



Recalibration of mutually consistent garnet–biotite and garnet–cordierite geothermometers[☆]

Yasunari Kaneko^{a,*}, Takashi Miyano^b

^aDoctoral Programs in Geoscience, The University of Tsukuba, Ibaraki 305-8571, Japan

^bInstitute of Geoscience, The University of Tsukuba, Ibaraki 305-8571, Japan

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Abstract

Garnet–biotite and garnet–cordierite geothermometers have been consistently calibrated, using the results of Fe^{2+} –Mg cation exchange experiments and utilizing recently evaluated nonideal mixing properties of garnet. Nonideal mixing parameters of biotite (including Fe, Mg, Al^{VI} , and Ti) and of cordierite (involving Fe and Mg) are evaluated in terms of iterative multiple least-square regressions of the experimental results. Assuming the presence of ferric Fe in biotite in relation to the coexisting Fe-oxide phases (Case A), and assuming the absence of ferric Fe in biotite (Case B), two formulae of garnet–biotite thermometer have been derived. The garnet–cordierite geothermometer was constructed using Margules parameters of garnet adopted in the garnet–biotite geothermometers. The newly calibrated garnet–biotite and garnet–cordierite thermometers clearly show improved conformity in the calculated temperatures. The thermometers give temperatures that are consistent with each other using natural garnet–biotite–cordierite assemblages within ± 50 °C. The effects of ferric Fe in biotite on garnet–biotite thermometry have been evaluated comparing the two calibrations of the thermometer. The effects are significant; it is clarified that taking ferric Fe content in biotite into account leads to less dispersion of thermometric results.

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1. Introduction

The Fe^{2+} –Mg exchanges between ferromagnesian minerals such as garnet, biotite, and cordierite are widely used as geothermometers. Since the pioneering studies of Ferry and Spear (1978) and Perchuk and Lavrent'eva (1983), numerous versions of these geothermometers have been proposed. Several previous

studies, including experimental and empirical calibrations of garnet–biotite thermometers, have treated the minerals as ideal solid solutions (Thompson, 1976; Holdaway and Lee, 1977; Ferry and Spear, 1978; Perchuk and Lavrent'eva, 1983; Perchuk, 1991). The nonideal behavior of garnet was edgingly introduced (e.g. Goldman and Albee, 1977; Lavrent'eva and Perchuk, 1981; Pigage and Greenwood, 1982; Hodges and Spear, 1982; Ganguly and Saxena, 1984, 1985; Perchuk et al., 1985; Hoinkes, 1986; Aranovich et al., 1988; Williams and Grambling, 1990; Perchuk, 1991). In the same manner, various versions of garnet–cordierite geothermometers have been proposed (empirical and ideal mixing; Thompson, 1976; Holdaway and

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* Corresponding author. Tel.: +81-29-853-4308; fax: +81-29-853-4308.

E-mail address: ykaneko@arsia.geo.tsukuba.ac.jp (Y. Kaneko).

Lee, 1977; experimental and ideal mixing: Wells, 1979; Perchuk and Lavrent'eva, 1983; Perchuk et al., 1985; Aranovich and Podlesskii, 1989; experimental and nonideal mixing: Nichols et al., 1992). Later calibrations have included the nonideal behavior of garnet, as well as those of biotite and cordierite (e.g. Indares and Martignole, 1985; Bhattacharya et al., 1988, 1992; Dasgupta et al., 1991; Kleemann and Reinhardt, 1994; Gessmann et al., 1997; Holdaway et al., 1997; Dwivedi et al., 1998; Holdaway, 2000).

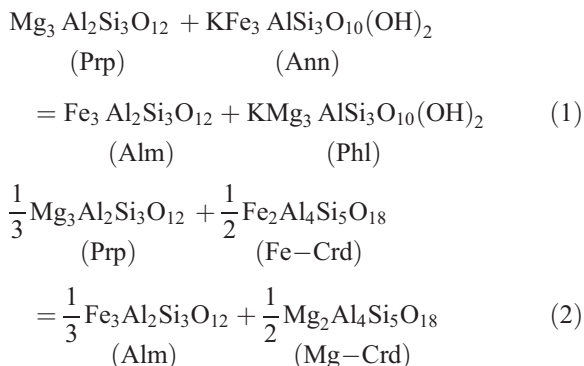
The presence of Fe^{3+} in garnet and biotite was first introduced to the garnet–biotite geothermometer by Williams and Grambling (1990); they used natural compositional data of the minerals for their calibration. Holdaway et al. (1997) applied the presence of Fe^{3+} in the minerals to Fe^{2+} –Mg cation exchange experiments and reconstructed the thermometer. However, detecting the amounts of Fe^{3+} in biotite remains to be difficult to some extent. Therefore, two garnet–biotite thermometer formulae were calibrated in this study, assuming the absence and the presence, respectively, of Fe^{3+} in biotite. The influence of employing Fe^{3+} in biotite in garnet–biotite thermometric calculations has also been examined by comparison of the results obtained by the two formulae. Holdaway (2000) confronted recently published sets of garnet Margules and have advocated the use of averaged values of these Fe–Mg–Ca garnet Margules. We have also used the averaged values and evaluated nonideal behaviors of biotite and cordierite solid solutions consistently.

Dwivedi et al. (1998) constructed a garnet–cordierite thermometer estimating Fe–Mg nonideality in cordierite through a multiple linear regression method. Their calibrations were based on the Mukhopadhyay et al. (1997) ternary Margules parameters and on the Berman (1990) quaternary parameters for garnets. Their calibration, however, includes a misformulation of the Margules equation; the term $W_{\text{FeMgCa}}X_{\text{Ca}}(X_{\text{Mg}} - X_{\text{Fe}})$ in their Eq. (5) is superfluous. The Mn and Ca contents in the experimental garnets were disregarded in their calibrations. Data of Fe^{3+} content in cordierite have not accumulated yet. However, cordierite possibly has some low- Fe^{3+} content. In this study, we have refined the garnet–cordierite thermometer by considering the Mn and Ca contents in experimental garnets and Fe^{3+} content in experimental cordierite.

Generally, the application of different geothermometers (i.e. garnet–biotite and garnet–cordierite) to an equilibrium assemblage in a rock sample (or in a microscopic area) should ideally calculate identical temperatures. However, the thermometers, which have been calibrated on the basis of the different set of experimental and/or natural data, may give different results. Although several authors (e.g. Perchuk et al. 1985; Perchuk, 1991) have attempted to construct internally consistent geothermobarometers, they have adopted nearly ideal solid solution models of related minerals. Their calibrations of the two thermometers produced discrepancies of up to ca. 100 °C. We have reconstructed garnet–biotite thermometers using a different approach to the thermodynamic equilibrium expression of the cation exchange reactions that were adopted in Holdaway et al. (1997) and Holdaway (2000). The expression used here permits straightforward and comprehensible regression procedures, and it gives simple thermometer equations. Mutually consistent garnet–biotite and garnet–cordierite geothermometers were calibrated through the iterative multiple least-square regression method using the same garnet interaction parameters in both garnet–biotite and garnet–cordierite thermometric calibrations.

2. Thermodynamic modeling

The Fe^{2+} –Mg cation exchange reactions between garnet–biotite and garnet–cordierite are expressed as follows (the mineral abbreviations of Kretz, 1983 are used throughout):



Solution models of the minerals were assumed to be (1) quaternary (Fe^{2+} , Mg, Ca, and Mn) asymmetric

solid solution for garnet, (2) quintuple (Fe^{3+} , Fe^{2+} , Mg, Al^{VI} , and Ti) symmetric solid solution for biotite, and (3) binary (Fe^{2+} and Mg) symmetric solid solution for cordierite. Margules equations for the garnet solid solution were taken from Berman (1990). Holdaway (2000) compared several sets of ternary Fe–Mg–Ca garnet Margules parameters with fixed M–Fe, Mn–Mg, and Mn–Ca parameters in the thermometric calibrations and showed that differences between the sets did not have significant effects on the thermometric results. He recommended averaged values (AV) of Berman and Aranovich (1996; BA), Ganguly et al. (1996; GA), and Mukhopadhyay et al. (1997; MU) for thermodynamic formulations. We confronted these sets of Margules parameters by fitness of calibration to the garnet–biotite and garnet–cordierite experiments. The orders of goodness of fitness (R^2) are $\text{MU} > \text{AV} > \text{GA} > \text{BA}$ for garnet–biotite and $\text{BA} > \text{AV} > \text{GA} > \text{MU}$ for garnet–cordierite. As a result, the averaged values (AV), which constantly give good results for both garnet–biotite and garnet–cordierite thermometric calibrations, were used in this study except for the volumetric terms (W_V). Volumetric interaction parameters were adopted from Geiger (1999). The interaction parameters of the enthalpic and entropic terms (W_H and W_S) for binary solid solutions including Mn were taken from Ganguly et al. (1996) for Mn–Fe, Ganguly and Cheng (1994) for Mn–Ca, and Holdaway et al. (1997) for Mn–Mg. The values of the parameters used in the present study are listed in Table 1. The temperatures calculated by our calibrations and those of Holdaway (2000) will be examined below in a later section; discrepancies may have been due to the interaction parameter of Mn–Fe binary and the multiple regression procedure used in the respective calibrations.

