The applicability of the GRIPS geobarometry in metapelitic assemblages

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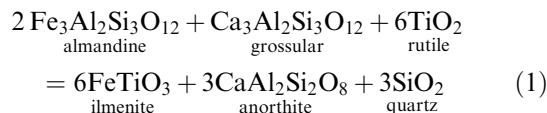[2]*Department of Earth Sciences, James Lee Science Building, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

ABSTRACT   Although the garnet-rutile-ilmenite-plagioclase-silica (quartz) (GRIPS) geobarometer has been experimentally calibrated and widely applied, its applicability to metapelitic rocks has not yet been discussed carefully. In this paper, this barometer was recalibrated by fitting the available reversed-phase equilibrium data incorporating different combinations of activity models of garnet, plagioclase and ilmenite. The resultant GRIPS barometer formalisms reproduce the experimental pressures well within ±0.2 kbar. The GRIPS and garnet-aluminium silicate-plagioclase-quartz (GASP) barometer values are concordant within ±1 kbar for pressures above ∼6 kbar for natural metapelites, but the difference of pressure determinations between these two barometers becomes larger when pressure and/or the grossular content of garnet decrease. However, the pressure difference is independent of either temperature, or almandine in garnet, or anorthite in plagioclase, or iron content in ilmenite. After testing and application of the GRIPS barometer to aluminosilicate-bearing metapelites and metapelitic assemblages within limited geographical areas as well as within contact thermal aureoles, it is concluded that this barometer may be applied to low- to high-grade, medium- to high-pressure metapelites. The application of the GRIPS barometer to metapelites is not advocated in situations where calcium is deficient in garnet ($X_{Ca}^{grt} < 0.05$) or plagioclase ($X_{Ca}^{pl} < 0.17$), or for pressures below ∼6 kbar.

Key words: applicability; calibration; geobarometer; GRIPS; metapelite.

INTRODUCTION

Ilmenite and rutile are common minerals in TiO_2-saturated, low- to high-grade metapelites. Although occurring as minor or accessory minerals, they play an important role in deciphering metamorphic $P–T$ conditions. Through reversed-phase equilibrium experiments, Bohlen & Liotta (1986) thermodynamically bracketed the garnet-rutile-ilmenite-plagioclase-silica (quartz) (GRIPS) geobarometer net-transfer reaction

$$2 \underset{\text{almandine}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + 6 \underset{\text{rutile}}{TiO_2}$$
$$= 6 \underset{\text{ilmenite}}{FeTiO_3} + 3 \underset{\text{anorthite}}{CaAl_2Si_2O_8} + 3 \underset{\text{quartz}}{SiO_2} \qquad (1)$$

under physical conditions of 10.6–14.4 kbar at 800–1100 °C using synthetic stoichiometric pure ilmenite, rutile, plagioclase and impure garnet (1/3 grossular + 2/3 almandine) as well as natural, pure quartz from Brazil. Four reversals tightly constrain this equilibrium in $P–T$ space.

This GRIPS barometer is widely used in metamorphic petrology (e.g. Robinson *et al.*, 2004), with different authors choosing their preferred activity models of the minerals. Although the GRIPS geobarometer has been widely applied, its applicability to metapelitic rocks has not yet been discussed carefully, to our knowledge. In recent years, mixing models of garnet, plagioclase and ilmenite have been greatly improved (e.g. Fuhrman & Lindsley, 1988; Feenstra & Peters, 1996; Holdaway, 2001), which has paved the way for improved application of this barometer. In this paper, this barometer was calibrated by combining different activity models of garnet, plagioclase and ilmenite, which allowed its applicability to be fully tested for metapelitic assemblages.

CALIBRATION OF THE GRIPS GEOBAROMETER

Thermodynamic background

It is well known that the Gibbs free energy of a reaction system is

$$\Delta G = 0 = \Delta G^0 + RT \ln K \qquad (2)$$

For each end-member mineral phase, the Gibbs free energy contribution to ΔG^0 is (Holland & Powell, 1990):

$$\Delta_f G = \Delta H^0_{(1,298.15)} - T \cdot \Delta S^0_{(1,298.15)} + \int_{298.15}^{T} C_P \, dT$$

$$- T \int_{298.15}^{T} \frac{C_P}{T} dT$$

$$+ P \cdot [V^0_{(1,298.15)} + \alpha V(T - 298.15)] - \frac{\beta V}{2} P^2 \quad (3)$$

For the GRIPS reaction (1), substituting Eq. (3) into Eq. (2), we obtain the GRIPS barometer model as

$$\Delta H^0_{(1,298.15)} - T \cdot \Delta S^0_{(1,298.15)}$$

$$= -\int_{298.15}^{T} \Delta C_P \, dT + T \int_{298.15}^{T} \frac{\Delta C_P}{T} dT + \frac{\Delta(\beta V)}{2} P^2$$

$$- P[\Delta V^0_{(1,298.15)} + \Delta(\alpha V)(T - 298.15)] + 6RT \ln \gamma^{grt}_{Fe}$$

$$+ 3RT \ln \gamma^{grt}_{Ca} - 6RT \ln \gamma^{ilm}_{Fe} - 3RT \ln \gamma^{pl}_{Ca}$$

$$- 3RT \ln K^{ideal}_d \quad (4)$$

in which the delta items are the corresponding thermodynamic items of reaction (1), and the γ-related items are the activity coefficients of the corresponding minerals.

When ignoring the heat capacity, thermal expansion and compressibility coefficients of the minerals, the GRIPS barometer model is simplified as:

$$\Delta H^0_{(1,298.15)} - T \cdot \Delta S^0_{(1,298.15)}$$

$$= -P \cdot \Delta V^0_{(1,298.15)} + 6RT \ln \gamma^{grt}_{Fe} + 3RT \ln \gamma^{grt}_{Ca}$$

$$- 6RT \ln \gamma^{ilm}_{Fe} - 3RT \ln \gamma^{pl}_{Ca} - 3RT \ln K^{ideal}_d \quad (5)$$

Activity models of the mineral solid solutions

Garnet solid solution

Natural metapelitic garnet consists essentially of a Fe-Mg-Ca-Mn quaternary solid solution. However, there are very few garnet activity models to describe this quaternary system, as most of the existing activity models rely on binary and/or ternary solid solutions. Direct measurements of the quaternary mixing properties of garnet are rare. Koziol (1996) studied the displacement of the garnet-aluminium silicate-plagioclase-quartz (GASP) equilibrium to determine the activity of garnet but failed to retrieve the Margules parameters because of limited data. Currently, there are three quaternary garnet solid solution models (Berman, 1990; Ganguly *et al.*, 1996; Holdaway, 2001) derived from fitting the existing experimental data and/or natural data. The Holdaway (2001) garnet model is the average of three models (Berman, 1990; Ganguly *et al.*, 1996; Mukhopadhyay *et al.*, 1997). These models include separate expressions of almandine, pyrope, grossular and spessartine.

