Original Calibration of a Garnet Geobarometer in Metapelite

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Abstract: In many metapelitic assemblages, plagioclase is either CaO-deficient or even absent. In such cases, all the widely applied, well-calibrated plagioclase-related geobarometers lose their usage. Fortunately, it has been found that a net-transfer reaction including intracrystalline \( \text{Fe}^{2+} - \text{Ca}^{2+} \) exchange in garnet is pressure-sensitive, therefore, a garnet geobarometer can be empirically calibrated under pressure–temperature (P–T) conditions of 430–895 °C and 1–15 kbar. The chemical composition range of the calibrant garnet is \( X_{\text{Ca}} = 0.02 - 0.29 \) and \( X_{\text{Fe}} = 0.42 - 0.91 \), and covers the majority of garnet in metapelites. The total error of this geobarometer was estimated to be within ±1.3 kbar. The application of this garnet geobarometer to metamorphic terranes certifies its applicability, and this geobarometer can play a unique role, especially when plagioclase is absent or CaO-deficient. Metamorphic P–T conditions can be simultaneously determined by the garnet–biotite pair through the application of the present garnet geobarometer in combination with a well-calibrated garnet-biotite geothermometer.

Keywords: application; calibration; garnet; geobarometer; metapelite

1. Introduction

In the past eighty years, people have developed nearly 60 different kinds of geothermometers and 50 different kinds of geobarometers calibrated based on the partitioning or exchange of major elements between mineral phases formed at thermodynamic equilibrium. These geothermobarometers have been extensively used in determining metamorphic or magmatic pressure–temperature (P–T) conditions. Therefore, calibrating precise and accurate geothermometers and geobarometers is extremely important work for petrologists such as the well-calibrated, widely-used Al-in-hornblende geobarometer [1–5] applied to estimate the formation pressure of hornblende crystallizing from granitoid magma, as well as the phengite geobarometer [6,7] applied to eclogite to decipher metamorphic pressure of high or ultra-high pressure metamorphism. There are other precise, minor element geothermometers applied to estimate metamorphic temperature including the Ti-in-quartz geothermometer [8,9], Zr-in-rutile geothermometer [10–14], and the Ti-in-zircon thermometer [12,15], etc. In recent years, based on the physical properties of the minerals, Raman-spectra geobarometers have also been developed [16–27].

It is well known that garnet-bearing metapelites is perfectly sensitive to P–T change and thus can act as an ideal research target in unraveling the metamorphic evolution of orogenic belts [27–37]. However, plagioclase is always CaO-poor or even absent in many metapelitic assemblages, which makes most of the commonly adopted plagioclase-related geobarometers unusable [38–54].

However, it was found that the metamorphic pressure was in negative relation to the Fe/Ca ratio of garnet at every 25 °C interval (Figure 1) for the natural metapelite samples collected from the literature (Table S1). Therefore, it can be inferred that the following net-transfer reaction including intracrystalline \( \text{Fe}^{2+} - \text{Ca}^{2+} \) exchange in garnet is pressure-sensitive and thus can be calibrated as a geobarometer. The mineral abbreviations are as follows hereafter: Alm, almandine; Grt, garnet; Ttn, titanite; Grs, grossular; Ilm, ilmenite; Qtz, quartz. This further suggests that model reaction (1) is
a potentially perfect geobarometer. Therefore, in this contribution, the garnet geobarometer was empirically calibrated using natural metapelite samples, and its applicability was certified through application to natural metamorphic terranes.

The activity model of asymmetric Fe–Mg–Ca–Mn quaternary garnet [49] was preferred and adopted. Therefore, Equation (2) can be approximately simplified to Equation (3)

\[ \Delta G = 0 = \Delta H - T \Delta S + (P - 1) \Delta V + 3RT \ln \left( \frac{X_{\text{Grt}}}{X_{\text{Fe}}} \right) + 3RT \ln \left( \frac{\gamma_{\text{Grt}}^{\text{Grt}}}{\gamma_{\text{Fe}}^{\text{Grt}}} \right) - 3RT \ln \left( \frac{\gamma_{\text{Ilm}}^{\text{Grt}}}{\gamma_{\text{Ilm}}^{\text{Grt}}} \right) \]