The equilibrium conditions of reactions (1) and (2) are generally described by Eq. (3) using changes of enthalpy ($\Delta H_T^{\circ(m)}$), entropy ($\Delta S_T^{\circ(m)}$), and volume ($\Delta V_{298}^{\circ(m)}$) of reaction (m), where m denotes 1 or 2:

$$\Delta H_T^{\circ(m)} - T\Delta S_T^{\circ(m)} + \Delta V_{298}^{\circ(m)}(P - 1) + nRT \ln K_D^{(m)} + nRT \ln K_\gamma^{\text{Grt}} + nRT \ln K_\gamma^{\text{M}} = 0 \quad (3)$$

in which $K_D^{(m)}$, K_γ^{Grt} , and K_γ^{M} represent the distribution coefficient of reaction (m) and the nonideal mixing

Table 1
Margules parameters of garnet used in this study

	W_H (J/mol)	W_S (J/mol K)	W_V (J/bar)	Ref. for W_H and W_S
MgCa	25,759	12.87	0.184	AV
CaMg	66,114	18.98	0.012	AV
FeCa	19,932	9.67	0.157	AV
CaFe	–1304	–0.34	0.099	AV
FeMg	–5672	–5.99	0.000	AV
MgFe	11,622	5.50	0.000	AV
MnFe	1617	0.00	0.024	GA
FeMn	1617	0.00	0.024	GA
MnCa	1425	0.00	0.065	GC
CaMn	1425	0.00	0.065	GC
MnMg	41,249	23.01	0.038	HO
MgMn	41,249	23.01	0.038	HO

W_H , W_S , and W_V are enthalpic, entropic, and volumetric terms of Margules parameters, respectively. Values of volumetric terms were taken from Geiger (1999). BA: Berman and Aranovich (1996), GA: Ganguly et al. (1996), GC: Ganguly and Cheng (1994), HO: Holdaway et al. (1997), AV: Averaged values of BA, GA, and MU.

terms of garnet and mineral M, respectively. M indicates Bt, Crd, or in some cases Grt. P is pressure (bar), T is temperature (K), and R is the gas constant (8.31441 J/bar). The number of sites involved with cation exchange reactions is n . The distribution coefficient is expressed as the following equation, using the mole fraction (X_i^{M}) of component i in each mineral (M) (Fe^{2+} is denoted as Fe in subscript for clarity):

$$K_D^{(m)} = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{Grt}} (X_{\text{Mg}}/X_{\text{Fe}})^{\text{M}} \quad (4)$$

Bearing the relation $nRT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}}) = W_H - TW_S + W_V(P - 1)$ in mind, the nonideal mixing terms of garnet, biotite, and cordierite are represented as the following equations:

$$\begin{aligned} nRT \ln K_\gamma^{\text{Grt}} &= nRT \ln(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Grt}} \\ &= nRT \ln \gamma_{\text{Fe}}^{\text{Grt}} - nRT \ln \gamma_{\text{Mg}}^{\text{Grt}} \end{aligned} \quad (5)$$

$$\begin{aligned} nRT \ln K_\gamma^{\text{Bt}} &= -(W_{\text{H,FeMg}}^{\text{Bt}} - TW_{\text{S,FeMg}}^{\text{Bt}})(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) \\ &\quad - (W_{\text{H,Al}}^{\text{Bt}} - TW_{\text{S,Al}}^{\text{Bt}})X_{\text{Al}}^{\text{Bt}} \\ &\quad - (W_{\text{H,Ti}}^{\text{Bt}} - TW_{\text{S,Ti}}^{\text{Bt}})X_{\text{Ti}}^{\text{Bt}} \end{aligned} \quad (6)$$

$$nRT \ln K_\gamma^{\text{Crd}} = -(W_{\text{H,FeMg}}^{\text{Crd}} - TW_{\text{S,FeMg}}^{\text{Crd}})(X_{\text{Mg}}^{\text{Crd}} - X_{\text{Fe}}^{\text{Crd}}) \quad (7)$$

For simplification, W_V^{Bt} and W_V^{Crd} were set to nil. The details of nonideal mixing terms for garnet are described in Appendix A.

Volumes (in J/bar) of mineral end-members were taken from Mukhopadhyay et al. (1997) for garnets (Alm: $V_{298}^\circ = 11.529$ and Prp: $V_{298}^\circ = 11.318$), Berman (1988) for biotite (Ann: $V_{298}^\circ = 15.483$ and Phl: $V_{298}^\circ = 14.997$), Robie and Hemingway (1995) for Mg-cordierite ($V_{298}^\circ = 23.322$), and Mukhopadhyay and Holdaway (1994) for Fe-cordierite ($V_{298}^\circ = 23.706$). The resulting volume changes of reactions (1) and (2) were -0.295 and -0.122 J/bar, respectively. The volume change for reaction (1) is identical to that used in Holdaway (2000). Although the value of reaction (2) that has been adopted in Dwivedi et al. (1998) is slightly larger (-0.13 J/bar) than ours, we chose the present value to maintain the consistency of the two thermometers.

3. Experimental data and treatments

3.1. Garnet–biotite

Several assumptions were made for treating the experimental data of garnet and biotite in order to calibrate garnet–biotite thermometers. At first, accepting the estimations by Holdaway et al. (1997) and Holdaway (2000) regarding Fe^{3+} cations, the content and site possession of the cations were considered as follows. Fe^{3+} is present in the octahedral sites of garnet and biotite. Fe^{3+} is assumed to be 3% of the total Fe (Fe^{T}) in the case of garnets. Fe^{3+} in biotite of Case A is present depending on the oxidation state, and it was assumed to be 7% of Fe^{T} for the Ferry and Spear (1978) experiments (graphite–methane–buffer) and 15% of Fe^{T} for the Perchuk and Lavrent'eva (1983) experiments (QFM- or NNO-buffers). No Fe^{3+} is present in biotite of Case B, i.e. all Fe cations are present as ferrous Fe. Second, Mn and Ca contents of garnet were $X_{\text{Mn}}^{\text{Grt}} = X_{\text{Ca}}^{\text{Grt}} = 0$ for the Ferry and Spear (1978) experiments. In accord with the manner of Holdaway et al. (1997), $X_{\text{Mn}}^{\text{Grt}}$ and $X_{\text{Ca}}^{\text{Grt}}$ values listed in Kleemann and Reinhardt (1994) with a factor of 0.6 were used for the Perchuk and Lavrent'eva (1983) experiments. Kleemann and Reinhardt (1994) assumed that $X_{\text{Mn}}^{\text{Grt}}$ and $X_{\text{Ca}}^{\text{Grt}}$ under equilibrium conditions were identical to those of the starting materials.

Perchuk and Lavrent'eva (1983), however, reported that Mn and Ca were dissolved into the fluid and that these components were in low concentrations in products. Third, Al at the octahedral sites in biotite was assumed to be 0.1 atoms per formula unit (apfu) for the Ferry and Spear (1978) experiments, as discussed by Holdaway (2000); moreover, the values of Kleemann and Reinhardt (1994) multiplied by 1.2 were used for the Perchuk and Lavrent'eva (1983) experiments, in the same manner as those of Holdaway et al. (1997) and Holdaway (2000). The values used in Kleemann and Reinhardt (1994) were based on biotite analyses and the estimates of Al^{VI} (half of total Al – 1, 11 oxygen base) of Aranovich et al. (1988). However, natural biotite frequently contains a larger Al^{VI} than $(\text{Al} - 1)/2$. Fourth, Ti content in biotite was $X_{\text{Ti}}^{\text{Bt}} = 0$ for the Ferry and Spear (1978) experiments and 0.053 apfu for the Perchuk and Lavrent'eva (1983) experiments (the average of three analyses by Perchuk and Lavrent'eva, 1983). Finally, runs with the garnet $\text{Alm}_{80}\text{Prp}_{20}$ of Ferry and Spear (1978) were excluded because the brackets with the $\text{Alm}_{80}\text{Prp}_{20}$ data were much larger than those with the $\text{Alm}_{90}\text{Prp}_{10}$ (Ferry and Spear, 1978). Only runs of Perchuk and Lavrent'eva (1983), in which the Al content of biotite was analyzed by Aranovich et al. (1988), were used in the present calibrations. Because Holdaway (2000) showed that excluding the experiments of Gessmann et al. (1997) gave better results in fitness of calibration to the experimental results, this study also excluded the Gessmann et al. (1997) experiments. All data used for the calibrations are shown in Appendix B, in the on-line version of this article.

3.2. Garnet–cordierite

To render the results obtained with the garnet–biotite and garnet–cordierite thermometers consistent, almost all treatments, which were applied to the garnet in the previous section, were performed for the garnet–cordierite experiments. Fe^{3+} is assumed to be 3% of Fe^{T} in garnet. Mn and Ca contents in the garnets of the Perchuk and Lavrent'eva (1983) and Aranovich and Podlesskii (1983) experiments were assumed to be 60% of the starting materials. $X_{\text{Mn}}^{\text{Grt}}$ was equal to zero, and $X_{\text{Ca}}^{\text{Grt}}$ was 60% of the starting materials (0.07 apfu) for the Hensen and Green (1971) experiments. The $X_{\text{Ca}}^{\text{Grt}}$ value was consistent

with that of the produced phases (6 mol%), as analyzed by Hensen and Green (1971). $X_{\text{Mn}}^{\text{Grt}}$ and $X_{\text{Ca}}^{\text{Grt}}$ were zero for the Bertrand et al. (1991) experiments because the synthetic starting materials included neither Mn nor Ca. In the case of cordierite, Mn was ignored in all of the experiments. We checked effects of the presence of Fe^{3+} in cordierite assuming Fe^{3+} was 0%, 1.5%, 3.0%, or 4.5% of Fe^{T} . The results showed that the goodness of fitness (R^2) of regression increases with the increasing percentage of Fe^{3+} . These assumptions of Fe^{3+} content have little effect on the thermometric results by garnet–cordierite; the difference is less than ± 1 °C. Khomenko et al. (2001) showed by Mössbauer analysis that their 21 cordierite samples, in which X_{Mg} ranges from 0.19 to 0.97, have contained Fe^{3+} from 0% to 1.5% of Fe^{T} . Experimental and natural cordierite used in this study fall within this X_{Mg} range. Cerný and Chapman (1997) and Geiger et al. (2000) also showed low- Fe^{3+} contents in Fe- and Mg-cordierites, respectively. We adopted the assumption that Fe^{3+} content is 1.5% of Fe^{T} in cordierite in the present calibration of the garnet–cordierite thermometer. Differing from the garnet–biotite experiments, the natural logarithm of the distribution coefficient ($\ln K_{\text{D}}$) between garnet and cordierite as a function of the experimental temperature (T_{exp}) fluctuated over more than 3σ discrepancy (σ is the standard deviation). This fact shows that some experimental runs possibly have not achieved equilibrium. To exclude less equilibrated experimental data, several runs, those which gave more than 100 °C discrepancy between the T_{exp} and the estimated temperature by preliminary calculations (i.e. 2 runs at 900 °C of Bertrand et al., 1991 and 1 run at 1000 °C of Hensen and Green, 1971), were omitted. The 100 °C discrepancy corresponds to 3σ (100.15 °C) of difference between the T_{exp} and the temperature calculated by preliminary formulation. The data used for the regressions are listed in Appendix C, in the on-line version of this article.

