad \Delta V < 0$$

In order to study the reactions responsible for Ti and Al substitution in Maniwaki biotites, the extreme normalization schemes have been used (Dymek, 1983). The first one assumes that:

$$\text{Total cation charges} = 44$$

and does not take into account a possible charge excess due to an unknown quantity of Fe^{3+} and to substitutions originating through reactions (9) and (10). The second normalization:

$$\text{Total cations} - (K + Na + Ca) = 14$$

implies a complete occupancy of octahedral and tetrahedral sites. This model does not take into account the possibility of vacancies. Due to the analytical uncertainty in the amount of Fe^{3+}, H_2O, and octahedral vacancies, it is not possible to give a definite crystallo-chemical model of our biotites.

In Figure 2, the Ti content of Maniwaki biotites shows a positive correlation with the charge excess (charge excess = total cation charges −44, when the second normalization scheme is used). In the Ti vs Charges diagram, the data points are scattered around the line labeled Charge excess = 2Ti which corresponds to reaction (12) and/or (13). As Ti and Al^{vi} or Al^{iv} do not show significant correlation, substitution according to (12) and (14) seems predominant over (9), (10), and (11). Discriminating between (12) and (13) necessitates data on H_2O content in order to calculate the oxy-biotite component (reaction 13). In spite of the analytical uncertainty, a $(H_2O + Cl + F)$ content between 2 and 3% is estimated from microprobe analysis of biotites. This, together with the presence of vacancies after normalization on a 44-charge basis, lead us to favour reaction (12) rather than reaction (13).

Assuming that all the Ti is incorporated into the biotite according to reaction (12), biotite stoichiometry can be recalculated allowing 1 vacancy for each Ti.

$$\text{Total cations} - (K + Ca + Na) + Ti = 14$$

This cationic normalization scheme, takes into account the vacancies and significantly affects only the Al^{vi} and Al^{iv} contents of biotite (Table 2). However, its application to the Maniwaki biotites leads to small deficiencies in total positive charges (13.5 < Total positive charges < 14), suggesting that other substitutional mechanisms also partici-

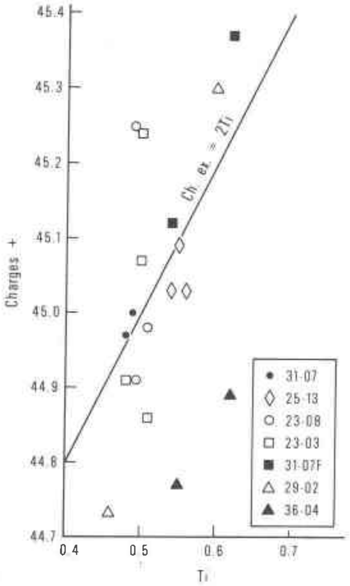

Fig. 2. Total positive charges, calculated with 14 cation normalization, *vs.* Ti-content in biotite from Maniwaki area.

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[3] ( ) site vacancy.

Table 3. K_D and temperature estimates in °C obtained with garnet core and matrix biotite compositions

ROCK-TYPE	METAPELITES			SEMIPELITE	GRANULITES	
SAMPLE	31-07	25-13	23-03	31-02F	29-02	36-04
K_D	0.383-0.386	0.388-0.364	0.345-0.426	0.385-0.426	0.333-0.327	0.369-0.389
Thompson	808-811	812-862	766-786	810-854	746-752	789-814
Goldman & Albee	954-960	878-945	828-852	936-980	794	835-878
Ferry & Spear	940-976	978-1065	900-932	974-1051	866-878	938-980

pate, in a much lesser extent. Nevertheless, this last scheme gives the best approximation of biotite stoichiometry and it will be used for further treatment of our data.

In the Al^{vi}/Al^{iv} diagram (Fig. 3), all the points are located below the line $Al^{vi} = Al^{iv} - 2$ indicating that Al^{vi} is introduced into the biotite via reaction (14), and that an additional reaction, (9) or (10), is responsible for an excess in Al^{iv}. This effect is more pronounced in granulite samples.

The two principal reactions (12 and 14) responsible for Al^{vi} and Ti substitution in biotite imply a volume decrease (ΔV_s). The compensation for this volume decrease is acheived by the replacement of Mg ions by larger Fe^{2+} ions. The corresponding increase in Fe^{2+}/Mg ratio results in an increase in K_D, and thus, in the calculated T if an ideal model is used. This is in keeping with the observation that in high-grade rocks with Ti-rich biotites, Ferry and Spear's calibration gives temperatures higher than those obtained by independent estimates (Grew, 1981; Indares, 1982). The ΔV_s caused by the Ti substitution is much larger than the ΔV_s caused by the Al^{vi} substitution, and the effect of the latter on the K_D is therefore much smaller. This is supported by the fact that Maniwaki pelites and quartzofeldspathic gneisses do not show an appreciable difference in the K_D of biotite–garnet pairs, although biotites have significantly different Al^{vi} contents (Table 2).

