Empirical calibration of geobarometers for the assemblage garnet + hornblende + plagioclase + quartz

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Abstract

Four geobarometers for garnet amphibolites and granulites have been calibrated and are based on the equilibrium

6 anorthite + 3 albite + 3 tremolite = 2 grossular + 1 pyrope + 3 pargasite + 18 quartz

and its Fe end-member equivalent.

Literature data representing 19 natural samples that equilibrated from 3.5 to 14 kbar and from 520 to 800 °C are fitted to the general equation

$$-RT \ln K_{eq} = A - BT + (P - 1)C,$$

where T is in kelvins and P is in bars, using a weighted least-squares method.

Isopleths of $\ln K_{eq}$ in P-T space are quite flat; slopes at 600 °C and 5 to 10 kbar range from -7 to $+13$ bars/°C. Propagated analytical errors produce a corresponding error in pressure of ± 200 to 600 bars (1σ). When errors in T and the regressed parameters are also propagated, the accuracy is estimated to be not better than ± 5000 bars.

Applications show that these calibrations are consistent with other calibrated mineral equilibria, but caution is advised in applying the barometers outside the range of mineral compositions employed here, or to rocks that equilibrated at high temperatures ($> \sim 700$ °C), because of the potential for re-equilibration of garnet and hornblende on cooling.
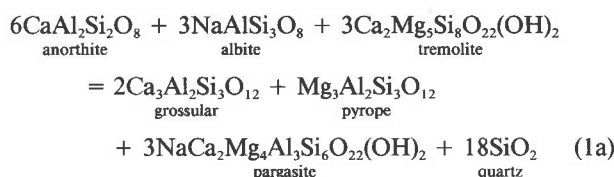
Introduction

Several authors (e.g., Thompson, 1982; Hodges and Crowley, 1985) have suggested that a geobarometer for metamorphosed mafic rocks might be developed based on a reaction involving quartz, plagioclase, garnet, and Tschermak exchange in amphibole (hornblende). Such a geobarometer would be extremely useful because of its applicability in a variety of metamorphic terranes and its resistance to retrograde re-equilibration.
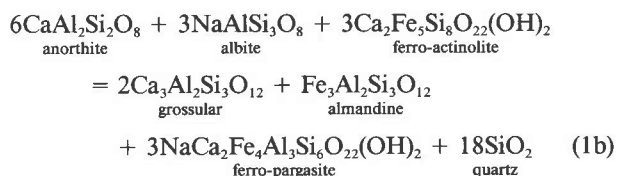
Data that are well-constrained with respect to pressure and temperature have recently become available (Griffin et al., 1980; Krogh, 1980; Jen and Kretz, 1981; Spear, 1982 and unpub. data; Selverstone et al., 1984; Stoddard, 1985; Spear and Rumble, 1986; Thompson and Leclair, 1987). Thus, it is now possible to calibrate empirically a geobarometer for garnet-bearing amphibolites and hornblende-bearing granulites.

Technique

Many equilibria may be written among quartz and the components of plagioclase, garnet, and amphibole. The reactions of interest are

$$6CaAl_2Si_2O_8 + 3NaAlSi_3O_8 + 3Ca_2Mg_5Si_8O_{22}(OH)_2$$
$$\text{anorthite} \qquad \text{albite} \qquad \text{tremolite}$$

$$= 2Ca_3Al_2Si_3O_{12} + Mg_3Al_2Si_3O_{12}$$
$$\text{grossular} \qquad \text{pyrope}$$

$$+ 3NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 18SiO_2 \quad (1a)$$
$$\text{pargasite} \qquad \text{quartz}$$

and

$$6CaAl_2Si_2O_8 + 3NaAlSi_3O_8 + 3Ca_2Fe_5Si_8O_{22}(OH)_2$$
$$\text{anorthite} \qquad \text{albite} \qquad \text{ferro-actinolite}$$

$$= 2Ca_3Al_2Si_3O_{12} + Fe_3Al_2Si_3O_{12}$$
$$\text{grossular} \qquad \text{almandine}$$

$$+ 3NaCa_2Fe_4Al_3Si_6O_{22}(OH)_2 + 18SiO_2 \quad (1b)$$
$$\text{ferro-pargasite} \qquad \text{quartz}$$