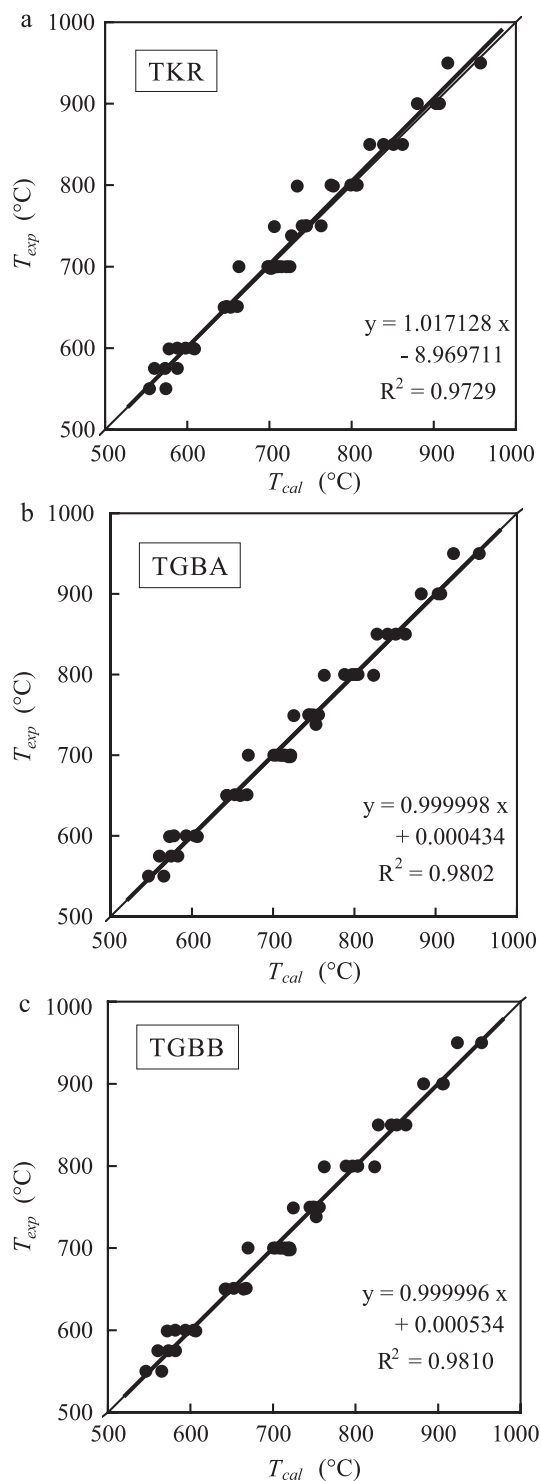


Fig. 1. Calculated temperatures (T_{cal}) versus experimental temperatures (T_{exp}) for garnet–biotite pairs. (a) TKR: Kleemann and Reinhardt (1994), (b) TGBA: this study with Fe^{3+} correction (Case A), and (c) TGBB: this study without Fe^{3+} correction (Case B). Formulation of multiply regressed straight line and goodness of fitness (R^2) are also shown in each diagram.

4. Construction of geothermometers

4.1. Garnet–biotite

To obtain the interaction parameters in biotite solid solution that can fully account for the distribution of $K_D^{(1)}$ versus the T_{exp} , Eq. (3) was rewritten in terms of reaction (1) and was rearranged as follows for the multiple regressions:

$$\begin{aligned} \Delta H_T^{\circ(1)} - T\Delta S_T^{\circ(1)} + (\Delta V_{298}^{\circ(1)} + W_V^{\text{Grt}})(P - 1) \\ + 3RT \ln K_D^{(1)} + W_H^{\text{Grt}} - TW_S^{\text{Grt}} \\ - (W_{\text{H,FeMg}}^{\text{Bt}} - TW_{\text{S,FeMg}}^{\text{Bt}})(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) \\ - (W_{\text{H,Al}}^{\text{Bt}} - TW_{\text{S,Al}}^{\text{Bt}})X_{\text{Al}}^{\text{Bt}} \\ - (W_{\text{H,Ti}}^{\text{Bt}} - TW_{\text{S,Ti}}^{\text{Bt}})X_{\text{Ti}}^{\text{Bt}} = 0 \end{aligned} \quad (8)$$

$$\begin{aligned} (\Delta V_{298}^{\circ(1)} + W_V^{\text{Grt}})(P - 1) + 3RT \ln K_D^{(1)} + W_H^{\text{Grt}} \\ - TW_S^{\text{Grt}} - (W_{\text{H,Ti}}^{\text{Bt}} - TW_{\text{S,Ti}}^{\text{Bt}})X_{\text{Ti}}^{\text{Bt}} \\ = -\Delta H_T^{\circ(1)} + T\Delta S_T^{\circ(1)} \\ + (W_{\text{H,FeMg}}^{\text{Bt}} - TW_{\text{S,FeMg}}^{\text{Bt}})(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) \\ + (W_{\text{H,Al}}^{\text{Bt}} - TW_{\text{S,Al}}^{\text{Bt}})X_{\text{Al}}^{\text{Bt}} \end{aligned} \quad (9)$$

The interaction parameters for Ti substitution in biotite ($W_{\text{H,Ti}}^{\text{Bt}} = 310,990$ J, $W_{\text{S,Ti}}^{\text{Bt}} = 370.390$ J/K)

(a) Case A; assuming the presence of Fe^{3+} in biotite

$$T = \frac{-37,612.9 + (-0.295 + W_V^{\text{Grt}})(P - 1) + W_H^{\text{Grt}} - 16,234.6(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) - 262,165.9X_{\text{Al}}^{\text{Bt}} - 310,990X_{\text{Ti}}^{\text{Bt}}}{-5.160 - 3R \ln K_D^{(1)} + W_S^{\text{Grt}} - 12.066(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) - 300.664X_{\text{Al}}^{\text{Bt}} - 370.39X_{\text{Ti}}^{\text{Bt}}} \quad (10a)$$

(b) Case B; assuming the absence of Fe^{3+} in biotite

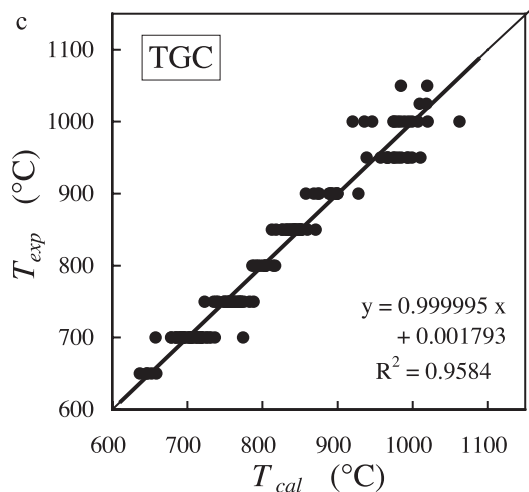
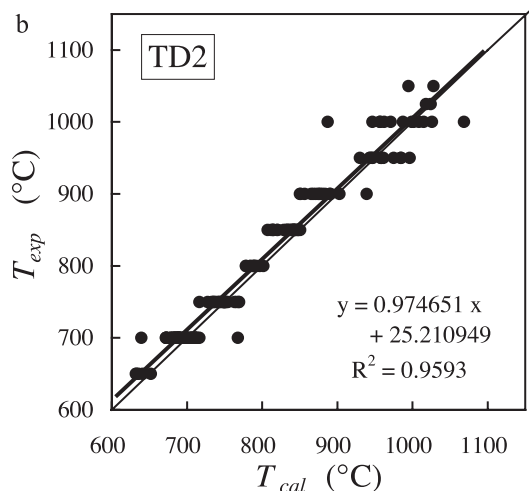
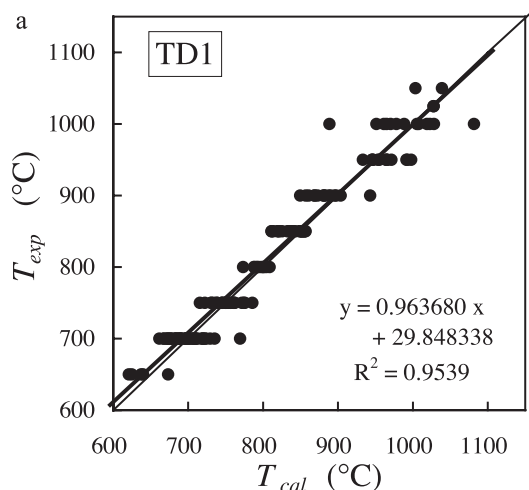
$$T = \frac{-38,889.9 + (-0.295 + W_V^{\text{Grt}})(P - 1) + W_H^{\text{Grt}} - 15,667.5(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) - 256,595.2X_{\text{Al}}^{\text{Bt}} - 310,990X_{\text{Ti}}^{\text{Bt}}}{-7.880 - 3R \ln K_D^{(1)} + W_S^{\text{Grt}} - 12.238(X_{\text{Mg}}^{\text{Bt}} - X_{\text{Fe}}^{\text{Bt}}) - 309.871X_{\text{Al}}^{\text{Bt}} - 370.39X_{\text{Ti}}^{\text{Bt}}} \quad (10b)$$

The calculated temperatures for each experimental run are listed in Appendix B. Both of the formulae reproduced the experimental temperature better than did the Kleemann and Reinhardt (1994) thermometer (Fig. 1).