In conclusion, in high-grade biotite–garnet assemblages, Ti and Al^{vi} substitutions will alter the K_D so that an ideal mixing in the biotite solid solution does not seem tenable. A correction scheme for the two substitutions is thus needed.

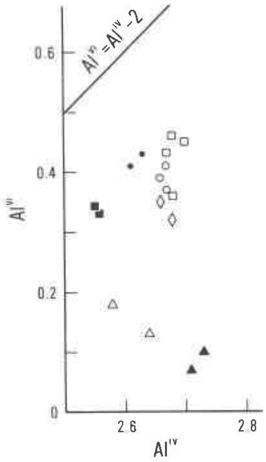

Fig. 3. Al^{vi} *vs.* Al^{iv} in biotite from Maniwaki area calculated on the basis of $\sum$ cations + Ti − (K + Na) = 14

Affects of Ti and Al on the LnK_D vs. $1/T$ Relation

Due to the departure from ideality of both garnet and biotite solid solutions, the equilibrium constant of reaction (1) should be rewritten as:

$$K = K_D \times \frac{\gamma^{bi}_{Fe}\gamma^{bi}_{Mg}}{\gamma^{ga}_{Fe}\gamma^{ga}_{Mg}} \tag{16}$$

As K can be calculated at any temperature from the experimental data of Ferry and Spear (1978), independent temperature data (Indares and Martignole, 1984) will constrain the value of the γ-term in equation (16).

Components in biotite solid solution include an aluminous component ($KAl_7O_{10}(OH)_2$), a titaniferous component ($KTi_2AlSi_3O_{10}$) resulting from substitution (12) and (13), annite ($KFe_3AlSi_3O_{10}(OH)_2$) and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$). The Al and Ti components represent the most likely Al and Ti substitution mechanisms in biotites. In a quaternary biotite solid solution, using a regular symmetrical model (Ganguly and Kennedy, 1974) the activity coefficients of Fe and Mg terms are given by:

$$RT\ln(\gamma^{bi}_{Fe}/\gamma^{bi}_{Mg}) = W^{bi}_{FeMg}(X^{bi}_{Mg} - X^{bi}_{Fe}) + (W^{bi}_{FeAl} - W^{bi}_{MgAl}) \cdot X^{bi}_{Al} + (W^{bi}_{FeTi} - W^{bi}_{MgTi})\,X^{bi}_{Ti} \tag{17}$$

As in the biotite solid solution W_{FeMg} is probably close to zero (Wones, 1972; Ferry and Spear, 1978) equation (17) involves two unknowns, namely:

$$(W^{bi}_{FeAl} - W^{bi}_{MgAl}) = m$$

and

$$(W^{bi}_{FeTi} - W^{bi}_{MgTi}) = n$$

The values m and n are thus the two unknowns after developing the γ-term in equation (16). Two least square regressions (Dahl, 1980) can now be performed from known K_D, K' (equation 4) and corresponding K calculated according to independent temperature estimates, for $K' = K'_1$ (using model A for the nonideality of garnet) and $K' = K'_2$ (using model B).

Data used for the regressions are from biotite–garnet pairs of the Maniwaki area (Table 4). The corresponding K_D obtained by applying rigorous equilibrium criteria are

Table 4. Minor element contents and K_D of the bi–ga pairs for the $RT\ln \Delta K/X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}$ *vs.* $X_{\mathrm{Ti}}^{\mathrm{bi}}/X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}$ regression ($\Delta K = K/K'$)

SAMPLE	GA	BI	X_{Ca}^{ga}	X_{Mn}^{ga}	$X_{Al^{vi}}^{bi}$	X_{Ti}^{bi}	K_D
31-07	Vc	D	0.05	0.01	0.10	0.08	0.387
	Vc	E	0.05	0.01	0.09	0.08	0.383
25-13	IVc	B	0.04	0.01	0.08	0.12	0.436
	IVc	E	0.04	0.01	0.08	0.10	0.391
23-03	A	D	0.07	0.04	0.09	0.09	0.364
	A	A	0.07	0.04	0.10	0.10	0.346
31-02F	1c	Vb	0.03	0.01	0.08	0.09	0.427
	VIIa	VIa	0.03	0.01	0.08	0.11	0.387
29-02	IIIc	IXa	0.08	0.02	0.05	0.10	0.333
	IIIc	VIa	0.07	0.02	0.05	0.08	0.326
36-04	VIb	VIIIa	0.05	0.02	0.05	0.09	0.391

thought to correspond to peak temperatures of 800°C (Indares and Martignole, 1984).

If

$$y = \frac{RT\ln (K/K')}{X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}}, \quad x = X_{\mathrm{Ti}}^{\mathrm{bi}}/X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}$$

and

$$K' = K'_1 \text{ or } K'_2,$$

a linear equation y = m + nx can be fitted through the data points (Fig. 4) for each regression with intercept and slope values of m and n representing the two unknowns. If model A is used, m = −464 and n = −6767 with a correlation coefficient of 0.92 and a standard error on the slope of 1015 and m = −1590 and n = −7451 with a correlation coefficient of 0.93 and a standard error on the slope of 1192 when model B is used.

