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CALIBRATION OF THE SGAM THERMOBAROMETER FOR PELITIC ROCKS USING DATA FROM PHASE-EQUILIBRIUM EXPERIMENTS AND NATURAL ASSEMBLAGES

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ABSTRACT

The assemblage quartz (S) - Garnet - Aluminosilicate - Mica (SGAM) is common in amphibolite-grade metapelitic rocks; yet the equilibrium Alm + Ms = Ann + 2 Al_2SiO_5 + Qtz is rarely used as a barometer because of difficulties relating primarily to the lack of experimental calibration. We present a calibration of the above equilibrium determined using linear programming analysis (LIP) of data from phase-equilibrium experiments and natural assemblages. Pressure and temperature of the natural assemblages were constrained independently by aluminosilicate polymorph occurrences, and by Grossular - Aluminosilicate - quartz (S) - Plagioclase (GASP) barometry and garnet-biotite thermometry. The calibration of the above equilibrium yields a slope almost identical to that of GASP. Application to several sets of published compositions shows that this calibration offers distinct improvements over previous calibrations. Pressures determined using the new calibration are consistent with the aluminosilicate polymorph present and with GASP barometry, where available. Also, some SGAM results show systematic spatial variations, suggestive of field gradients, which are not evident in the GASP results. Some differences between the two barometers probably reflect contrasting kinetics of the two systems.

Keywords: thermometry, barometry, biotite, garnet, muscovite, linear programming.

SOMMAIRE

L'assemblage quartz (S) - Grenat - Aluminosilicate - Mica (SGAM) est répandu dans les roches métapélitiques du facies amphibolite. Malgré ce fait, on se sert rarement de l'équilibre Alm + Ms = Ann + 2 Al_2SiO_5 + Qtz comme baromètre, surtout à cause du manque de calibrage expérimental. Nous présentons ici le calibrage requis, déterminé au moyen de programmation linéaire de données dérivées à la fois d'expériences sur les équilibres impliquant ces phases et d'observations sur les assemblages naturels. La pression et la température des assemblages naturels ont été contraintes indépendamment par la nature du polymorphe de Al_2SiO_5, et les résultats barométriques en utilisant l'assemblage Grossulaire - Aluminosilicate - quartz (S) - Plagioclase (GASP) et thermométriques fondés sur couples grenat - biotite. Le calibrage de l'équilibre cité donne une pente presqu'identique à celle du GASP. L'application du SGAM à plusieurs cas publiés montre que notre calibrage offre une nette amélioration par rapport aux calibrages antérieurs. La pression déduite au moyen du nouveau calibrage concorde avec la nature du polymorphe de Al_2SiO_5 et la barométrie selon le GASP, où disponible. De plus, certains des résultats obtenus avec l'équilibre SGAM montrent des variations spatiales systématiques, qui font penser à des gradients sur le terrain, et qui ne sont pas évidentes avec le GASP. Certaines des différences entre les deux baromètres résulteraient probablement des contrastes dans la cinétique des deux systèmes.

(Traduit par la Rédaction)

Mots-clés: thermométrie, barométrie, biotite, grenat, muscovite, programmation linéaire.

INTRODUCTION

There are two major barometers for pelitic rocks, GASP (Garnet - Aluminosilicate - quartz (S) - Plagioclase) and GRAIL (Garnet - Rutile - Aluminosilicate - Ilmenite - quartz), initially calibrated by Ghent (1976) and Bohlen *et al.* (1983), respectively. However, both have disadvantages. Metamorphic plagioclase is commonly complexly zoned and heterogeneous at the scale of a thin

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section, leading to uncertainty over which composition to take as representative of equilibrium. Thus GASP pressures for a single sample can be variable. GRAIL is not commonly used because small grain-size and small modal amounts of the Ti-bearing phases make potential candidates for GRAIL difficult to recognize in the field. Indeed, metamorphic assemblages with both ilmenite and rutile are not commonly reported. A third barometer, using the assemblage garnet - biotite - plagioclase - muscovite, was calibrated by Ghent & Stout (1981), and is less commonly used. It has the same disadvantage as the GASP barometer because of the use of plagioclase. For these reasons, we have investigated the system quartz (S) - Garnet - Aluminosilicate - Mica (hereafter referred to as SGAM) as a possible thermobarometer.

PREVIOUS CALIBRATIONS OF SGAM

SGAM, which involves the minerals quartz, garnet, aluminosilicate, muscovite, and biotite, shows promise as a thermobarometer. The three equilibria for the SGAM assemblage, written with the high-temperature assemblage on the right-hand side, are the two net-transfer reactions

$$\mathrm{Alm + Ms = Ann + 2\,Al_2SiO_5 + Qtz} \quad \text{(A)}$$

$$\mathrm{Phl + 2\,Al_2SiO_5 + Qtz = Prp + Ms} \quad \text{(B)}$$

and the garnet–biotite exchange reaction

$$\mathrm{Alm + Phl = Prp + Ann} \quad \text{(C)}$$

(see Table 1 for mineral abbreviations). Only two of these are linearly independent, and the position of the invariant point defined (Fig. 1) is dependent on mineral compositions.

SGAM, though a widespread assemblage, has not been calibrated experimentally. In spite of this, reaction A has been examined and used in thermobarometric studies in recent years. Thompson (1976a, b) deduced the relative stabilities of various assemblages but did not suggest a quantitative barometer. Tracy *et al.* (1976) and Tracy (1978) used equilibrium A qualitatively to make rough estimates of pressure (*e.g.*, 7 kbar). Fletcher & Greenwood (1979) calculated the position for equilibrium A using thermodynamic data principally from Helgeson *et al.* (1978) and Zen (1973). Although the pressures determined by Fletcher & Greenwood using SGAM were found to be consistent with those determined using other barometers, these authors were reluctant to place weight on the results because the thermodynamic data came from a variety of different sources. "Quantitative" barometers based on equilibrium A were derived by Robinson (1983), Hodges & Crowley (1985) and Holdaway *et al.* (1988). All used data from natural assemblages to derive a single expression for P in terms of T and the mineral compositions. Robinson's (1983) calibration (reported in an abstract) appears to be in error because all pressures calculated using this calibration fall approximately along a line in P–T space, and at temperatures below about 475°C the barometer yields negative pressures. The calibrations of Hodges & Crowley (1985) and Holdaway

TABLE 1. MINERAL NAMES, FORMULAS AND ABBREVIATIONS USED IN TEXT

Almandine	Alm	$\mathrm{Fe_3Al_2Si_3O_{12}}$
Andalusite	And	$\mathrm{Al_2SiO_5}$
Annite	Ann	$\mathrm{KFe_3AlSi_3O_{10}(OH)_2}$
Biotite	Bt	$\mathrm{(K,Na,Ba)_1(Fe,Mg,Ti,Al)_3Al(Si,Al)_3O_{10}(OH,F,Cl)_2}$
Enstatite	En	$\mathrm{MgSiO_3}$
Fayalite	Fa	$\mathrm{Fe_2SiO_4}$
Ferrosilite	Fs	$\mathrm{FeSiO_3}$
Forsterite	Fo	$\mathrm{Mg_2SiO_4}$
Grossular	Grs	$\mathrm{Ca_3Al_2Si_3O_{12}}$
Garnet	Grt	$\mathrm{(Fe,Mg,Ca,Mn)_3Al_2Si_3O_{12}}$
Kyanite	Ky	$\mathrm{Al_2SiO_5}$
Muscovite	Ms	$\mathrm{KAl_2AlSi_3O_{10}(OH)_2}$
Phlogopite	Phl	$\mathrm{KMg_3AlSi_3O_{10}(OH)_2}$
Pyrope	Prp	$\mathrm{Mg_3Al_2Si_3O_{12}}$
Quartz	Qtz	$\mathrm{SiO_2}$
Sillimanite	Sil	$\mathrm{Al_2SiO_5}$

Abbreviations are those suggested by Kretz (1983).