were identical with those of Holdaway et al. (1997) and Holdaway (2000) because the experimental compositions of biotite did not vary sufficiently in Ti content to evaluate its effect. Multiple least-square regressions were performed for the right-hand side (RHS) of Eq. (9) regarding $\Delta S_T^{\circ(1)}$, $W_{\text{H,FeMg}}^{\text{Bt}}$, $W_{\text{S,FeMg}}^{\text{Bt}}$, $W_{\text{H,Al}}^{\text{Bt}}$, and $W_{\text{S,Al}}^{\text{Bt}}$. The iterative multiple regression procedure can be outlined as follows. Step 1 includes a calculation of the left-hand side (LHS) of Eq. (9) using T_{exp} as T and a regression of the RHS of Eq. (9). Step 2 is a computation of temperature (T_{cal}) using the regression results of Step 1 in a thermometer equation. Step 3 is a calculation of the best-fitted straight line of T_{cal} versus T_{exp} (i.e. $T_{\text{exp}} = \mathbf{a}T_{\text{cal}} + \mathbf{b}$). Step 4 involves calculating the LHS of Eq. (9) using $T_{\text{mod}} = \mathbf{a}T_{\text{exp}} + \mathbf{b}$ as T and regressing the RHS of Eq. (9). Step 5 is a computation of temperature using the regressed results from Step 4. Step 6 is a recalculation of the best-fitted straight line, $T_{\text{exp}} = \mathbf{a}T_{\text{mod}} + \mathbf{b}$. Step 7 includes a calculation of the LHS of Eq. (9) and a regression of the RHS of Eq. (9), using $\mathbf{a}T_{\text{mod}} + \mathbf{b}$ as T . Step 8 is a formulation of temperature using the results of Step 7. Step 9 is a repetition of Steps 6 to 8, until the slope (\mathbf{a}) and intercept (\mathbf{b}) of a best-fitted linear line become 1 ± 0.00001 and 0 ± 0.01 , respectively. The resulting equations for the garnet–biotite thermometer are as follows:

4.2. Garnet–cordierite

A similar procedure was carried out for the reconstruction of the garnet–cordierite thermometer. Iterative multiple regressions were performed regarding



$\Delta S_T^{\circ(2)}$, $W_{\text{H,FeMg}}^{\text{Crd}}$, and $W_{\text{S,FeMg}}^{\text{Crd}}$ in this case. The equilibrium condition Eq. (3) of reaction (2) was rewritten and rearranged as follows:

$$\begin{aligned} \Delta H_T^{\circ(2)} - T\Delta S_T^{\circ(2)} + (\Delta V_{298}^{\circ(2)} + W_V^{\text{Grt}})(P - 1) \\ + RT\ln K_D^{(2)} + W_H^{\text{Grt}} - TW_S^{\text{Grt}} \\ - (W_{\text{H,FeMg}}^{\text{Crd}} - TW_{\text{S,FeMg}}^{\text{Crd}})(X_{\text{Mg}}^{\text{Crd}} - X_{\text{Fe}}^{\text{Crd}}) = 0 \quad (11) \end{aligned}$$

$$\begin{aligned} (\Delta V_{298}^{\circ(2)} + W_V^{\text{Grt}})(P - 1) + RT\ln K_D^{(2)} + W_H^{\text{Grt}} - TW_S^{\text{Grt}} \\ = -\Delta H_T^{\circ(2)} + T\Delta S_T^{\circ(2)} \\ + (W_{\text{H,FeMg}}^{\text{Crd}} - TW_{\text{S,FeMg}}^{\text{Crd}})(X_{\text{Mg}}^{\text{Crd}} - X_{\text{Fe}}^{\text{Crd}}) \quad (12) \end{aligned}$$

The resulting equation for the garnet–cordierite geothermometer is therefore represented by the following expression (assuming $\text{Fe}^{3+} = 0.015\text{Fe}^{\text{T}}$ in cordierite):

$$T = \frac{-26,144.7 + (-0.122 + W_V^{\text{Grt}})(P - 1) + W_H^{\text{Grt}} - 80.44(X_{\text{Mg}}^{\text{Crd}} - X_{\text{Fe}}^{\text{Crd}})}{-12.7094 - R\ln K_D^{(2)} + W_S^{\text{Grt}} + 1.642(X_{\text{Mg}}^{\text{Crd}} - X_{\text{Fe}}^{\text{Crd}})} \quad (13)$$

The calculated temperatures for the experimental runs are listed in Appendix C. The experimental temperatures were better reproduced by the present formulation than by the Dwivedi et al. (1998) calibrations (Fig. 2).

5. Evaluation and application of the thermometers

In order to test the reliability of the newly calibrated geothermometers, the calculated temper-

Fig. 2. Calculated temperatures (T_{cal}) versus experimental temperatures (T_{exp}) for garnet–cordierite pairs. (a) TD1: Dwivedi et al. (1998)-T1 (with Mukhopadhyay et al., 1997 Margules parameters), (b) TD2: Dwivedi et al. (1998)-T2 (with Berman, 1990 Margules parameters), and (c) TGC: this study. Formulation of multiply regressed straight line and goodness of fitness (R^2) are also shown in each diagram.

atures were compared with those calculated by recently reported thermometers. Garnet–biotite pairs in pelitic rocks in Maine (data from Holdaway et al., 1997) and garnet–cordierite pairs listed in Dwivedi et al. (1998) were used. The calibrated garnet–biotite geothermometer with the Fe^{3+} correction in biotite (Case A) computed nearly identical temperatures with those of Holdaway (2000) (Fig. 3). The thermometer, assuming that there was no Fe^{3+} in biotite (Case B), calculated 5–15 °C lower temperatures than did both Holdaway (2000) and the Case A thermometers. The garnet–cordierite geothermometer of this study calculated temperatures that were approximately 10–40 °C lower than those of Dwivedi et al. (1998), as shown in Fig. 4. The observed differences may have resulted from the incorporation

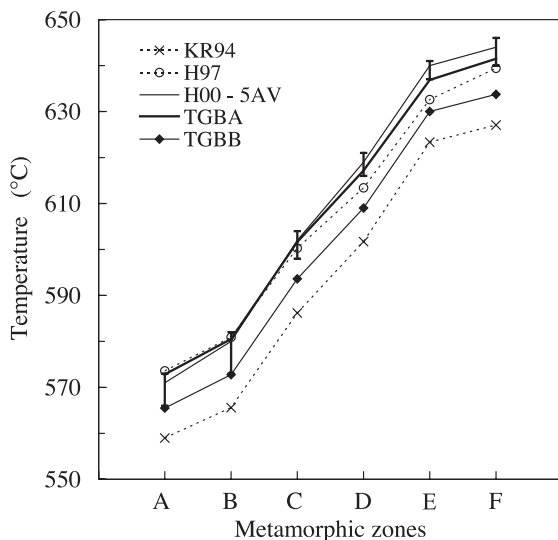


Fig. 3. Comparison of estimated temperatures for pelitic rocks in Maine calculated by various methods of garnet–biotite thermometers. Chemical compositional data were taken from Holdaway et al. (1997). KR94: Kleemann and Reinhardt (1994), H97: Holdaway et al. (1997), H00-5AV: Holdaway (2000)-5AV, TGBA: this study with Fe^{3+} correction (Case A), TGBB: this study without Fe^{3+} correction (Case B). Vertical bars represent temperature ranges calculated by 5BA, 5GA, 5MU, and 5AV formulae of Holdaway (2000). Metamorphic zones are A: staurolite zone, B: sillimanite–staurolite zone, C: andalusite–staurolite zone, D: sillimanite-I zone, E: sillimanite-II zone, F: sillimanite–alkali feldspar zone.

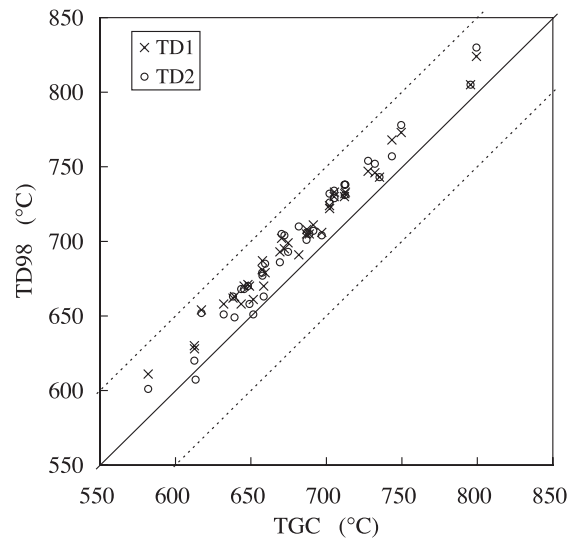


Fig. 4. Comparison of temperatures calculated by the present and Dwivedi et al. (1998) formulations of garnet–cordierite thermometers. TD1: Dwivedi et al. (1998)-T1 (with Mukhopadhyay et al., 1997 Margules parameters), TD2: Dwivedi et al. (1998)-T2 (with Berman, 1990 Margules parameters). Dashed lines represent ± 50 °C discrepancies.

of the Mn and Ca contents in the experimental garnets into the present calibration.

