# Garnet-biotite geothermometry revised: New Margules parameters and a natural specimen data set from Maine

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## ABSTRACT

The garnet-biotite geothermometer has been recalibrated using recently obtained Margules parameters for iron-magnesium-calcium garnet, Mn interactions in garnet, and Al interactions in biotite, as well as the Fe oxidation state of both minerals. Fe-Mg and  $\Delta W_{Al}$ Margules parameters for biotite have been retrieved by combining experimental results on <sup>16</sup>Al-free and <sup>16</sup>Al-bearing biotite using statistical methods. Margules parameters, per mole of biotite are

$$W_{MgFe}^{Bt} = 40719 - 30T \text{ J/mole},$$
  
 $\Delta W_{AI}^{Bt} = W_{FeAI}^{Bt} - W_{MgAI}^{Bt} = 210190 - 245.40T \text{ J/mole},$   
 $\Delta W_{Ti}^{Bt} = W_{FeTi}^{Bt} - W_{MgTi}^{Bt} = 310990 - 370.39T \text{ J/mole}.$ 

Based on this model, the exchange reaction  $\Delta H$  is 41952 J/mol and  $\Delta S$  is 10.35 J/(K mol). Estimated uncertainty for this geothermometer is 25 °C.

This geothermometer was tested on two data sets. The first consisted of 98 specimens containing garnet and biotite from west-central Maine, which formed under reducing  $f_{O_2}$  with graphite, a limited range of P (~3 to 4.5 kbar), and a moderate range in T (~550–650 °C), and which were all analyzed on a single microprobe using the same standards. Results indicate that the Maine staurolite zone averages 574 °C compared with 530 °C previously calculated and that the muscovite-breakdown T is consistent with experimental data. The second set consisted of cordierite-garnet granulites without hypersthene from Ontario. Results here suggest an average T of 662 °C, compared with significantly lower or higher Ts calculated from other geothermometers.

This model reproduces the Perchuk and Lavrent'eva (1983) experimental  $T_s$  with a standard deviation of 12 °C and discriminates the assemblages in the Maine data set better than other models.

## INTRODUCTION

The garnet-biotite Fe-Mg exchange geothermometer is the most widely used thermometer for estimating T of equilibration of medium-grade pelitic metamorphic rocks. The landmark experimental calibrations of Ferry and Spear (1978) and Perchuk and Lavrent'eva (1983) form the basis for this geothermometer, together with recent modifications that account for nonideality in the garnet and biotite (e.g., Ganguly and Saxena 1984, Indares and Martignole 1985, Williams and Grambling 1990, Berman 1990, McMullin et al. 1991, Bhattacharya et al. 1992, Kleemann and Reinhardt 1994). The combination of Berman's (1990) garnet model and Kleemann and Reinhardt's (1994) biotite model appears to be the best overall calibration currently available. However, when applied to any given rock suite, these and other contributions have yielded disparate results. This may be due to the following: (1) The original calibrations of Ferry and Spear (1978) and Perchuk and Lavrent'eva (1983) were assumed to involve ideal or nearly ideal Fe-Mg substitution in garnet and biotite by McMullin et al. (1991) and Kleemann and Reinhardt (1994) and should be corrected for both garnet and biotite Fe-Mg nonideality. (2) Disparities may have resulted from errors in garnet and biotite mixing properties. (3)  $Fe^{3+}$  in garnet and biotite plays a significant role in the calibration compositions and in natural rocks and, when not incorporated, may have produced discrepancies. The resulting errors are significant.

Using robust regression methods (least absolute deviation), Mukhopadhyay et al. (1997) have statistically evaluated and applied the available volume, experimental  $(K_{\rm D},$  binary and ternary GASP equilibria), and calorimetric data for the Fe-Mg-Ca interactions in garnet to arrive at a self-consistent set of asymmetric Margules parameters ( $W^{H}$ ,  $W^{S}$ ,  $W^{V}$ , and  $W_{FeMgCa}$ ) with statistical uncertainties, and compared their results with previous work. In this contribution we: (1) determine the best possible estimates of Fe<sup>3+</sup> to apply to synthetic and natural garnet and biotite; (2) re-determine the Ferry and Spear (1978) exchange equation from first principles taking into account Fe3+ and Fe-Mg nonideality in synthetic garnet and biotite; (3) use the Ferry and Spear (1978) and Perchuk and Lavrent'eva (1983) experiments, the Mukhopadhyay et al. (1997) garnet Margules parameters, the Ganguly and Cheng (1994) experimental Mn garnet Margules, the biotite and garnet Fe<sup>3+</sup> data, and the best available biotite  $\Delta Ti$  Margules to evaluate  $W_{MgFe}^{HBt}$ ,  $W_{MgFe}^{SBt}$ ,  $\Delta W_{Al}^{HBt}$  and  $\Delta W_{Al}^{SBt}$ ; (4) combine these data to produce a new garnet-biotite calibration; (5) present a 98-sample garnet-biotite data set from graphite-bearing pelitic metamorphic rocks of westcentral Maine; (6) use this data set and another from high-T cordierite+garnet rocks to evaluate the relative accuracy and precision of this revised garnet-biotite geothermometer and previous calibrations; and (7) estimate error for this revised geothermometer.

# DISCUSSION OF PREVIOUS, LARGELY EXPERIMENTAL, RESULTS

This study draws mainly on data from Ferry and Spear (1978, FS), Perchuk and Lavrent'eva (1983, PL), and Kleemann and Reinhardt (1994). Ferry and Spear (1978, p. 115) apparently made mass-balance corrections for small changes in garnet composition that resulted from the shifts in average biotite composition. We have also followed this procedure. The FS brackets using  $Alm_{80}Prp_{20}$  are much wider than those at  $Alm_{90}Prp_{10}$  and were not used by them in their least-squares regression. Kleemann and Reinhardt (1994) used all the data reported by Ferry and Spear (1978). Following Ferry and Spear (1978), we only used the data for the  $Alm_{90}Prp_{10}$  experiments, because brackets for  $Alm_{80}Prp_{20}$  were too wide to be useful for constraining the reaction.

In their analysis, Kleemann and Reinhardt (1994) misplotted the 800 °C points in their Figure 5, and these incorrect values apparently were used in their regression. Unweighted linear regression of their corrected data (their Table 3) gives  $\Delta H = 50089$  J/mol and  $\Delta S = 20.26$ J/(K·mol), rather than 60759 and 31.98 as stated in their paper. This does not nullify the major conclusion of their work regarding  $\Delta W_{\rm Al}^{\rm bi}$ , but requires that  $\Delta W_{\rm Al}^{\rm bi}$  be increased.

Another aspect concerns the <sup>[6]</sup>Al contents of the PL experimental biotite as given by Kleemann and Reinhardt (1994, KR), taken from Al analyses by Aranovich et al. (1988). Because no Si analyses were made, Aranovich et al. (1988) assumed that <sup>[6]</sup>Al<sup>Bt</sup> = (Al - 1)/2. Kleemann and Reinhardt (1994) appear to have increased <sup>[6]</sup>Al<sup>Bt</sup> by about 3.5% over this ideal formula. Pelitic biotite from Maine (see below) shows  $25 \pm 6\%$  more <sup>[6]</sup>Al than would result from the ideal calculation, <sup>[6]</sup>Al<sup>Bt</sup> =  $1.25 \times (Al - 1)/2$ , suggesting that there may be significantly more

<sup>161</sup>Al<sup>Bt</sup> than implied by the ideal calculation. For this study we tested both the KR <sup>161</sup>Al<sup>Bt</sup> and these values multiplied by 1.2. This ambiguity introduces negligible uncertainty in the resultant *T* determinations.

Sengupta et al. (1990) estimated biotite Ti Margules parameters from natural data. Kleemann and Reinhardt (1994) incorrectly divided these one-site values by three. In addition, their assumption of average Ti content of experimental biotite of 0.105 pfu is based on one analysis by Aranovich et al. (1988), which contrasts with three analyses by Perchuk and Lavrent'eva (1983, p. 236) averaging Ti = 0.056. We have adopted an average value close to the latter (see below).

Finally, Perchuk and Lavrent'eva (1983) state that newly formed garnet was poor in Ca and Mn relative to starting material compositions, although analytical data are lacking. Kleemann and Reinhardt (1994) assumed that the product garnet contained the same Ca and Mn as the starting garnet. Failure to account for dilution of Ca and Mn in product garnet because of loss of these ions to the fluid and growth of garnet from the surrounding minerals may have a deleterious effect on the results of calculations.