where \( P \) is pressure (in bar); \( T \) is temperature (in K), and \( \Delta G \) (in J), \( \Delta H \) (in J), \( \Delta S \) (in J/K), and \( \Delta V \) (in J/bar) are the Gibbs free energy, enthalpic, entropic, and volumetric changes of the model reaction (Equation (1)), respectively. The three items enclosed in the last parentheses refer to the activities of the quartz, ilmenite, and titanite phase components, respectively. The term \( X_j^{\text{Grt}} = [j/(Fe + Mg + Ca + Mn)] \) denotes the molar fraction of cation \( j \) in the garnet solid solution. The \( \gamma_{\text{Grt}}^{\text{Grt}} \) and \( \gamma_{\text{Fe}}^{\text{Grt}} \) stand for the activity coefficients of the grossular and almandine components in the garnet solid solution, respectively. \( R \) is the gas constant (=8.3144 J/K·mol).

In metapelite, quartz is essentially the pure phase, and ilmenite and titanite are also chemically very near the pure phases. Therefore, Equation (2) can be approximately simplified to Equation (3)

\[ \Delta G = 0 = \Delta H - T \Delta S + (P - 1) \Delta V + 3RT \ln \left( \frac{X_{\text{Ca}}^{\text{Grt}}}{X_{\text{Fe}}^{\text{Grt}}} \right) + 3RT \ln \left( \frac{\gamma_{\text{Ca}}^{\text{Grt}}}{\gamma_{\text{Fe}}^{\text{Grt}}} \right) \]

The activity model of asymmetric Fe–Mg–Ca–Mn quaternary garnet [49] was preferred and adopted. The difference of excess chemical potential between the grossular and almandine components in garnet solid solution can be described as

\[ 3RT \ln \left( \frac{\gamma_{\text{Ca}}^{\text{Grt}}}{\gamma_{\text{Fe}}^{\text{Grt}}} \right) = aT(K) + bP(\text{bar}) + c \]

where \( a, b, \) and \( c \) are polynomials and are listed respectively as

Fe₃Al₂Si₃O₁₂ + 3 CaTiSiO₅ = Ca₃Al₂Si₃O₁₂ + 3 FeTiO₃ + 3 SiO₂

(1)

Alm in Grt    Ttn    Grs in Grt    Ilm    Qtz

2. Calibration

Thermodynamic equilibrium of the model exchange reaction (Equation (1)) can be described as

\[ \Delta G = 0 = \Delta H - T \Delta S + (P - 1) \Delta V + 3RT \ln \left( \frac{X_{\text{Ca}}^{\text{Grt}}}{X_{\text{Fe}}^{\text{Grt}}} \right) + 3RT \ln \left( \frac{\gamma_{\text{Ca}}^{\text{Grt}}}{\gamma_{\text{Fe}}^{\text{Grt}}} \right) - 3RT \ln \left( \frac{\gamma_{\text{Ilm}}^{\text{Grt}}}{\gamma_{\text{Ilm}}^{\text{Grt}}} \right) \]

where \( P \) is pressure (in bar); \( T \) is temperature (in K), and \( \Delta G \) (in J), \( \Delta H \) (in J), \( \Delta S \) (in J/K), and \( \Delta V \) (in J/bar) are the Gibbs free energy, enthalpic, entropic, and volumetric changes of the model reaction (Equation (1)), respectively. The three \( a \) items enclosed in the last parentheses refer to the activities of the quartz, ilmenite, and titanite phase components, respectively. The term \( X_j^{\text{Grt}} = [j/(Fe + Mg + Ca + Mn)] \) denotes the molar fraction of cation \( j \) in the garnet solid solution. The \( \gamma_{\text{Grt}}^{\text{Grt}} \) and \( \gamma_{\text{Fe}}^{\text{Grt}} \) stand for the activity coefficients of the grossular and almandine components in the garnet solid solution, respectively. \( R \) is the gas constant (=8.3144 J/K·mol).

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where \( a, b, \) and \( c \) are polynomials and are listed respectively as

Fe₃Al₂Si₃O₁₂ + 3 CaTiSiO₅ = Ca₃Al₂Si₃O₁₂ + 3 FeTiO₃ + 3 SiO₂

(1)
was found. These regressed parameters (Table 1, model H01) into Equation (8), the formulation of the garnet geobarometer is described as

\[ P = 1 - \frac{\Delta H}{\Delta V} + T \Delta S/\Delta V - (1/\Delta V) [3RT \ln (X_{\text{Fe}}^{\text{Grt}} / X_{\text{Ca}}^{\text{Grt}})] + aT + bP + c \]  

where the \( \Delta \)-related items are unknowns to be determined through multiple regression analysis.