Comparing the thermometric results of the present and reported thermometers, and evaluating the consistency between the constructed garnet–biotite and garnet–cordierite thermometers, temperatures were calculated for pelitic rocks selected from the Bushveld contact aureole, the regionally metamorphic Limpopo Belt, and other published data. In the pelitic rocks, garnet, biotite, and cordierite coexist in apparent equilibrium. The compositional data of the minerals and the calculated temperatures are listed in Appendix D, in the on-line version of this article. In the cases involving the application of the thermometers to natural assemblages, there are some difficulties in estimating the Fe^{3+} content in biotite. Direct analyses of Fe^{3+} in natural biotite cannot be achieved with only a microprobe; moreover, it is currently hard to find enough numbers of data including the Fe^{3+} content in biotite for evaluating the present garnet–biotite thermometers. Fe^{3+} in biotite is known to vary according to oxygen fugacity (e.g. Williams and Grambling, 1990; Guidotti and Dyar, 1991; Dyar et al., 2002). It is therefore

thought that the Fe^{3+} content in biotite and the Fe-oxide phases share a significant relationship. We tentatively fixed the Fe^{3+} content in the natural biotites on the basis of the Fe-oxide phases present with the mineral, using Williams and Grambling (1990) and Guidotti and Dyar (1991) as references. For the Case A thermometer, the Fe^{3+} content was $\text{Fe}^{3+} = 0.11\text{Fe}^{\text{T}}$ in biotite coexisting with ilmenite (no magnetite), and $\text{Fe}^{3+} = 0.22\text{Fe}^{\text{T}}$ in biotite coexisting with magnetite (no ilmenite); the average of the former two values ($\text{Fe}^{3+} = 0.165\text{Fe}^{\text{T}}$) was used for biotite coexisting with both of the Fe-oxides. No Fe^{3+} correction was made for the Case B biotite, and the total Fe was considered to be ferrous. The Fe^{3+} content in natural garnet was assumed to be 3% of the Fe^{T} ; this assumption was made in a manner similar to that of the experimental garnet in the calibration processes.

For the experimental data used here, the two different formulations of the garnet–biotite thermometer computed consistent temperatures (Fig. 5), as expected from the calibration procedure using the iterative multiple regressions. The thermometer with

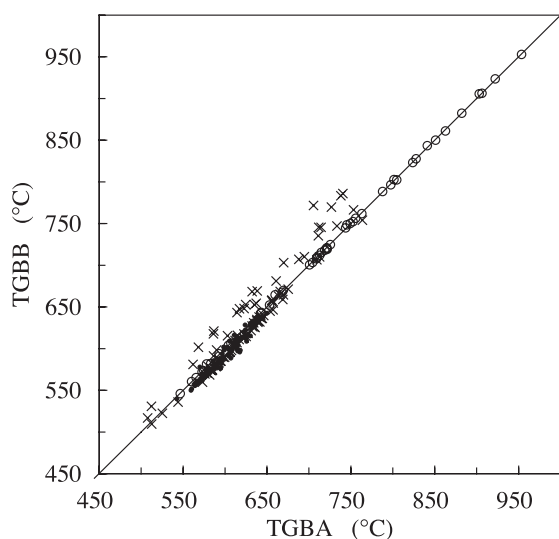


Fig. 5. Comparison of temperatures calculated by the two garnet–biotite geothermometers with and without Fe^{3+} correction. TGBA: with Fe^{3+} correction (Case A), TGBB: without Fe^{3+} correction (Case B). Open circles: experimental garnets and biotites used in the present calibrations, dots: natural garnets and biotites in Maine (Holdaway et al., 1997), crosses: natural garnets and biotites listed in Appendix D.

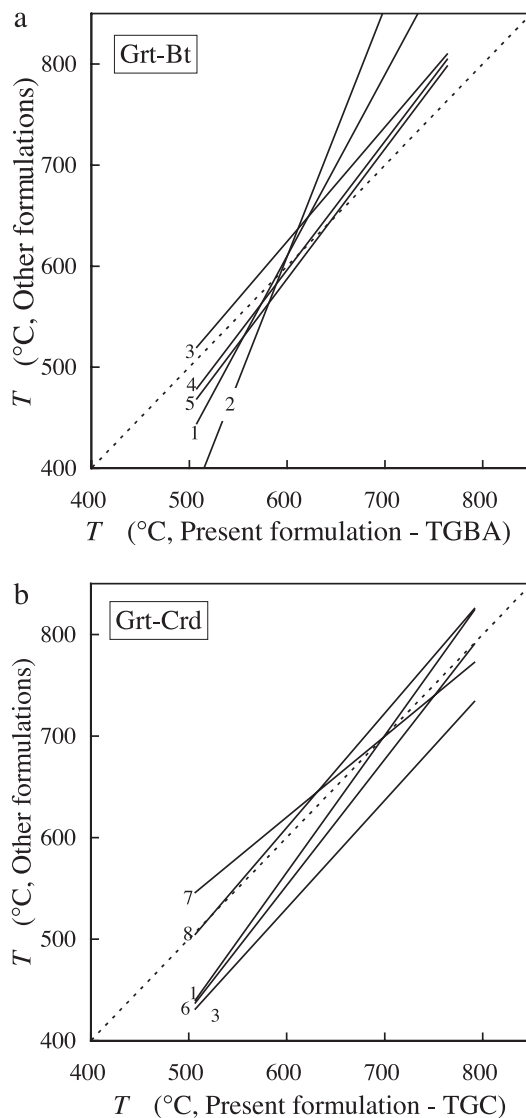


Fig. 6. Calculated temperatures by the present calibrations versus published thermometers. (a) Garnet–biotite thermometers (TGBA—this study versus various published thermometers), (b) garnet–cordierite thermometers (TGC—this study versus various published thermometers). 1: Thompson (1976), 2: Ferry and Spear (1978), 3: Perchuk and Lavrent'eva (1983), 4: Bhattacharya et al. (1992) with Hackler and Wood (1989) garnet solution model, 5: Kleemann and Reinhardt (1994), 6: Wells (1979), 7: Bhattacharya et al. (1988), 8: Dwivedi et al. (1998)–T2 (with Berman, 1990 Margules parameters). Each line represents a least-square regression line. Mineral data used are listed in Appendix D.

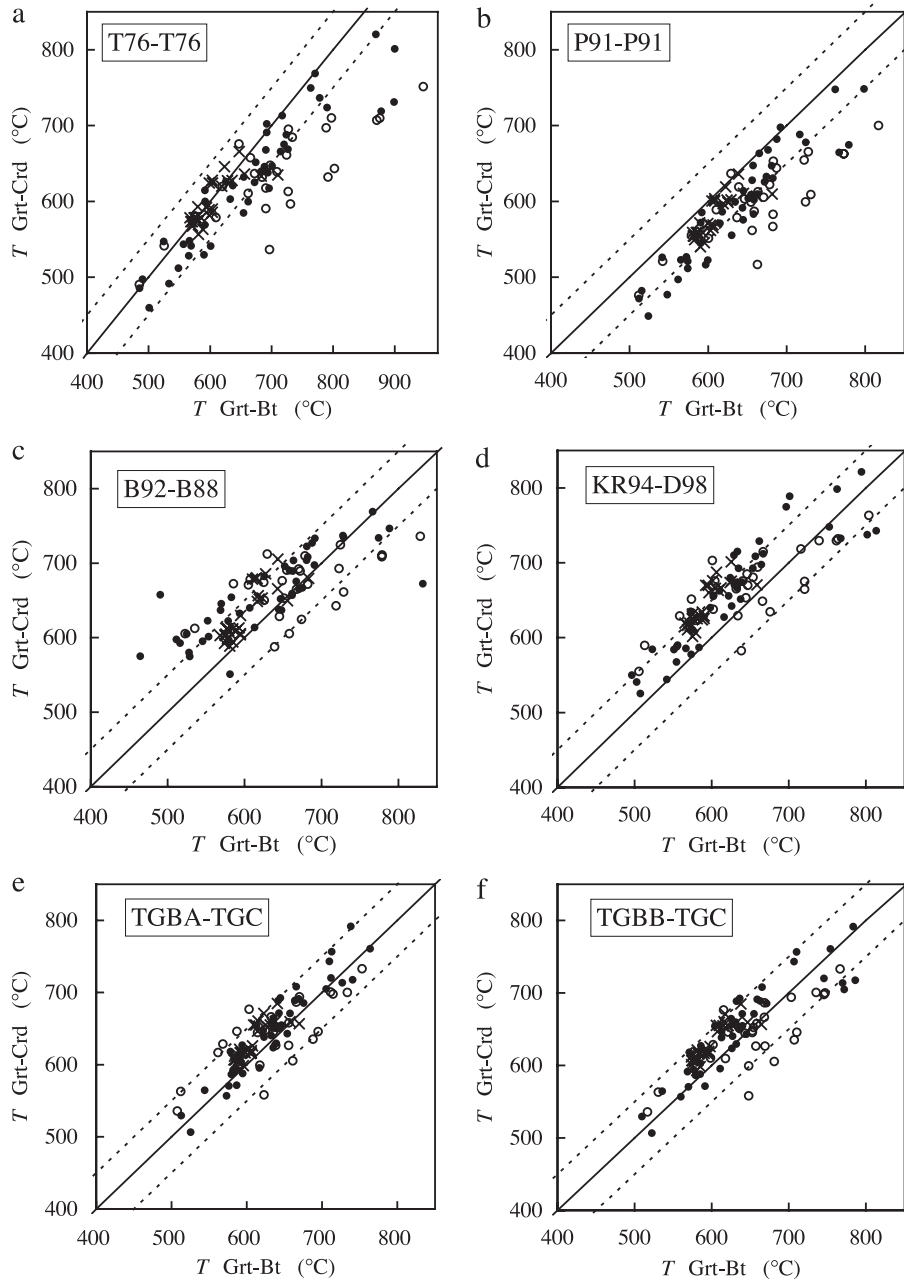


Fig. 7. Garnet–biotite temperatures versus garnet–cordierite temperatures for natural garnet–biotite–cordierite assemblages. (a) Thompson (1976), (b) Perchuk (1991), (c) Bhattacharya et al. (1992) versus Bhattacharya et al. (1988), (d) Kleemann and Reinhardt (1994) versus Dwivedi et al. (1998), (e) TGBA (this study) vs. TGC (this study), (f) TGBB (this study) vs. TGC (this study). Open and solid dots represent data from the regionally metamorphosed Limpopo Belt and the Bushveld contact aureole, respectively. Crosses denote data of various grades of metapelitic rocks taken from literatures. Compositional data of minerals are listed in Appendix D. Dashed lines represent ± 50 °C discrepancies. The present calibrations of Case A garnet–biotite and garnet–cordierite thermometers compute consistent temperatures within a range of ± 50 °C.

the Fe^{3+} correction (Case A) calculated slightly higher temperatures than that without the Fe^{3+} correction (Case B) for the Maine data, as mentioned above. The finding suggests that the presence of Fe^{3+} in biotite leads to an underestimation of temperature by the Case B thermometer. Contrary to the Maine data, for the natural garnet and biotite listed in Appendix D, the Case A thermometer sporadically calculated somewhat lower temperatures than did the Case B thermometer. The quantities of Fe^{3+} in the biotites from Maine were well constrained in comparison with the quantities in the minerals shown in Appendix D. The downward deviation suggests that the Fe^{3+} content in biotite listed in Appendix D was possibly overestimated, which resulted in an underestimation of temperature by the Case A thermometer.