# Estimation of $FE^{3+}$ in biotite and garnet

Because natural and synthetic biotite and garnet contain Fe<sup>3+</sup> and biotite contains more Fe<sup>3+</sup> than garnet (Williams and Grambling 1990; Dyar 1990; Guidotti and Dyar 1991; Rebbert et al. 1995; M.D. Dyar, unpublished data), failure to account for Fe<sup>3+</sup> significantly affects calibration and use of the garnet-biotite geothermometer. As pointed out by Guidotti and Dyar (1991), unless specific Fe<sup>3+</sup> measurements or estimates are made, the high Fe<sup>3+</sup> percentages (7-46%) in biotite preclude the possibility of good quality garnet-biotite geothermometry in all rocks except, possibly, those formed under very reducing conditions. In pelitic rocks, the best specimens for garnetbiotite geothermometry are those that crystallized with graphite and ilmenite free of hematite component. Such rocks probably formed at  $f_{0}$ , slightly above the quartzfayalite-magnetite (QFM) oxygen buffer (e.g., Holdaway et al. 1988; Williams and Grambling 1990). The synthetic minerals used for the calibration of Ferry and Spear (1978) were produced under conditions of the graphitemethane buffer, which is more reducing than QFM. Mössbauer analysis of biotite synthesized by John Brady (personal communication) according to the recipe of Ferry and Spear (1978) indicates Fe3+/Fe, values of 6.6-7.4% (M.D. Dyar, unpublished data). For simplicity in equations, we designate Fe for Fe<sup>2+</sup>, Fe<sup>3+</sup> for Fe<sup>3+</sup>, and Fe<sub>t</sub> for  $Fe^{2+}$  +  $Fe^{3+}$ . An average of 11.6 ± 3.3%  $Fe^{3+}$  is measured in natural reduced biotite from Maine (Guidotti and Dyar 1991). This amount is supported by wet chemical analyses (Guidotti 1984, p. 426; M.D. Dyar, unpublished data). The experiments of Perchuk and Lavrent'eva (1983) were conducted with the nickel-nickel oxide (NNO) buffer, more oxidizing than QFM. Guidotti and Dyar (1991) and Rebbert et al. (1995) show that if biotite

contains significant Mg or Al, its Fe<sup>3+</sup> content is mainly a function of  $f_{0,}$ . For our work we assume that natural reduced biotite has 11.6% Fe3+, FS synthetic biotite has 7% Fe<sup>3+</sup>, and PL synthetic biotite has between 15 and 19% Fe3+. Biotite Fe3+ is assumed to be in octahedral sites. The available data are insufficient to evaluate the Tand compositional effects on Fe<sup>3+</sup> content, but the results of Guidotti and Dyar (1991) suggest that they are minor. Woodland and O'Neill (1993) show that there is a small but finite amount of Fe<sup>3+</sup> in almandine produced over a range of  $f_{o}$ , and T at crustal P. Fe<sup>3+</sup> contents of typical Maine garnet is 2% and of garnet synthesized at high P by John Brady is 4% (M.D. Dyar, unpublished data). For our work we assumed all synthetic and natural garnet contains 3% Fe3+ and that it replaces Al in octahedral sites.

# Calibration of the garnet-biotite exchange equilibrium from Ferry and Spear (1978) data

The FS experimental data were first used to evaluate the geothermometer for simple reduced systems free of <sup>16</sup>Al<sup>Bt</sup>; then  $W_{Mg}^{Et}$ , and  $\Delta W_{A1}^{Bt}$  were determined using the Al-bearing PL experimental biotite and garnet combined with the FS calibration. Because there are no analyses of Al and Si for the FS product biotite, zero <sup>16</sup>Al<sup>Bt</sup> was assumed. This assumption appears reasonable because <sup>16</sup>Al<sup>Bt</sup> was absent in annite synthesized by Rebbert et al. (1995) over a range of  $f_{O_2}$ . If FS biotite did contain <sup>16</sup>Al, systematic errors in  $\Delta H$  and  $\Delta S$  would be produced, which, for aluminous biotite, would tend to be compensated for by systematic errors in Al Margules using our method (discussed below).

For the 3-site Fe-Mg exchange equilibrium

$$Fe_{3}Al_{2}Si_{3}O_{12} + KMg_{3}AlSi_{3}O_{10}(OH)_{2}$$

$$AIm Phl$$

$$= Mg_{3}Al_{2}Si_{3}O_{12} + KFe_{3}AlSi_{3}O_{10}(OH)_{2}$$
(1)
$$Pyp Ann$$

we assume  $\Delta C_{\rm P} = 0$  in the *T* range of the FS experiments (550–800 °C). Therefore

$$3RT \ln K_{\rm D}K_{\rm y} = -(\Delta H + P\Delta V) + T\Delta S \qquad (2)$$

where

$$K_{\rm D} = \frac{X_{\rm Mg}^{\rm Grt}/X_{\rm Fe}^{\rm Grt}}{X_{\rm Me}^{\rm Bt}/X_{\rm Fe}^{\rm Bt}}, \qquad K_{\gamma} = \frac{\gamma_{\rm Mg}^{\rm Grt}/\gamma_{\rm Fe}^{\rm Grt}}{\gamma_{\rm Mo}^{\rm Bt}/\gamma_{\rm Fe}^{\rm Bt}}.$$

Equation 2 can be rewritten as

$$\ln K_{\rm D}K_{\rm \gamma} = \frac{1}{T} \left[ \frac{-(\Delta H + P\Delta V)}{3R} \right] + \frac{\Delta S}{3R}.$$
 (3)

In the FS experiments, garnet composition was maintained at approximately  $Fe_{t_{0.9}}$  Mg<sub>0.1</sub>, allowing 2 mol% of biotite to vary in composition as it equilibrated with 98 mol% of garnet. Assuming that 3% of the garnet Fe<sub>t</sub> is Fe<sup>3+</sup>, the revised garnet composition is, on average, Fe<sub>0.8972</sub> Mg<sub>0.1028</sub>. For an asymmetric garnet solid solution, (following Mukhopadhyay et al. 1993) we can write

 
 TABLE 1.
 Experimentally determined Fe-Mg fractionation data between coexisting garnet and biotite at 2.07 kbar based on FS experimental data

T (°℃)	$X_{Mg}^{Grt}/X_{Fe_t}^{Grt}$	$X^{\scriptscriptstyle { m Bt}}_{\scriptscriptstyle { m Mg}}/X^{\scriptscriptstyle { m Bt}}_{\scriptscriptstyle { m Fe_{t}}}$	In K <sub>D1</sub>	a Gri a Gri a Fe	a Bt / a Bt Fe	In $K_{eq}$
799 799 738 749 698 698 651 651 599 599	0.1049 0.1165 0.1044 0.1161 0.1100 0.1160 0.1094 0.1152 0.1085 0.1138	0.3333 0.4085 0.3699 0.4389 0.4205 0.4205 0.4493 0.4728 0.5129 0.5504 0.6447	-1.157 -1.255 -1.265 -1.330 -1.341 -1.355 -1.464 -1.493 -1.624 -1.734	0.1338 0.1469 0.1363 0.1490 0.1450 0.1517 0.1474 0.1538 0.1502 0.1561	0.4169 0.4975 0.4749 0.5436 0.5415 0.5707 0.6109 0.6491 0.7026 0.7826	-1.137 -1.220 -1.248 -1.295 -1.317 -1.325 -1.422 -1.440 -1.542 -1.612
550 550	0.1078 0.1133	0.6129 0.7036	-1.738 -1.826	0.1535 0.1596	0.7737 0.8430	-1.618 -1.664

*Note:* for the last three columns, garnet is assumed to contain 3% <sup>[6]</sup>Fe<sup>3+</sup>, and biotite 7% <sup>[6]</sup>Fe<sup>3+</sup>, garnet non-ideality is based on Mukhopadhyay et al. (1997), and biotite non-ideality is assumed to be  $W_{Mofe}^{\text{st}} = 40719 - 30$  *T* J/mol (see text). Fe<sub>1</sub> = total Fe,  $K_{D_1} = K_D$  based on total Fe. Calculation methods described in text.

$$3RT \ln\left(\frac{\gamma_{Mg}^{Gri}}{\gamma_{Fe}^{Gri}}\right) = 2X_{Mg}X_{Fe}(W_{FeMg}^{Gri} - W_{MgFe}^{Gri}) + X_{Fe}^2W_{MfEe}^{Gri} - X_{Mg}^2W_{EeMg}^{Gri}$$
(4)

and for a symmetric biotite solid solution

$$3RT \ln\left(\frac{\gamma_{Mg}^{Bt}}{\gamma_{Fe}^{Bt}}\right) = W_{MgFe}^{Bt}(X_{Fe} - X_{Mg})$$
(5)

where all Margules parameters, W, are for free energy, unless specified as  $W^{\vee}$ ,  $W^{\mu}$ , or  $W^{s}$ . To calculate the activity ratio of the FS garnet compositions, we have adopted the Fe-Mg garnet mixing model of Mukhopadhyay et al. (1997, 3-site Ws) at 2070 bar, the *P* of the experiments, in J/mol, K, bar:

$$W_{\rm FeMg}^{\rm Grt} = -24\,166 + 22.09T - 0.034P \tag{6}$$

$$W_{\text{MgFe}}^{\text{Grt}} = 22265 - 12.40T + 0.050P.$$
 (7)

The regression for end-member reaction thermodynamic values also depends on biotite Fe-Mg mixing nonideality. On the basis of data of Perchuk and Lavrent'eva (1983) we obtained  $W_{MgFe}^{Bi} = 40719 - 30T$  J/mol (3-site Ws, see below). An unweighted linear regression of calculated equilibrium constants for Equation 1 gives the relationship

$$\ln K_{\rm eq} = -\frac{1707.71}{T} + 0.415 \tag{8}$$

which is significantly different from that obtained assuming ideal garnet and biotite and zero  $Fe^{3+}$  (Table 1, Fig. 1).

Berman (1988) gives  $\Delta V$  of Reaction (1) as 0.311 J/bar. Recasting Equation 8 into the form of Equation 3 at 2070 bar, we obtain values for  $\Delta H$  of 41952 J/mol, and  $\Delta S$  of 10.35 J /(K·mol) for our preferred biotite model (see Table 2 for  $\Delta H$  and  $\Delta S$  based on various combinations of



**FIGURE 1.** Plots of FS data vs. 1/T. (A) ln  $K_{Dt}$  (including no Fe<sup>3+</sup> corrections). (B) ln  $K_{eq}$  for garnet with 3% <sup>[6]</sup>Fe<sup>3+</sup>, biotite with 7% 6Fe3+, garnet Margules parameters of Mukhopadhyay et al. (1997) and biotite Margules parameter  $W_{MgFe}^{Bi} = 40719 -$ 30 T (J/mol). Other possible  $\Delta H$  and  $\Delta S$  solutions to the FS data are given in Table 2.

omitting the Fe<sup>3+</sup> correction, ideal and non-ideal mixing of garnet and biotite, and various values of  $W_{MgFe}^{Bt}$ .