Plagioclase solid solution

Presently, two activity models of ternary Ca-Na-K plagioclase solid solutions (Fuhrman & Lindsley, 1988; Elkins & Grove, 1990) are available which have been extensively used.

Ilmenite solid solution

Natural metapelitic ilmenite always contains nearly pure ilmenite ($FeTiO_3$) and small amounts of pyrophanite ($MnTiO_3$) and sometimes detectable proportions of hematite (Fe_2O_3) and geikielite ($MgTiO_3$), but usually negligible amounts of corundum (Al_2O_3). Ilmenite in metapelitic rocks with ~5 mol.% of pyrophanite component is quite common (Feenstra & Peters, 1996). In fact, in the collated natural metapelitic ilmenite from the literature, more than 97 mol.% of the solid solution consists of ilmenite and pyrophanite components, while the geikielite component ranges between 0% and 10.8% ($\bar{x} = 1.5\%$), hematite between 0% and 10.6% ($\bar{x} = 1.3\%$), and corundum between 0% and 0.8% ($\bar{x} = 0.05\%$). These minor components total 2.8% ($\bar{x}$) and have been assumed to be ideal, except for ilmenite and pyrophanite which mix non-ideally.

O'Neill *et al.* (1989) experimentally determined the activity–composition relationships for the binary ilmenite ($FeTiO_3$–$MnTiO_3$) solid solution for the wide chemical composition range of $X_{ilm} = 0.15$–0.77 for temperature between 1050 and 1300 K by emf measurements using an electrochemical technique with calcia- and yttria-stabilized zirconia solid electrolytes. They have shown that the ilmenite-pyrophanite solid solution shows small positive deviations from ideality and the solution may be described by a regular solution model with a single interaction parameter (W^{ilm}_{FeMn}) of 2.2 ± 0.3 kJ mol^{-1}, independent of temperature. This value is comparable with that ($W^{ilm}_{FeMn} = 1757.4$ J mol^{-1}) derived by Pownceby *et al.* (1987) through fitting their unpublished data on Fe-Mn exchange reaction between garnet and ilmenite.

Feenstra & Peters (1996) experimentally determined the activities in the $FeTiO_3$–$MnTiO_3$ binary ilmenite solid solution by redox reversals at 1 bar and 700–900 °C using asymmetric mixing models:

$$a^{ilm}_{FeTiO3} = X^{ilm}_{Fe} \cdot \exp\{(X^{ilm}_{Mn})^2[-23234.0 + 27062.0 X^{ilm}_{Fe}$$

$$+ T(22.06 - 4.82 X^{ilm}_{Fe})]/RT\} \quad (6)$$

Although different activity models of ilmenite solid solution have been determined for the binary ilmenite-hematite (e.g. Burton, 1984; Andersen & Lindsley, 1988), the binary ilmenite-geikielite (Berman & Aranovich, 1996) and the ternary ilmenite-hematite-geikielite (e.g. Ghiorso, 1990; Andersen *et al.*, 1991) systems, we have found that the simplified Fe-Mn binary system describes well the ilmenite solid solution because of the negligible presence of other components in natural metapelitic ilmenites.

Quartz and rutile

These minerals are essentially pure phases, and hence their activities may be reasonably taken as unity.

Calibration of the GRIPS barometer

The Bohlen & Liotta (1986) reversed equilibria of the GRIPS reaction involve pure minerals except for impure garnet and they correctly stated that this reaction lies at pressures lower than those for the end-member GRIPS reaction because of the free energy of mixing of almandine and grossular in garnet. The equilibrium line in the P–T space of the end-member GRIPS reaction may be computed by inputting the experimental P, T and garnet compositions (Bohlen & Liotta, 1986) of the GRIPS reaction as well as the activity models of garnet into Eq. (4) or (5). In the calibration, the volume of the GRIPS reaction was taken as $\Delta V^0_{(1,298.15)} = 9.209$ J bar^{-1} (Holland & Powell, 1990).

Modelling of the GRIPS experiments (Bohlen & Liotta, 1986) needs only the garnet activity models, because other minerals involved in the experiments are pure phases. There are now three quaternary garnet solution models (Berman, 1990; Ganguly *et al.*, 1996; Holdaway, 2001). The calibration used here lies in two categories: one involves the C_p, α and β parameters of the minerals (Holland & Powell, 1990) and the other does not. Thus, there are actually six barometer models, i.e. three garnet activity models, multiplied by the two categories. The regressed parameters of the GRIPS barometer are listed in Table 1 which actually yields six GRIPS barometer formalisms. Each of these formulae reproduces the GRIPS experimental pressures well within ± 0.2 kbar. This is not surprising because Berman (1990) and Ganguly *et al.* (1996) used the same Margules parameters (W^H_{FeCa}, W^S_{FeCa}, W^H_{CaFe} & W^S_{CaFe}) and Holdaway (2000, 2001) differs a little. From this point of view, these barometer formulae are all valid to the experimental data. It is noted that when incorporating the C_p, α and β items of the minerals, the standard deviation of the derived ΔH of the reaction is large (Table 1), irrespective of the garnet activity model used.

Table 1. Derived enthalpy and entropy of the GRIPS reaction by fitting the experimental data (Bohlen & Liotta, 1986) using different quaternary solid solution models of garnet

Garnet model	$\Delta H^0_{(1,298.15)}$ (J mol^{-1})	$\Delta S^0_{(1,298.15)}$ (J K^{-1} mol^{-1})	SD (kbar)	*R*-value
Including C_p, α and β of the minerals (Holland & Powell, 1990)				
Berman (1990)	−1678.0 (±6553.0)	122.79 (±5.3)	±0.2	0.994
Ganguly *et al.* (1996)	−1558.6 (±6589.3)	123.48 (±5.4)	±0.2	0.994
Holdaway (2001)	−3445.9 (±6571.8)	121.76(± 5.4)	±0.2	0.994
Excluding C_p, α and β of the minerals				
Berman (1990)	24652.9 (±5791.6)	160.59 (±4.7)	±0.2	0.997
Ganguly *et al.* (1996)	24772.4 (±5828.3)	161.28 (±4.7)	±0.2	0.997
Holdaway (2001)	22885.0 (±5810.6)	159.56 (±4.7)	±0.2	0.997

Natural plagioclase and ilmenite are solid solutions, and hence the activity models of these minerals should be incorporated into the GRIPS barometer formulae in order to accurately infer the metamorphic pressures. Incorporating different activity models of garnet, plagioclase and ilmenite in the above barometer formulae (corresponding parameters in Table 1 derived from the GRIPS experiments), 30 versions of this barometer are obtained as listed in Table 2. Of course, these formulae all reproduce the experimental pressures well within ± 0.2 kbar. Again, this is not unexpected because ilmenite, rutile and quartz are pure phases in the experiments (Bohlen & Liotta, 1986) and their activities are unity.