For Reactions 1a and 1b at equilibrium, one may write:

$$-RT \ln K_{eq1} = \Delta H_1 - T\Delta S_1 + (P - 1)\Delta V_1 \quad (2a)$$

and

$$-RT \ln K_{eq2} = \Delta H_2 - T\Delta S_2 + (P - 1)\Delta V_2, \quad (2b)$$

where

$$K_{eq1} = \frac{a_{Grs}^2 a_{Prp}^3 a_{Prg}^3 a_{Qtz}^{18}}{a_{An}^6 a_{Ab}^3 a_{Tr}^3}$$

$$K_{eq2} = \frac{a_{Grs}^2 a_{Alm} a_{Fe-Prg}^3 a_{Qtz}^{18}}{a_{An}^6 a_{Ab}^3 a_{Fe-Act}^3}$$

and a_{Grs}, a_{Prp}, and a_{Alm} are the activities of grossular, pyrope, and almandine, respectively, in garnet; a_{Prg}, a_{Tr}, a_{Fe-Prg}, and a_{Fe-Act} are the activities of pargasite, tremolite, ferro-pargasite, and ferro-actinolite, respectively, in amphibole; a_{An} and a_{Ab} are the activities of anorthite and albite in plagioclase; and a_{Qtz} is the activity of SiO_2 in quartz [mineral abbreviations after Kretz (1983)]. Assuming that

ΔH, ΔS, and ΔV are independent of pressure and temperature, data from natural samples may be fitted to the equation

$$-RT \ln K_{eq} = A - BT + (P - 1)C, \qquad (3)$$

with K_{eq} defined as above. A, B, and C are best considered as fit parameters for the barometer calibrations rather than as estimates of the thermodynamic properties of the end-member equilibria. This is because nonideal mixing in amphibole, heat capacities, and changes of volume with pressure and temperature were not considered in our calculations.

ACTIVITY MODELS

Garnet and plagioclase

Several models for the activity of various components in garnet have been suggested in the literature (e.g., Wood, 1975; Saxena, 1979; Ghent and Stout, 1981; Newton and Haselton, 1981; Hodges and Spear, 1982; Ganguly and Saxena, 1984; Brey et al., 1986), but no one model has produced a significantly better fit to the data than the others. For the present calibrations, the Hodges and Spear (1982) activity expressions were chosen:

$$a_{Prp} = \{X_{Prp}\exp[(13800 - 6.28T)$$
$$(X_{Grs}^2 + X_{Alm}X_{Grs} + X_{Grs}X_{Sps})/RT]\}^3$$
$$a_{Grs} = \{X_{Grs}\exp[(13800 - 6.28T)$$
$$(X_{Prp}^2 + X_{Alm}X_{Prp} + X_{Prp}X_{Sps})/RT]\}^3$$
$$a_{Alm} = \{X_{Alm}\exp[(13800 - 6.28T)(-X_{Prp}X_{Grs})/RT]\}^3.$$

X_{Prp}, etc., are the mole fractions of phase components in garnet as defined in Appendix 1; R is the gas constant in $J/(mol \cdot K)$. These activity expressions are believed to be valid only for low-spessartine garnets ($X_{Sps} < 0.20$).

Several plagioclase activity models have also been presented in the literature (e.g., Orville, 1972; Saxena and Ribbe, 1972; Newton et al., 1980; Hodges and Royden, 1984; Ashworth and Evirgen, 1986; etc.). Although many activity models were tested and found to produce statistically similar results, the activity model for anorthite component in plagioclase presented in Hodges and Royden (1984) was used because it allowed for temperature dependence and fitted the data slightly better than other models:

$$a_{An} = X_{An}\exp[(610.34/T) - 0.3837],$$
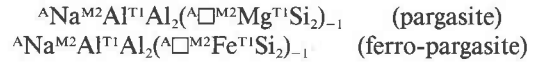
where X_{An} is the mole fraction of anorthite (see App. 1). The activity for albite component in plagioclase was assumed to be ideal (see Orville, 1972):

$$a_{Ab} = X_{Ab},$$
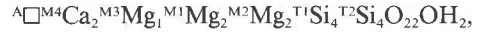
where X_{Ab} is the mole fraction of albite (see App. 1). These expressions are believed to be valid for intermediate plagioclases ($0.15 \leq X_{An} \leq 0.60$).

Amphibole

The amphibole components for Reactions 1a and 1b are related chemically by the following exchanges:

$$^A Na^{M2}Al^{T1}Al_2(^A\square^{M2}Mg^{T1}Si_2)_{-1} \quad \text{(pargasite)}$$
$$^A Na^{M2}Al^{T1}Al_2(^A\square^{M2}Fe^{T1}Si_2)_{-1} \quad \text{(ferro-pargasite)}$$

operating on the components tremolite,

$$^A\square^{M4}Ca_2{}^{M3}Mg_1{}^{M1}Mg_2{}^{M2}Mg_2{}^{T1}Si_4{}^{T2}Si_4O_{22}OH_2,$$

and ferro-actinolite,

$$^A\square^{M4}Ca_2{}^{M3}Fe_1{}^{M1}Fe_2{}^{M2}Fe_2{}^{T1}Si_4{}^{T2}Si_4O_{22}OH_2,$$

respectively, where A, M1, M2, M3, M4, T1, and T2 refer to the alkali, metal (octahedral), and tetrahedral sites in the amphibole structure, and $\square$ refers to the alkali site vacancy. It is assumed that Si can occupy either of two tetrahedral positions (T1 or T2), but that any tetrahedrally coordinated Al can only occupy one (T1).