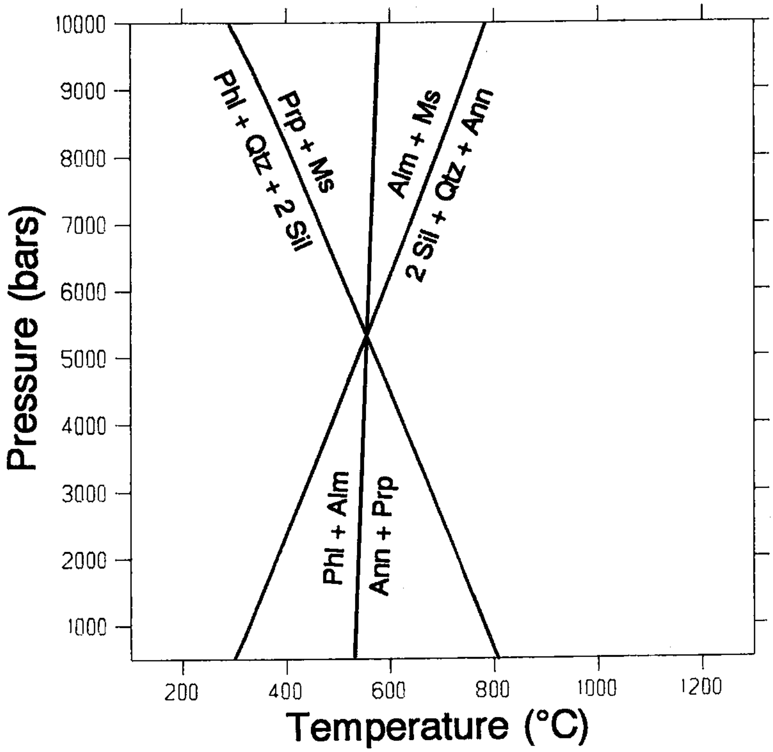

FIG. 1. SGAM equilibria considered in this study. Intersection defines P and T of equilibration of assemblage. See Table 1 for abbreviations.

et al. (1988) are compared later with the new calibration.

CALIBRATION METHODOLOGY

The positions of equilibria in P–T space, such as those in Figure 1, are calculated by evaluating the equation,

$$\Delta_r G^{P,T} = 0 = \sum_i^n \nu_i \left[\begin{array}{c} \Delta_f H_i^\circ - T \cdot S_i^\circ \\ + \int_{Tr}^{T} Cp_i \, dT - T \cdot \int_{Tr}^{T} \left(\frac{Cp_i}{T}\right) dT \\ + V_i^\circ (P - Pr) + \int_{Pr}^{P} (V_i - V_i^\circ) dP \end{array} \right] + R \cdot T \cdot \ln K \qquad (1)$$

where ν_i is the reaction coefficient for phase i and n is the number of phases (see Table 2 for other notation). Evaluation of equation 1 requires values for enthalpies of formation, third-law entropies, heat capacity terms, and expansivity and compressibility terms for all phases. These were taken from Berman (1988, 1990) for all phase components except annite, whose properties were determined in this study. For naturally occurring solid-solutions, one also requires activity models in order to evaluate the equilibrium constant, K.

For equilibrium A

$$K = \frac{a_{Ann}}{a_{Alm} \times a_{Ms}} \qquad (2)$$

where

$$a_{Ann} = a_{Ann}^{id} \cdot \gamma_{Ann}$$

$$a_{Alm} = a_{Alm}^{id} \cdot \gamma_{Alm}$$

$$a_{Ms} = a_{Ms}^{id} \cdot \gamma_{Ms}$$

assuming unit activities for quartz and aluminosilicate. The ideal (configurational) term for almandine, a_{alm}^{id} equals $(X_{Fe}^{Grt})^3$. The ideal terms for both micas (a_{Ann}^{id}, a_{Ms}^{id}) were evaluated using an algorithm and program described by McMullin (1990, in prep.). This formulation of ideal activity of micas produces only very slightly different pressures (less

TABLE 2. GLOSSARY OF NOTATION AND SYMBOLS USED IN TEXT

P, Pr	Pressure (bars, kilobars), Reference pressure (1 bar)
T, Tr	Temperature (K, °C), Reference temperature (298.15 K)
$\Delta G_i^{P,T}$	Gibbs free energy of formation of phase i from the elements at P and T
$\Delta_r G^{P,T}$	Gibbs free energy of reaction at P and T
$\Delta H_i^{P,T}$	Apparent enthalpy of formation of phase i from the elements at P and T (kJ/mol)
$\Delta_f H_i^\circ$	Enthalpy of formation of pure phase i from the elements (kJ/mol)
$\Delta_r H_i^{P,T}$	Enthalpy of reaction at P and T
$S_i^{P,T}$	Entropy of pure phase i at P and T (J/mol/K)
S_i°	Third-law entropy of pure phase i (J/mol/K)
$\Delta_r S^{P,T}$	Entropy of reaction at P and T
V_i°	Molar volume of pure phase i (J/bar)
Cp_i	Heat capacity of pure phase i
$\Delta_r V^{P,T}$	Volume of reaction at P and T
W_{H12}, W_{S12}, W_{V12}	Margules parameters for excess enthalpy (kJ/mol), entropy (J/mol/K), and volume (J/bar)
a_i^{id}	Ideal activity of component i
γ_i	Activity coefficient of component i
a_i	Activity of phase $i = a_i^{id} \cdot \gamma_i$
X_e^i	Mole fraction of element e in phase i
K	Equilibrium constant
K_D	Distribution coefficient
R	Gas constant

than 200 bars) compared with the following formulations:

$$a_{Ann}^{id} = X_K^{Bt} \cdot (X_{Fe}^{Bt})^3 \cdot (X_{OH}^{Bt})^2$$

$$a_{Ms}^{id} = X_K^{Ms} \cdot (X_{Al}^{Ms})^2 \cdot (X_{OH}^{Ms})^2$$

where

$$X_K^{Bt} = \frac{K}{K+Na+Ba+Ca}$$

$$X_{Fe}^{Bt} = \frac{Fe}{Fe+Mg+Al+Ti+Mn}$$

$$X_{OH}^{Bt} = \frac{OH}{OH+F+Cl}$$

$$X_K^{Ms} = \frac{K}{K+Na}$$

$$X_{Al}^{Ms} = \frac{Al}{Al+Fe+Mg+Ti+Mn}$$

and

$$X_{OH}^{Ms} = \frac{OH}{OH+F+Cl} .$$

Calculated temperatures are the same for both formulations. The activity coefficients (γ) are described by Margules parameters. Activity models for garnet and muscovite were taken from Berman (1990) and Chatterjee & Froese (1975), respectively. In using the Chatterjee & Froese model, we assume that NaK_{-1} is the only substitution of importance in muscovite. The muscovite-bearing assemblages used by us contain muscovite with a mole fraction of Al in the octahedral sites of greater than 0.93. Application of the SGAM calibration derived here to assemblages with muscovite with a significantly lower content of octahedrally coordinated Al may result in errors in calculated pressure.

In the evaluation of nonideality in biotite, there are several types of substitution to consider. K, Na, Ca and Ba occur on the XII-fold or "A" site; Fe, Mg, Ti, Al, and Mn occupy octahedrally coordinated sites, and OH, F, and Cl are found in the hydroxyl site. In biotite, the "A" site is predominantly filled by K (>0.9 ions per unit formula). Although muscovite shows considerable nonideality in Na–K mixing on the "A" site, Na–K nonideality in biotite is considered to be negligible, as biotite rarely contains more than 0.05 Na ions per formula unit (Guidotti 1984). In metamorphic biotite, the substitution of F and Cl for OH is dependent on the complex interplay of several factors, most notably the halogen content of the bulk rock, the Mg/(Mg + Fe) ratio, and metamorphic grade (Guidotti 1984). A clearer understanding of the role of halogens in the hydroxyl site is hampered by limited data (Guidotti 1984), but it appears that, in most examples of metamorphic biotite, F and Cl typically constitute less than 0.10 ions per formula unit (2 sites). Therefore, nonideal mixing on this site has been ignored.

Octahedrally coordinated sites in biotite contain Fe, Mg, Al, Ti, with Mn typically present in negligible amounts (<0.01 atoms per 3 sites: Guidotti 1984). A significant problem in calculating the position of SGAM equilibria is that effects of nonideal mixing involving these cations in biotite are largely unknown. Indares & Martignole (1985) estimated solution parameters of biotite using the Fe–Mg exchange equilibrium between garnet and biotite (equilibrium C) and compositional data from natural assemblages. However, because it is an exchange reaction, they could only determine the differences between the Fe and Mg Margules parameters (*i.e.*, MgTi - FeTi and MgAl - FeAl). In our calibration of SGAM, we initially considered all interactions among the octahedrally coordinated cations Fe, Mg, Al, and Ti. As it became clear that the data discussed below were insufficiently constraining for the purpose of deriving a unique estimate of each solution parameter, we set the Ti–Al interaction to zero. In addition, the Fe–Mg interaction was assumed to be zero on the basis of the observed negligible excess volume of mixing between the Fe and Mg end-members (Hewitt & Wones 1984).