As no phase equilibria experimental data were available to calibrate the garnet geobarometer, therefore, this geobarometer was empirically calibrated using natural metapelite samples in this work. Valid natural metapelite samples (Table S1) were selected from the literature according to the following criteria: (a) equilibrium texture of the assemblage is clearly described; (b) accurate chemical compositions of the minerals are reported including at least the nine components SiO\(_2\), TiO\(_2\), Al\(_2\)O\(_3\), FeO, MnO, MgO, CaO, Na\(_2\)O, and K\(_2\)O, and the total oxides ranged from 99.5 wt % to 100.5 wt %; (c) samples with CaO-deficient garnet (\( X_{\text{Ca}}^{\text{Grt}} \) < 0.02) or CaO-deficient plagioclase (\( X_{\text{Pl}}^{\text{Ca}} \) < 0.17) were excluded from the dataset due to larger pressure errors propagated from even smaller analytical errors of the CaO component of garnet or plagioclase [49,56]; and (d) samples plotted into the wrong Al\(_2\)SiO\(_5\) stability field by the garnet-biotite geothermometer [55] in agreement with the GASP geobarometer [49], respectively. These two geothermobarometers were demonstrated to be the most accurate among the different versions as demonstrated by [57] through extensive comparative studies. The garnet composition of these calibrant samples can be summarized as \( X_{\text{Ca}} = 0.02 \pm 0.29 \) and \( X_{\text{Fe}} = 0.42 \pm 0.91 \), which covers about 90% of metapelitic garnet found in nature. In the calibration, the ferric iron contents of biotite and garnet were assumed to be 11.6 mol % and 3 mol % of the total iron, respectively, following [49,55]. These ferric contents were determined by available Mössbauer studies for some representative metapelite samples [58–60]. If hematite is present, the Fe\(^{3+}\) fractions of the garnet and biotite are \( \pm 5\% \) and \( \pm 20\% \) of the total iron, respectively [58–60]. As for the calibrant samples (Table S1), however, no hematite was found.

Each sample constitutes an equation in the form of Equation (8), therefore, the calibrant samples constructed an overdetermined equation set. Regression of this set of equations yielded the unknowns of Equation (8) as listed in Table 1 (model H01) with the standard deviation of \( \pm 0.81 \) kbar. Inserting these regressed parameters (Table 1, model H01) into Equation (8), the formulation of the garnet geobarometer is described as

\[ P(\text{bar}) = \frac{-8904.5 + 24.542T(\text{K}) + 0.45RT \ln (X_{\text{Ca}}^{\text{Grt}} / X_{\text{Fe}}^{\text{Grt}}) + 0.15aT + 0.15c}{1 - 0.15b} \]  

\[ (9) \]
Application of the garnet geobarometer (Equation (9)) to the calibrant samples (Table S1) showed that the reproduced pressures were well within ±1.0 kbar when compared to the well-calibrated GASP geobarometer [49] for the 493 (76.6%) samples, within ±1.0–1.5 kbar for the 114 (17.7%) samples, and within ±1.5–1.8 kbar for remaining 37 (5.7%) samples (Table 2; Figure 2a). Furthermore, the 596 (93.7%) calibrant samples were plotted into the correct Al$_2$SiO$_5$ stability field (Figure 2b) by the present garnet geobarometer in combination with the well-calibrated garnet-biotite geothermometer [55].

**Table 1.** Regressed parameters in calibrating the garnet geobarometer using different activity models of garnet *.

| Model | Solution | Symmetry   | $\Delta H/\Delta V$ (bar) | $\Delta S/\Delta V$ (bar/K) | $1/\Delta V$ (bar/J) | R  |
|-------|----------|------------|---------------------------|-----------------------------|----------------------|----|
| H01   | Fe–Mg–Ca–Mn | asymmetric | 8905.5 (±454.1)           | 24.542 (±0.528)             | −0.150               | 0.941 |
| B90   | Fe–Mg–Ca–Mn | asymmetric | 8974.4 (±454.5)           | 24.634 (±0.529)             | −0.151               | 0.941 |
| BA96  | Fe–Mg–Ca  | asymmetric | 9626.3 (±478.5)           | 24.605 (±0.556)             | −0.155               | 0.935 |
| G96   | Fe–Mg–Ca–Mn | asymmetric | 9076 (±472.6)             | 24.365 (±0.549)             | −0.150               | 0.936 |
| M97   | Fe–Mg–Ca  | asymmetric | 7331.8 (±457.1)           | 23.160 (±0.527)             | −0.148               | 0.940 |
| W     | Fe–Mg–Ca–Mn | symmetric  | 7815.3 (±925.9)           | 25.663 (±0.659)             | −0.142               | 0.949 |

* Activity model of garnet: H01 = reference [49] preferred in this work, B90 = reference [61], BA96 = reference [62], G96 = reference [63], M97 = reference [64], W = symmetric quaternary a-X model with all Margules parameters derived in this work.