With respect to these exchanges, two extreme possibilities for modeling the activities of amphibole components may be considered. The first assumes independent mixing on each amphibole site. Disadvantages of this approach include (1) the site occupancies are very dependent on the amount of Fe^{3+}, (2) the estimated activities are susceptible to analytical errors, and (3) the partitioning of Fe and Mg among the sites must be known. The second extreme assumes complete local charge balance associated with pargasite exchange. Although several models between and including these extremes were tested, the data were best-fitted (correlation coefficients were greatest) using two models representing partial local charge balance associated with the pargasite and ferro-pargasite exchanges. For model 1,

$$a_{Prg} = 16 X_{T1Al}^2 X_{T1Si}^2 X_{ANa}$$
$$a_{Tr} = X_{T1Si}^4 X_{A\square}$$
$$a_{Fe-Prg} = 16 X_{T1Al}^2 X_{T1Si}^2 X_{ANa}$$
$$a_{Fe-Act} = X_{T1Si}^4 X_{A\square}.$$

For model 2,

$$a_{Parg} = 4 X_{M2Al} X_{M2Mg} X_{ANa}$$
$$a_{Trem} = X_{M2Mg}^2 X_{A\square}$$
$$a_{Fe-Parg} = 4 X_{M2Al} X_{M2Fe} X_{ANa}$$
$$a_{Fe-Acti} = X_{M2Fe}^2 X_{A\square}.$$

Consequently, each model was adopted in turn for calibrating the reactions.

Mg and Fe were assumed to be equipartitioned among the M1, M2, M3, and M4 sites. Fe was calculated to a minimum value of Fe^{3+}, consistent with amphibole stoichiometry (typically all Fe^{2+}), using the method of Spear and Kimball (1984). Amphibole site-occupancy assignments are described in Appendix 1. Because no nonideal correction of the amphibole activity was made for other amphibole components, the activity models are believed to be applicable only to amphiboles similar in composition to those employed for calibration of the barometers.

TABLE 1. Preferred pressures, temperatures, and calculated equilibrium constants for samples used in calibration

Sample	P (bars)	T (°C)	$\ln(K_{eq})$ for model 1		$\ln(K_{eq})$ for model 2	
			Fe	Mg	Fe	Mg
Selverstone et al. (1984)[1]						
(1) Z3-N	8000 ± 500	540	+0.87	−2.33	+1.13	−2.59
(2) FH-1M	7000 ± 500	550	−1.00	−4.61	+0.27	−3.72
(3) FH-1P	7500 ± 500	545	−0.13	−4.00	+1.33	−3.02
(4) FH-1P (core)	9500 ± 1000	530	+4.19	−0.82	+4.24	−0.28
Spear (1982)[2,3]						
(5) 73-20A	5250 ± 500	560	−2.34	−6.41	−3.26	−6.48
(6) 73-20C	5300 ± 500	575	−1.30	−5.53	−1.16	−4.69
(7) 73-28A	5500 ± 500	610	−3.36	−7.44	−2.32	−5.63
(8) 73-29D	5275 ± 500	570	−1.52	−5.86	−0.79	−4.39
(9) 73-30S	5000 ± 500	535	−3.96	−7.78	−1.76	−6.30
Our unpublished data, west-central New Hampshire[2,4]						
(10) 71-49H	3750 ± 500	520	−4.45	−9.87	−2.73	−7.17
Thompson and Leclair (1987)[2,5]						
(11) A-1	7000 ± 1000	610	−0.71	−9.95	+0.31	−3.15
(12) A-2	5000 ± 1000	550	−2.32	−9.62	−1.95	−6.00
Griffin et al. (1980)[2,6,7]						
(13) 152733	7000 ± 1000	640	+2.86	−1.98	−0.53	−4.03
(14) 152735	7300 ± 1000	615	+2.40	−1.43	−0.04	−4.10
Stoddard (1985)[2,6,7,8]						
(15) 74-C-248B	6200 ± 1000	690	+0.44	−3.99	−1.93	−5.25
Jen and Kretz (1981)[2,6,7,8]						
(16) J-99	5250 ± 1500	625	−2.33	−7.58	−3.40	−7.47
Krogh (1980)[2,6,8]						
(17) MA-1	12200 ± 2000	755	+7.10	+5.60	+4.53	+1.88
(18) MA-2	13650 ± 2000	805	+8.97	+7.35	+5.89	+3.51
(19) KV-1	10700 ± 2000	720	+5.64	+4.12	+3.34	+0.70

[1] Pressures and temperatures calculated using intersection of garnet-plagioclase-kyanite-quartz equilibrium of Hodges and Crowley (1985) and P-T path of Selverstone et al. (1984).