We have not considered the ferric iron content of biotite in this study. Guidotti & Dyar (1991) found that biotite in the presence of graphite generally has about 4% of the total iron as octahedrally coordinated Fe^{3+}, with 8 ± 3% tetrahedrally coordinated Fe^{3+} irrespective of the assemblage and grade. All the data used here to refine the solution properties of biotite are from low $f(O_2)$ environments. The experiments of Ferry & Spear (1978) were done using the graphite–methane buffer, and all the natural assemblages used here, with the possible exception of some of the assemblages of Indares & Martignole (1985), contain graphite. The experiments of LeBreton & Thompson (1988) were carried out in the absence of water and could not rely on conventional oxygen buffers. However, LeBreton & Thompson noted that their high-pressure assemblage probably resulted in high $f(H_2)$, and thus the ferric iron content of their biotite probably is low.

Therefore, in our calibration the adjustable parameters were the enthalpy of annite and the Margules parameters W^{Bt}_{13} (MgTi), W^{Bt}_{14} (MgAl), W^{Bt}_{23} (FeTi), and W^{Bt}_{24} (FeAl). In fitting for these parameters, we used the method of linear programming (LIP), which was first introduced to the petrological literature by Greenwood (1967, 1968) and used to derive thermodynamic properties by Gordon (1973, 1977). Techniques of linear and nonlinear programming (collectively, mathematical programming) have been used extensively since then by a number of investigators to calibrate thermodynamic properties from phase-equilibrium data (*e.g.*, Day & Halbach 1979, Day & Kumin 1980, Halbach & Chatterjee 1982, Berman & Brown 1984, Berman *et al.* 1986, Berman 1988, 1990). An assessment of the techniques of linear and nonlinear programming, and of their advantages and disadvantages, is beyond the scope of this paper and is discussed extensively by the authors above, particularly by Berman *et al.* (1986). It should be emphasized that what we present below is an empirical fit to the data considered (Table 3). Thus all errors, such as analytical errors and those relating to the choices of solution models for other phases, are incorporated into the biotite parameters derived here.

DATA SOURCES

Two kinds of data are considered here. First, there are thermodynamic data, including standard-state properties, heat capacities, expansivity and compressibility values and solution parameters. The enthalpy of formation of annite determined in this study and the enthalpies, entropies, and molar volumes for all other phases involved in SGAM are given in Table 4. The heat capacity terms and thermal expansivity and compressibility terms for all phase components in the LIP analysis were taken from Berman (1988, 1990). Solution parameters for muscovite are from Chatterjee & Froese (1975), those for garnet from Berman (1990), and both sets are given, along with the empirical solution-parameters for biotite determined during this study, in Table 5.

The $S°$ of annite was calculated as 421.01 J/mol/K using the exchange reaction

$$\mathrm{Phl} + 3\ \mathrm{FeO} = \mathrm{Ann} + 3\ \mathrm{MgO}, \qquad \text{(D)}$$

the entropies of phlogopite and periclase taken from Berman (1990) and (1988), respectively, and

TABLE 3. PHASE-EQUILIBRIUM DATA (EXPERIMENTS AND NATURAL ASSEMBLAGES) USED TO DERIVE ENTHALPY OF ANNITE AND SOLUTION PARAMETERS OF BIOTITE

Equilibrium	Ref*	Parameters constrained§	Uncertainties for LIP (see text)
Phl + Alm = Ann + Prp	1	$\Delta_f H_{Ann}{}^\circ$	6°C, 0.01 X_{Ann}
	2†	$W^{Bt}_{13} - W^{Bt}_{23}$, $W^{Bt}_{14} - W^{Bt}_{24}$	30°C
	3†	"	30°C
	4†	"	(see text)
	5†	"	50°C
	6‡	"	30°C
Alm + Ms = Ann + 2 Sil + Qtz	2†	W^{Bt}_{13}, W^{Bt}_{14}, W^{Bt}_{23}, W^{Bt}_{24}	0.5 kbar, 30°C
	3†	"	0.5 kbar, 30°C
Alm + Ms = Ann + 2 Ky + Qtz	2†	"	0.5 kbar, 30°C
Alm + Ms = Ann + 2 And + Qtz	4†	"	0.5 kbar, 30°C

* Refs: (1) Ferry & Spear (1978), (2) Pigage (1982), (3) Holdaway *et al.* (1988), (4) Ferry (1980), (5) Indares & Martignole, (6) LeBreton & Thompson (1988).

§ Component order for Bt: 1 = Mg, 2 = Fe, 3 = Ti, 4 = Al. Notation of Berman & Brown (1984).

† Data from natural assemblages.

‡ Experiments with natural minerals.

the entropy of FeO, from Helgeson *et al.* (1978). The value for the contribution of the electronic configuration and crystal-field stabilization (Helgeson *et al.* 1978, p. 51) was determined to be 4.7 J/cation by averaging the values for the two exchange equilibria

$$\mathrm{Fo} + 2\,\mathrm{FeO} = \mathrm{Fa} + 2\,\mathrm{MgO} \tag{E}$$

$$\mathrm{En} + \mathrm{FeO} = \mathrm{Fs} + \mathrm{MgO} \tag{F}$$

(entropies of Fo, Fa, En, and Fs from Berman 1988). The molar volume of annite was set at 15.483 J/bar (from Hewitt & Wones 1984).

P–T–X data derived from phase-equilibrium experiments and from natural assemblages also are considered in this study, and used as constraints on the fit parameters. Phase-equilibrium data on four equilibria from six sources (Table 3) were used to determine the enthalpy of annite, and the solution properties of biotite. One study of the garnet–biotite equilibrium (C), notable by its absence from Table 3, is that of Perchuk & Lavrent'eva (1983). This data-set was considered in the early phase of this study because Perchuk & Lavrent'eva used garnet and biotite of natural composition. However, we found several problems with these data. First, we were unable to ascertain the starting compositions used in their experiments. Second, the run products were found to be extremely heterogeneous (particularly garnet), making it extremely difficult to determine which compositions were in equilibrium. Third, as the compositions of the run products are listed only as Mg-numbers, the data cannot be used as constraints on Ti and Al solution parameters.

TABLE 4. ENTHALPIES, ENTROPIES AND VOLUMES

Mineral	ΔH_f° (kJ/mol)	S° (J/mol/K)	V° (J/bar)
Alm	−5267.216‡	340.007‡	11.511
And	−2589.972	91.434	5.147
Ann	−5142.0*	421.01†	15.483§
Ky	−2594.22	82.430	4.412
Ms	−5976.74	293.157	14.087
Phl	−6210.391‡	334.346‡	14.977‡
Prp	−6286.548	266.359	11.316
aQtz	−910.7	41.46	2.269
Sil	−2586.091	95.93	4.983

* Value fit by LIP in this study. † Calculated using equilibrium D (see text). § From Hewitt & Wones (1984). ‡ From Berman (1990). All other values from Berman (1988).

TABLE 5. SOLUTION (MARGULES) PARAMETERS

Biotite:*

ij	W_{Hij} (kJ/mol)	W_{Sij} (J/mol/K)	W_{Vij} (J/bar)
13	58.865		
14	75.0		
23	30.921		
24	63.721		

Component order: 1 = Mg, 2 = Fe, 3 = Ti, 4 = Al.

Garnet:†

ijk	W_{Hijk} (kJ/mol)	W_{Sijk} (J/mol/K)	W_{Vijk}(J/bar)
112	21.56	18.79	0.1
122	69.2	18.79	0.1
113	20.32	5.08	0.17
133	2.62	5.08	0.09
223	0.23	0.0	0.01
233	3.72	0.0	0.06
123	58.825	23.87	0.265
124	45.424	18.79	0.1
134	11.47	5.08	0.13
234	1.975	0.0	0.035

Component order: 1 = Ca, 2 = Mg, 3 = Fe, 4 = Mn.

Muscovite:§

ijk	W_{Hijk} (kJ/mol)	W_{Sijk} (J/mol/K)	W_{Vijk} (J/bar)
112	12.23	−0.7104	-0.6653
122	19.456	−1.6543	−0.4561

Component order: 1 = K, 2 = Na.