Equation 2 can be rewritten

$$\Delta H - T\Delta S + P\Delta V + 3RT \ln K_{\rm D} + 3RT \ln \left(\frac{\gamma_{\rm Mg}^{\rm Gr}}{\gamma_{\rm Fc}^{\rm Gr}}\right) + 3RT \ln \left(\frac{\gamma_{\rm Fc}^{\rm Bt}}{\gamma_{\rm Mg}^{\rm Bt}}\right) = 0.$$
(9)

Using the values obtained above and the biotite Margules

TABLE 2.	$\Delta H$ and $\Delta S$ of the garnet-biotite exchange reaction,
	Equation 1, from Ferry and Spear (1978) and
	incorporating various assumptions

<sup>(6)</sup> Fe <sup>3+</sup>	Garnet Mg-Fe	WHBI (J/moł)	W <sup>SBt</sup> [J/(K mol)]	Δ <i>H</i> (J/mol)	∆ <i>S</i> [J/(K mol)]
none	Berman	0	0	60759*	31,98*
none	Berman	0	0	50167	20.18
none	ideal	0	0	52635	20.20
none	non-ideal	0	0	42624	16.09
cor.	non-ideal	0	0	42927	15.24
cor	non-ideal	8500	0	36698	5.84
cor.	non-ideal	9000	0	36331	5.29
cor.	non-ideal	9500	0	35968	4.74
cor.	non-ideal	34135	24	41005	9.60
cor.	non-ideal	39372	29	41979	10.50
cor.	non-ideal	44608	34	42948	11.40
cor.	non-ideal	38872	29	42344	11.08
cor.	non-ideal	39872	29	41609	9.95
cor.	non-ideal	40719	30	41952	10.35
cor.	non-ideal	41219	30	41584	9,80
cor.	non-ideal	39872	29	41609	9.95

Note: AH and AS calculated using unweighted linear regressions of equilibrium constant data. 16]Fe3+ corrections (cor.) -3% for garnet, 7% for biotite. Garnet non-ideality is based on Margules parameters of Mukhopadhyay et al. (1997) except where given as ideal or Berman (1990). For  $W_{MaFe}^{HBt} > 0$ , only values used in Tables 4 and 5 are shown. Bold set was used for Figure 1B and is our preferred model (Table 5). \* Kleemann and Reinhardt (1994) values.

parameters derived below, the equation for the revised FS geothermometer is

$$T(K) = \frac{41952 + 0.311P + G + B}{10.35 - 3R \ln K_{\rm D}}$$
(10)

where R = 8.31441 and P is in bar, and G and B, evaluated in terms of Margules parameters, are given by

$$G = 3RT \ln\left(\frac{\gamma_{Mg}^{Gri}}{\gamma_{Fe}^{Gri}}\right), \qquad B = 3RT \ln\left(\frac{\gamma_{Fe}^{Bt}}{\gamma_{Mg}^{Bt}}\right).$$
(11)

Because G and B are T dependent, Equation 10 must be solved by iteration.

A Fortran computer program for the PC was written to solve Equation 10. Fe<sup>3+</sup> may be accounted for in the biotite and garnet. The method calculates  $K_{\rm D}$  and initial G and B using a starting T of 600 °C, an estimated P and the equations of Mukhopadhyay et al. (1993). Equation 10 is then solved to give an approximate T. The previous T is averaged with the new T (to avoid oscillation) and used to solve for a new G and B. The process is repeated until the specified convergence interval (0.02 °C) is reached. This program may be obtained by writing Holdaway and providing a 3.5-inch disk.

#### Margules parameters for garnet

For this study, we adopt the Mukhopadhyay et al. (1997) Margules parameters for the Fe-Mg-Ca interactions in garnet, including a ternary  $W_{\text{FeMgCa}}^{\text{Gn}}$  parameter. The values for Mn are as follows. WGrt is very low (Koziol 1990) and the value of 1425 J/mol (Ganguly and Cheng 1994) appears reasonable. W<sub>MnFe</sub> is 1860 J/mol (Pownceby et al. 1987, Ganguly and Cheng 1994). For  $W_{MnMg}^{Grt}$ , the

Source	$ \begin{array}{c} \Delta \mathcal{W}_{Al}^{Bt} \\ = (\mathcal{W}_{FeA}^{Bt} - \mathcal{W}_{MgAI}^{Bt}) \end{array} $	$ \begin{array}{c} \Delta \mathcal{W}_{T_{I}}^{Bt} \\ = (\mathcal{W}_{FeT_{I}}^{Bt} - \mathcal{W}_{MgTi}^{Bt}) \end{array} $	T <sub>Ave</sub> °C
Indares and Martignole (1985)	- 19 958	-93 525	795
Sengupta et al. (1990)	-45 124	-55.518	750
Hoisch (1991)	7605	-8270	600
McMullin et al. (1991)	-11279	-27.944	~600
Patiño Douce et al. (1993)	22 200*	-12300*	900
Kleeman and Reinhardt (1994)	$233355 - 282.3 T^{**}$	-54414 + 3517	575-950
This report	210190 - 245.40 T	310990 - 370.39 T	575-950

**TABLE 3.** Mixing properties for AI and Ti (in J/mol) for 12-O biotite and the average *T* at which they were determined, derived mainly from natural parageneses

Note: All values are per mole of biotite, 12-O formula. Only the preferred models are given for Indares and Martignole (1985, Model B), for Hoisch (1991, Model 2), and for Patiño Douce et al. (1993, Model 1).

\* These values are on an ordered basis, for two M2 sites, and cannot be directly compared with the others.

\*\* Based on an incorrect analysis of the Ferry and Spear (1978) experiments. Correct regression results would produce higher values.

† These values are based on Sengupta et al. (1990, Table 4) which is on a per ion basis. Kleeman and Reinhardt (1994) incorrectly divided the Sengupta et al. (1990) values by 3.

30345 - 15.6T J/mol value based on experiments of Ganguly and Cheng (1994) is consistent with the Wood et al. (1994) high-*T* determination and is reasonably consistent with the results of Williams and Grambling (1990) on natural assemblages and with our own observations (see below). These garnet Mn values were used for our calculations.

## Margules parameters for biotite

There is considerable variability in previously proposed Margules parameters for biotite. Table 3 lists previously determined values for  $\Delta W_{\text{Ti}}^{\text{Bt}}$ . The first four entries, based on a model with disordered octahedral sites, show a strong *T* effect. We assumed  $\sigma$  in *T* of 50 °C, 75 °C for McMullin et al. (1991), and  $\sigma$  in  $\Delta W_{\text{Ti}}^{\text{Bt}}$  of 20 000 J, 25 000 for Indares and Martignole (1985), and did a York-type linear regression of these entries. (Approximate error estimates are based on our evaluation of the work and on the range of *T* used.) This results in  $\Delta W_{\text{Ti}}^{\text{Bt}} = 310 990 - 370.39 T$  J/mol, and these values were used for our calculations. These represent the best values possible because of the low and uncertain Ti content of experimental biotite and the low Ti content of the Maine biotite (discussed below).

Fe<sup>3+</sup> in reduced biotite is small, hard to measure accurately, and probably correlated with Fe<sub>t</sub>; thus a meaningful Margules parameter for <sup>16</sup>Fe<sup>3+</sup> is impossible to retrieve. Guidotti and Dyar (1991) measured as much as 0.4 Fe<sup>3+</sup> per 12 O atoms in oxidized biotite (46% of the Fe<sub>t</sub>, 14% of the octahedral sites, assuming no<sup>[4]</sup>Fe<sup>3+</sup>), suggesting that the ideality assumption fits small amounts of <sup>16]</sup>Fe<sup>3+</sup> in reduced biotite.

# Al-Fe-Mg interactions in biotite

Kleemann and Reinhardt (1994) suggested that the large difference between the FS and PL calibrations is mainly because of <sup>[6]</sup>Al<sup>Bt</sup> in the PL experiments and have used this conclusion to calculate strongly *T*-dependent Margules parameters for <sup>[6]</sup>Al<sup>Bt</sup>. There are four additional variables that might contribute to the difference between the two calibrations: (1) Mg-Fe in biotite, (2) Fe<sup>3+</sup> in bi-

otite (3) overestimation of Ca and Mn content of garnet, and (4) Ti in biotite, although <sup>161</sup>Al<sup>Bt</sup> contributes the most (Kleemann and Reinhardt 1994). With no correction for <sup>161</sup>Al<sup>Bt</sup>, any version of the FS calibration applied to the PL chemical data gives substantially higher *T* than experimental *T* above 600 °C (Fig. 2A).