[2] T estimated using the garnet-hornblende geothermometer (Graham and Powell, 1984).

[3] P estimated at T using P-T path of Spear and Rumble (1986).

[4] P based on aluminosilicate triple point of Holdaway (1971).

[5] P estimated at T using garnet-plagioclase-muscovite-biotite and garnet-plagioclase-muscovite-quartz thermobarometers of Hodges and Crowley (1985).

[6] T estimated using garnet-clinopyroxene geothermometer (Ellis and Green, 1979).

[7] P estimated using the garnet-plagioclase-orthopyroxene-quartz geobarometers of Bohlen et al. (1983) and Newton and Perkins (1982).

[8] P calculated using garnet-plagioclase-clinopyroxene-quartz equilibrium (Newton and Perkins, 1982).

DATA SET

Sample selection

In order to be used for calibration, samples had to have (1) (at least) the minerals garnet, hornblendic amphibole, intermediate plagioclase, and quartz; (2) no significant evidence for retrogression; and (3) well-constrained temperatures and pressures. A literature search produced seven appropriate data sets (Griffin et al., 1980; Krogh, 1980; Jen and Kretz, 1981; Spear, 1982; Selverstone et al., 1984; Stoddard, 1985; Thompson and Leclair, 1987). In addition, our unpublished data were also used.

Calibration pressures, temperatures, and compositions

Pressures and temperatures for the samples used for calibration were determined using a variety of mineral equilibria as described in the footnotes of Table 1. Most mineral compositions were taken directly from complete microprobe analyses; the only exceptions involve some plagioclase compositions, which were determined using the electron microprobe, but only reported as ranges of anorthite content. Assumptions regarding K content for these plagioclases do not significantly affect calculated equilibrium constants, and the plagioclases were assumed to be binary solid solutions between anorthite and albite. Unless otherwise indicated, mineral compositions were considered to represent matrix rim compositions. Table 1 presents the pressures, temperatures, and calculated equilibrium constants used for calibration of the geobarometers.

CALIBRATION

Calibration of the geobarometers requires fitting Equation 3 to the data set, using a linear-regression routine to solve for the parameters A, B, and C. This was done using a weighted least-squares method; pressure was chosen as the dependent variable because it is the least well constrained of the variables P, T, and ln (K_{eq}). Weighting was assigned according to the assumed errors in thermobarometrically determined pressures, with the exception of
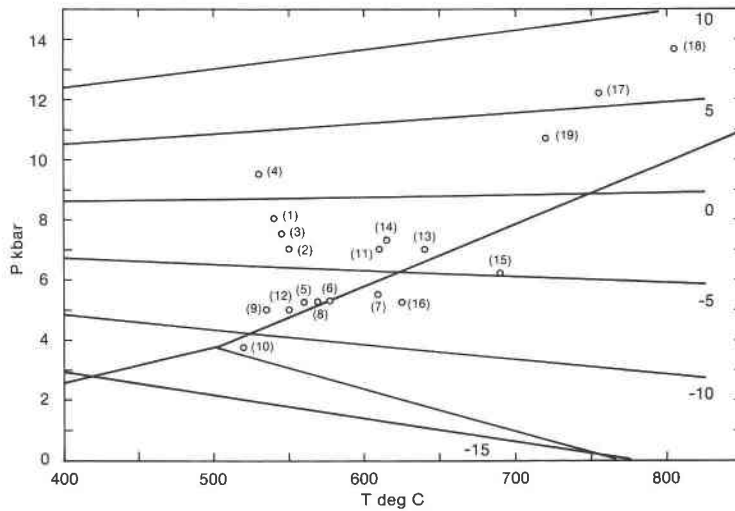
Fig. 1. *P-T* diagram with isopleths of K_{eq} for the Mg end-member reaction and amphibole model 1. Aluminosilicate phase diagram is after Holdaway (1971). Positions of calibration samples are plotted for reference (dots); numbers correspond to those used in Table 1.

sample FH-1P (core). Because of questions concerning mineral compositions, the weight for this sample was assigned to be one half that of other samples in the suite. No correlation among *P*, *T*, and K_{eq} was assumed. This assumption is justified because many of the pressure estimates for the samples were essentially independent of temperature, and most of the mole fractions used to calculate the equilibrium constants were not those used to estimate pressure and temperature. Quality of fit was evaluated based on the magnitude of the multiple correlation coefficient (*R*).