Differences between temperatures calculated by reported thermometers and the present thermometers are shown in Fig. 6. The garnet–biotite thermometers of Thompson (1976) and Ferry and Spear (1978) give lower and higher temperatures at lower ($T < 550$ °C) and higher ($T > 600$ °C) temperature regions, respectively, than the present Case A garnet–biotite thermometer. The Perchuk and Lavrent'eva (1983) garnet–biotite thermometer gives temperatures that are 15–40 °C higher than those calculated by the Case A thermometer. The garnet–biotite calibrations of Bhattacharya et al. (1992) and Kleemann and Reinhardt (1994) result in slightly lower temperatures at $T < 600$ °C, and higher temperatures at $T > 650$ °C, than the Case A thermometer. The garnet–cordierite thermometer of Wells (1979) gives lower temperatures than the present calibration of the garnet–cordierite thermometer at $T < 700$ °C, and the method of Bhattacharya et al. (1988) reflects the opposite pattern. The Perchuk and Lavrent'eva (1983) calibration of the thermometer computes more than 50 °C lower temperatures than do the present calibration. The Dwivedi et al. (1998) garnet–cordierite thermometer gives slightly higher temperatures than the present thermometer as previously shown in Fig. 4.

The correspondences between temperatures computed by several sets of garnet–biotite and garnet–cordierite thermometers are shown in Fig. 7. Sets of calibrations of the Thompson (1976) and Perchuk (1991) thermometers give constantly higher garnet–

biotite temperatures than garnet–cordierite, and the values fluctuated widely. A set of the Bhattacharya et al. (1988, 1992) methods computed scattered temperatures; the scattering became significantly large within higher (>750 °C) and lower (<550 °C) temperature regions. The Kleemann and Reinhardt (1994) garnet–biotite and Dwivedi et al. (1998) garnet–cordierite set of thermometers gave slightly higher garnet–cordierite temperatures and resulted in the frequent scattering of more than 50 °C discrepancies. The present calibrations revealed better correspondence between garnet–biotite and garnet–cordierite thermometers than those associated with the above-mentioned methods. The calibration of the garnet–biotite thermometer with the Fe^{3+} correction (Case A) produced less scattered results than did calibration without the Fe^{3+} correction (Case B). This result suggests that the presence of Fe^{3+} in biotite appreciably affects the garnet–biotite thermometric calculation. It should be noted that the Fe^{3+} correction was based on the rough assumption that the Fe^{3+} quantity in natural biotite may have been related to the occurrence of Fe-oxide phases. A precise estimate of the Fe^{3+} content in natural biotite (e.g. by Mössbauer analysis) may improve the results obtained with the Case A garnet–biotite thermometer. With accurate value of Fe^{3+} quantity in natural biotite, in addition, the Case A thermometer may achieve better consistency with the garnet–cordierite thermometer.

6. Error estimation and limitation of the thermometers

The absolute errors of the calibrated thermometers were estimated on the basis of standard deviations of differences between experimental and calculated temperatures. These standard deviations are ± 15.0 , ± 14.7 , and ± 22.2 °C for Cases A and B (i.e. the garnet–biotite thermometers) and for the garnet–cordierite thermometer, respectively. For the experiments, absolute errors, including analytical errors for the experimental products, measurement errors for the experimental conditions, and the systematic error of the calibrations and incorrect estimation of Fe^{3+} , could be estimated with 2σ confidence at less than ± 30 and ± 45 °C for the

garnet–biotite and garnet–cordierite thermometers, respectively.

The garnet–biotite thermometers were calibrated with $X_{\text{Fe}^{2+}}=0.21-0.92$, $X_{\text{Mg}}=0.04-0.73$, $X_{\text{Mn}}=0-0.04$, $X_{\text{Ca}}=0-0.07$ garnets and $X_{\text{Fe}^{3+}}=0.02-0.10$, $X_{\text{Fe}^{2+}}=0.12-0.68$, ($X_{\text{Fe}^{\text{T}}}=0.14-0.73$), $X_{\text{Mg}}=0.18-0.70$, $X_{\text{Al}^{\text{VI}}}=0.03-0.18$, $X_{\text{Ti}}=0-0.02$ biotites under conditions of 550–950 °C and 2.07–6 kbar. The garnet–cordierite thermometer was evaluated with $X_{\text{Fe}^{2+}}=0.19-0.85$, $X_{\text{Mg}}=0.09-0.75$, $X_{\text{Mn}}=0-0.04$, $X_{\text{Ca}}=0-0.08$ garnets and $X_{\text{Fe}^{\text{T}}}=0.05-0.60$, $X_{\text{Mg}}=0.40-0.95$ cordierites in the ranges of 650–1050 °C and 4–12 kbar. The calibrated thermometers can be safely applied to minerals within these compositional ranges. Caution should be exercised when applying the thermometers to the biotite, which has high Al^{VI} and Ti contents, because experimental biotites used for the calibrations contained small amounts of Al^{VI} and Ti; moreover, the Ti was less varied. Most natural biotites listed in Appendix D, however, have $X_{\text{Ti}}>0.02$. This implies that the interaction parameters of Ti substitution in biotite have been reasonably estimated and shows applicability of the present thermometer for relatively high-Ti biotites (up to about $X_{\text{Ti}}=0.1$, see Fig. 7 and Appendix D). Highly oxidized biotite should also be treated with caution because the calibration was carried out only using reduced biotites. High-Mn garnets were not included among the present calibrations; however, the application of the present thermometers to natural assemblages demonstrated their applicability for such garnets (up to $X_{\text{Mn}}^{\text{Grt}}=0.28$; see Fig. 7 and Appendix D). Generally, extrapolations of the thermometers to temperature ranges beyond those of the calibrations should be done with great caution. However, the iterative regression processes did achieve reproduction of the linear relation of T_{exp} versus T_{cal} , i.e. T_{exp} versus $\ln K_{\text{D}}$. Therefore, the extrapolation may be applicable at lower and higher temperatures; however, in this paper, the thermometers were confirmed only within a range of 500–750 °C.

7. Conclusions

The garnet–biotite and garnet–cordierite thermometers have been consistently recalibrated. These ther-

metric formulations were calibrated by iterative multiple regressions. Two formulations of garnet–biotite thermometer have been derived based on the presence and absence of Fe^{3+} in biotite. Fe^{3+} content in biotite was estimated in terms of oxidation state. The garnet–biotite thermometer with the Fe^{3+} correction in biotite calculates less scattered temperatures than does the thermometer without Fe^{3+} correction in biotite for natural garnet–biotite pairs. Precise estimates of the Fe^{3+} content in biotites are indispensable to improve thermometric calculations involving biotite. The garnet–cordierite thermometer has been calibrated based on the presence of Fe^{3+} in cordierite as 1.5% of Fe^{T} . Mn and Ca in garnet have been also taken into account in accord with the present garnet–biotite thermometer. The present garnet–cordierite thermometer gives lower temperatures than previously reported thermometers. The resulting temperatures for natural pelites, including garnet–biotite–cordierite assemblages, that were obtained by the present thermometers are consistent within ± 50 °C. These thermometers have been applied to both regionally metamorphosed pelitic rocks and contact metamorphic pelites, and they give reasonable and consistent results within the temperature range of 500–750 °C. The absolute errors of the thermometers were estimated to be about ± 30 and ± 45 °C for the garnet–biotite and garnet–cordierite thermometers, respectively.

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Appendix A

The nonideal mixing terms of garnet were formulated by the expression of Berman (1990) and the interaction parameters cited in the main text. The

general forms of them are as follows (the superscript Grt is ignored for clarity):

$$\begin{aligned}
 3RT \ln K_{\gamma}^{\text{Grt}} &= 3RT \ln (\gamma_{\text{Fe}}^{\text{Grt}} / \gamma_{\text{Mg}}^{\text{Grt}}) \\
 &= 3RT \ln \gamma_{\text{Fe}}^{\text{Grt}} - 3RT \ln \gamma_{\text{Mg}}^{\text{Grt}} \\
 &= W_{\text{FeMg}} X_{\text{Mg}}^2 - W_{\text{MgFe}} X_{\text{Fe}}^2 \\
 &\quad + (W_{\text{FeCa}} - W_{\text{MgCa}}) X_{\text{Ca}}^2 \\
 &\quad + (W_{\text{FeMn}} - W_{\text{MgMn}}) X_{\text{Mn}}^2 \\
 &\quad + 2(W_{\text{MgFe}} - W_{\text{FeMg}}) X_{\text{Mg}} X_{\text{Fe}} \\
 &\quad + (2W_{\text{CaFe}} - W_{\text{FeMgCa}}) X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad + (W_{\text{FeMgCa}} - 2W_{\text{CaMg}}) X_{\text{Mg}} X_{\text{Ca}} \\
 &\quad + (2W_{\text{MnFe}} - W_{\text{FeMgMn}}) X_{\text{Fe}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeMgMn}} - 2W_{\text{MnMg}}) X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeCaMn}} - W_{\text{MgCaMn}}) X_{\text{Ca}} X_{\text{Mn}} \quad (\text{A1})
 \end{aligned}$$

$$\begin{aligned}
 W_{\text{FeMgCa}} &= (W_{\text{FeMg}} + W_{\text{MgFe}} + W_{\text{FeCa}} + W_{\text{CaFe}} \\
 &\quad + W_{\text{MgCa}} + W_{\text{CaMg}}) / 2 - C_{\text{FeMgCa}} \\
 (C_{\text{FeMgCa}} &= 0) \quad (\text{A2})
 \end{aligned}$$

$$\begin{aligned}
 W_{\text{FeMgMn}} &= (W_{\text{FeMg}} + W_{\text{MgFe}} + W_{\text{FeMn}} + W_{\text{MnFe}} \\
 &\quad + W_{\text{MgMn}} + W_{\text{MnMg}}) / 2 - C_{\text{FeMgMn}} \\
 (C_{\text{FeMgMn}} &= 0) \quad (\text{A3})
 \end{aligned}$$

$$\begin{aligned}
 W_{\text{FeCaMn}} - W_{\text{MgCaMn}} &= (W_{\text{FeCa}} + W_{\text{CaFe}} + W_{\text{FeMn}} + W_{\text{MnFe}} - W_{\text{MgCa}} \\
 &\quad - W_{\text{CaMg}} - W_{\text{MgMn}} - W_{\text{MnMg}}) / 2 - C_{\text{FeCaMn}} \\
 &\quad - C_{\text{MgCaMn}} \quad (C_{\text{FeCaMn}} = C_{\text{MgCaMn}} = 0) \quad (\text{A4})
 \end{aligned}$$