* Values fit during this study. † Solution model of Berman (1990). § Solution model of Chatterjee & Froese (1975). Component order notation of Berman & Brown (1984).

Treatment of experimental data

For reversed experimental data, the P and T quoted for any experiment is determined to lie on one side or the other of the equilibrium studied, giving rise to an inequality in the sign of the free energy of reaction (equation 1). Given this information, it is desirable to use, in the LIP analysis, values of P and T for an experiment that have been adjusted to take account of the experimental uncertainties. The uncertainties for LIP analysis, listed in column 4 of Table 3, were utilized to adjust the nominal P, T, and composition for the experiment so as to move the P–T–X constraint away from the equilibrium position. For example, for an equilibrium with positive slope and phase i as a reactant, the nominal pressure for a "reactants stable" experiment was increased, the nominal temperature was decreased, and X_i was decreased (if i is a product, then X_i was increased). For a "product stable" experiment, P is decreased, T is increased and X_i in increased (see Fig. 2). In

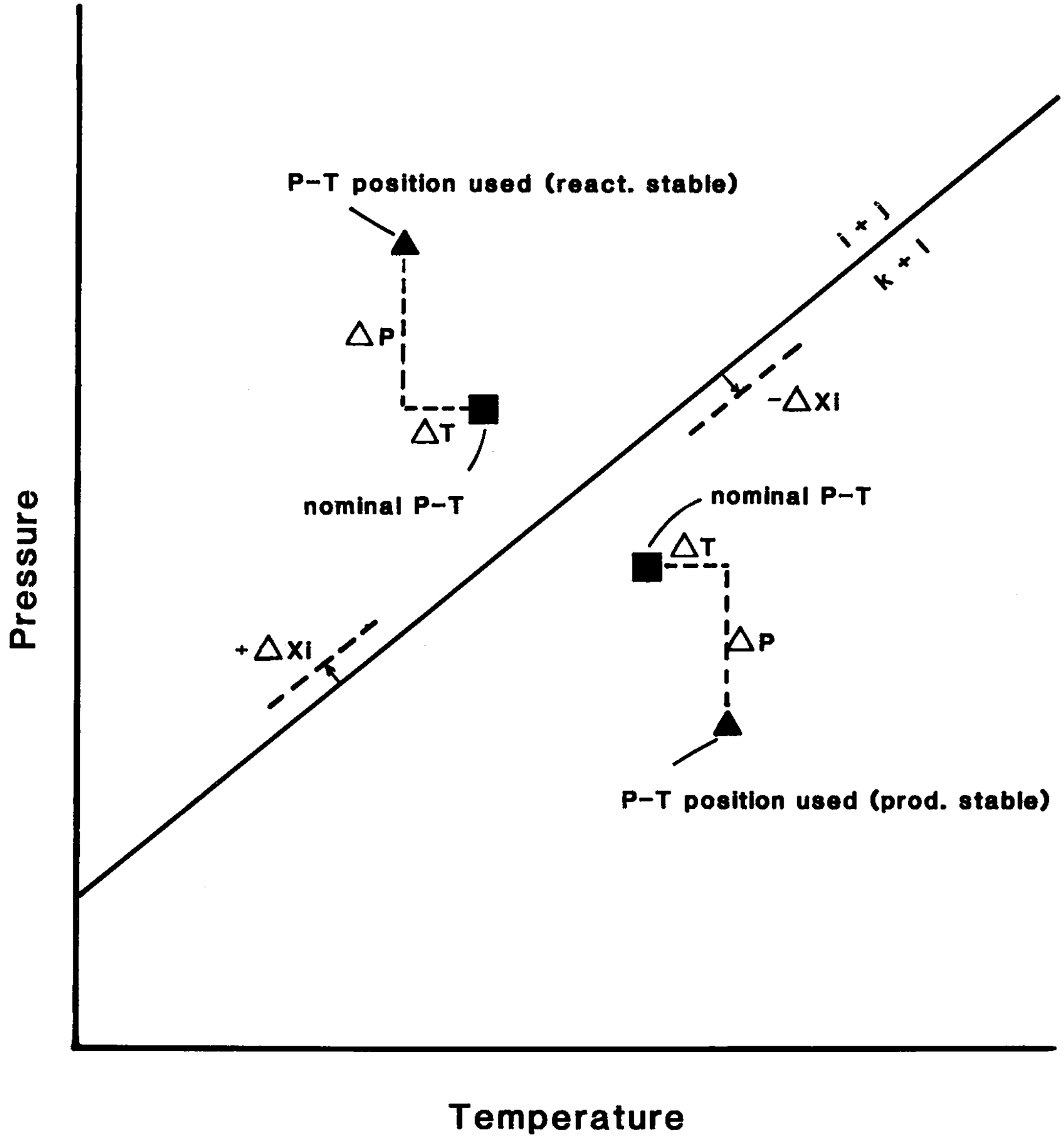

FIG. 2. Adjusted experimental brackets for LIP analysis of data for a reaction with positive slope and phase component i as reactant.

all cases, these adjustments render the constraint provided by the experiment less stringent.

The temperature uncertainties listed for the data of Ferry & Spear (1978) are those quoted by them. Two of their biotite compositions were adjusted to include 0.06 mole fraction Al. This is the amount suggested by Ferry & Spear to account for slight excess volume in the synthetic pure annite used as starting material for these two experiments. The experiments of LeBreton & Thompson (1988) were melting experiments on assemblages of natural minerals, not phase-equilibrium reversals. Therefore, these experiments were treated as equilibrated natural assemblages (see below).

Treatment of data on natural assemblages

Although the type of information conveyed by data on natural assemblages is different from that of phase-equilibrium experiments (Berman *et al.* 1986), we treated the two types of data simultaneously in the LIP analysis. This was done by constructing "brackets" for the natural data that are identical in algebraic structure to brackets from experimental data (Fig. 3A). Accordingly, each rock gives rise to one "bracket" centered around the estimated *P–T* conditions for that rock, with the bracket width reflecting the level of confidence in the estimates of *P*, *T*, and analytical error. All calculations of *P–T* conditions were made using the PTAX software, part of the GEØ-CALC package (Berman *et al.* 1987, Brown *et al.* 1988). Initial estimates of temperature of equilibration of each assemblage were based on garnet–biotite thermometry, and pressure estimates were based on aluminosilicate polymorph occurrence or on GASP barometry, with most weight given to rocks with coexisting aluminosilicate polymorphs. The *P–T* estimates are based on standard-state properties and solution parameters of garnet from Berman (1988, 1990). As an initial estimate, we used values for the solution properties of biotite midway between ideal (zero) and those formulated by Indares & Martignole (1985). We used the plagioclase solution model of Fuhrman & Lindsley (1988) for the activity of anorthite in the GASP equilibrium. Once a *P* and *T* of equilibration had been determined, it was assumed that the reactants and products were stable at *P–T* points an arbitrary ΔP and ΔT removed from the preliminary *P–T* estimates (Fig. 3A). For samples containing one ASK polymorph (andalusite, sillimanite, kyanite) in which the initial *P–T* estimate from garnet–biotite and GASP lay close to one of the ASK boundaries (*i.e.*, an isograd), that boundary was taken as one limit of the adjustment offset, whereas the other limit was set by a judgement of the uncertainty in the *P–T* estimate (Fig. 3B). As with experimental data, the ΔP and ΔT offsets were applied so as to make the data point less constraining on the final parameters than the nominal *P* and *T*. Using this process rocks containing two aluminosilicate polymorphs are the most constraining. Rocks containing a single polymorph but with *P–T* estimates close to a polymorph boundary (isograd) are less constraining. Rocks for which only GASP barometry was available are the least constraining.

The LIP uncertainties for natural assemblages given in Table 3 are the values used in the calibration. In the initial stages of refinement, larger uncertainties, incorporating the range of conditions calculated using both ideal solution models and those of Indares & Martignole (1985), were used to ensure that initial estimates would not exert excessive influence on the final results. We have not indicated uncertainties in *P* for equilibrium C in Table 3 as varying the size of the uncertainty in *P* for this extremely steep reaction has negligible effect on the fit parameters. The data of LeBreton & Thompson (1988) are from melting experiments on natural minerals, not reversals. Thus these data were treated in the same way as the natural assemblages, in that each experiment provided two half-brackets. The run products of LeBreton & Thompson were somewhat inhomogeneous, probably owing to the large grain-size of the garnet used as starting material (LeBreton & Thompson 1988, p. 229). However, there is no estimate of the extent of inhomogeneity. In the absence of specific data on the degree of heterogeneity, we used larger uncertainties in temperature than those quoted by LeBreton and Thompson (1988). Indares & Martignole (1985) quoted composition ranges rather than single analyses, and these ranges are incorporated as uncertainties in composition for these data.