After testing and application of these 30 formulae, the P(3) and P(18) formalisms preferred are expressed, respectively, as

$\mathrm{P}_{(3)}(\mathrm{bar})$

$$
= \{566809.6 + 0.222306T^2 - 1103.3T \ln T
$$
$$
+ 9845.36T - 90744.8T^{0.5} - 14310700.0T^{-1}
$$
$$
+ 2.05 \times 10^{-5}P^2 + T(2Fea + Caa - 3Fa)
$$
$$
+ P(2Feb + Cab - 3Fb) + (2Fec + Cac - 3Fc)
$$
$$
+ 3RT \ln\left[\frac{4(X^{\mathrm{grt}}_{\mathrm{Fe}})^2(X^{\mathrm{grt}}_{\mathrm{Ca}})}{(X^{\mathrm{ilm}}_{\mathrm{Fe}})^2(X^{\mathrm{pl}}_{\mathrm{Ca}})(1 + X^{\mathrm{pl}}_{\mathrm{Ca}})^2}\right]
$$
$$
- 6(1 - X^{\mathrm{ilm}}_{\mathrm{Fe}})^2[-23234.0 + 27062.0X^{\mathrm{ilm}}_{\mathrm{Fe}}
$$
$$
+ T(22.06 - 4.82X^{\mathrm{ilm}}_{\mathrm{Fe}})]\}
$$
$$
/\{9.209 + 6.7 \times 10^{-5}[T(K) - 298.15]\} \quad (7)
$$

and

$\mathrm{P}_{(18)}(\mathrm{bar})$

$$
= \{-22885.0 + 159.56T(K)
$$
$$
+ 3RT \ln\left[\frac{4(X^{\mathrm{grt}}_{\mathrm{Fe}})^2(X^{\mathrm{grt}}_{\mathrm{Ca}})}{(X^{\mathrm{ilm}}_{\mathrm{Fe}})^2(X^{\mathrm{pl}}_{\mathrm{Ca}})(1 + X^{\mathrm{pl}}_{\mathrm{Ca}})^2}\right]
$$
$$
+ T(2Fea + Caa - 3Fa) + P(2Feb + Cab - 3Fb)
$$
$$
+ (2Fec + Cac - 3Fc) - 6(1 - X^{\mathrm{ilm}}_{\mathrm{Fe}})^2
$$
$$
\times [-23234.0 + 27062.0X^{\mathrm{ilm}}_{\mathrm{Fe}}
$$
$$
+ T(22.06 - 4.82X^{\mathrm{ilm}}_{\mathrm{Fe}})]\}/9.209 \quad (8)
$$

in which Fea, Feb, Fec, Caa, Cab, Cac, Fa, Fb and Fc terms are the polynomials describing the activity coefficients of garnet and plagioclase, which have been given in the appendix in Wu *et al.* (2004). The GRIPS barometer P(3) (Eq. 7) has incorporated the C_p, α and β parameters (Holland & Powell, 1990) of the minerals involved, the garnet activity model of Holdaway (2001), the plagioclase activity model of Fuhrman & Lindsley (1988) and the ilmenite activity model of Feenstra & Peters (1996). Barometer P(3) needs iteration in its application. The GRIPS barometer P(18) (Eq. 8) has excluded the C_p, α and β items of the

Table 2. GRIPS barometer formalisms through different combinations of different activity models of garnet, plagioclase and ilmenite

Barometer	Garnet activity model	Plagioclase activity model	Ilmenite activity model
(a) Including C_p, α and β of the minerals (Holland & Powell, 1990)			
P(1)	Holdaway (2001)	Fuhrman & Lindsley (1988)	ideal
P(2)	Holdaway (2001)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(3)	Holdaway (2001)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(4)	Holdaway (2001)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(5)	Holdaway (2001)	Elkins & Grove (1990)	Feenstra & Peters (1996)
P(6)	Berman (1990)	Fuhrman & Lindsley (1988)	ideal
P(7)	Berman (1990)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(8)	Berman (1990)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(9)	Berman (1990)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(10)	Berman (1990)	Elkins & Grove (1990)	Feenstra & Peters (1996)
P(11)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	ideal
P(12)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(13)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(14)	Ganguly et al. (1996)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(15)	Ganguly et al. (1996)	Elkins & Grove (1990)	Feenstra & Peters (1996)
(b) Excluding C_p, α and β of the minerals			
P(16)	Holdaway (2001)	Fuhrman & Lindsley (1988)	ideal
P(17)	Holdaway (2001)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(18)	Holdaway (2001)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(19)	Holdaway (2001)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(20)	Holdaway (2001)	Elkins & Grove (1990)	Feenstra & Peters (1996)
P(21)	Berman (1990)	Fuhrman & Lindsley (1988)	ideal
P(22)	Berman (1990)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(23)	Berman (1990)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(24)	Berman (1990)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(25)	Berman (1990)	Elkins & Grove (1990)	Feenstra & Peters (1996)
P(26)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	ideal
P(27)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	O'Neill et al. (1989)
P(28)	Ganguly et al. (1996)	Fuhrman & Lindsley (1988)	Feenstra & Peters (1996)
P(29)	Ganguly et al. (1996)	Elkins & Grove (1990)	O'Neill et al. (1989)
P(30)	Ganguly et al. (1996)	Elkins & Grove (1990)	Feenstra & Peters (1996)

minerals and includes the same activity models as that of barometer P(3), and thus does not need any iteration in its application.

Even though all the GRIPS formalisms yield similar pressure estimates for any given sample collated in the section *Electronic Appendices*, we prefer P(3) or P(18) because they incorporate the most accurate activity models of garnet (Holdaway, 2000, 2001), plagioclase (Fuhrman & Lindsley, 1988) and ilmenite (Feenstra & Peters, 1996).

TEST AND APPLICATION OF THE GRIPS GEOBAROMETER

Electronic appendices

The data files used in this analysis of the GRIPS and GASP geobarometers are provided as an electronic appendix. Tables S1–S4 provide the data used in the analysis. The complete results of the analysis are provided in Figs S1–S7. Representative figures from these appendices are provided in the printed copy and are identified with the equivalent numbers, namely Figs 1–7. Thus for each of the Figs 1–7 printed in the paper, the full figure is available in the appendices.

Natural metapelites collated from the literature

To test the applicability of the GRIPS barometer, 87 natural metapelites (Tables S1–S4) have been collated

which span P and T conditions of 2.2–11.1 kbar and 450–730 °C, respectively. The temperature and pressure values are determined simultaneously by applying the garnet-biotite thermometer (Holdaway, 2000) and GASP barometer (Holdaway, 2001), respectively. Ferric iron contents of ilmenite are determined according to the method of Droop (1987). Ferric iron contents of garnet are assumed to be 3 mol.% of the total FeO. After theoretical modelling and analyses of natural metapelites, Todd (1998) suggested that the GASP barometer be used with great caution when the product $X_{Ca}^{grt} \cdot X_{Ca}^{pl}$ is < 0.05. Holdaway (2001) found that GASP barometer can only be accurately used for $X_{Ca}^{pl} > 0.17$ and $X_{Ca}^{grt} > 0.03$. For the metapelites collated in this paper, the composition criteria of $X_{Ca}^{pl} > 0.17$ and $X_{Ca}^{grt} > 0.03$ have been applied. These samples are to be used to test the accuracy and applicability of the GRIPS barometer.