**Figure 2.** Performance of the present garnet geobarometer applied to the calibrant samples (Table S1). (a) Pressures determined by the present garnet geobarometer versus those by the GASP geobarometer [49]. The dashed black and solid red lines define ±1.0 kbar and ±1.5 kbar deviations, respectively; and (b) in combination with the garnet-biotite geothermometer [55], the present garnet geobarometer plotted 93.7% of the calibrant samples into the correct Al$_2$SiO$_5$-stability field. R, multiple correlation coefficient; s.d., standard error. Al$_2$SiO$_5$ phase diagram: the sold lines are from [65], whereas the dashed line is from [66].
Therefore, it can be concluded that the total error of the present garnet geobarometer is expected to be less than ±1.3 kbar. However, the total error can be anticipated from the main error sources. Taking the calibrant samples (Table S1) as examples, the analytical errors of ±2% of the Fe or Ca cations of the garnet translated to pressure errors of ±0.11 kbar or ±0.09 kbar, respectively. The standard error of the garnet-biotite geothermometer was ±25 °C [55]. If this temperature error is adopted, the propagated pressure errors of the garnet geobarometer will be well restricted to ±0.54 kbar for all the calibrant samples. Furthermore, the estimation errors of Fe$^{3+}$ of garnet, when taken as ±15%, would introduce pressure errors of around ±0.05–0.10 kbar. In fact, the Fe$^{3+}$ content of garnet in metapelite is generally as small as 0–5% of the total iron [58–60]. Therefore, the total error of the present garnet geobarometer is expected to be less than ±1.3 kbar, further considering the consistency between the garnet and GASP [49] geobarometers within the error of ±1 kbar for most of the calibrant samples (Table S1; Figure 2a).

Error distribution is another criterion in judging the accuracy of a geothermometer or a geobarometer. Again taking the calibrant samples (Table S1) as examples, it was found that the misfit of the present garnet geobarometer was not related to either pressure (Figure 3a) or temperature (Figure 3b) or the chemical composition of garnet (Figure 3c,d). Therefore, it can be concluded that the present garnet geobarometer shows no bias in estimating pressure conditions.

### Table 2. Pressure accordance of samples (Table S1) determined by the GASP geobarometer [49] and the garnet geobarometers incorporating different activity models of garnet based on data listed in Table S1.

| Model | Solution          | Symmetry   | ±1.0 kbar | ±1.0–1.5 kbar | ±1.5–1.8 kbar | >±1.8 kbar |
|-------|------------------|------------|-----------|---------------|---------------|------------|
| H01   | Fe–Mg–Ca–Mn      | asymmetric | 76.6%     | 17.7%         | 5.7%          | 0.0%       |
| B90   | Fe–Mg–Ca–Mn      | asymmetric | 77.3%     | 16.6%         | 6.1%          | 0.3%       |
| BA96  | Fe–Mg–Ca         | asymmetric | 56.4%     | 18.3%         | 10.4%         | 14.9%      |
| G96   | Fe–Mg–Ca–Mn      | asymmetric | 73.0%     | 19.3%         | 3.9%          | 3.9%       |
| M97   | Fe–Mg–Ca         | asymmetric | 70.0%     | 19.7%         | 7.0%          | 3.3%       |
| W     | Fe–Mg–Ca–Mn      | symmetric  | 80.3%     | 15.4%         | 4.3%          | 0.0%       |

Note: Symbols of the garnet a–X models are the same as those in Table 1.