The resulting equations of the nonideal mixing terms are as follows:

$$\begin{aligned}
 W_{\text{H}}^{\text{Grt}} &= W_{\text{FeMg}} X_{\text{Mg}}^2 - W_{\text{MgFe}} X_{\text{Fe}}^2 \\
 &\quad + (W_{\text{FeCa}} - W_{\text{MgCa}}) X_{\text{Ca}}^2 \\
 &\quad + (W_{\text{FeMn}} - W_{\text{MgMn}}) X_{\text{Mn}}^2 \\
 &\quad + 2(W_{\text{MgFe}} - W_{\text{FeMg}}) X_{\text{Mg}} X_{\text{Fe}} \\
 &\quad + (2W_{\text{CaFe}} - W_{\text{FeMgCa}}) X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad + (W_{\text{FeMgCa}} - 2W_{\text{CaMg}}) X_{\text{Mg}} X_{\text{Ca}} \\
 &\quad + (2W_{\text{MnFe}} - W_{\text{FeMgMn}}) X_{\text{Fe}} X_{\text{Mn}}
 \end{aligned}$$

$$\begin{aligned}
 &\quad + (W_{\text{FeMgMn}} - 2W_{\text{MnMg}}) X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeCaMn}} - W_{\text{MgCaMn}}) X_{\text{Ca}} X_{\text{Mn}} \\
 &= -1891 X_{\text{Mg}}^2 - 3874 X_{\text{Fe}}^2 - 1942 X_{\text{Ca}}^2 \\
 &\quad - 13,211 X_{\text{Mn}}^2 + 11,529 X_{\text{Mg}} X_{\text{Fe}} \\
 &\quad - 20,278 X_{\text{Fe}} X_{\text{Ca}} - 24,668 X_{\text{Mg}} X_{\text{Ca}} \\
 &\quad - 14,202 X_{\text{Fe}} X_{\text{Mn}} - 12,219 X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad - 25,418 X_{\text{Ca}} X_{\text{Mn}} \quad (\text{A5})
 \end{aligned}$$

$$\begin{aligned}
 W_{\text{S}}^{\text{Grt}} &= W_{\text{FeMg}} X_{\text{Mg}}^2 - W_{\text{MgFe}} X_{\text{Fe}}^2 \\
 &\quad + (W_{\text{FeCa}} - W_{\text{MgCa}}) X_{\text{Ca}}^2 \\
 &\quad + (W_{\text{FeMn}} - W_{\text{MgMn}}) X_{\text{Mn}}^2 \\
 &\quad + 2(W_{\text{MgFe}} - W_{\text{FeMg}}) X_{\text{Mg}} X_{\text{Fe}} \\
 &\quad + (2W_{\text{CaFe}} - W_{\text{FeMgCa}}) X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad + (W_{\text{FeMgCa}} - 2W_{\text{CaMg}}) X_{\text{Mg}} X_{\text{Ca}} \\
 &\quad + (2W_{\text{MnFe}} - W_{\text{FeMgMn}}) X_{\text{Fe}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeMgMn}} - 2W_{\text{MnMg}}) X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeCaMn}} - W_{\text{MgCaMn}}) X_{\text{Ca}} X_{\text{Mn}} \\
 &= -2.00 X_{\text{Mg}}^2 - 1.83 X_{\text{Fe}}^2 - 1.07 X_{\text{Ca}}^2 \\
 &\quad - 7.67 X_{\text{Mn}}^2 + 7.66 X_{\text{Mg}} X_{\text{Fe}} - 7.01 X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad - 5.87 X_{\text{Mg}} X_{\text{Ca}} - 7.59 X_{\text{Fe}} X_{\text{Mn}} - 7.75 X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad - 11.42 X_{\text{Ca}} X_{\text{Mn}} \quad (\text{A6})
 \end{aligned}$$

$$\begin{aligned}
 W_{\text{V}}^{\text{Grt}} &= W_{\text{FeMg}} X_{\text{Mg}}^2 - W_{\text{MgFe}} X_{\text{Fe}}^2 \\
 &\quad + (W_{\text{FeCa}} - W_{\text{MgCa}}) X_{\text{Ca}}^2 \\
 &\quad + (W_{\text{FeMn}} - W_{\text{MgMn}}) X_{\text{Mn}}^2 \\
 &\quad + 2(W_{\text{MgFe}} - W_{\text{FeMg}}) X_{\text{Mg}} X_{\text{Fe}} \\
 &\quad + (2W_{\text{CaFe}} - W_{\text{FeMgCa}}) X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad + (W_{\text{FeMgCa}} - 2W_{\text{CaMg}}) X_{\text{Mg}} X_{\text{Ca}} \\
 &\quad + (2W_{\text{MnFe}} - W_{\text{FeMgMn}}) X_{\text{Fe}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeMgMn}} - 2W_{\text{MnMg}}) X_{\text{Mg}} X_{\text{Mn}} \\
 &\quad + (W_{\text{FeCaMn}} - W_{\text{MgCaMn}}) X_{\text{Ca}} X_{\text{Mn}} \\
 &= 0.000 X_{\text{Mg}}^2 + 0.000 X_{\text{Fe}}^2 - 0.009 X_{\text{Ca}}^2 \\
 &\quad - 0.005 X_{\text{Mn}}^2 + 0.000 X_{\text{Mg}} X_{\text{Fe}} - 0.009 X_{\text{Fe}} X_{\text{Ca}} \\
 &\quad + 0.067 X_{\text{Mg}} X_{\text{Ca}} - 0.005 X_{\text{Fe}} X_{\text{Mn}} \\
 &\quad - 0.005 X_{\text{Mg}} X_{\text{Mn}} + 0.005 X_{\text{Ca}} X_{\text{Mn}} \quad (\text{A7})
 \end{aligned}$$