Test of the GRIPS barometer

At present, there are at least 32 versions of the garnet-biotite thermometer and at least nine versions of the GASP barometer which have been calibrated empirically or experimentally, or empirically and experimentally and may be applied to retrieve the $P–T$ conditions of metapelites. After extensive comparison, Wu & Cheng, in press concluded that the Holdaway (2000) garnet-biotite thermometer and the Holdaway (2001) GASP barometer are the most accurate and
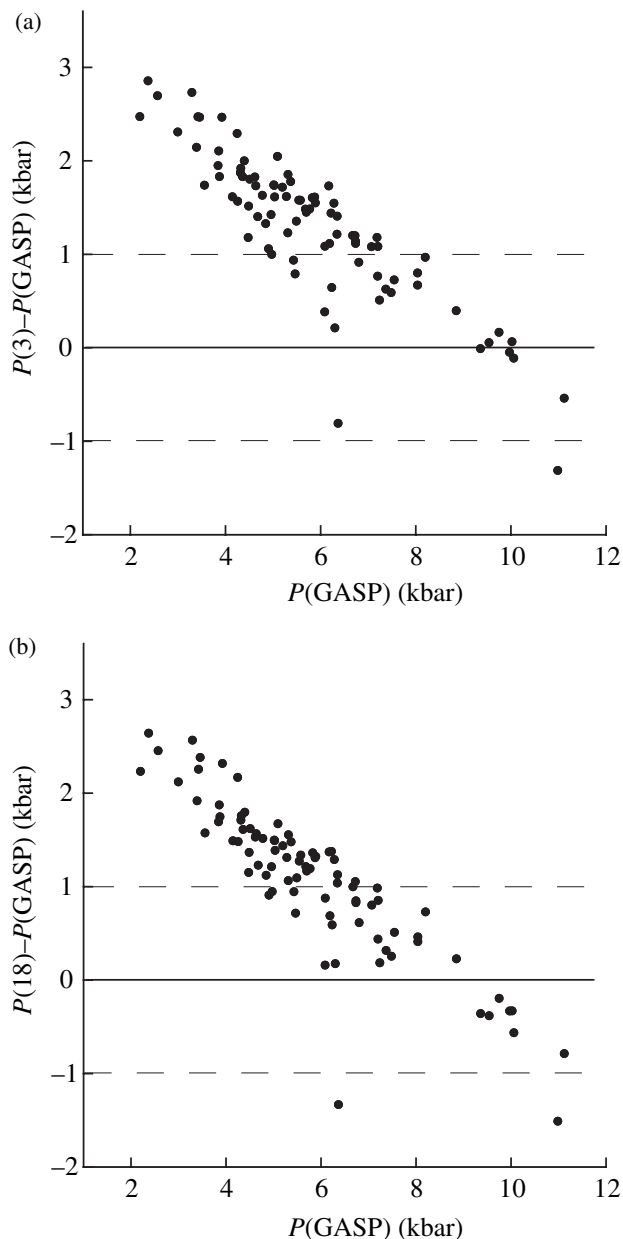
Fig. 1. The GASP pressures v pressure differences between GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ v $P(GASP)$; (b) $P(18)$–$P(GASP)$ v $P(GASP)$.
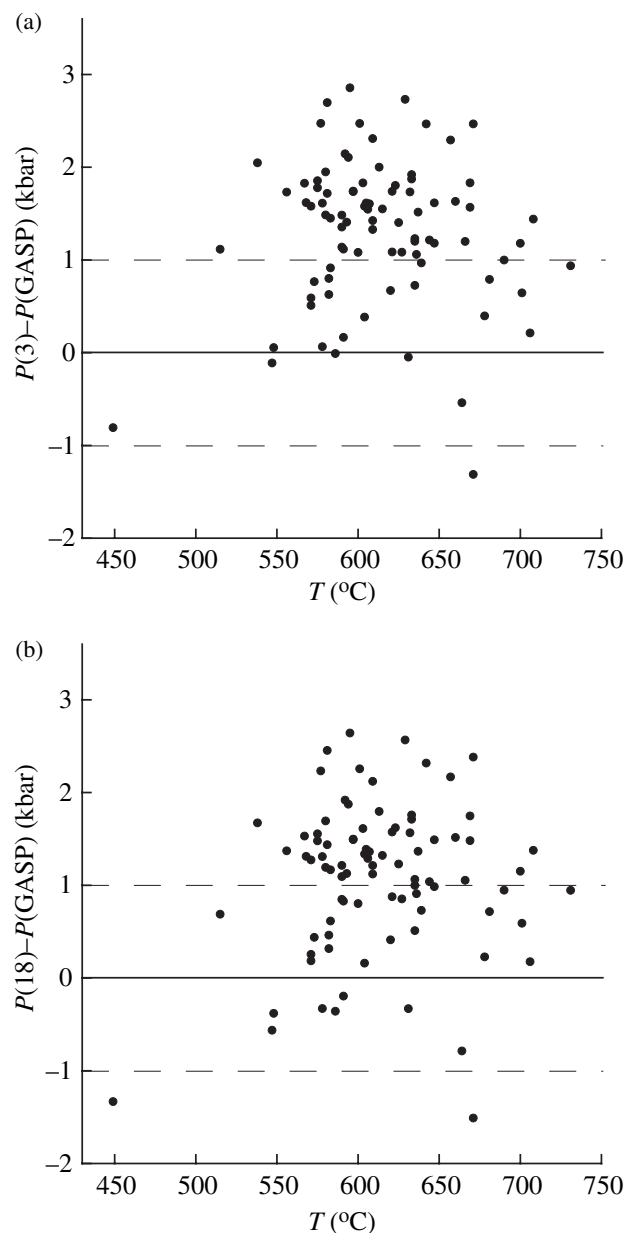
Fig. 2. Temperature v pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ v T °C; (b) $P(18)$–$P(GASP)$ v T °C.

valid thermobarometers. Therefore, the GASP and GRIPS pressures are compared to test the applicability of the GRIPS barometer. In this paper hereafter, the garnet-biotite thermometer is referred as Holdaway (2000) and the GASP barometer as Holdaway (2001) when no specific notes are addressed.

It has been found that all the GRIPS barometer formulations incorporating the plagioclase activity model of Elkins & Grove (1990) always overestimate pressures compared with the GASP barometer (Tables S1–S4; Figs S1–S7). Therefore, it is concluded

that the GRIPS barometer should not be incorporated with the Elkins & Grove (1990) plagioclase model. Other GRIPS formulations, surprisingly, give identical pressure values, within error (Tables S1–S4; Figs 1–7), irrespective of the activity models of garnet, plagioclase and ilmenite incorporated. It is thus concluded that the GRIPS barometers are almost independent of the activity models selected, except for the Elkins & Grove (1990) plagioclase model.