RESULTS

The goal of the LIP analysis was to produce a solution in which (1) experimental data were fit within their uncertainties (Table 3), (2) the natural data were fit within the narrowest brackets possible while maintaining consistency within the entire data-set, and (3) absolute values of the derived Margules parameters were as small as possible. The third point was necessary because it was found that the data were not sufficiently constraining to determine unique values for each of the Margules parameters. The parameters so determined thus do not yield a valid representation of the mixing properties of biotite. They do, however, provide a reasonable calibration of the SGAM equilibria,

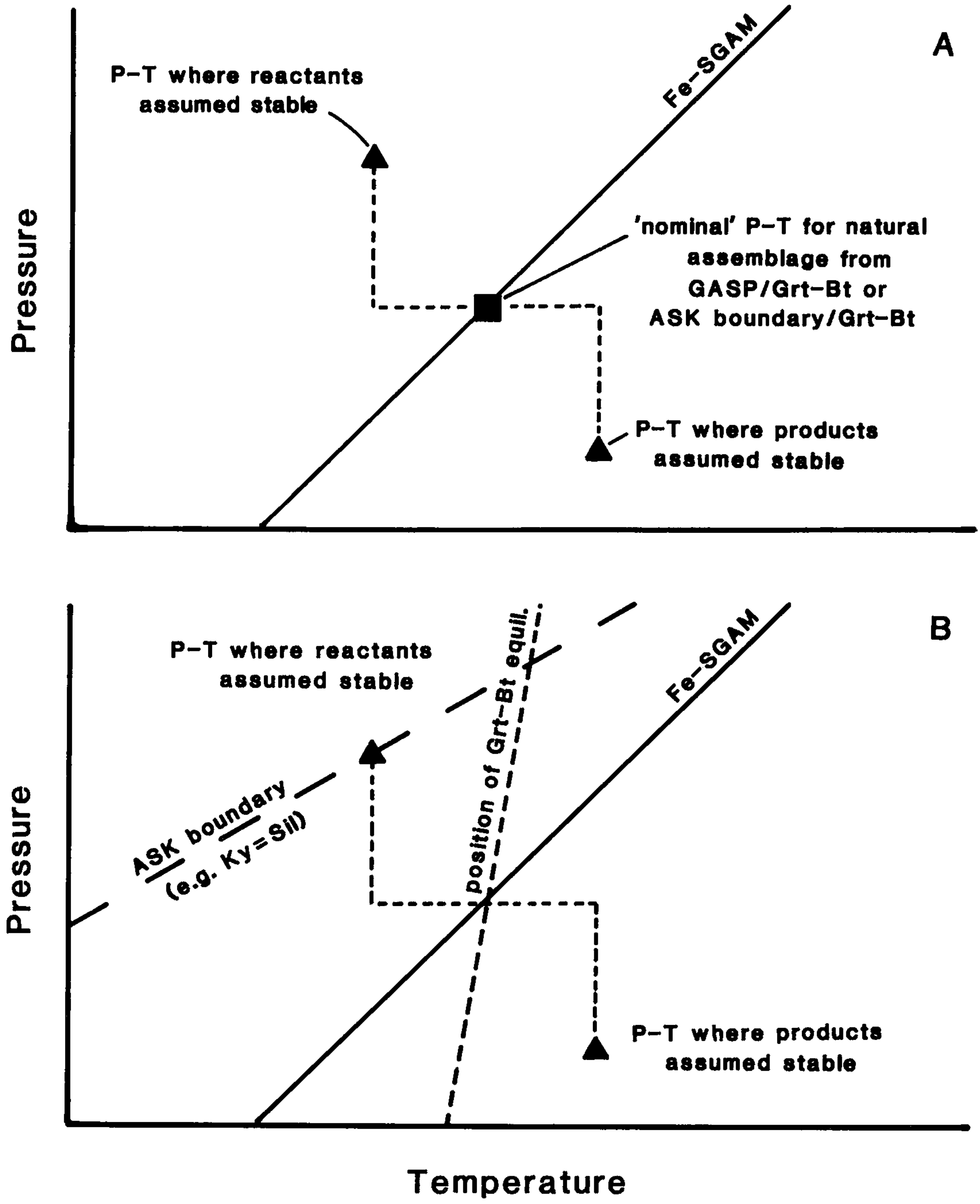

FIG. 3. A. *P–T* "brackets" used for natural assemblages where nominal *P–T* defined by GASP - Grt-Bt (one ASK polymorph), or where nominal *P–T* defined by ASK boundary (two or more Al_2SiO_5 polymorphs) and Grt-Bt thermometer. B. "Brackets" defined for assemblages with one ASK polymorph (*e.g.*, Sil), but that give a GASP - Grt-Bt *P–T* close to an Al_2SiO_5 polymorphic transformation (*e.g.*, Ky-Sil).

representing (within uncertainties) the natural and experimental phase-equilibrium data with the following exceptions.

1. Two of the three samples of Pigage (1982), which contain sillimanite only, fall within the kyanite field close to the kyanite–sillimanite boundary (<20°C).
2. One of the andalusite-bearing samples of Ferry (1980) plots in the sillimanite field by about 30°C.

The final set of fit-parameters (standard-state values and solution parameters) are given in Tables 4 and 5.

APPLICATION

The utility of the new calibration can be tested against independent published calibrations to determine whether it offers any improvement in

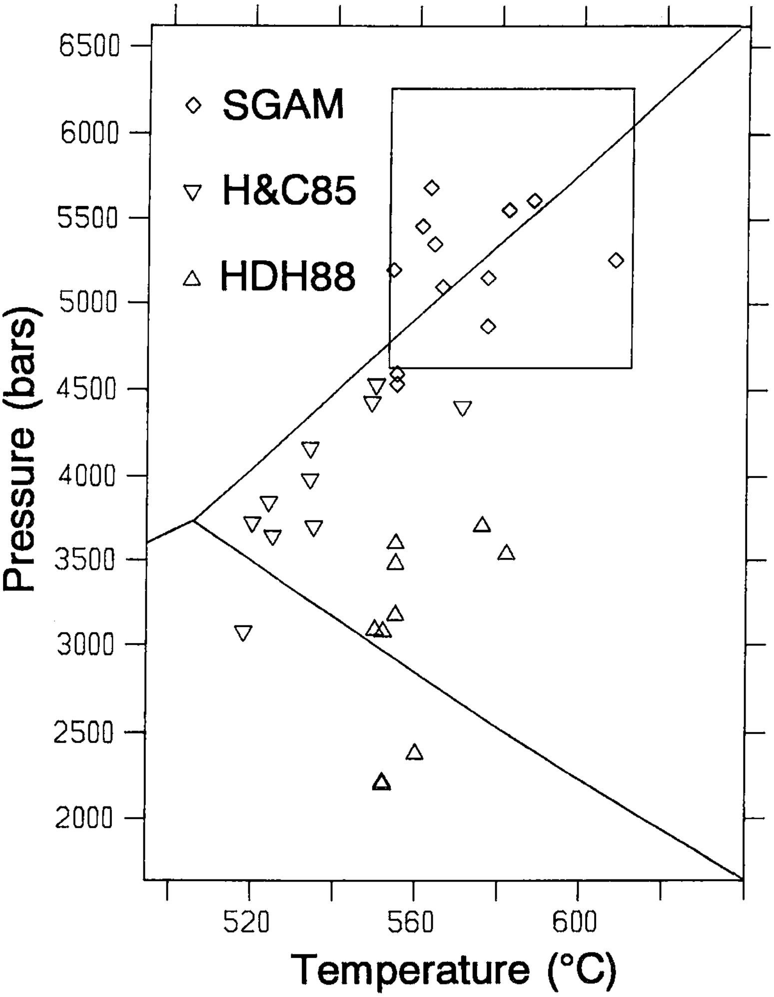

FIG. 4. Pressures and temperatures determined for data of Pigage (1982) using three different calibrations. Values are tabulated in Table 6. The box in the center of the diagram shows the P–T range defined by GASP for the same samples. Note that the new calibration (diamonds) is consistent with GASP. Also shown are the P and T values determined using the calibrations of Holdaway *et al.* (1988) (upright triangles) and Hodges & Crowley (1985) (inverted triangles). These last two calibrations both give pressures that are judged to be too low, because the Pigage samples come from an area that straddles the Ky–Sil isograd.

precision, consistency, and ability to perform well where applied to minerals having compositions different from those used to calibrate the model. An "improved calibration" should not only produce good results for data that older models could not handle; it should also deal well with data that were previously handled satisfactorily. In the following paragraphs, it is shown that these tests are well met by the new calibration.