### 3. Error Consideration

The standard error propagation method [67] can hardly be applied to infer the total error of the garnet geobarometer, because of its complex formulation (Equation (9)). However, the total error can be anticipated from the main error sources. Taking the calibrant samples (Table S1) as examples, the analytical errors of ±2% of the Fe or Ca cations of the garnet translated to pressure errors of ±0.11 kbar or ±0.09 kbar, respectively. The standard error of the garnet-biotite geothermometer was ±25 °C [55]. If this temperature error is adopted, the propagated pressure errors of the garnet geobarometer will be well restricted to ±0.54 kbar for all the calibrant samples. Furthermore, the estimation errors of Fe$^{3+}$ of garnet, when taken as ±15%, would introduce pressure errors of around ±0.05–0.10 kbar. In fact, the Fe$^{3+}$ content of garnet in metapelite is generally as small as 0–5% of the total iron [58–60]. Therefore, the total error of the present garnet geobarometer is expected to be less than ±1.3 kbar, further considering the consistency between the garnet and GASP [49] geobarometers within the error of ±1 kbar for most of the calibrant samples (Table S1; Figure 2a).

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![Figure 3](image-url)

**Figure 3.** Distribution of the pressure misfit of the present garnet geobarometer based on the calibrant metapelite samples (Table S1). P (Grt) misfit of the present garnet geobarometer is defined as the pressure difference determined by the garnet (this work) and the GASP [49] geobarometers. (a) Misfit vs. pressure; (b) misfit vs. temperature; (c) misfit vs. $X_Fe$ of garnet; and (d) misfit vs. $X_Ca$ of garnet.
4. Application

The present garnet geobarometer can be combined with the garnet-biotite (GB) geothermometer [35] to simultaneously yield metamorphic P–T conditions of metapelite, regardless of the presence or absence of plagioclase or Al₂SiO₅ phases in the assemblage. Several application examples are given below and the application examples are listed in Table S2. These samples were not included in the calibration of the garnet geobarometer.

The garnet geobarometer was first applied to the metapelite samples (Table S2) in the Ivrea Zone, Northern Italy [68]. Except for one sample (70197-10), which yielded a larger pressure error (±1.58 kbar), the garnet geobarometer yielded similar pressure estimates (±1.48 kbar) with the GASP geobarometer [49], and all these sillimanite-bearing samples were correctly placed into the sillimanite stability field (Figure 4b). Furthermore, for the three sillimanite-bearing metapelite samples collected from within 100 m away at the Molodezhnaya Station, eastern Antarctica [69], the garnet and GASP geobarometers yielded identical pressure estimates (Table S2; Figure 4a), although the chemical compositions of the garnet were different.

As for the Fe- and Al-rich graphitic metapelite (Table S2) collected from the Transangarian region of the Yenisei Ridge, eastern Siberia, Russia [70], the GASP geobarometer misplotted the andalusite-bearing samples into the kyanite- or sillimanite-stability field (Figure 4b) due to CaO-deficiency in plagioclase. The garnet geobarometer, however, correctly plotted the samples into the andalusite-stability field (Figure 4b). Regarding the andalusite- and/or sillimanite-bearing metapelite (Table S2) sampled in the Augusta quadrangle, south-central Maine [71], the garnet geobarometer correctly plotted these samples into the correct Al₂SiO₅ stability field (Figure 4b), with the exception of two samples (5, 102) where the CaO content of garnet was fairly diluted. The GASP geobarometer [49], however, lost usage here due to absence of plagioclase.

The applicability of the garnet geobarometer can also be tested through its application to Al₂SiO₅-absent metapelite. In the Furulund Group, Sulitjelma, Scandinavian Caledonides [72], the garnet and the GBPQ [50] geobarometers yielded similar pressure estimates within error of ±1 kbar for most of the samples (Table S2; Figure 4c).

![Figure 4](image_url)

Figure 4. Application of the present garnet geobarometer to natural metapelite samples (Table S2) not included in the calibration. To simultaneously obtain P–T conditions, the garnet-biotite geothermometer [35] was combined with either the present garnet, or the GASP [49] or the GBPQ [50] geobarometers. (a) Sillimanite-bearing metapelite in the mafic complex contact aureole, Ivrea Zone, Northern Italy (BB00; [68]), and sillimanite-bearing metapelite at the Molodezhnaya Station, eastern Antarctica (G81; [69]); (b) Andalusite-bearing metapelite in the contact aureole in the Transangarian region of the Yenisei Ridge, eastern Siberia, Russia (L01; [70]), and andalusite- or sillimanite-bearing metapelite in the Augusta quadrangle, south-central Maine (NH81; [71]); and (c) Comparison of the present garnet and the GBPQ [50] geobarometers to Al₂SiO₅-free metapelite in the Furulund Group, Sulitjelma, Scandinavian Caledonides [72].