It has also been found that the pressure difference between the GRIPS and GASP barometers becomes larger and larger as pressure decreases. Below ~6 kbar,
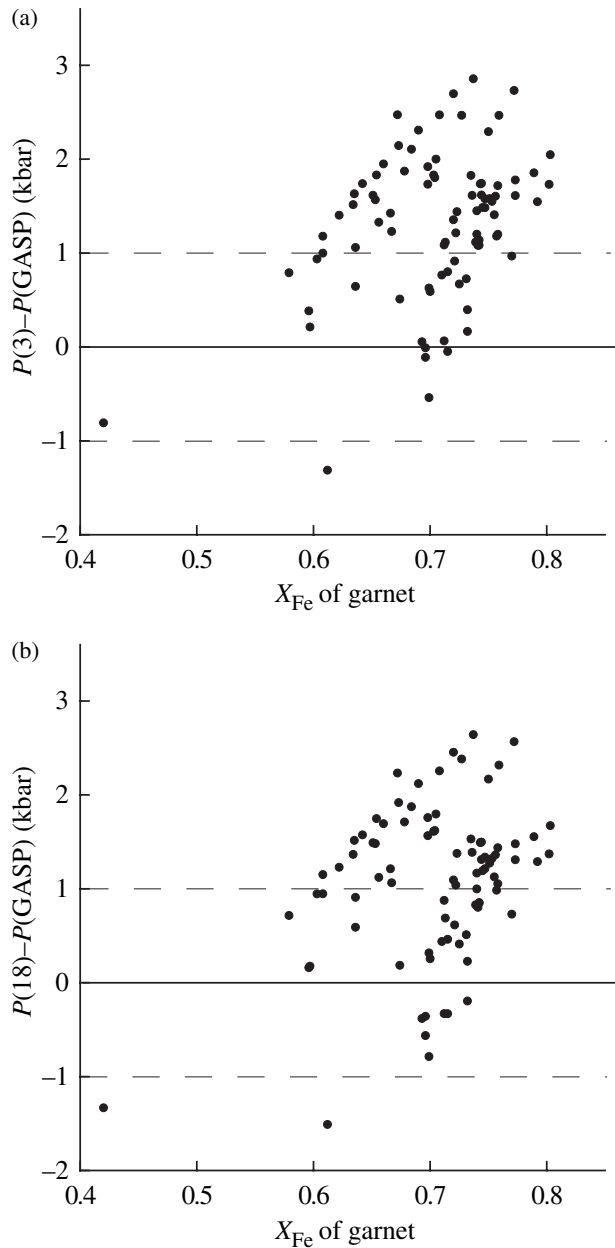
Fig. 3. Almandine contents of garnet *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ *v* X_{Fe} Grt; (b) $P(18)$–$P(GASP)$ *v* X_{Fe} Grt.

Fig. 4. Anorthite contents of plagioclase *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ *v* X_{Ca} Plag.; (b) $P(18)$–$P(GASP)$ *v* X_{Ca} Plag.

the difference exceeds ±1 kbar and the GRIPS pressures are always higher than the GASP pressures (Tables S1–S4; Fig. 1). However, the pressure difference is independent of temperature (Fig. 2), which suggests that these two barometers have nearly identical temperature dependence.

It is clear that the pressure difference between the GRIPS and GASP barometers has almost no relationship with either grossular components in garnet (Fig. 3), or anorthite components in plagioclase (Fig. 4) or iron fractions in ilmenite (Fig. 5). But, the
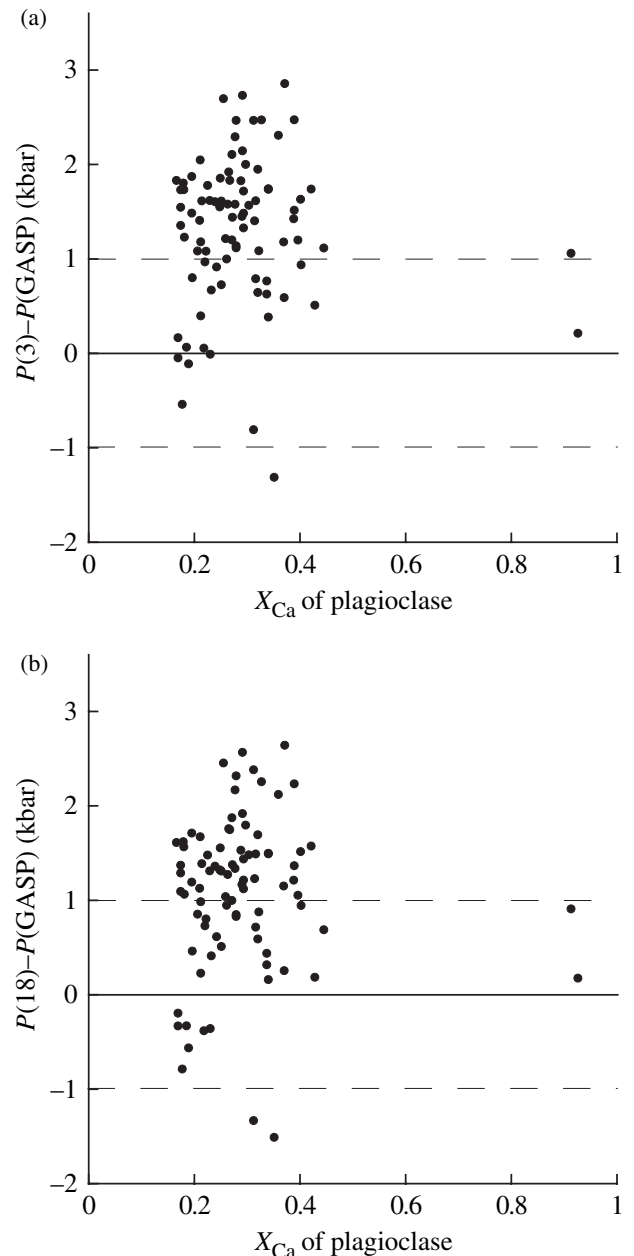
pressure difference becomes larger when the grossular component in garnet decreases (Fig. 6), and when the calcium fraction is below 0.05 the pressure difference is always larger than 1 kbar.