Starting from the experimentally derived equation of Ferry and Spear (1978), two more elaborated expressions of the LnK_D *vs.* $1/T$ relationships, depending on the correction model for garnet, can be formulated that now account for deviations from ideality in both garnet and biotite solid solution.

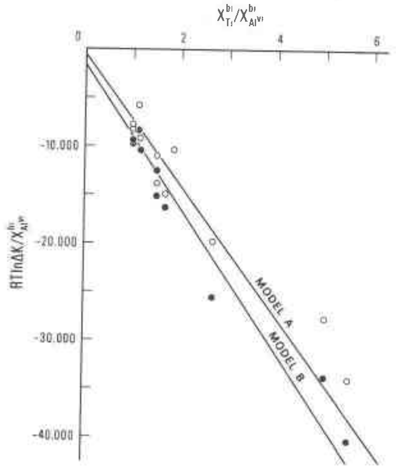

Fig. 4. Plot of the data used for the $RT\ln \Delta K/X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}$ *vs.* $X_{\mathrm{Ti}}^{\mathrm{bi}}/X_{\mathrm{Al^{vi}}}^{\mathrm{bi}}$ regression ($\Delta K = K/K'$). Full circles: points obtained according to model A. Open circles: points obtained according to model B.

$$T^{\circ}\mathrm{K} = \frac{12454 + 0.057P(\mathrm{bar}) + 3(-454\,X_{\mathrm{Al}}^{\mathrm{bi}} - 6767\,X_{\mathrm{Ti}}^{\mathrm{bi}}) - 3(-(3300 - 1.5T))X_{\mathrm{ca}}^{\mathrm{ga}}}{4.662 - 5.9616\ \ln K_D} \qquad (18)$$

$$T^{\circ}\mathrm{K} = \frac{12454 + 0.057P(\mathrm{bar}) + 3(-1590\,X_{\mathrm{Al}}^{\mathrm{bi}} - 7451\,X_{\mathrm{Ti}}^{\mathrm{bi}}) - 3(-3000(X_{\mathrm{Ca}}^{\mathrm{ga}} + X_{\mathrm{Mn}}^{\mathrm{ga}}))}{4.662 - 5.9616\ \ln K_D} \qquad (19)$$

Discussion

Each of the proposed expressions (18) and (19) is thus a combination of an experimental calibration of the ideal part of the exchange reaction between biotite and garnet and an empirical calibration of the deviation from the ideal model. The source of error inherent to the empirical calibration based on independent temperature estimates has a minor incidence on estimated temperature, because this procedure is applied only to the non-ideal part of the system.

Application of this thermometer to biotite–garnet assemblages from the Maniwaki area for which appropriate equilibrium criteria have been used (Indares and Martignole, 1984), gives temperatures for peak conditions ranging from 740°C to 870°C using equation (18) and from 740°C to 850°C when equation (19) is used (Fig. 5). For the corresponding K_D's these temperatures are distributed within ±50°C along the K_D/T line of Thompson (1976). This confirms Thompson's calibration applied to high-grade metamorphic rocks. However, the relations proposed in this paper have a greater domain of application because they permit temperature calculations for samples representing compositional departures from a fixed average Ti and $\mathrm{Al^{vi}}$ content implicitly included in Thompson's calibration.

Due to the lack of published data on garnet cores and coexisting isolated biotites, application of equations (18) and (19) to other granulite terranes is not possible at the moment. But when enough analysis of such mineral pairs become available, further test of the calibration and a choice between the two corrections for garnet may be possible. Refinements of Ti and Al interaction parameters will also be possible for a larger compositional range.

Finally, as the calculated Ti and Al interaction parameters are somewhat dependent on the substitutional model adopted, application of our calibration to upper amphibolite facies rocks should be done with caution. In fact, the validity of the calibration is limited to cases where Ti and Al substitutions take place according to reactions (12) and (14).

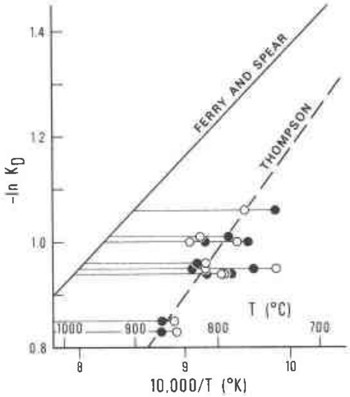

Fig. 5. $\ln K_D$ *vs.* 10000/T°(K) plot from biotite–garnet pairs of Maniwaki area, according to the calibration proposed here. K_D lines from Thompson (broken line) and Ferry and Spear (for 7 Kbar, full line) are shown for comparison. Full circles: points obtained according to equation 18. Open circles: points obtained according to equation 19.

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