Values for the regressed parameters are presented in Table 2 and lead to the following calibrations, where *P* is in bars and *T* is in kelvins: for model 1,

$$P_{Mg} = [120\,593 + T(10.3 - 8.314 \ln K_{eq})]/14.81$$
$$P_{Fe} = [117\,993 + T(-47.8 - 8.314 \ln K_{eq})]/11.29,$$

and, for model 2,

$$P_{Mg} = [44\,724 + T(51.9 - 8.314 \ln K_{eq})]/9.19$$
$$P_{Fe} = [-4\,948 + T(81.8 - 8.314 \ln K_{eq})]/9.52.$$

Figure 1 shows a pressure-temperature diagram contoured for $\ln(K_{eq})$ using the Mg end-member reaction and amphibole model 1. *P* and *T* of samples used for calibration are shown for reference. Slopes at 600 °C and 5 to 10 kbar are quite shallow and range from −4 to +6 bars/°C. Also, $\ln(K_{eq})$ changes very rapidly with changes in pressure. This sensitivity to pressure and insensitivity to temperature is characteristic of all the calibrations; for example, the total range of slopes at 600 °C and 5 to 10 kbar for the four calibrations is −7 to +13 bars/°C.

Errors in calibration

In any calibration, there are two errors of concern: the accuracy and the precision. The precision for barometers is the ability to measure differences in pressure between rocks of similar compositions and depends on the errors in determining temperature and in mineral compositions (i.e., K_{eq}). The accuracy represents the ability of a calibration to produce the "true" pressure and is a function of the error not only in K_{eq} and *T*, but also in the fit

TABLE 2. Regressed values for fit parameters *A*, *B*, and *C*; associated errors (1σ); and correlation coefficients (*R*) and matrices

		Regressed values			
		A (J)	*B* (J/k)	*C* (J/bar)	*R*
Model 1–Mg		120 593 ± 58 818	−10.30 ± 67.15	−14.81 ± 2.13	0.922
Model 1–Fe		117 993 ± 41 659	47.79 ± 48.87	−11.29 ± 1.43	0.937
Model 2–Mg		44 724 ± 24 559	−51.93 ± 28.20	−9.19 ± 0.88	0.961
Model 2–Fe		−4 948 ± 25 684	−81.76 ± 30.43	−9.52 ± 0.97	0.956

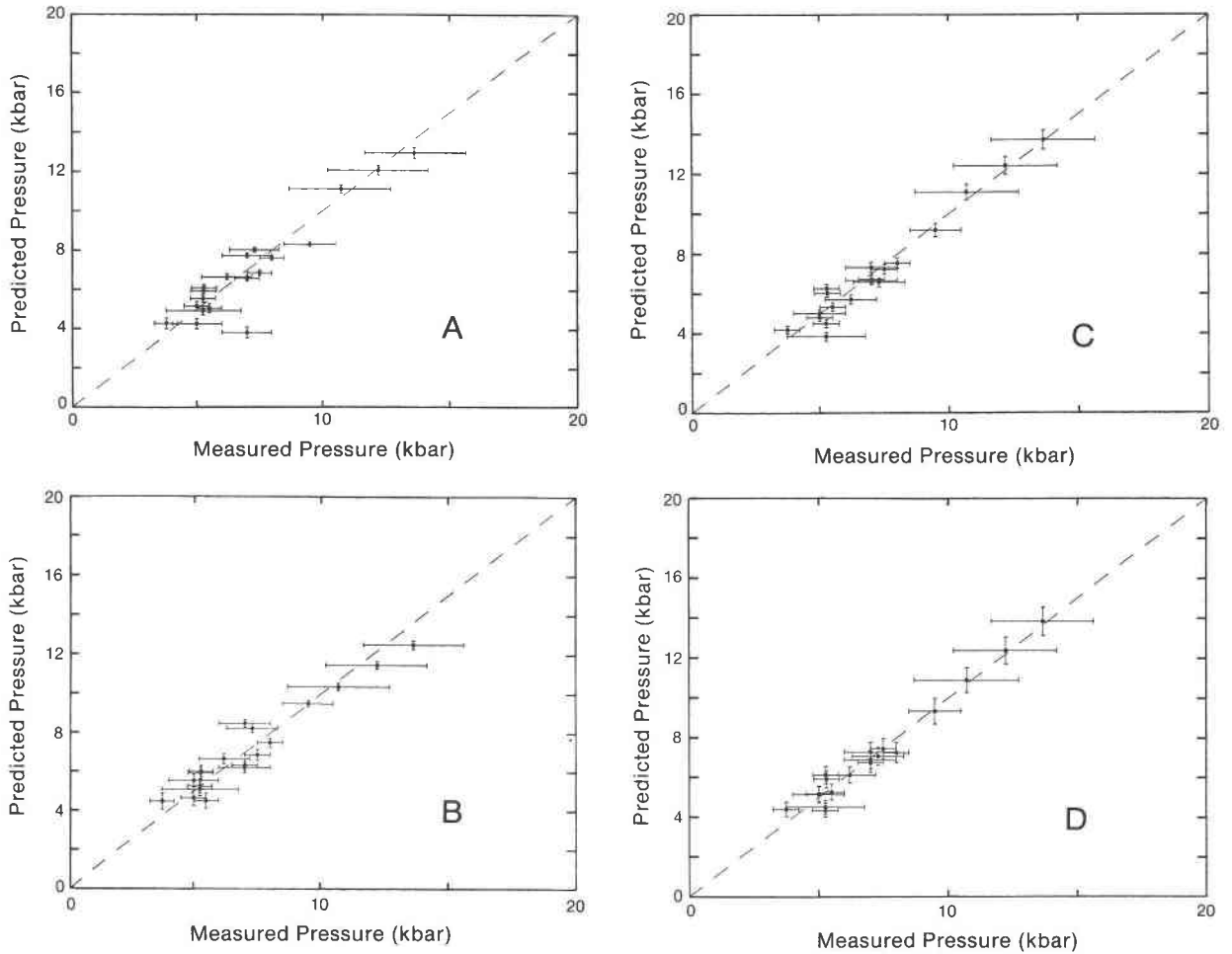|		Correlation matrices					
		Model 1			Model 2		
Mg	*A*	1.000	0.9950	0.4538	1.000	0.9913	0.3289
	B	0.9950	1.000	0.3738	0.9913	1.000	0.2111
	C	0.4538	0.3738	1.000	0.3289	0.2111	1.000
Fe	*A*	1.000	0.9987	0.5052	1.000	0.9984	0.1444
	B	0.9987	1.000	0.4852	0.9984	1.000	0.1228
	C	0.5052	0.4852	1.000	0.1444	0.1228	1.000