Application of the GRIPS barometer to metapelites within limited geographical areas

The GRIPS barometer shows small pressure deviations compared with the GASP barometer to metapelitic
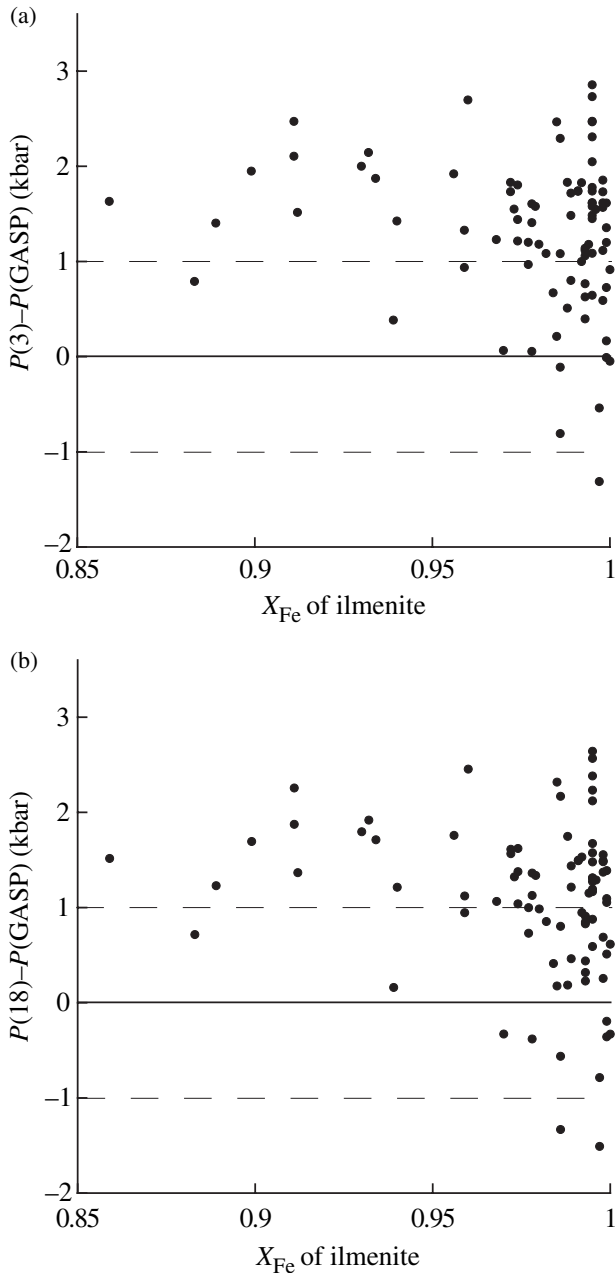
Fig. 5. Ferrous iron contents of ilmenite *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ *v* X_{Fe} Ilm; (b) $P(18)$–GASP *v* X_{Fe} Ilm.

Fig. 6. Grossular contents of garnet *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4. (a) $P(3)$–$P(GASP)$ *v* X_{Ca} Grt; (b) $P(18)$ – $P(GASP)$ *v* X_{Ca} Plag.

rocks when pressure is above ∼6 kbar. To test its applicability further, this barometer is now applied to low- to medium-pressure metapelites within limited geographic areas.

The Baltimore metapelites within 500 m, USA

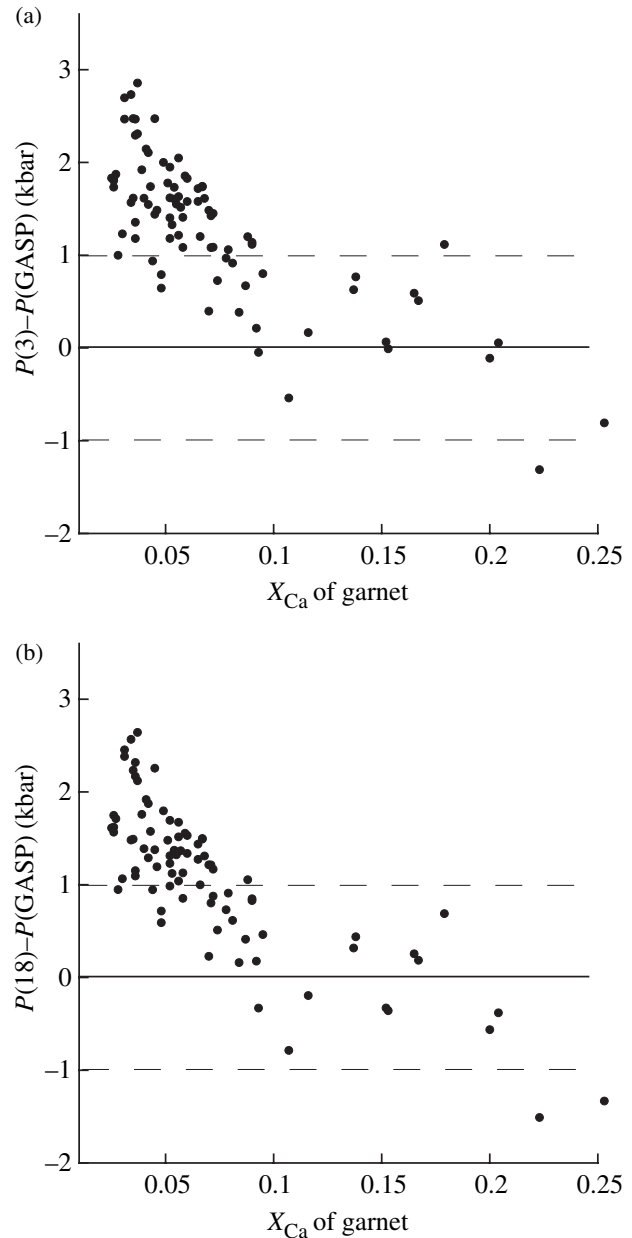Thirteen samples were collected by Lang (1991) from the two metamorphic mineral assemblages: a stauro-