The PL experimental data set has the following characteristics: (1) there were 35 experiments that included biotite Al determinations (by Aranovich et al. 1988); (2) experimental T ranged from 575-950 °C; (3) Fe/(Fe + Mg) in biotite ranged from 17-78% and in garnet from 23-95%; (4) <sup>161</sup>Al<sup>B1</sup> was substantial, limited in range, but not very precisely measured; (5) Ca and Mn were not measured but have substantially decreased in the product garnet from the known starting garnet compositions (Perchuk and Lavrent'eva 1983); (6) the Ti content of biotite is not well known and an average value must be assumed because the starting biotite compositions are not given by Perchuk and Lavrent'eva (1983); (7) their approach to determining the equilibrium garnet and biotite compositions as the most shifted compositions is questionable; however, the fact that their results lend themselves to the analysis below and that our results appear to compare well with previous calibrations suggest that they may have approached equilibrium compositions. Thus, this data set is especially valuable for determining biotite Fe-Mg Margules parameters, including T dependence, but of somewhat less value for determining biotite Al Margules parameters, and of no value in determining or testing garnet Mn or Ca interactions and biotite Ti interactions. However, assumption of incorrect Margules parameters for Mn, Ca, or Ti, or assumption of too much Ca and Mn in the product garnet or too much Ti in the product biotite substantially impairs the quality and contributes to systematic errors in the Fe-Mg-Al parameters retrieved through bringing the FS and PL experimental results into agreement (see below).

The basic procedure used to retrieve biotite Margules parameters is an iterative stepwise linear regression. Two steps were applied to T calculations using the PL chemical and experimental data to derive biotite Margules pa-



**FIGURE 2.** The effect of  $\Delta W_{A1}^{B1}$  on  $T_{calc}$ . Open symbols are FS experiments, containing no  ${}^{(6)}Al^{B1}$ , and closed symbols are PL experiments, containing  ${}^{(6)}Al^{B1}$ . Both diagrams are calculated using our calibration except for Al in biotite. (A)  $\Delta W_{A1}^{B1} = 0$ . (B)  $\Delta W_{A1}^{B1} = 210190 - 245.40 T$  J/mol as determined by this study. Note that the *Ts* calculated for the PL data with  $\Delta W_{A1}^{B1} = 0$  (case A) fan out at high *T* and those calculated with the  $\Delta$ Al Margules parameters (case B) do not. B represents our preferred model.

rameters: (1) For a particular set of Mg-Fe biotite Margules parameters and related FS calibration (Table 2), a permissible set of Al Margules parameters for biotite was identified to give a set of  $T_s$  ( $T_{calc}$ ) calculated from PL compositions that coincided on a least-squares linear regression line (e.g., Fig. 2B) with the PL experimental  $T_s$ ( $T_{exp}$ ). (2) Statistical parameters were used to show which possible combinations of biotite Margules parameters produced the minimum average deviation of each  $T_{calc}$ from its respective  $T_{exp}$ . This approach does not necessarily invalidate the use of published values of  $\Delta W_{Ti}$  given above.

To account for incompletely known compositional aspects of the experimental biotite, four complete sets of calculations were made; for 15% and 19% Fe<sup>3+</sup>, and 1.0 and 1.2 times the KR <sup>16</sup>[Al<sup>Bt</sup>. Using the Mukhopadhyay et al. (1997) garnet Margules parameters, the Mn and Ti parameters given above, and trial values of  $W_{MgFe}^{HBt}$  and  $W_{MgFe}^{SBt}$  we adjusted  $\Delta W_{Al}^{HBt}$  and  $\Delta W_{Al}^{SBt}$  by successive approximation until the linear regression equation of the calculated line ( $T_{calc}$  vs.  $T_{exp}$ ) had a slope of 1.0000 and each point on the line from the intercept to the highest Thad  $|T_{calc} - T_{exp}| \leq 0.01$  °C. These tight constraints coupled with the new FS calibration for each set of Mg-Fe Margules parameters allowed us to depend on the statistical parameters.

The process of fitting the data involved changing the Mg-Fe biotite Margules parameters incrementally, such that each new fit was compared with the previous calculation. We used the statistic sum of squares due to deviation, a measure of the failure of the least squares line to fit the data points, defined as SST (total sum of the squares) less SSR (sum of the squares due to the regression), seeking a minimum value. Varying the  $\Delta W_{AI}$  Margules parameters within the above T slope and intercept limits produced SST - SSR which varied by no more than  $\pm 10$  °C<sup>2</sup>. As long as the  $T_{calc}$  vs.  $T_{exp}$  line had the characteristics given above, each statistical parameter,  $\sigma_{PL}$ (standard deviation of  $|T_{calc} - T_{exp}|$ ), SST – SSR, goodness of fit, and r<sup>2</sup>, served as adequate tests of how well the individual  $T_{\text{catc}}$  determinations conformed to the regression line, and hence to  $T_{exp}$ . For additional information on these statistical methods see Devore (1991).

An important observation is that our minimum values of SST - SSR were higher than appeared reasonable if we assumed, as did Kleemann and Reinhardt (1994), that the product garnet contained the same Ca and Mn as the starting garnet. This apparently resulted from overestimation of the Ca and Mn contents of the garnet, thus increasing the scatter of the results. After achieving a preliminary fit of the various biotite Margules parameters, a factor ( $\Delta$ CaMn) was added to dilute successively apparent garnet Ca and Mn by a fraction of the starting compositions and to allow Fe and Mg to increase proportionally. Reduction of the average Ca and Mn values substantially improved the statistical fit, consistent with Perchuk and Lavrent'eva's (1983) observations of substantially reduced Ca and Mn in the product garnet. Presumably, cordierite or biotite in the experiments contributed to the growth of garnet. The values of the biotite Margules parameters varied slightly with  $\Delta CaMn$ , so that it was necessary to find the value of  $\Delta$ CaMn that would produce a minimum in SST - SSR at the final optimum Margules parameters for biotite. The optimum value of  $\Delta$ CaMn is 60%.

Similarly, SST – SSR was improved by reducing the apparent average biotite Ti content of 0.105 pfu assumed by Kleemann and Reinhardt (1994) to 0.056 pfu, as determined by averaging three analysis of reaction products by Perchuk and Lavrent'eva (1983). For our analysis, the assumed Ti of 0.105 was decreased with a variable factor ( $\Delta$ Ti). If the calculations assumed  $\Delta$ Ti > 50%, a  $\Delta$ Ti vs.

TABLE 4.	Self-consistent sets of molar $W_{MgFe}^{HBt}$ , $W_{MgFe}^{SBt}$ , $\Delta W_{Al}^{HBt}$
	and $\Delta W_{Al}^{SBt}$ derived from PL experimental data on
	the biotite-garnet exchange equilibrium

_				
	Inc	reasing WHB	at constant W <sup>SBt</sup> →	•
		N	/SBL = 0	
N	W HBI MGEe	8500	9000	9500
2	$\Delta W_{Al}^{HB1}$	295168	299863	304518
÷.	$\Delta W_{AI}^{SBI}$	332.46	338.82	345.18
9	SST - SSR	8512	8449	8514
VBr		W	/SBt = 24	
ţ			34135	
an	$\Delta W_{AI}^{HB1}$		259988	
st	$\Delta W_{Al}^{SBt}$		300.99	
101	SST – SSR		4922	
at		N	$M_{MOFe}^{(SBt)} = 29$	
10		38872	39372	39872
VSE	$\Delta W_{Al}^{HBt}$	247958	252618	248380
2	$\Delta W_{Ai}^{SBt}$	287,48	294.00	300.33
ů,	SST – SSR	4890	4845	4894
eas		W	$\frac{1}{MOEe} = 34$	
Č.	W HBt MgFe		44608	
=	$\Delta W_{Ai}^{HBt}$		24558	
$\downarrow$	$\Delta W_{AI}^{SBt}$		287.28	
	SST - SSR		4932	

Note: <sup>(6)</sup>Fe<sup>3+BL</sup> is 15% of Fe<sub>1</sub>, <sup>(6)</sup>Al<sup>Bt</sup> is 1.0 × KR value (see text). Values for  $\Delta H$  and  $\Delta S$  of Equation (1) are given in Table 2 as indicated by  $W_{MGFe}^{BE}$  and  $W_{MGFe}^{BE}$ . Bold set represents optimum values (see Table 5, third entry). See text for additional details.

SST – SSR plot had a slope twice as large as the slope assuming  $\Delta Ti < 50\%$ . Apparently, the Ti content is sufficiently variable that progressive reduction to zero Ti content successively improves the statistics of the regression. We conclude that above 50%, a larger reduction in SST – SSR results from making the average Ti content more accurate, and below 50%, a smaller reduction in SST – SSR results from decreasing the randomness of Ti content by reducing average Ti toward zero. We used the value of 50% for  $\Delta Ti$ , equivalent to assuming average Ti of 0.053 pfu, consistent with the Perchuk and Lavrent'eva (1983) reaction product analyses.

The correction factors discussed above improved the accuracy of Ca, Mn, and Ti estimates and minimized the effect of Ca, Mn, and Ti on the regression by compensating for errors in average estimated amounts of these elements and possibly for systematic errors in Margules parameters for these elements. In addition, introduction of a temperature dependence for the biotite Fe-Mg Margules parameter substantially reduces SST – SSR. This is true for any set of garnet Fe-Mg Margules parameters. Incorporation of these three factors [ $\Delta$ CaMn,  $\Delta$ Ti, and  $W_{\rm MgFc}^{\rm SBt}$ ], not previously considered, leads to greatly improved SST – SSR and apparently improved biotite Margules parameters.

The results of a number of possible biotite Margules parameter sets for 15% Fe<sup>3+</sup>,  $1.0 \times \text{KR}^{16}\text{Al}^{B1}$  are given in Table 4 along with SST – SSR. Each set in Table 4 gives a regression line with a slope of one and an intercept of zero, and each is a possible self-consistent set of symmetric Margules parameters for the geothermometer.