Pressures and temperatures have been calculated for the sample compositions given by Pigage (1982) and are shown on Figure 4 and tabulated in Table 6. The new calibration of the SGAM barometer yields pressures and temperatures consistent with the field assemblages, particularly the Ky–Sil isograd crossing Pigage's area (Fig. 5). However, the calibrations of Holdaway *et al.* (1988) and Hodges & Crowley (1985) yield pressures that are too low. The difference between the new calibration and that of Holdaway *et al.* (1988) results from the fact that the garnet grains analyzed by Pigage (1982) have a quarter of the Mn content of those used by Holdaway *et al.* (1988) in their calibration. Hodges & Crowley (1985) were very careful to note that their calibration is enormously imprecise (on the order of 10 kbar) owing to the nature of the data used in their calibration.

Figure 5 shows the areal distribution of pressures calculated from the data of Pigage (1982). With some scatter within the bounds of that expected to arise from analytical error alone (250 bars at the 2σ level), SGAM pressures increase from north to south. This areal distribution of pressures could represent a field gradient of appropriate magnitude

TABLE 6. PRESSURES (BARS) AND TEMPERATURES (°C) CALCULATED FOR DATA OF PIGAGE (1982) AND HODGES & SPEAR (1982) USING SGAM AND GASP/GARNET-BIOTITE

	SGAM						GASP	
	This study*		H&C(1985)†		HDH(1988)‡		This study*	
Sample #	P	T	P	T	P	T	P	T
Pigage (1982)								
373	4864	577	-	-	-	-	5999	583
121	5094	566	-	-	-	-	4794	565
367	5149	577	3631	525	2395	560	6078	581
82	5196	554	3710	520	3103	550	5053	553
398	4591	555	3687	535	3092	552	4725	555
492	5455	561	3968	534	3494	555	4805	557
223	5350	564	3834	524	3191	555	4730	560
2-376	5615	588	4416	549	3551	582	6260	592
2-13	4532	555	3062	518	2212	552	5062	558
74	5257	608	4390	571	2225	552	6213	612
59	5555	582	4517	550	3717	576	5666	582
40	5693	563	4153	534	3631	555	4624	558
Hodges & Spear (1982)								
HS-78b	3716	477	1845	466	1863	480	4453	481
HS-80d	3769	525	2098	495	1551	520	3874	525
HS-90a	3770	498	2123	486	1996	496	4426	501
HS-92d	3985	501	2275	491	2123	502	4558	504
HS-145e	3170	505	1836	501	1434	511	4301	511
HS-146d	3565	480	1736	466	1593	469	2524	475

* Calculated using models given in text.

† Calculated using calibration of Hodges & Crowley (1985).

‡ Calculated using calibration of Holdaway *et al.* (1988).

GASP/garnet-biotite conditions calculated using the plagioclase solution model of Fuhrman & Lindsley (1988), the garnet model of Berman (1990), and the biotite model from this study.

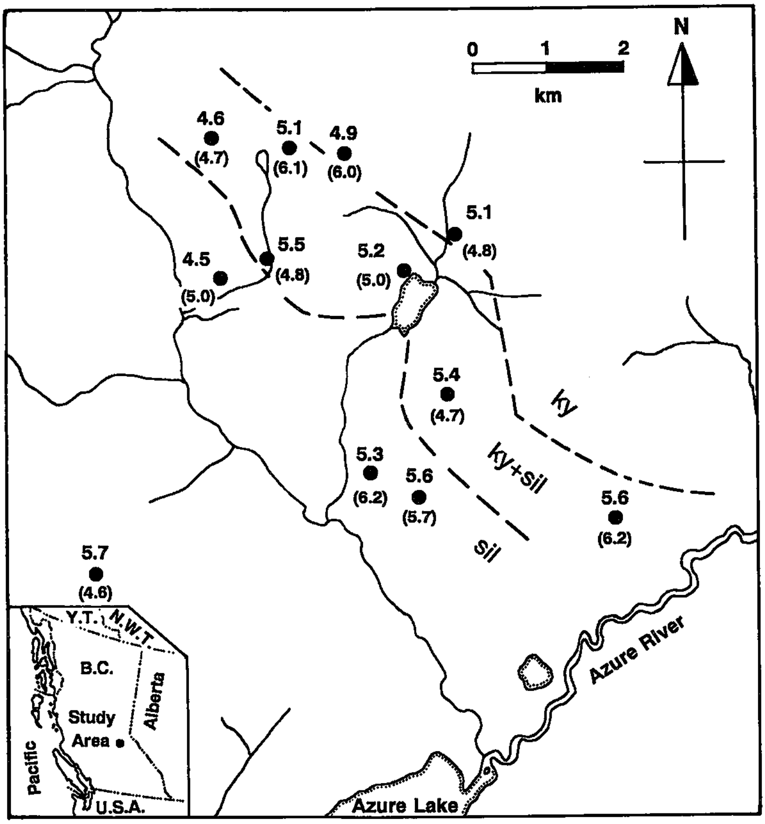

FIG. 5. Map from Pigage (1982) showing the distribution of SGAM pressures calculated with the calibration of SGAM presented here. Values in parentheses are GASP pressures for the same samples. Dashed lines show boundaries (isograds and minor faults) between Ky, Ky + Sil, and Sil zones.

consistent with the observed isograds (Fig. 5). In contrast, GASP pressures do not show any consistent spatial variations (Fig. 5).

Figure 6 shows the pressures and temperatures calculated for the data of Holdaway *et al.* (1988). The data are tabulated in Table 7. The central box in Figure 6 shows the P–T range defined by GASP barometry and garnet-biotite thermometry. The new calibration is required to be consistent with this range by virtue of its inclusion in the LIP analysis. Generally, all three calibrations give the same pressures and temperatures. However, the new calibration gives a slightly narrower range of pressure for the samples than do the two older calibrations. The Holdaway *et al.* (1988) calibration gives slightly higher temperatures because they incorporate nonideality in Mn solution in garnet (Ganguly & Saxena 1984, 1985); in this area the garnet is quite Mn-rich (13–22% Sps). The wide spread of the P–T data represents a field gradient in P (and T?) for the area (Holdaway *et al.* 1988). The difference between the Holdaway *et al.* calibration and the GASP and garnet-biotite box arises from the fact that Holdaway *et al.* used staurolite-breakdown criteria and field evidence to estimate an average P for the area of 3.1 kbar, on which they calibrated the barometer.

The areal distribution of the pressures determined for the Holdaway *et al.* (1988) data is complicated, but is similar to that given by Holdaway *et al.* In general, the pressures increase from northeast to southwest. There are some irregularities that probably result from later plutonism or postmetamorphic folding, as shown by the presence of folded isograds (Holdaway *et al.* 1988).