lite assemblage (staurolite + garnet + biotite + quartz + muscovite + plagioclase + ilmenite + magnetite), and a staurolite-kyanite assemblage (kyanite + staurolite + garnet + biotite + quartz + muscovite + plagioclase + ilmenite + rutile + pyrrhotite). These rocks are randomly distributed along a 0.5-km-long exposure at the Hunt Valley Mall, north of Baltimore, Maryland, USA. Among these samples, six contain kyanite and are not calcium-deficient. The *P* and *T* values of these rocks determined simulta-
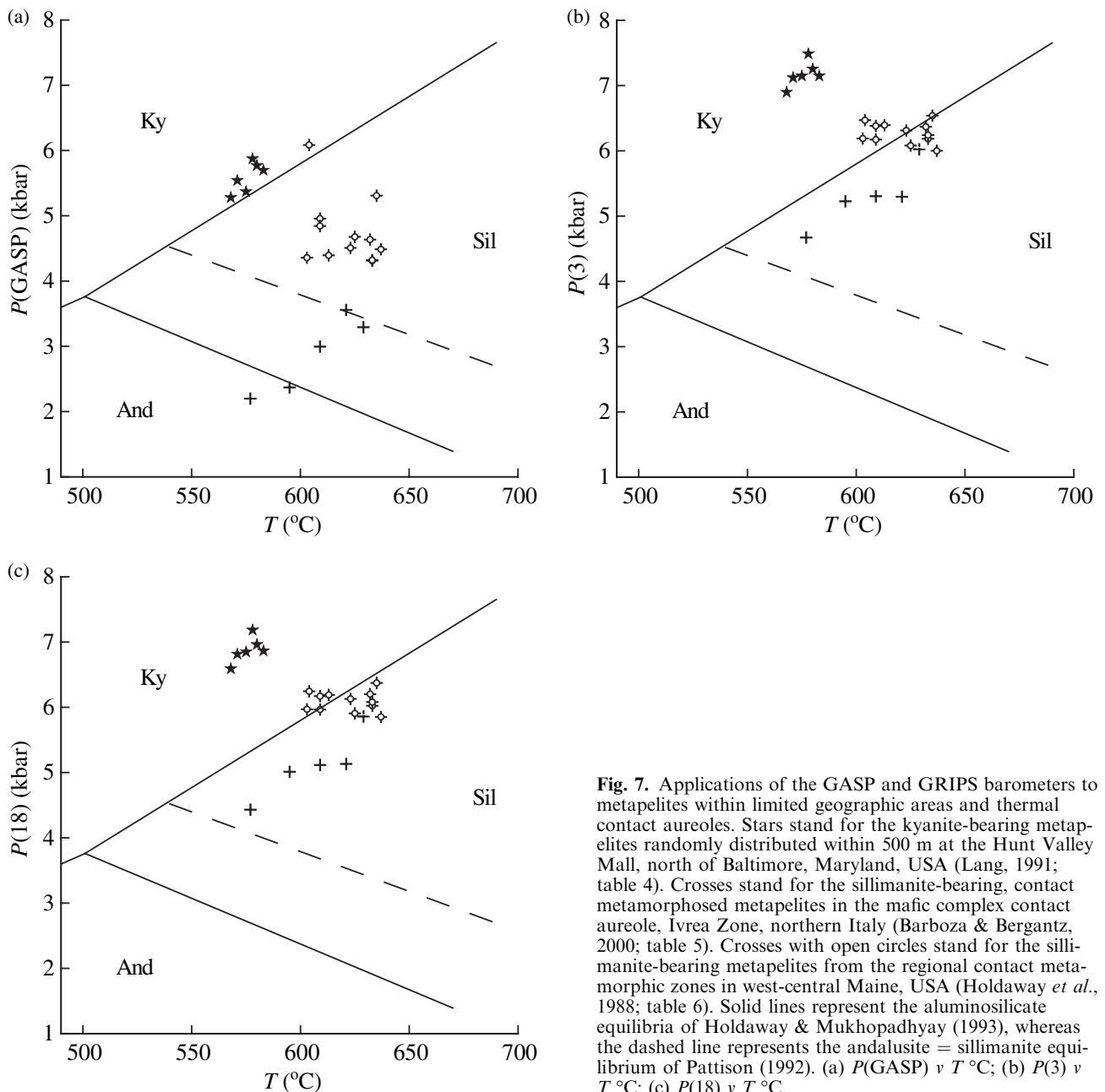
Fig. 7. Applications of the GASP and GRIPS barometers to metapelites within limited geographic areas and thermal contact aureoles. Stars stand for the kyanite-bearing metapelites randomly distributed within 500 m at the Hunt Valley Mall, north of Baltimore, Maryland, USA (Lang, 1991; table 4). Crosses stand for the sillimanite-bearing, contact metamorphosed metapelites in the mafic complex contact aureole, Ivrea Zone, northern Italy (Barboza & Bergantz, 2000; table 5). Crosses with open circles stand for the sillimanite-bearing metapelites from the regional contact metamorphic zones in west-central Maine, USA (Holdaway *et al.*, 1988; table 6). Solid lines represent the aluminosilicate equilibria of Holdaway & Mukhopadhyay (1993), whereas the dashed line represents the andalusite = sillimanite equilibrium of Pattison (1992). (a) P(GASP) v T °C; (b) P(3) v T °C; (c) P(18) v T °C.

neously by the garnet-biotite thermometer and GASP barometer are 568–580 °C and 5.3–5.9 kbar, respectively (Table S2, Fig. 7). Thus the P–T conditions are believed to be constant, within error. The GRIPS barometer also reflects such a constant-pressure metamorphism, with P(3) yielding pressure values between 6.9 and 7.5 kbar and P(18) yielding between 6.6 and 7.2 kbar (Table S2, Fig. 7). The GRIPS pressures are 1.3–1.6 kbar higher than the GASP pressures, and the GRIPS barometer correctly assigns all the samples to the kyanite-stability field (Fig. 7).

Metapelites in the mafic complex contact aureole, Ivrea Zone, northern Italy

Near the Italian–Swiss border, northern Italy, a Late Carboniferous–Early Permian mafic intrusive complex is exposed. Emplacement of a major part of the mafic complex occurred during decompression from ambient pressures at the thermal maximum during the regional granulite facies episode (Barboza & Bergantz, 2000). Final emplacement caused anatexis and metamorphism only within a narrow (2–3 km) aureole in the proximal supracrustal rocks. These events overprint

the regional amphibolite to granulite facies prograde metamorphic zonation (Barboza & Bergantz, 2000). Simultaneous application of the garnet-biotite thermometer and GASP barometer yields the *P* and *T* values of these sillimanite-bearing rocks to be 577–629 °C and 2.2–3.6 kbar, respectively (Table S3, Fig. 7); and thus, the metamorphic pressure may be assumed constant, within error. Although the GRIPS barometer also reflects such a constant-pressure metamorphism, with P(3) yielding pressure values between 4.7 and 6.0 kbar and P(18) yielding between 4.4 and 5.9 kbar (Table S3, Fig. 7), the GRIPS barometer erroneously assigned several sillimanite-bearing samples to the kyanite-stability field (Fig. 7).

Metapelites in the regional contact metamorphic zones in west-central Maine, USA

Holdaway *et al.* (1988) studied the west-central Maine regional contact metamorphic zones which cover a large area and suggested that M3 metamorphism occurred at 3.1 kbar and M5 at 3.8 kbar. The GASP barometer shows no obvious pressure difference between M3 and M5 and therefore they can be regarded as constant around 4.7 kbar, within error (Table S4, Fig. 7). The GRIPS barometer P(3) also yields constant pressure values of 6.0–6.5 kbar and averaged to be 6.3 kbar, while the GRIPS barometer P(18) gave constant pressure values of 5.9–6.4 kbar and an average pressure from both of 6.1 kbar as obtained (Table S4, Fig. 7). Although the GRIPS barometer has assigned all the samples to the sillimanite-stability field (Fig. 7), it yielded 1.4–1.6 kbar higher pressures than GASP.