Fig. 2. Plots of calibrant data on predicted pressure, i.e., $\{T[B - R \ln(K_{eq})] - A\}/1000C$, vs. measured pressure diagrams for the Mg and Fe end-members of models 1 (**A** and **B**) and 2 (**C** and **D**). Dashed lines show the fit of the models to the data. Error bars correspond to estimated errors in measured P (horizontal) and propagated errors in T and K_{eq} (vertical).

parameters A, B, and C. This latter error is important when comparing different thermobarometers.

Errors may be propagated for the general function $Z = f(i, j, \ldots)$ according to the error propagation equation

$$\sigma_z^2 = (\partial z/\partial i)^2\sigma_i^2 + (\partial z/\partial j)^2\sigma_j^2 + 2(\partial z/\partial i)(\partial z/\partial j)\sigma_i\sigma_j\Omega_{ij}$$
$$+ \text{(higher-order terms)},$$

where $\sigma_{i,j}$ = error in i, j, etc. and Ω_{ij} = correlation between i and j.

The errors reflecting both the precision and the accuracy of the predicted pressure have been propagated for the expression

$$P = [-A + T(B - R \ln K_{eq})]/C$$

according to the above error-propagation equation (neglecting higher-order terms) using the data for the calibration samples as references.

Precision

The precision was determined as follows. For each calibration sample, an error of ± 50 °C was assigned to T and a 2.5% error to each mole fraction (1σ). Furthermore,

perfectly negative correlation between the components X_{T1Al} and X_{T1Si}; X_{ANa} and $X_{A\square}$; and X_{M2Al} and X_{M2Mg} was also assumed. No correlation between any other components was assumed.

Figure 2 shows plots of the data employed in the calibration with the resulting propagated 1σ errors in predicted pressure (vertical bars); also shown are the estimated errors in measured pressure (horizontal bars) and the fit of each model to the data (dashed line). The unweighted errors in predicted pressure correspond to approximately ± 200 to 600 bars. This reflects the very strong pressure-dependence of the equilibrium constants and suggests that the barometers should prove to be quite precise.