Figure 7 shows the pressures and temperatures calculated using the data of Hodges & Spear (1982). The data are tabulated in Table 6. This data-set was not part of the LIP analysis. The central box

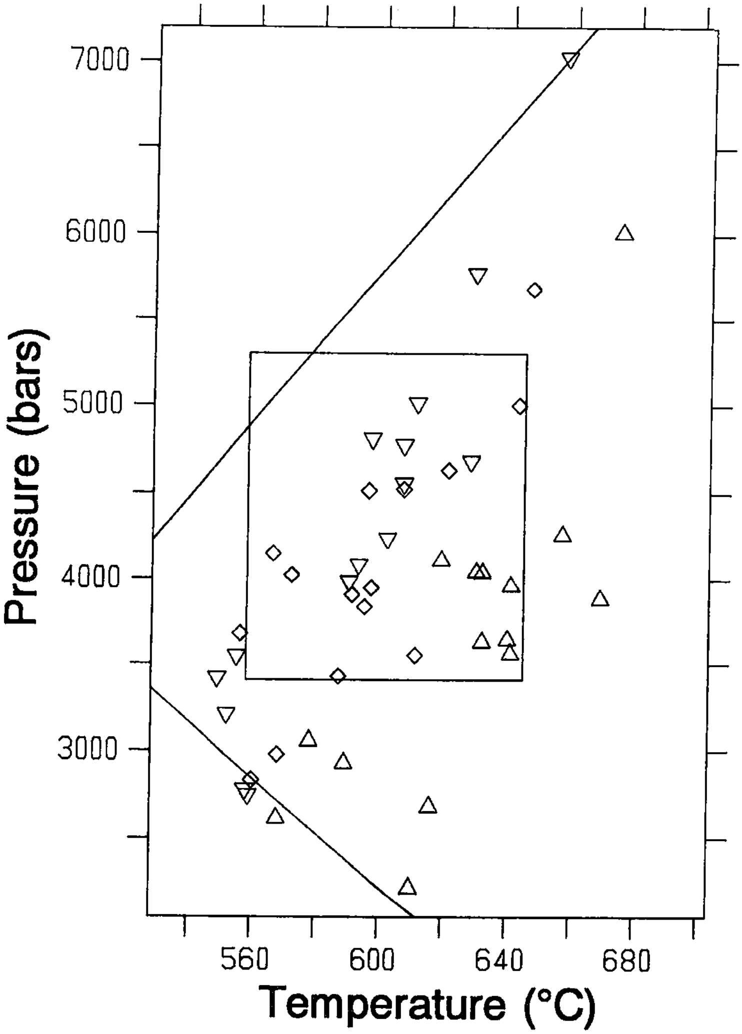

FIG. 6. Pressures and temperatures for the data of Holdaway *et al.* (1988). The box represents the *P–T* range for the samples using GASP and garnet – biotite thermometry. The new calibration of the SGAM barometer (diamonds) is consistent with this *P–T* range. The calibrations of Holdaway *et al.* (1988) (upright triangles) and Hodges & Crowley (1985) (inverted triangles) are in the same range, with slightly more scatter.

is again the *P–T* range defined using GASP barometry and garnet–biotite thermometry. It is clear that only the new calibration is consistent with these values of *P* and *T*. The new calibration is also consistent with the field observations of all three aluminosilicate polymorphs in the area. The other two calibrations yield pressures that are too low.

The areal distribution of the pressures calculated using the data of Hodges & Spear (1982) shows an increase in pressure from east to west (Fig. 8). Calculated GASP pressures do not show this gradient (Fig. 8). The aluminosilicate bathograd drawn by Hodges & Spear is based on the absence of andalusite and is thus only a crude estimate of an isobar. Nevertheless, the SGAM pressures increase in the appropriate sense across the bathograd, within the precision of the calibration. As noted above, these data were not used in the

TABLE 7. PRESSURES (BARS) AND TEMPERATURES (°C) CALCULATED FOR DATA OF HOLDAWAY *ET AL.* (1988) USING SGAM AND GASP/GARNET-BIOTITE

	SGAM						GASP	
	This study*		H&C(1985)†		HDH(1988)‡		This study*	
Sample #	P	T	P	T	P	T	P	T
4a	4024	572	3532	555	2631	568	5211	578
47	4151	566	3406	549	3071	578	4099	566
19	3675	556	3194	552	2944	589	4012	558
63	2977	568	2763	558	2232	610	3885	573
30	2832	560	2735	559	2699	616	3409	563
8	4631	621	4998	611	4056	632	4634	621
140	3908	591	3973	590	3643	632	4719	595
77-3	4514	596	4793	597	4129	619	4496	596
77-2	4522	607	4759	607	4058	630	4693	608
76	3948	597	4540	607	3976	641	3647	596
56	3837	595	4073	593	3575	641	3799	595
91	3550	611	4669	628	3900	669	4799	617
73	3431	587	4225	602	3655	640	3663	588
87	4998	643	5755	629	4274	657	4206	639
86	5676	647	7013	657	6026	675	5299	645

* Calculated using models as given in text.

† Calculated using the calibration of Hodges & Crowley (1985).

‡ Calculated using the calibration of Holdaway *et al.* (1988).

GASP/garnet-biotite conditions calculated using the plagioclase solution model of Fuhrman & Lindsley (1988), the garnet model of Berman (1990), and the biotite model from this study.

LIP analysis, and thus the results here indicate that the pressures calculated with the new calibration seem to be both accurate and precise.

Temperatures for the above data-sets do not show gradients, which may reflect the poorer precision of the garnet-biotite thermometer. For garnet compositions common to pelitic rocks, temperature precision is rarely better than ±30°C. Thus the garnet-biotite thermometer demonstrates quantitative gradients in temperature only in areas of high thermal gradient (aureoles) or over large areas. The data of Raeside *et al.* (1988), from a thermal aureole, and the data of Chipera & Perkins (1988), for a large area showing pronounced change in grade, are suitable for examinations. The new parameters give almost identical temperatures to the calibration preferred by Raeside *et al.* (1988) on the basis of the field assemblages. Raeside *et al.* (1988) determined a range in T of 436–675°C. The lowest reported temperature (317°C) in Raeside *et al.* (1988) is incorrect (R.P. Raeside, pers. comm. 1991). The new calibration gives a range of 431–654°C.

Chipera & Perkins (1988) examined a number of calibrations of the garnet–biotite thermometer, using data from an upper amphibolite to granulite assemblage. Their preferred calibration (that of Perchuk & Lavrent'eva 1983) yielded what Chipera & Perkins considered the most accurate and precise temperatures for the area (600–750°C).

The temperatures determined using the new calibration differ slightly from the preferred values of Chipera & Perkins. The temperatures are slightly higher and show a slightly wider range, from 550 to 820°C, still consistent with the mineralogical estimates of the grade of the rocks examined. Second, similar temperatures (within the ±30°C range) were determined for five out of six sample pairs that have different compositions but that come from the same, or a nearby locality. Temperatures for these sample pairs and the temperatures calculated by Chipera & Perkins using eight different calibrations are tabulated in Table 8.

The new calibration has been applied to a number of data-sets from the literature (to date, 17) and to new data collected for a regional metamorphic study (McMullin 1990). A limiting factor in applying this calibration to older data is the relative paucity of studies that are based on

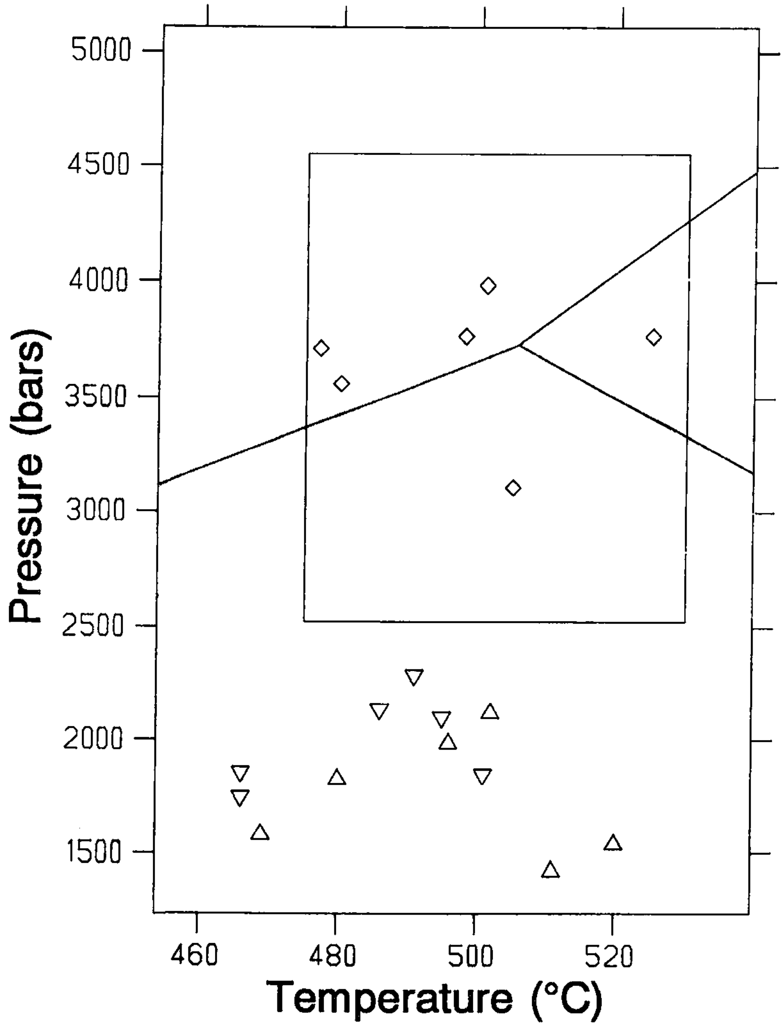

FIG. 7. Pressures and temperatures for the data of Hodges & Spear (1982). Box represents the GASP and garnet – biotite pressures and temperatures for the area. Other symbols as for previous diagrams.