DISCUSSION

The inconsistency between the GRIPS and GASP barometers may not be explained by a single cause. If the end-member calibrations are consistent, then at higher pressures, the two systems should agree best, and at lower pressures they might diverge because of error(s) in the activity model(s) (M. J. Holdaway, pers. comm.). It is noted that in the higher pressure region the barometers agree quite well, at least up to 11 kbar for the collated samples (Fig. 1). At lower pressures (< 6 kbar) the discrepancy becomes larger. Such a phenomenon preliminarily suggests that the two barometer experiments are consistent at least at higher pressures. But, because no much higher pressure samples have been collected, it is not clear if these two sets of experiments are really consistent.

It appears that the problem does not lie in the activity of ilmenite because it is very close to 1.0 for the collated metapelitic ilmenite. It also appears that such a pressure difference is independent of either temperature, almandine in garnet, anorthite in plagioclase, or iron content in ilmenite. But, it is clear that the discrepancy between the two barometers becomes larger when calcium is low in garnet ($X_{Ca}^{grt} < 0.05$),

thus it may be anticipated that there are somewhat inherent errors in the garnet activity model(s) used in applying the GRIPS barometer for low-Ca garnet. However, such a conclusion can hardly be verified. Presumably, such errors in the garnet activity model(s) would also apply to the GASP calibration.

Perhaps the inconsistency between the GRIPS and GASP barometers at lower pressures can be ascribed to multiple reasons. However, it does not appear likely that the GRIPS experiments are metastable because such an explanation is quite spurious. Another possibility may be that there are inherent errors in extrapolating the experimental GRIPS reaction curve (10.6–14.4 kbar) to much lower pressures, and further experimental calibration of the GRIPS barometer at lower pressures is needed to resolve the matter.

It is reasonable that the GRIPS barometer is applied simultaneously combining the garnet-ilmenite thermometer in order to maintain thermodynamic consistency. The garnet-ilmenite Fe-Mn exchange geothermometer has been experimentally calibrated by Ono (1980), Docka (1984), Kress *et al.* (1985), Pownceby *et al.* (1987, 1991) and Feenstra & Engi (1998). Unfortunately, application of these garnet-ilmenite thermometers usually yields apparently erroneous temperature estimates, because the range of chemical compositions of most metapelitic ilmenite exceeds those involved in these experiments, i.e. natural metapelitic ilmenites are almost pure ilmenite and are not rich in Mn compared with the experimental ilmenite. Thus, the present garnet-ilmenite thermometer finds little use in metapelites, and temperature estimates are therefore based on the well-calibrated garnet-biotite thermometer. However, as the GRIPS barometer derived in this paper incorporates the same activity model of garnet involved in the thermobarometers, the thermodynamic consistency between the GRIPS barometer and the garnet-biotite thermometer has been maintained.

The most widely used GASP barometer in metapelites has a primary difficulty in that the metapelitic garnet is typically Ca-deficient. Relatively large errors accompany the analysis of minor components in addition to errors resulting from uncertainty in the activity of the grossular component in garnet at substantial dilution. As a consequence, GASP pressure values may have built-in systematic errors for low-Ca garnet and, similarly, metapelitic low-Ca plagioclase. Accordingly, the GRIPS barometer should not be applied to calcium-deficient garnet or plagioclase.

In many rocks, one or more of the phases, usually the titanium oxides, are present at levels of < 1 modal percent. In addition, ilmenite may have been oxidized during retrogression and/or weathering resulting in the formation of rutile or anatase (Bohlen & Liotta, 1986). Rutile has also been noted as a product of retrogression of titaniferous biotite. But such retrograde development of TiO_2 is usually recognized by textural examination.

Reliable pressure values can be obtained from rocks in which the ilmenite and rutile occur as inclusions in garnet as well as discrete grains in the matrix (Bohlen & Liotta, 1986). If the compositions of ilmenite and rutile within garnet grains and in the host-rock matrix are similar, equilibrium may be inferred. Zoned garnet containing inclusions of ilmenite and rutile throughout might possibly be used to elucidate a portion of the *P–T–t* path, assuming that the complete assemblage was at equilibrium during formation of the zonation in the garnet (Bohlen & Liotta, 1986).

It is well known that ion-exchange thermometers may suffer from post-peak cooling and re-exchange of ions such as the garnet-biotite Fe-Mg and garnet-ilmenite Fe-Mn exchange thermometers. On the other hand, most barometers are based on net transfer reactions which involve breaking of the silica tetrahedra, thus leading to generally significantly higher closure temperature than ion-exchange thermometers (e.g. Frost & Chacko, 1989). Sometimes, the ion re-exchange may continue after the net transfer reactions have ceased. This introduces an additional uncertainty into thermobarometry of granulites in that the temperatures at which barometers close are not known (Frost & Chacko, 1989). Such a phenomenon should be kept in mind when applying the garnet-biotite thermometer and the GRIPS barometer.

Amphibolite to granulite facies metapelites may still undergo post-peak retrograde net transfer reaction, i.e. the garnet rim may break down to other minerals (Kohn & Spear, 2000; Kohn *et al.*, 2001). This significantly affects the *P–T* computation and should be critically checked according to the X_{Mn} and Fe/(Fe + Mg) ratios of garnet zoning profile. Peak *P–T* conditions should be anticipated from garnet growth rim compositions paired with matrix mineral compositions at equilibrium.

CONCLUSIONS

After calibration, testing and application of the GRIPS barometer, it is found that this barometer may be used in cases of low- to high-grade, medium- to high-pressure metapelites. This barometer is especially useful when aluminosilicate is absent in the rocks, where the well-calibrated GASP barometer cannot be used. But, in cases where the GASP is applicable, the GRIPS barometer is not recommended because there still remains much more experimental work to be done. Furthermore, the application of the GRIPS barometer is not recommended to metapelites in which calcium is deficient in garnet ($X_{Ca}^{grt} < 0.05$) or plagioclase ($X_{Ca}^{pl} < 0.17$), or pressures below ~6 kbar.

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SUPPLEMENTARY MATERIAL

The authors have provided supplementary appendices to the paper, which are available from http://www.blackwell-synergy.com.

Fig. S1. The GASP pressures *v* pressure differences between GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S2. Temperatures *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S3. Almandine contents of garnet *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S4. Anorthite contents of plagioclase *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S5. Ferrous iron contents of ilmenite *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S6. Grossular contents of garnet *v* pressure differences between the GASP and GRIPS barometers of the metapelites listed in Tables S1–S4.

Fig. S7. Applications of the GASP and GRIPS barometers to metapelites within limited geographic areas and thermal contact aureoles.

Table S1. Application of the GASP and GRIPS barometers to aluminosilicate-bearing metapelites.

Table S2. The Ky-bearing metapelites within 500 m at the Hunt Valley Mall, north of Baltimore, Maryland, USA (Lang, 1991).

Table S3. Sillimanite-bearing metapelites from the mafic complex contact aureole, Ivrea Zone, northern Italy (Barboza & Bergantz, 2000).

Table S4. Sillimanite-bearing metapelites from the regional contact metamorphic zones in west-central Maine, USA (Holdaway *et al.*, 1988).