Accuracy

To calculate the accuracy, a 2.5% error in each mole fraction and a ± 150 °C error in T was assumed. In addition it was assumed that the regressed parameters had errors and correlations as indicated by the regressions (see Table 2).
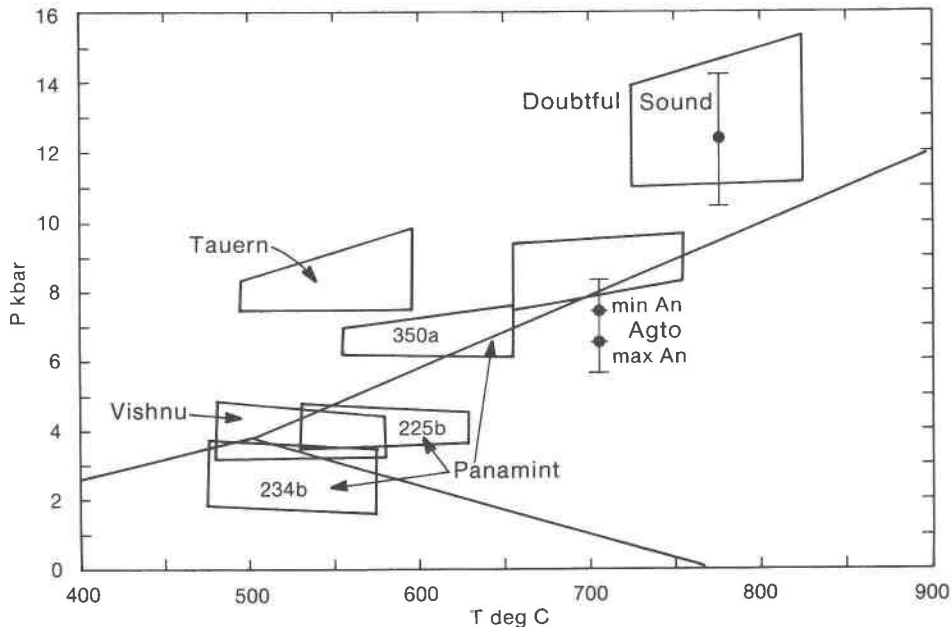
Fig. 3. *P* vs. *T* plot of the simultaneous solution of all four calibrations at an estimated temperature (trapezoids) using data for samples MCD-350a, PML-225b, and PML-234b (Panamint calcic schists; Labotka, 1987), 17A-71 (Vishnu Group; Clark, 1978), FH-1R (Tauern Window garbenschists; Selverstone et al., 1984), 91141 (Agto metadolerites; Glassley and Sorensen, 1980), and 36511 (Doubtful Sound feldspathic granulite; Oliver, 1977). Preferred *P-T* positions of the samples, when known (dots with error bars), and aluminosilicate phase diagram after Holdaway (1971) shown for reference.

Some errors in parameters are quite large relative to the values of the parameters ($\sigma_{B2} \approx B2$), but neglecting the higher-order terms of the error-propagation equation does not affect the estimated accuracy by more than 10%. Propagated errors in K_{eq}, *T*, *A*'s, *B*'s, and *C*'s are not plotted, but the accuracy is not better than ±5000 bars for both Reactions 1a and 1b. This accuracy is of the same magnitude as that estimated by Hodges and Crowley (1985) for other empirical barometers.

DISCUSSION

In order to test the consistency and possible compositional limitations of the calibrations, seven samples from four terranes were chosen representing wide ranges of pressures, temperatures, and mineral compositions. The Panamint Range calcic schists are part of a low-pressure (andalusite-sillimanite facies), contact-metamorphic terrane (samples MCD-350a, PML-225b, PML-234b; Labotka et al., 1980, and Labotka, 1987); plagioclases are extremely calcic (An_{81}–An_{94}), and hornblendes show a wide range of Si and Al contents. Data presented for the Doubtful Sound, New Zealand, feldspathic granulites (sample 36511; Oliver, 1977) indicate that these rocks equilibrated at very high pressures and temperatures. Sample 91141 (Glassley and Sorensen, 1980) is from an intermediate-pressure, high-temperature granulite terrane near Agto, West Greenland, and has very strongly reversely zoned plagioclases (An_{48}–An_{77}). Pressures have not before been determined for the last two samples (FH-

1R and 17A-71), which come from the Tauern Window suite (Selverstone et al., 1984) and from the Vishnu Group schists of the Grand Canyon (Clark, 1978).

Figure 3 shows the simultaneous solution of all four calibrations with the garnet-hornblende thermometer of Graham and Powell (1984). For the Doubtful Sound granulite, an average of the garnet-hornblende and garnet-clinopyroxene (Ellis and Green, 1979) temperatures was used. Also shown are the preferred pressure-temperature positions for each sample (if known) with appropriate errors in pressure. Pressures for the Agto metadolerite (91141) and Doubtful Sound feldspathic granulite (36511) samples were estimated using garnet-plagioclase-orthopyroxene-quartz and garnet-plagioclase-clinopyroxene-quartz equilibria (Newton and Perkins, 1982; Bohlen et al., 1983). Pressures for the Panamint schists (MCD-350a, PML-225b, PML-234b) could not be reliably determined based on mineral equilibria, but stratigraphic overburden calculations and presence of andalusite in pelitic schists nearby suggest pressures of 2.5 to 3 kbar (Labotka, 1981). Both the maximum and minimum anorthite contents of plagioclase were used for applying the garnet-plagioclase-orthopyroxene-quartz geobarometers to the Agto metadolerite data, and the corresponding *P-T* positions are plotted for comparison. Anorthite content within this range only negligibly affects K_{eq} for our calibrations. Sample 36461 was also used for estimating the preferred temperature and pressure for the Doubtful Sound suite.