The T center of mass for Fe-Mg in biotite of the 35 PL calculations (1047.3 K) is the T at which all best-fit  $W_{MgFe}^{Bt}$  lines must intersect, regardless of the value of  $W_{MgFe}^{SBt}$ . Thus, the procedure for stepwise refinement was (1) find the minimum SST – SSR for  $W_{MgFe}^{HBi}$  with  $W_{MgFe}^{SBi}$ = 0, (2) increase  $W_{MgFe}^{SBt}$  incrementally with  $W_{MgFe}^{Bt}$  constant (9000 J/mol for the case in Table 4) at 1047.3 K, (3) when the optimum set is found, bracket it with increments of 5 J/(K mol) in  $W_{MgFe}^{SBI}$  and 500 J/mol in  $W_{MgFe}^{HBI}$ , (4) test any series of three or four vertical or horizontal sets near the minimum with a second degree polynomial fit and, where necessary, change  $W_{MgFe}^{SBt}$ ,  $W_{MgFe}^{HBt}$ , or both in increments of one J/(K mol) or 100 J/mol respectively until the minimum SST - SSR is found (bold set, Table 4). Each of these individual tests (Table 4) begins with a new FS calibration (Table 2) using the applicable Mg-Fe biotite Margules parameters, and each involves successive approximation to bring the  $T_{calc}$  vs.  $T_{exp}$  regression line to a slope of one and an intercept of zero. Correlations exist between the biotite Mg-Fe and  $\Delta Al$  Margules parameters as seen by the fact that the  $\Delta Al$  Margules parameters vary consistently with the Mg-Fe Margules parameters for the same original data set (Table 4).

Table 5 compares the four alternative sets and an asymmetric biotite model (second entry, see footnote), each derived using the method shown in Table 4. These values suggest that a symmetric approximation for biotite is adequate. Each of the five sets could be used as a garnetbiotite geothermometer, because each is within the estimated Fe<sup>3+</sup> and <sup>161</sup>Al compositional range of the PL biotite. Values of the H and S  $\Delta Al$  biotite Margules parameters change substantially between 1.0 and  $1.2 \times KR$ <sup>16]</sup>Al<sup>Bt</sup>, but the change in  $\Delta W_{Al}^{Bt}$  is much less. Of the symmetric determinations, 15% Fe<sup>3+</sup> and 1.2  $\times$  KR <sup>[6]</sup>Al<sup>B1</sup> (Table 5, first entry) appears to be the best because it gives the lowest SST - SSR and provides near-minimum values for Al Margules parameters, which in turn provide a wider spread of T for a suite of rocks and the lowest value of T for the staurolite zone (assemblage A) in Maine (see below). Also, the values of <sup>161</sup>Al<sup>B1</sup> are probably the most accurate with this  $1.2 \times \text{correction}$ . As further justification for the validity of these Al Margules parameters, we note that a York regression of the first four values in Table 3, determined independently of our values, gives very similar results to those in Table 5, No. 1 (Holdaway et al., unpublished manuscript). This set of biotite Margules parameters along with the final garnet parameters and the appropriate  $\Delta H$  and  $\Delta S$  (Table 2) constitute our recommended garnet-biotite geothermometer.

Previous studies concerning the Fe-Mg interaction in biotite have suggested that the interaction is ideal (e.g., Ganguly and Saxena 1984, McMullin et al. 1991, Kleemann and Reinhardt 1994) or that there is a nonideality of about 13400 J/mol (Sack and Ghiorso 1989, Dasgupta et al. 1991, Bhattacharya et al. 1992). Our results are consistent with 13400 J/mol (14525 J/mol at 600 °C, 13400 J/mol at 637 °C). Values near zero give significantly larger  $\sigma_{PL}$  (c.f. Table 5) if the  $T_{cale}$  and  $T_{exp}$  of Per-

	<sup>[6]</sup> Fe <sup>3+BI</sup>	<sup>[6]</sup> Al <sup>BI</sup> Fac,	₩ <sup>HBt</sup> MgFe	WSBt MgFe	$\Delta W_{\rm Al}^{\rm HBt}$	$\Delta W_{\rm Al}^{\rm SB1}$	SST - SSR	$\sigma_{PL}$	$\Delta_{PL}$
		Our calib	rations, Margu	iles parameter	s of Mukhopadhy	ay et al. (1997	) and this report		
(1)	15%	1.2	40719	30	210190	245.40	4817	11.9	0.0
(1)**	15%	1.2	41219	29.8	215031	250.12	4774	11.9	0.0
(1)	15%	1.0	39372	29	252618	294.00	4845	11.9	0.0
(1)	19%	1.2	41219	30	213303	243.57	5014	12.2	0.0
(1)	19%	1.0	39872	29	256405	292.07	5046	12.2	0.0
				Previ	ous calibrations				
(2)	0%	1.0	0	0	0	0	6961	15.6	-5.8
(3)	0%	1.0	0	0	-11279	0	high	86.7	138.3
(4)	0%	1.0	0	0	233355	282,3	6831	14.5	-1.8

**TABLE 5.** Various optimum combinations of  $W_{MgFe}^{HBt}$ ,  $W_{MgFe}^{SBt}$ ,  $\Delta W_{Al}^{HBt}$  and  $\Delta W_{Al}^{SBt}$  [J/mol and J/(K mol)] applied to the PL experimental data\*

Notes: (1) Five optimum sets, each determined by procedure summarized in Table 4. The bold set is considered best of these because it tends to minimize SST – SSR,  $\sigma_{PL}$ ,  $\Delta W_{Al}^{\text{Bel}}$  and  $\Delta W_{Al}^{\text{Sel}}$ , and for reasons given in the text. Appropriate  $\Delta H$  and  $\Delta S$  of Equation (1) given in Table 2. (2) PL calibration. (3) Berman (1990) with McMullin et al. (1991) calibration. Because the PL calculated and experimental *T* were not reconciled, very high SST – SSR,  $\sigma_{PL}$ , and  $\Delta_{PL}$  result. (4) KR calibration.

\* Last 3 column entries: SST - SSR = sum of the squares due to deviation (see text);  $\sigma_{PL}$  = standard deviation of  $|T_{calc} - T_{exp}|$ ;  $\Delta_{PL}$  = average of  $T_{calc} - T_{exp}$ .

 $\frac{T_{calc} - T_{exp}}{**}$ Asymmetric biotite model.  $W_{FeMg}^{HBt} = 40219$ ,  $W_{FeMg}^{SBt} = 30.2$ .  $W_{FeAl}^{St} = -26912 + 62.95$  T,  $W_{MgAl}^{St} = -237102 + 308.35$  T using method of Holdaway et al. (unpublished manuscript).

chuk and Lavrent'eva (1983) are brought into agreement using our procedure (Table 4). Our work also shows that an entropy interaction parameter in biotite is mandated by the  $W_{MgFe}^{SGa}$  and  $W_{FeMg}^{SGa}$  of Mukhopahdyay et al. (1997). However, our results also show that even zero-entropy garnet Margules parameters (e.g., Berman 1990) would require a small entropy interaction parameter for biotite.

Although the approach to equilibrium of the Perchuk and Lavrent'eva (1983) results is questioned, the fact that they lend themselves well to this statistical analysis supports their validity. In addition, they are the only available experimental determinations for Al-rich biotite. It is highly unlikely that the higher-*T* experiments are wholly incorrect, and this analysis depends strongly on these values. Our results support as well as refine the Margules parameters of Kleemann and Reinhardt (1994) on <sup>[6]</sup>Al<sup>Bt</sup>, and show that other factors such as Fe<sup>3+</sup> (and perhaps garnet Ca and Mn and biotite Ti) are also important in explaining the discrepancy between the FS and PL experiments.

In summary, increased <sup>161</sup>Al<sup>Bt</sup>, a *T*-dependent value for  $W_{MgFe}^{Bt}$ , decreased Ca and Mn in garnet and Ti in biotite, and Fe<sup>3+</sup> in biotite significantly reduce SST – SSR and  $\sigma_{PL}$ , and provide improved values of  $\Delta W_{Al}^{HBt}$  and  $\Delta W_{Al}^{SBt}$ . These new values are important for calculating the best possible *T* for natural occurrences.

## Specimen data set from west-central Maine

We have analyzed 98 garnet-biotite pairs from graphite-bearing pelitic metamorphic rocks of west-central Maine [specimens provided by Holdaway, Guidotti, Dutrow, and J.M. Novak (Novak and Holdaway 1981)]. This Buchan-style regional metamorphism was produced by heat from adjacent plutons. The region experienced several metamorphic episodes: M2 (~399 Ma), with the sequence staurolite-andalusite, sillimanite; M3 (~356–394 Ma), staurolite, staurolite-sillimanite, sillimanite, and late Paleozoic metamorphism (~296-325 Ma), sillimanite, sillimanite-alkali feldspar. All analyzed rocks experienced the Acadian M3 event or the late Paleozoic event, but some M3 rocks contain andalusite preserved from M2 (Holdaway et al. 1988, Guidotti and Holdaway 1993). The samples show no petrographic indication of retrogression and were collected from the region surrounded by the cities of Augusta, Lewiston, Norway, Rumford, Oquossoc, Phillips, and Farmington. M3 specimens crystallized at P between 2 and 4 kbar (Holdaway et al. 1988 estimated 3.1 kbar), and the late Paleozoic specimens crystallized at P between 3.5 and 5.5 kbar (estimated average P = 4.5 kbar). The mineral assemblages, event, assemblage designation, and number of garnet-biotite pairs for each are given below. Each specimen also contains muscovite, quartz, hematite-free ilmenite, and graphite  $\pm$  accessory phases tourmaline, apatite, and zircon. Several specimans also contain plagioclase.