Finally, the present garnet geobarometer was applied to the poikiloblastic garnet collected from the Wopmay Orogen, Canada [73]. The garnet was rich in inclusion assemblages (plagioclase + biotite + quartz ± kyanite ± sillimanite ± ilmenite ± titanite) and the detailed chemical composition of only one sample (sample 3) was reported. The garnet zoning of sample 3 (Figure 5a) was characterized...
by monotonically decreasing \( X_{Mn} = \frac{\text{Mn}}{(\text{Fe} + \text{Mg} + \text{Ca} + \text{Mn})} \) and \( \text{Fe}# = \frac{\text{Fe}}{(\text{Fe} + \text{Mg})} \) ratios from the core to the rim, showing typical bell-shaped \( X_{Mn} \) and \( \text{Fe}# \) curves of the growth zoning of garnet derived from thermodynamic modeling for metapelite [30]. The \( \text{Ca}/\text{Fe} \) ratio of the garnet also decreased from 0.24 in the core to 0.08 in the rim, which implies that crystallization of the garnet from the core to the rim occurred during decompression. A prominent feature of the inclusion assemblages is that for every zone from the core to the rim of the garnet, the anorthite content of the plagioclase inclusion increased gradually from 0.25 to 0.38, similar to the zoned plagioclase porphyroblast in the matrix [73]; while the chemical composition of the biotite inclusion changed gradually from the core part to the rim part of the garnet. For example, the \( X_{Fe} = \frac{\text{Fe}}{(\text{Fe} + \text{Mg} + \text{Al}^{VI} + \text{Ti})} \) ratio of the biotite inclusion gradually decreased from 0.47 in the core domain to 0.41 in the rim domain of the garnet [73]. Furthermore, no reaction texture was found between the garnet interior and the adjacent inclusion minerals, and therefore, the local thermodynamic equilibrium among the inclusion minerals and the respective garnet zonation was attained and kept [73]. Quite similar \( P-T \) conditions of each inclusion assemblage and the adjacent garnet interior were obtained for every interior zone of the garnet, by simultaneous application of the GB geothermometer [55] in agreement with either the present garnet geothermometer (this work), or the GBPQ geobarometer [57], or the GASP geobarometer [49], as depicted in Figure 5b and Table S3. The identical near isothermal decompression \( P-T \) paths derived by different geobarometers (decreasing from 9.7-8.7 kbar in the core to 5.1-4.8 kbar in the rim) recorded in the garnet zonation (Figure 5b) suggest that large scale tectonic exhumation had occurred, as concluded earlier in [73]. This successful application suggests that the garnet geobarometer can be applied to decipher pressure conditions of the garnet zoning, provided that the corresponding temperatures of the zonation are known.

![Figure 5](image)

**Figure 5.** Chemical composition of the zoned garnet (a) and application of the garnet-biotite geothermometer [55] in concert with different geobarometers to the inclusion assemblages (b). Data were taken from [73] as listed in Table S3. \( \text{Al}_2\text{SiO}_5 \) phase diagram: the solid lines are from reference [65], whereas the dashed line is from [66].

5. Discussion

At present, there are only three experimentally calibrated geobarometers based on reversed phase equilibrium experiments: the GASP geobarometer [74–77], the garnet–rutile–ilmenite–plagioclase–silica (GRIPS) geobarometer [42], and the garnet–rutile–aluminosilicate–ilmenite–quartz (GRAIL) geobarometer [39,47]. The GASP geobarometer [49] is much more widely used for \( \text{Al}_2\text{SiO}_5 \)-plagioclase-bearing metapelite and its accuracy and precision have been demonstrated to be perfect after extensive comparative studies [57]. Therefore, in this contribution, the GASP geobarometer [49] was used as the benchmark to estimate the validity of the newly calibrated garnet geobarometer.