References

- Aranovich, L.Ya., Podlesskii, K.K., 1983. The cordierite–garnet–sillimanite–quartz equilibrium: experiments and applications. In: Saxena, S.K. (Ed.), *Kinetics and Equilibrium in Mineral Reactions. Advances in Physical Geochemistry*, vol. 3. Springer-Verlag, New York, pp. 173–198.
- Aranovich, L.Ya., Podlesskii, K.K., 1989. Geothermobarometry of high-grade metapelites: simultaneously operating reactions. In: Daly, J.S., Cliff, R.A., Yardley, W.V.D. (Eds.), *Evolution of Metamorphic Belts. Special Publication*, vol. 43. Geological Society, London, pp. 45–61.
- Aranovich, L.Ya., Lavrent'eva, I.V., Kosyakova, N.A., 1988. Calibration of the biotite–garnet and biotite–orthopyroxene geothermometers corrected for the variable Al level in biotite. *Geokhimiya* 5, 668–676.
- Berman, R.G., 1988. Internally-consistent thermodynamic data for minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$. *J. Petrol.* 29, 445–522.
- Berman, R.G., 1990. Mixing properties of Ca–Mg–Fe–Mn garnets. *Am. Mineral.* 75, 328–344.
- Berman, R.G., Aranovich, L.Ya., 1996. Optimized standard state and solution properties of minerals: I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system $\text{FeO}-\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$. *Contrib. Mineral. Petrol.* 126, 1–24.
- Bertrand, P., Ellis, D.J., Green, D.H., 1991. The stability of sapphirine–quartz and hypersthene–sillimanite–quartz assemblages: an experimental investigation in the system $\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ under H_2O and CO_2 conditions. *Contrib. Mineral. Petrol.* 108, 55–71.
- Bhattacharya, A., Mazumdar, A.C., Sen, S.K., 1988. Fe–Mg mixing in cordierite: constraints from natural data and implications for cordierite–garnet geothermometry in granulites. *Am. Mineral.* 73, 338–344.
- Bhattacharya, A., Mohanty, L., Maji, A., Sen, S.K., Raith, M., 1992. Non-ideal mixing in the phlogopite–annite binary: constraints from experimental data on Mg–Fe partitioning and reformulation of the biotite–garnet geothermometer. *Contrib. Mineral. Petrol.* 111, 87–93.
- Bucher-Nurminen, K., Ohta, Y., 1993. Granulite and garnet–cordierite gneisses from Dronning Maud Land, Antarctica. *J. Metamorph. Geol.* 11, 691–703.
- Cerný, P., Chapman, R., 1997. Lithium in sekaninaite from the type locality, Dolní Bory, Czech Republic. *Can. Mineral.* 35, 167–173.
- Dasgupta, S., Sengupta, P., Guha, D., Fukuoka, M., 1991. A refined garnet–biotite Fe–Mg exchange geothermometer and its application in amphibolites and granulites. *Contrib. Mineral. Petrol.* 109, 130–137.
- Dwivedi, S.B., Mohan, A., Lal, R.K., 1998. Recalibration of Fe–Mg exchange reaction between garnet and cordierite as a thermometer. *Eur. J. Mineral.* 10, 281–289.
- Dyar, M.D., Lowe, E.W., Guidotti, C.V., Delaney, J.S., 2002. Fe^{3+} and Fe^{2+} partitioning among silicates in metapelites: a synchrotron micro-XANES study. *Am. Mineral.* 87, 514–522.
- Earley III, D., Stout, J.H., 1991. Cordierite–cumingtonite facies rocks from Gold Brick District, Colorado. *J. Petrol.* 32, 1169–1201.
- Ferry, J.M., Spear, F.S., 1978. Experimental calibration of partitioning Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.* 66, 113–117.
- Ganguly, J., Cheng, W., 1994. Thermodynamics of (Ca,Mg,Fe,Mn)–garnet solid solution: new experiments, optimized data set, and applications to thermo-barometry. *International Mineralogical Association 16th General Meeting Abstracts*, Pisa, pp. 134–135.
- Ganguly, J., Saxena, S., 1984. Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and applications to geothermo-barometry. *Am. Mineral.* 69, 88–97.
- Ganguly, J., Saxena, S., 1985. Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and applications to geothermo-barometry: clarifications. *Am. Mineral.* 70, 1320.
- Ganguly, J., Cheng, W., Tirone, M., 1996. Thermodynamics of aluminosilicate garnet solid solution: new optimized model, and thermometric applications. *Contrib. Mineral. Petrol.* 126, 137–151.
- Geiger, C.A., 1999. Thermodynamics of (Fe^{2+} , Mn^{2+} , Mg, Ca) $_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet: a review and analysis. *Mineral. Petrol.* 66, 271–299.
- Geiger, C.A., Rager, H., Czank, M., 2000. Cordierite III: the site occupation and concentration of Fe^{3+} . *Contrib. Mineral. Petrol.* 140, 344–352.
- Gessmann, C.K., Spiering, B., Raith, M., 1997. Experimental study of Fe–Mg exchange between garnet and biotite: constraints on the mixing behavior and analysis of the cation-exchange mechanisms. *Am. Mineral.* 82, 1225–1240.
- Gil Ibarra, J.L., Martinez, F.J., 1982. Petrology of garnet–cordierite–sillimanite gneisses from the El Tormes thermal dome, Iberian Hercynian Foldbelt (W Spain). *Contrib. Mineral. Petrol.* 80, 14–24.
- Goldman, D.S., Albee, A.L., 1977. Correlation of Mg/Fe partitioning between garnet and biotite with $^{18}\text{O}/^{16}\text{O}$ partitioning between quartz and magnetite. *Am. J. Sci.* 277, 750–767.
- Guidotti, C.V., Dyar, M.D., 1991. Ferric iron in metamorphic biotite and its petrologic and crystallochemical implications. *Am. Mineral.* 76, 161–175.
- Hackler, R.T., Wood, B.J., 1989. Experimental determination of Fe and Mg exchange between garnet and olivine and estimation of Fe–Mg garnet mixing properties. *Am. Mineral.* 74, 994–999.
- Harris, N.B.W., Holt, R.W., Drury, S.A., 1982. Geobarometry, geothermometry, and late Archean geotherms from the granulite facies terrain of South India. *J. Geol.* 90, 509–527.
- Hensen, B.J., Green, D.H., 1971. Experimental study of the stability of cordierite and garnet in pelitic compositions at high pressure and temperature: I. Compositions with excess aluminosilicate. *Contrib. Mineral. Petrol.* 33, 309–330.
- Hodges, K.V., Spear, F.S., 1982. Geothermometry, geobarometry and the Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire. *Am. Mineral.* 67, 1118–1134.
- Hoinkes, G., 1986. Effect of grossular-content in garnet on the partitioning of Fe and Mg between garnet and biotite. An empirical

- investigation on staurolite-zone samples from the Austroalpine Schneeberg Complex. *Contrib. Mineral. Petrol.* 92, 393–399.
- Holdaway, M.J., 2000. Application of new experimental and garnet Margules data to the garnet–biotite geothermometer. *Am. Mineral.* 85, 881–892.
- Holdaway, M.J., Lee, S.M., 1977. Fe–Mg cordierite stability in high-grade pelitic rocks based on experimental, theoretical, and natural observations. *Contrib. Mineral. Petrol.* 63, 25–43.
- Holdaway, M.J., Mukhopadhyay, B., Dyar, M.D., Guidotti, C.V., Dutrow, B.L., 1997. Garnet–biotite geothermometry revised: new Margules parameters and a natural specimen data set from Maine. *Am. Mineral.* 82, 582–595.
- Indares, A., Martignole, J., 1985. Biotite–garnet geothermometry in the granulite facies: the influence of Ti and Al in biotite. *Am. Mineral.* 70, 272–278.
- Khomenko, V.M., Langer, K., Geiger, C.A., 2001. Structural locations of the iron ions in cordierite: a spectroscopic study. *Contrib. Mineral. Petrol.* 141, 381–396.
- Kleemann, U., Reinhardt, J., 1994. Garnet–biotite thermometry revisited: the effect of Al^{VI} and Ti in biotite. *Eur. J. Mineral.* 6, 925–941.
- Kretz, R., 1983. Symbols for rock-forming minerals. *Am. Mineral.* 68, 277–279.
- Lavrent'eva, I.V., Perchuk, L.L., 1981. Phase correspondence in the system biotite–garnet: experimental data. *Dokl. Akad. Nauk SSSR* 260, 731–734.
- Likhanov, I.I., Reverdatto, V.V., Sheplev, V.S., Vershinin, A.E., Kozlov, P.S., 2001. Contact metamorphism of Fe- and Al-rich graphitic metapelites in the Transangarian region of the Yenisei Ridge, eastern Siberia, Russia. *Lithos* 58, 55–80.
- Mukhopadhyay, B., Holdaway, M.J., 1994. Cordierite–garnet–sillimanite–quartz equilibrium: I. New experimental calibration in the system FeO–Al₂O₃–SiO₂–H₂O and certain P–T–XH₂O relations. *Contrib. Mineral. Petrol.* 116, 462–472.
- Mukhopadhyay, B., Holdaway, M.J., Koziol, A.M., 1997. A statistical model of thermodynamic mixing properties of Ca–Mg–Fe²⁺ garnets. *Am. Mineral.* 82, 165–181.
- Nichols, G.T., Berry, R.F., Green, D.H., 1992. Internally consistent gahnitic spinel–cordierite–garnet equilibria in the FMASHZn system: geothermobarometry and application. *Contrib. Mineral. Petrol.* 111, 362–377.
- Nielsen, P.A., 1986. Metamorphism of the Arseno Lake area, N.W.T., Canada: an Abukuma facies series of Aphebian age. *Can. J. Earth Sci.* 23, 646–669.
- Okuyama-Kusunose, Y., 1993. Contact metamorphism in andalusite–sillimanite type Tono aureole, northeast Japan; reactions and phase relations in Fe-rich aluminous metapelites. *Bull. Geol. Surv. Japan* 44, 377–416.
- Palmeri, R., 1997. P–T paths and migmatite formation: an example from Deep Freeze Range, northern Victoria Land, Antarctica. *Lithos* 42, 47–66.
- Perchuk, L.L., 1991. Derivation of a thermodynamically consistent set of geothermometers and geobarometers for metamorphic and magmatic rocks. In: Perchuk, L.L. (Ed.), *Progress in Metamorphic and Magmatic Petrology: A Memorial Volume in Honor of D.S. Korzinskiy*. Cambridge Univ. Press, London, pp. 93–111.
- Perchuk, L.L., Lavrent'eva, I.V., 1983. Experimental investigation of exchange equilibria in the system cordierite–garnet–biotite. In: Saxena, S.K. (Ed.), *Kinetics and Equilibrium in Mineral Reactions. Advances in Physical Geochemistry*, vol. 3. Springer-Verlag, New York, pp. 199–239.
- Perchuk, L.L., Aranovich, L.Ya., Podlesskii, K.K., Lavrent'eva, I.V., Gerasimov, V.Yu., Fed'kin, V.V., Kitsul, V.I., Karsakov, L.P., Berdnikov, N.V., 1985. Precambrian granulites of the Aldan shield, eastern Siberia, USSR. *J. Metamorph. Geol.* 3, 265–310.
- Pigage, L.C., Greenwood, H.J., 1982. Internally consistent estimates of pressure and temperature: the staurolite problem. *Am. J. Sci.* 282, 943–969.
- Pitra, P., de Waal, S.A., 2001. High-temperature, low-pressure metamorphism and development of prograde symplectites, Marble Hall Fragment, Bushveld Complex (South Africa). *J. Metamorph. Geol.* 19, 311–325.
- Robie, R.A., Hemingway, B.S., 1995. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.*, vol. 2131. U.S. Government Printing Office, Washington. 461 pp.
- Scrimgeour, I., Smith, J.B., Raith, J.G., 2001. Palaeoproterozoic high-T, low-P metamorphism and dehydration melting in metapelites from the Mopunga range, Arunta Inlier, central Australia. *J. Metamorph. Geol.* 19, 739–757.
- Thompson, A.B., 1976. Mineral reactions in pelitic rocks: II. Calculation of some P–T–X(Fe–Mg) phase relations. *Am. J. Sci.* 276, 425–454.
- Visser, D., Senior, A., 1990. Aluminous reaction texture in orthoamphibole-bearing rocks: the pressure–temperature evolution of the high-grade Proterozoic of the Bamble sector, south Norway. *J. Metamorph. Geol.* 8, 231–246.
- Wells, P.R.A., 1979. Chemical and thermal evolution of Archaean sialic crust, southern West Greenland. *J. Petrol.* 20, 187–226.
- Williams, M.L., Grambling, J.A., 1990. Manganese, ferric iron, and the equilibrium between garnet and biotite. *Am. Mineral.* 75, 886–908.