- A. Staurolite + Garnet + Biotite ± Chlorite M3 (St, 24)
- B. Andalusite + Staurolite + Garnet + Biotite M3 (And-St, 11)
- C. Sillimanite + Staurolite + Garnet + Biotite M3 (Sil-St, 28)
- D. Sillimanite + Garnet + Biotite M3 (Sil I, 24)
- E. Sillimanite + Garnet + Biotite late Paleozoic (Sil II, 6)
- F. Alkali feldspar + Sillimanite + Garnet + Biotite late Paleozoic (Kfs-Sil, 5)

Rocks of assemblage B are interspersed throughout the higher-grade area of assemblage A, the staurolite zone. Many assemblage B rocks are from the same Augusta region as studied by Ferry (1980), but Ferry collected andalusite-bearing rocks that also contained coarse, visible garnet (J.M. Ferry, personal communication) from the highest-grade portion of the staurolite zone. Our B spec-

TABLE 6.	Peak-T partial stoichiometric analytical data and calculated	T using our preferred model for garnet-biotite pairs from
	Maine	о . О

		Ga	Irnet				Biotite			
Specimen	Fe*	Mg	Mn	Ca	Fe <sup>3+</sup>	Fe	Mg	[6]AI	Ti	- <i>T</i> °C
	1			Assemb	lage A, Staur	olite				
27	2.530	0,191	0,128	0.071	0.166	1.383	0.682	0.499	0,100	584
D084x	2.483	0.223	0.168	0.062	0.159	1.320	0.813	0.463	0,086	568
D084y	2,509	0.226	0,140	0.063	0.156	1.298	0.818	0.489	0.088	566
84	1.973	0.196	0.649	0.096	0.141	1.173	0.965	0.492	0.082	555
D123X	2.190	0.251	0.377	0.124	0.138	1.146	0.964	0.448	0.124	572
65-4	2.199	0.263	0.355	0.124	0.139	1.155	1.033	0,432	0.104	570
114	2.337	0.255	0.296	0.214	0,122	1,240	1.035	0.483	0.091	583
129-1	2 171	0.242	0.327	0.172	0.143	1 156	1.001	0.512	0.079	5/9
42-2	2,219	0.309	0.311	0.096	0 114	1,160	1.026	0.430	0.005	590
94-1	2.123	0.301	0.348	0.166	0.195	1.024	1.032	0.496	0.081	593
547A	2,163	0,238	0.385	0,165	0.161	1.081	1,099	0.412	0.079	548
544B	2,100	0.247	0.374	0.179	0.128	1.060	1.065	0.504	0.075	559
D124	2,129	0.283	0.416	0.109	0.128	1.058	1.084	0.487	0.098	568
52-3	2,183	0.286	0.355	0.118	0.132	1.063	1.103	0.496	0.086	565
D233	2.170	0.297	0.322	0.132	0,125	1.044	1.157	0.461	0.077	563
Ra-a48-66	2.227	0.288	0.240	0.183	0.151	1.065	1.103	0.472	0.078	569
Ra-d00-00	2,104	0.253	0.380	0.230	0.127	1.145	1,037	0.497	0.086	579
Ba-c4-66	2 152	0.372	0.309	0.113	0,185	1,047	1.087	0.531	0.085	579
Ra-a14-66	2 135	0.278	0.372	0.131	0.155	1.130	1.056	0.467	0.084	579
Ra-a33-66	2.173	0.326	0.305	0 149	0.115	1.028	1 168	0.437	0.004	573
Ra-a29-66	2.187	0.330	0.305	0.142	0.132	1.097	1.066	0.489	0.087	597
Ra-a76-66	2,184	0.333	0.296	0.116	0,122	1,063	1,064	0.402	0.080	591
Average T										574
				Assemblage B	3, Andalusite-	Staurolite				
5-4x	1.893	0,315	0.517	0.210	0.158	0.971	1.146	0.465	0.091	601
5-4y	1.941	0,287	0.507	0,232	0.137	1.023	1.146	0.454	0.081	588
3-3	1.990	0.320	0.503	0.114	0.130	0.952	1.197	0.518	0.080	574
61-2	2.017	0.332	0.394	0.182	0.130	0,973	1.215	0.483	0.064	583
1	1.948	0.313	0.451	0.124	0.121	0,976	1.216	0.482	0.071	5/5
N43	1.816	0.273	0.596	0.225	0.125	0.940	1.200	0.483	0.061	561
N147	2.097	0.267	0.404	0.180	0.144	1 062	1.032	0.490	0.000	577
42-5	2.041	0.250	0.516	0.138	0.165	1.104	1.028	0.458	0.097	576
N91C	2,165	0.270	0.350	0.150	0.126	1.126	1.014	0,468	0.089	577
Ra-a69-66	2.302	0.291	0.235	0.108	0.117	1,185	0.970	0,519	0,086	585
Average 7				locombiago (	Cillimonite	Ctourolite				581
14-2	2,120	0.253	0.508	0.047	0.260	1.041	0.942	0.470	0 103	579
23-7	2.169	0.312	0.317	0.125	0.182	1,119	0.946	0.472	0.121	613
53	2.221	0,328	0.284	0.100	0.117	1,118	1.048	0.495	0.096	591
137-1	2.271	0.321	0.228	0.108	0.135	1.089	1.035	0.482	0.101	584
6-3	1.954	0.344	0,425	0.208	0.079	1.050	1.052	0.516	0.139	617
N41	2.005	0.382	0.469	0.094	0.103	0.982	1,209	0.485	0.100	596
4-5	2,348	0.288	0.236	0.071	0.124	1.185	0.960	0.464	0.092	579
D237x	2 272	0.335	0.453	0.213	0,135	0.990	1.082	0.524	0.106	613
D237v	2 272	0.330	0.264	0.093	0.124	1,174	1.017	0.471	0.101	501
D267x	2.153	0.297	0.328	0.152	0.174	1 163	0.927	0.474	0.000	618
D267y	2.263	0.308	0.272	0.094	0.179	1.198	0.934	0.449	0.104	611
D330x	2,193	0.322	0.320	0.100	0.219	1.069	0.982	0.464	0.094	607
D330y	2.152	0.326	0.294	0.110	0.218	1.066	1.012	0.467	0.089	609
Ra-a93-66	2.097	0.319	0.342	0.203	0,187	1.059	1.069	0.470	0.094	606
Ra-b42-66	2.175	0.330	0.336	0.117	0.124	1.114	1.084	0.524	0.095	594
Ha-C35-66	2.251	0.308	0.299	0.098	0.126	1,133	1.017	0.497	0.101	586
Ra-a95-66	2.232	0,283	0.262	0.162	0.076	1.185	0.980	0.535	0.092	586
Ra-b41-66	2,130	0.293	0.347	0.189	0.076	1.185	1.014	0.528	0.107	597
0-J-73	2.070	0.310	0.371	0.170	0.062	1.179	1.032	0.500	0.101	605
O-K-15	1,981	0.244	0.516	0.015	0.100	1.208	0.003	0.493	0.098	614
Ra-b56-66	2,209	0.305	0.317	0.120	0.133	1.194	0.937	0.323	0.000	610
Ra-b86-66	2,062	0.307	0.410	0.164	0.075	1.183	1.054	0.490	0.106	603
Ra-c62-66	2.113	0.330	0.408	0.095	0.166	1.071	0.988	0.544	0.097	611
O-J-65	2,304	0.296	0.208	0.121	0.136	1.217	0.916	0.458	0.089	604
O-L-10	2.200	0.262	0.360	0.131	0.154	1.242	0.874	0.458	0.118	606
Ha-b53-66	2.057	0.313	0.397	0.202	0_139	1.019	1.129	0.448	0.089	589
Average /										600