detailed microprobe analyses of all phases, particularly of muscovite. In most of the cases studied, the SGAM pressures are similar (within 2 kbar) to the GASP pressures. The cases in which a large discrepancy occurs typically give a higher GASP pressure. The data of Crowley & Spear (1987) give very large discrepancies between SGAM and GASP (>3 kbar in some cases). This may reflect the complex tectonic uplift history of the area (Crowley & Spear 1987) and thus may indicate that the mechanism for the re-equilibration of the GASP assemblage is more sluggish than that of SGAM. Crowley & Spear (1987) stated that the analyses reported are "representative" but also stated that many of the minerals show extreme zonation. Thus the reported data may not represent equilibrium compositions. If there are real differences in the kinetics of the SGAM equilibria and GASP (or GRAIL), the discrepancies between the recorded temperatures and pressures should yield information on the *P–T* histories of the rocks. Comparison of SGAM with GASP and GRAIL also may help to identify disequilibrium assemblages.

CONCLUSIONS

There are two major conclusions to be made:

1. The new SGAM calibration produces tempera-

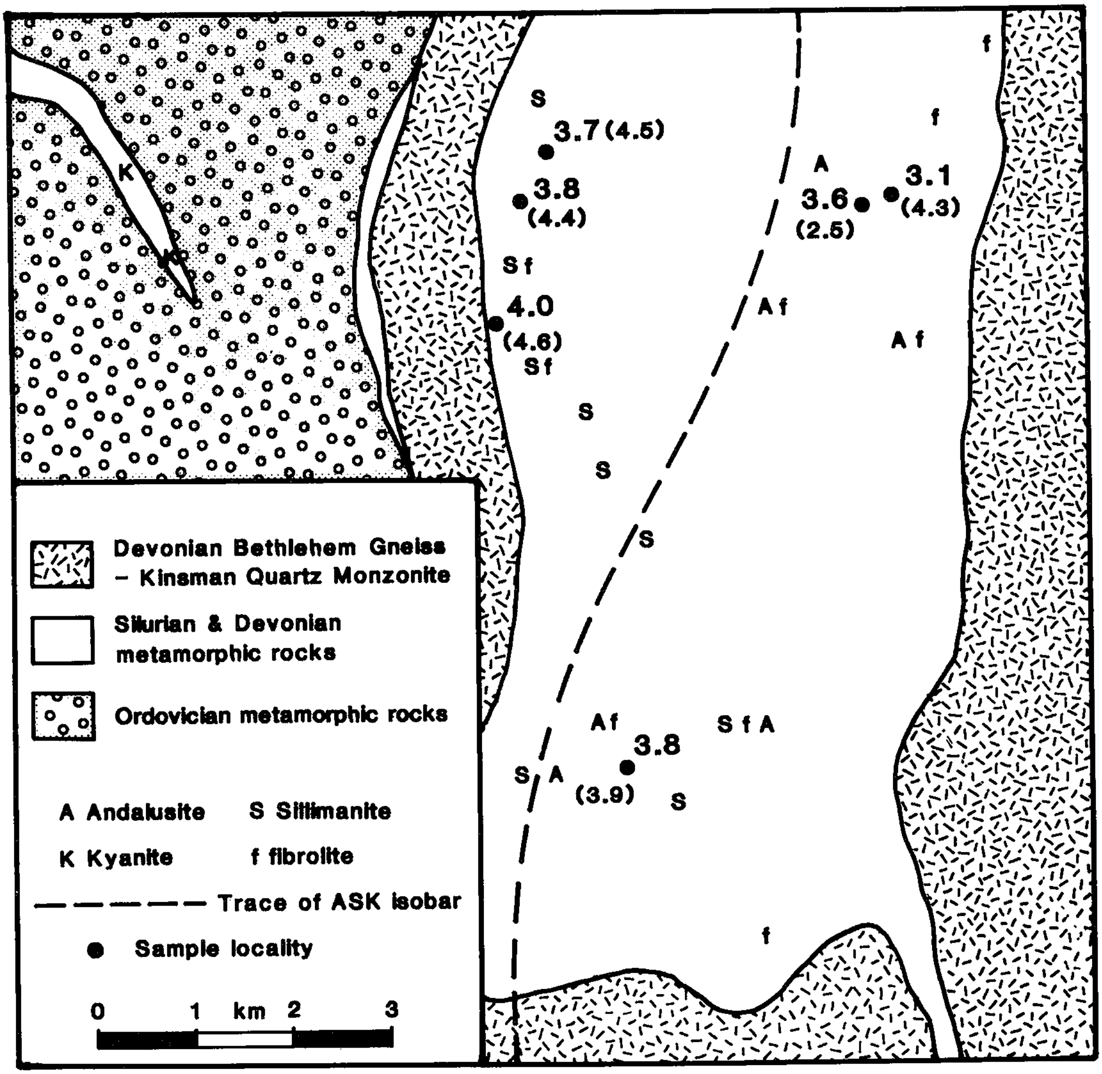

FIG. 8. Map showing the distribution of SGAM pressures from the data of Hodges & Spear (1982). GASP pressures are given in parentheses for comparison. ASK "isobar" trace after Hodges & Spear (1982).

tures and pressures that are consistent with occurrences of the aluminosilicate polymorphs and with GASP-derived pressures.

2. In one data-set, pressures determined using the new calibration show a field gradient not evident using GASP. The gradient matches both the sense and steepness that may be expected from field evidence.

It must be emphasized, however, that the Margules parameters for biotite determined here should be viewed as empirical fit-parameters rather than as an accurate representation of the solution properties of biotite. It should also be emphasized that the properties derived must be used in conjunction with the thermodynamic data-base of Berman (1988, 1990) in order to ensure thermodynamic consistency.

Although it was assumed during the calibration that the SGAM barometer "closes" at the same conditions as GASP, this need not be true. Differences in the behavior of the two systems may reflect differences in the kinetics of re-equilibration reactions. These differences, when better understood, may be exploited in the future to gain further insight into the histories of metamorphic rocks.

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TABLE 8. TEMPERATURES CALCULATED FOR SIX PAIRS OF SAMPLES FROM DATA OF CHIPERA & PERKINS (1988)

	Temperature calibrations								
Sample #	This study	TH	GA1	GA2	FS	PL	GS	IM1	IM2
BL1083C	744	717	631	656	790	697	548	683	673
BL1083E	763	697	617	604	761	684	685	675	698
DS2183B	622	608	553	553	632	621	592	562	581
DS2483	576	562	520	520	569	587	565	513	558
LS7884	677	654	586	562	697	654	588	595	587
SE0985A	702	675	601	615	728	669	533	626	619
RF2283	686	662	591	582	708	659	583	612	598
RF2583A	663	644	578	578	683	647	558	599	595
VM2683A	713	688	610	622	746	678	602	652	640
VR1383A	701	676	601	595	729	670	640	631	628
HS1483C	691	663	592	569	710	661	566	602	588
HS1583C	784	716	630	635	788	697	700	688	733

Sample pairs are from same or adjacent localities. Temperatures using other calibrations are from Table 3 of Chipera & Perkins (1988). Calibrations: TH = Thompson (1976b); GA1 = Goldman & Albee (1977), second parameter solution; GA2 = Goldman & Albee (1977), fifth rank solution; FS = Ferry & Spear (1978); PL = Perchuk & Lavrent'eva (1983); GS = Ganguly & Saxena (1984); IM1 = Indares & Martignole (1985) thermodynamic data only; IM2 = Indares & Martignole (1985), using both thermodynamic and experimental data. See Chipera & Perkins (1988) for further details.

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