The asymmetric quaternary \( \text{Fe–Mg–Ca–Mn} \) solid solution model of garnet adopted in this work [49] was constructed by combining the arithmetical averages of the corresponding Margules parameters of the different activity models of garnet [62–64]. Although such an approach is not ideally reasonable in thermodynamics, the validity and applicability of the resulting GASP geobarometer [49] have been repeatedly certified through application to natural metapelites. This in turn, at least from the practical perspective, suggests that the activity model of garnet [49] is applicable. However, in
the calibration of the present garnet geobarometer, when different activity models of garnet [61–64] were adopted, quite similar results were obtained (Table 1, Table 2 and Table S1; Figure 6). This phenomenon suggests that the pressure effect of the net-transfer reaction including intracrystalline Ca$^{2+}$–Fe$^{2+}$ exchange of garnet (Equation (1)) does exist, and furthermore, the description of the pressure effect is weakly related to the activity models of garnet. Therefore, to keep internal thermodynamic consistency between the present garnet geobarometer and the garnet-biotite geothermometer [55], we preferred to adopt the activity model of [49,55].

![Figure 6](image-url)

**Figure 6.** The GASP [49] versus garnet pressures calibrated by different activity models of garnet. The dashed black and solid red lines define ±1.0 kbar and ±1.5 kbar deviations, respectively. R, multiple correlation coefficient; s.d., standard error. (a) Activity model of [61]; (b) activity model of [62]; (c) activity model of [63]; (d) activity model of [64]; and (e) symmetric quaternary activity model with all Margules parameters derived in this work.

If different asymmetric ternary or quaternary solid solution models of garnet are adopted, the enthalpic (ΔH), entropic (ΔS), and volumetric (ΔV) changes of the model reaction (Equation (1)) can be estimated as −49.5−−62.1 kJ, −156.5−−163.6 J/K, and −6.45−−6.77 J/bar, respectively, as listed in Table 1. Furthermore, if the symmetric quaternary solid solution model is adopted, the corresponding parameters can be estimated as −55.0 kJ, −180.7 J/K, and −7.04 J/bar, respectively (Table 1). These derived parameters are somewhat similar to each other within error, although they differ to those directly derived from the thermodynamic dataset [78]. However, large pressure deviations between the garnet and the GASP [49] geobarometers can be easily obtained, if the garnet geobarometer is made by directly combining the ΔH, ΔS, and ΔV items from the dataset in [78], in combination with the different
garnet activity models [49,61–64] and symmetric quaternary a–X model. This implies that possible nonnegligible built-in errors of the thermodynamic dataset and/or the activity models of garnet do exist. It can be further inferred that errors of the newly developed garnet geobarometer may be buried in the derived $\Delta H$, $\Delta S$, and $\Delta V$ items (Table 1) and the errors of this geobarometer are compensated for by these parameters, similar to most of the empirically calibrated geothermobarometers.

Due to the lack of phase equilibrium experimental data, precision of the present garnet geobarometer cannot be determined. However, the above application examples suggest that this geobarometer can be used to estimate the metamorphic pressure for simple metapelitic assemblages. When combined with the GB geothermometer [55], metamorphic $P$–$T$ conditions can be simultaneously determined. However, further work is expected to be done to improve its accuracy, if more samples and/or phase equilibria experimental data are available.

Furthermore, pressure determined by the present garnet geobarometer represents the lower limit of pressure conditions for the ilmenite-bearing and titanite-absent assemblage. In contrast, if the assemblage contains titanite, but no ilmenite, the upper limit of pressure conditions can be obtained. Determination methods of minimum or maximum metamorphic $P$–$T$ conditions are given in [79].

6. Conclusions

This original calibration of a garnet geobarometer was empirically done under $P$–$T$ conditions of 430–895 °C/1–15 kbar, for the chemical composition of garnet of $X_{Ca} = 0.02$–0.29 and $X_{Fe} = 0.42$–0.91. This geobarometer yielded similar pressures for most of the calibrant samples within $\pm 1$ kbar compared to the well-calibrated GASP geobarometer, and plotted almost all of the calibrant samples in the correct $Al_2SiO_5$ stability field. Its total error is expected to be below $\pm 1.3$ kbar. This geobarometer may play a unique role in simple assemblage garnet + biotite, especially when plagioclase is Ca-deficient or even absent. It is not suggested that it be applied to Ca-deficient garnet ($X_{Ca} < 0.02$). An electronic spreadsheet (Table S4) is supplied to compute the $P$–$T$ conditions for the garnet-biotite pair, which is available in the Supplementary Materials.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/9/9/540/s1, Table S1: Natural metapelite samples used to calibrate the garnet geobarometer; Table S2: Application of the garnet geobarometer to natural metapelite samples not included in calibrating the garnet geobarometer; Table S3: Chemical compositions of the garnet zonation and the inclusion assemblages; Table S4: Combined spreadsheet of garnet geobarometer and garnet-biotite geothermometer.

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