#### TABLE 6—Continued

		Gai	rnet				Biotite			т
Specimen	Fe*	Mg	Mn	Ca	Fe <sup>3+</sup>	Fe	Mg	<sup>[6]</sup> AI	Ti	(°C)
				Assembla	ge D, Sillima	nite I				
50-3	2.213	0.297	0.344	0.070	0.199	1.125	0.899	0.486	0.149	615
63-1	2.042	0.271	0.450	0.145	0.225	1.099	0.918	0.464	0.130	611
D241	2.039	0.275	0.568	0.049	0.144	1.169	0.936	0.484	0.131	602
D202x	1,994	0.298	0.553	0.098	0.143	1,151	0.973	0.463	0.134	616
D202v	1.977	0.293	0.516	0.156	0.141	1.145	0.972	0.487	0,118	619
112-2	1 991	0.285	0 545	0.098	0.120	1 077	0.914	0.632	0.108	605
19-7	2 057	0.278	0.505	0.068	0 166	1 113	0.989	0.504	0.125	591
D176x	2,060	0 294	0 484	0.097	0 143	1 158	1 018	0.475	0.103	602
D176v	1 980	0.204	0 400	0.174	0.140	1 140	1 014	0 441	0.141	615
140-1	1.957	0.336	0.556	0.089	0.216	1.051	1.018	0.444	0.135	629
D196	2 023	0.314	0.400	0.003	0.137	1 108	1.062	0.454	0.128	605
20.1	1 705	0.314	0.433	0.124	0.177	1,005	1.031	0.497	0.123	626
D120A	1.795	0.309	0.004	0.154	0.124	1.003	1.052	0.473	0.124	600
DIZSA	1.920	0.290	0.003	0.000	0.134	0.000	1.002	0.450	0.160	639
0-1	1.072	0.300	0.514	0.169	0.157	1.012	1.160	0.430	0.085	614
4/-1	1.936	0.355	0.504	0.162	0.131	0.066	1,100	0.517	0.133	608
4	1.851	0.334	0.461	0.223	0.120	0.966	1,132	0.339	0.106	624
0.0.00	1.665	0.345	0.741	0.211	0.117	0.950	1.229	0.461	0.100	603
0-0-30	2.020	0.309	0.522	0.087	0.101	1,100	1.047	0.440	0.140	610
0-C-14	2,116	0.343	0.435	0.066	0.101	1.1/2	0.982	0.492	0.130	614
0-C-17	2,241	0.279	0.345	0.087	0.195	1.197	0.843	0.440	0.125	014
O-C-18	2.185	0.292	0.395	0.092	0.247	1.126	0.879	0,469	0.124	010
O-C-26	1.992	0.333	0.550	0.088	0.098	1.123	1.043	0.426	0.144	614
O-K-10	2.142	0.247	0.443	0,105	0.123	1.245	0.824	0.552	0.149	603
O-K-29	2.225	0.298	0.345	0.083	0.154	1,249	0.829	0.472	0.138	630
Average T										613
				Assembla	ge E, Sillima	nite II			0.445	
77-2	2.058	0.364	0.430	0.077	0.178	1.035	1.010	0,492	0.145	626
77-3	2,047	0.370	0,442	0.077	0,183	1.064	1.031	0,475	0.139	632
90	1.967	0.336	0.561	0.062	0.183	1.065	0.980	0,452	0.168	631
76	1,990	0.337	0.530	0.078	0.184	1.068	0.968	0.444	0.178	633
56	2.056	0.335	0.419	0.118	0.188	1.094	0.943	0.437	0.168	636
91	2.013	0.305	0.530	0.073	0.191	1.112	0.859	0.434	0.197	637
Average T										633
			Ass	semblage F, S	illimanite-All	ali Feldspar				
73	1.940	0.321	0.547	0.097	0.141	1.069	0.940	0.475	0.210	627
87	2,129	0.378	0.248	0.183	0.146	1.098	0.940	0.492	0.177	645
143	2,197	0.394	0.277	0.087	0.147	1,112	0.939	0.467	0.171	642
145	2.219	0.341	0.297	0.066	0.150	1,128	0.832	0.507	0.203	633
86	2.254	0.435	0.184	0.047	0.150	1,127	0.940	0.475	0,182	649
Average T										639

Note: Headings give stoichiometric amounts of eightfold Fe, Mg, Mn, and Ca for garnet and octahedral ions for 12-O biotite. Ts were calculated at P = 3.1 kbar for assemblages A-D, 4.5 kbar for assemblages E, F.

\* Garnet Fe is 97% of Fe, to remove Fe3+ (see text).

imens were collected over a broader area and probably from a wider range of conditions. Many contain finegrained garnet, not obvious in hand specimen. Rocks of assemblage B contain higher average Mg and Mn in the garnet than those of assemblage A. These are rocks that experienced earlier M2, and andalusite was preserved as a function of bulk composition, M3 grade and, in several cases, kinetic factors.

Assemblages C and D both occur as distinct metamorphic zones (Holdaway et al. 1988). Rocks of assemblage E are interspersed in the lower-grade part of the assemblage F area inside the alkali feldspar-sillimanite isograd. Assemblages E and F are found in the southern part of the region and result from the late Paleozoic metamorphism (Holdaway et al. 1988). Of the 98 garnet-biotite analyses, there are 11 pairs, each pair from the same outcrop or the same specimen.

All garnet and biotite were analyzed with the JEOL-

733 electron microprobe at SMU using the same standard file for both minerals (Tables 6, 7<sup>1</sup>). For each sample, several biotite grains surrounding, but not touching, a garnet were analyzed. The garnet was analyzed along a traverse, and only analyses with the highest Mg/Fe ratio (peak-*T*) were accepted. In these rocks biotite is 5–10 times as abundant as garnet. Considering that retrograde garnet rims occupy 5–40% of the garnet volume (most are 5–20%), retrograde exchange effects on the surrounding biotite compositions are seen to be minimal (discussed by Holdaway et al. 1988). Despite these observations, peak *T* may have decreased by up to 25 °C in some high grade specimens as a result of partial retro-

<sup>&</sup>lt;sup>1</sup> A copy of Table 7 may be obtained as document AM-97-638 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

_	$T_A(\sigma)$	$T_{\rm B}(\sigma)$	$T_{\rm C}(\sigma)$	$T_{D}(\sigma)$	$T_{\rm E}(\sigma)$	$\mathcal{T}_{F}(\sigma)$	% $\sigma_{\text{Ave}}$	$T_{\rm F} - T_{\rm A}$	$T_{\rm B} - T_{\rm A}$	$\Delta_{\rm ME}$
				Our calibra	tions (Table 7)					
(1) (2) (3) (4) (5)	<b>573.6(12.2)</b> 574.0(12.2) 574.5(11.5) 580.5(12.5) 582.2(11.7)	<b>580.9(8.4)</b> 581.4(8.4) 581.1(7.9) 588.1(8.5) 589.1(8.0)	<b>600.3(11.8)</b> 600.8(11.8) 599.5(11.0) 607.7(11.9) 607.7(11.2)	613.4(11.2) 613.8(11.1) 611.8(10.4) 620.8(11.3) 619.6(10.8)	<b>632.6(4.0)</b> 633.0(3.9) 629.9(3.9) 639.9(3.7) 637.8(3.6)	<b>639.4(9.0)</b> 639.8(9.0) 636.2(8.3) 646.9(9.3) 644.4(8.6)	<b>47.1</b> 47.1 47.3 47.6	<b>65.9</b> 65.7 61.7 66.4 62.2	<b>7.3</b> 7.4 7.2 7.6 6.9	<b>7.3</b> 7.3 6.8 7.4 6.9
				Previous	calibrations					
(6) (7) (8)	544.3(15.5) 530.4(25.2) 543.6(14.6)	541.7(12.7) 526.6(19.6) 541.8(11.2)	575.5(13.2) 575.2(23.0) 569.3(12.6)	588.5(13.4) 588.5(22.8) 576.7(12.4)	617.2(5.3) 626.4(9.6) 597.7(5.5)	632 2(15.5) 652 3(27.6) 611 5(14.6)	45.9 54.0 53.7	87.9 121.9 67.9	-2.6 -3.8 -1.8	7.1 14.0 7.7

TABLE 8. Average T (°C) and standard deviation of the Maine assemblages for various calibrations\*

*Note:* (1) 15% <sup>[6]</sup>Fe<sup>3+B]</sup>, 1.2 × <sup>[6]</sup>Al<sup>BI</sup> in PL, preferred set; (2) same with asymmetric biotite model; (3) 15% <sup>[6]</sup>Fe<sup>3+BI</sup>, 1.0 × <sup>[6]</sup>Al<sup>BI</sup> in PL; (4) 19% <sup>[6]</sup>Fe<sup>3+BI</sup>, 1.2 × <sup>[6]</sup>Al<sup>BI</sup> in PL; (5) 19% <sup>[6]</sup>Fe<sup>3+BI</sup>, 1.0 × <sup>[6]</sup>Al<sup>BI</sup> in PL; (6) PL calibration; (7) Berman (1990) with McMullin et al. (1991) calibration; (8) KR calibration. \* Last 4 column entries:  $\%\sigma_{AVE}$  = weighted average  $\sigma$  in *T* of assemblages A to F over  $\sigma$  of all specimens collectively, in percent.  $T_F - T_A = T$  difference between averages of assemblages F and A, similar for  $T_B - T_A$ ,  $\Delta_{ME}$  = Average difference in *T* between samples in 11 pairs from same outcrop or specimen.

gression. For each mineral, 4–8 analyses of 30 s, 60 000 counts, or, for later analyses, 80 000 counts per element were averaged. Biotite and garnet from a given specimen were analyzed successively in time and standards were analyzed every 1.5 to 2 h. Many biotite samples were analyzed for Fe<sup>3+</sup>, H<sub>2</sub>O, and F (Guidotti and Dyar 1991; M.D. Dyar, this study). For the remaining biotite, Fe<sup>3+</sup>, H<sub>2</sub>O, and F were estimated by grade (e.g., Guidotti and Dyar 1991). For garnet, 3% of Fe<sub>t</sub> was assigned to Fe<sup>3+</sup> as discussed above. Structural formulas for the biotite were calculated using the method described by Holdaway et al. (unpublished manuscript).

# **TESTING THE MODEL**

One way to test a geothermometer is to compare with experimental data that were not used in the regression. Our model was tested against the experimental results of Patiño Douce et al. (1993; T = 825-975 °C, P = 7-13kbar) and Le Breton and Thompson (1988; T = 850 °C, P = 10 kbar), which involved partial melting of pelitic rocks. Unfortunately, garnet and biotite compositions from both of these studies give low and nearly constant T (666-725 °C) with our geothermometer and give similar low Ts with most other geothermometers because the  $K_{\text{Di}}$  values (as defined in Table 1) do not vary systematically with T. For Patiño Douce et al. (1993)  $K_{Dt}$  values range from 0.29-0.41, and for Le Breton and Thompson (1988) they average 0.32. Apparently the biotite preferentially lost Fe to the melt or the gold capsules, or the equilibrium garnet composition was not adequately determined (Le Breton and Thompson 1988).

We also compared our geothermometer with the geothermometers of Perchuk and Lavrent'eva (1983), Kleemann and Reinhardt (1994), and Berman (1990, for garnet) combined with McMullin et al. (1991, for biotite). The Ferry and Spear (1978) calibration was not tested because it can only be correctly applied to biotite with low <sup>[6]</sup>Al<sup>Bt</sup>. In testing our garnet-biotite geothermometer, we used the PL experimental data set (Table 5) and the Maine natural data set (Table 8). For the experimental data set, the best overall indicators of accuracy are  $\sigma_{PL}$ 

and  $\Delta_{PL}$ . Our Maine data set is the best available natural set because it is large (98 samples), reduced in  $f_{0}$ , analyzed by the same microprobe, includes H<sub>2</sub>O and Fe<sup>3+</sup>, and is from two limited ranges of P. Use of the average biotite Fe<sup>3+</sup> content of 11.6% gave slightly better statistics than using individual Fe<sup>3+</sup> determinations and facilitated the direct comparison with geothermometers that do not distinguish between the oxidation states of Fe. In addition to individual values of  $\sigma$  for each assemblage, we used the last four statistics in Table 8 to compare calibrations. The most important overall statistic is  $\%\sigma_{Ave}$ , which should be minimized because this statistic gives the range of T for the individual assemblages relative to the overall spread of T and emphasizes that the assemblages should each represent the narrowest possible range of T relative to the total range. This is the case because application of any geothermometer to a set of natural data produces a considerable overlap between T populations for adjacent assemblages, and this overlap should be minimized to emphasize the distinction between assemblages or grades (Holdaway et al. unpublished manuscript). The four garnet-biotite geothermometers are also compared for lower granulite-facies pelitic rocks reported in the study of Chipera and Perkins (1988) (Table 9).

For the PL data set, all versions of our model (Table 5) give substantially lower  $\sigma_{PL}$  and  $\Delta_{PL}$  than those of Perchuk and Lavrent'eva (1983), Kleemann and Reinhardt (1994), and Berman (1990) with McMullin et al. (1991). Using the Maine data set, our model (Table 8, Nos. 1-5) gives lower  $\%\sigma_{Ave}$ ,  $\Delta_{Me}$  and  $T_{B} - T_{A}$  positive compared with the three previous models (Nos. 6-8). An exception is  $\mathscr{M}\sigma_{Ave}$  of the PL geothermometer. This lower value may result from the fact that with no nonideality corrections, the Perchuk and Lavrent'eva (1983) calibration closely mimics the complex compositions of many natural samples of biotite and garnet. The near duplication of <sup>161</sup>Al<sup>B1</sup> may actually do better statistically in dealing with the Al effect in a restricted compositional range of biotite than our attempts to measure 161AlBt of the experimental products and to apply the resulting Margules parameters.

In addition to the fact that our Margules parameters

F

E

D

С

B

Assemblage

TABLE 9.	Temperatures (°C), averages, and standard
	deviations for 15 garnet-cordierite-grade specimens
	from the English River subprovince (Chipera and
	Perkins 1988)

Specimen	PL	BM*	KR	This study
CH12	636	661	618	645
CH14	660	700	640	663
CH16	607	625	597	632
LS17	666	730	660	685
MN18	672	716	654	670
MN19	654	690	634	655
MN21	645	671	624	648
RF18	680	746	678	696
RF21	664	711	656	673
RF22	650	686	633	655
RF25	638	664	620	646
VM21	648	680	627	658
VM26	668	715	648	670
VM27	643	691	637	668
VR13	660	701	639	662
Average	652.7	692.4	637.8	661.7
σ	18.2	30.5	19.9	16.4
%σ**	1.97	3.16	2.18	1.75

<sup>\*</sup> BM = Berman (1990) with McMullin et al. (1991).

\*\* σ as a percentage of T (in K).

give lower  $\%\sigma_{Ave}$ , the actual average temperatures for the Maine assemblages appear to be reasonable (Table 8). Kleemann and Reinhardt (1994) expressed some concern that their method tends to underestimate *T* of high-grade rocks. For the Maine data set, the KR model not only gives lower *T*s than ours for all assemblages, but the *T* of assemblage B is lower than that of assemblage A. The Berman (1990) with McMullin et al. (1991) model also gives lower *T*s for assemblage B than for A. Thus the present model corrects well for the higher Mn and Mg content of assemblage B.

The average T of 574 °C for the Maine staurolite zone is, on average, 43 °C above the T estimated using the Ganguly and Saxena (1984) geothermometer (Holdaway et al. 1988). This difference is only partially explained by model errors in both formulations. The staurolite zone in Maine represents the upper part of the complete staurolite zone because all Maine M3 staurolite forms from a reaction that breaks the garnet-chlorite tie line (Holdaway et al. 1988, see also Spear 1993). According to the experiments of Richardson (1968), the first appearance of staurolite with quartz alone occurs at 540 °C at 3 kbar in pure H<sub>2</sub>O; staurolite with biotite, almandine, muscovite, and quartz should first appear at a T on the order of 20-30 °C higher, reduced slightly by impurities in the fluid and Mn in garnet. According to our garnet-biotite calibration, the first appearance of staurolite-biotite-almandine in Maine is at some T below the average staurolitezone T of 574 °C. This is also consistent with the estimate of Guidotti (1974) for the Maine rocks. Our somewhat higher T values for the staurolite grade assemblages are also consistent with the breakdown of staurolite with quartz. Richardson (1968), Dutrow and Holdaway (1989), and Holdaway et al. (1995) all indicate that at 3 kbar, staurolite and quartz break down at a T of 625  $^{\circ}$ C or

 $A = \underbrace{1}_{550} \underbrace{1}_{7} \circ C$ Fround 3. Frequency diagram of *T* values calculated for the

FIGURE 3. Frequency diagram of T values calculated for the assemblages of the Maine data set using our preferred model. X represents average T for each assemblage.

higher. Correction for impurities in the solid phases and fluid would reduce this figure to about 600 °C, near the average T of assemblage C, the staurolite breakdown assemblage in Maine (Table 8, No. 1). This value is also consistent with Guidotti's (1974) estimate. The average Tfor muscovite-sillimanite-alkali feldspar (assemblage F) is 639 °C, 20 °C below the estimated T of Holdaway et al. (1988, Model 2), based on muscovite stability relations with corrections for fluid and solid compositions. As pointed out by Holdaway et al. (unpublished manuscript) these rocks may have had assemblage F stabilized by substantially reduced  $f_{\rm H_2O}$ . Thus the T values determined by our geothermometer (Fig. 3, Table 6, 8) are preferred to the lower values of previous calibrations. The Ts calculated here for Maine also compare well with the petrogenetic grid of Spear and Cheney (1989). There are, however, risks associated with such comparisons because of the possibility that some grids have been based partly on previous lower-T garnet-biotite calibrations, rather than directly on experimental data.

Granulite-facies pelitic rocks of the English River subprovince, Canada, studied by Chipera and Perkins (1988) were also used to test the geothermometer at high grades. Fifteen samples were used from west of the Miniss River fault zone in pelitic rocks containing cordierite and garnet; all lacked muscovite, hypersthene, and spinel. Specimen, RF14, was rejected because it gave unreasonably high *T* with all geothermometers. Estimated *P* is 4 to 6 kbar, we assumed 5 kbar. These rocks formed above the muscovite + quartz breakdown *T* (Chatterjee and Johannes 1974; we estimate 25–50 °C) but below the *T* of formation of hypersthene with quartz. From consideration of the various solid-solid and solid-melt equilibria involved (e.g., Spear 1993, p. 366–369) we estimate that the cordierite-garnet rocks formed at significantly reduced  $X_{\rm H,0}$ at between 650 and 700 °C. Chipera and Perkins (1988) give little information to estimate  $f_{0_2}$ . For our calculations we assumed 11.6% Fe<sup>3+</sup> in biotite. The *T* values appear to be reasonable, averaging 662 °C (Table 9), above the *T* of Perchuk and Lavrent'eva (1983) and Kleemann and Reinhardt (1994) and below the *T* of Berman (1990) with McMullin et al. (1991).

A propagation of estimated errors in composition, Margules parameters,  $\Delta H$  and  $\Delta S$ , and experimental T and P into an error in calculated T produces errors on the order of 50 °C. However, in the procedure used here, we have the difficulty of the deterministic method necessary for the above results, and the related fact that there is a high degree of correlation between various Margules parameters, enthalpy and entropy (e.g., see Tables 2, 4), especially in the compositional range of common garnet and biotite. As a result, systematic errors in certain parameters are compensated for by systematic errors in others, resulting in true errors less than would be indicated by simple error propagation. Taking into account the 12  $^\circ\!C$   $\sigma$  value for the PL data, the good agreement between T estimated for natural assemblages and experimental results, and the small  $\sigma$  values for the Maine assemblages, which must, in part, reflect real variation in T, we estimate an uncertainty under optimum conditions for the determination of natural garnet-biotite T of about 25 °C.

# **FUTURE DIRECTIONS FOR RESEARCH**

In this study, we have attempted to account for all possible variables, including Fe3+, in deriving a calibration of the garnet-biotite geothermometer. The calibration was obtained largely through the application of statistical methods applied to available data, incorporating Margules parameters for biotite and garnet into both the FS and the PL experimental data sets. Additional primary research is needed to make further refinements in this geothermometer including: (1) experimental and calorimetric refinement of Margules parameters, especially for the Ca-rich and Fe-rich garnet compositions; (2) experiments on garnet-biotite at reducing conditions (QFM) over a range of carefully measured Al, Fe, and Mg contents, in systems free of Ca, Mn, and Ti, over a wide range of T; (3) studies involving Ti interactions in Fe-Mg-Al biotite; (4) a thorough analysis of errors associated with Fe-Mg exchange reactions. Statistical analysis in both natural and synthetic systems requires a large amount of data from carefully planned experiments, which have been designed in such a way as to prevent loss of Fe and Mg.

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