As can be seen, estimated pressures for the Panamint Range calcic schists using our calibrations are scattered, but broadly consistent with phase equilibria and structural reconstructions. A notable exception, however, is sample MCD-350a. The only significant compositional difference between this sample and the other Panamint samples is that its hornblende is much more aluminous. The scatter in pressure estimates may be due to disequilibrium among the minerals or to unknown activities of components in the feldspars or amphiboles.

Pressure estimates for the Agto metadolerites using minimum ("core") anorthite plagioclase compositions result in fair agreement between our barometers and the others. Although our calibrations indicate a higher pressure, they are still consistent within error with garnet-plagioclase-orthopyroxene-quartz and garnet-plagioclase-clinopyroxene-quartz geobarometers (Newton and Perkins, 1982; Bohlen et al., 1983). When maximum anorthite ("rim") plagioclase compositions are used, this difference is increased, but is still within error for the lower two pressure estimates (which are the two Fe calibrations). The differences in estimated pressures may be a result of differing activity models for the garnet and plagioclase components used in the geobarometers. Alternatively, the modal amounts of garnet and quartz are both very small for the Agto samples, and so the difference in pressures may also be due to diffusional re-equilibration in garnet on cooling or to retrograde quartz (i.e., unknown activity of SiO_2).

The pressure estimate for the Doubtful Sound feldspathic granulites using our calibrations is not particularly well constrained and has an error of ± 2000 bars. This may be due in part to retrograde re-equilibration since garnet-clinopyroxene (Ellis and Green, 1979) and garnet-hornblende (Graham and Powell, 1984) temperatures differ by about 100 to 150 °C. However, it is also seen that pressure estimates made using our calibrations are entirely consistent with the preferred value estimated from the two samples (36511 and 36461) using garnet-plagioclase-orthopyroxene-quartz and garnet-plagioclase-clinopyroxene-quartz geobarometry (Newton and Perkins, 1982; Bohlen et al., 1983).

The pressure indicated for sample FH-1R (Tauern Window) is high, but completely consistent with the pressure-temperature path determined by Selverstone et al. (1984). The estimated pressure for sample 17A-71 (Vishnu schist) is quite low and is consistent with the presence of cordierite in some samples from the same area (Clark, 1978).

Inspection of Figure 3 indicates that, with the exception of the Doubtful Sound granulites, the spread of calculated pressures using all models on a single data set varies from ± 500 to 1000 bars. This represents the internal consistency of the calibrations. It is suggested that the user of these barometers average the results and report the spread of the calculated pressures (with an additional $\pm \sim 500$ bars) as the precision.

TABLE 3. Compositional limits of minerals used for calibration

Hornblende (cations per 23 O)	
$6.1 \leq Si \leq 6.6$	$2.0 \leq Al \leq 3.2$
$0.0 \leq Ti \leq 0.275$	$0.975 \leq Mg \leq 2.7$
$1.7 \leq Fe \leq 2.8$	$0.0 \leq Mn \leq 0.05$
$1.5 \leq Ca \leq 1.9$	$0.35 \leq Na \leq 0.6$
$0.0 \leq K \leq 0.4$	$2.1 \leq Ca + Na + K \leq 2.75$
Garnet (cations per 12 O)	
$Mn \leq 0.45$ (i.e., $<15\%$ Sps)	
Plagioclase (cations per 8 O)	
$0.15 \leq Ca \leq 0.7$ (i.e., between An_{15} and An_{70})	

Limits of applicability

Application of the geobarometers to samples with different bulk compositions than those of the samples used for calibration may result in erroneous pressure estimates. In particular, preliminary application of the geobarometers to very calcic samples (Panamint schists) produces either scattered or high apparent pressures. We very strongly recommend that the user restrict application of the geobarometers to those samples within the compositional limits of the minerals (described in Table 3) that were used for calibration. It should also be noted that application of garnet and plagioclase solution models other than those of Hodges and Spear (1982) and Hodges and Royden (1984) will be inconsistent with the regressed A, B, and C parameters, possibly resulting in erroneous pressures.

CONCLUSIONS

Empirical thermobarometers, such as the ones presented here, serve two important purposes. First, they provide a statistical constraint within which to evaluate the internal consistency of different mineral equilibria in a suite of samples. Second, they provide a means by which pressure differences between samples or pressure changes recorded by a single sample may be measured.

The statistical correlations of the empirical barometers presented in this paper with the data on the minerals used for calibration ($R > 0.92$) demonstrate the consistency of garnet-hornblende-plagioclase-quartz equilibria with other common metamorphic equilibria. Calculated precisions indicate that pressure differences of ± 200 to 600 bars may be resolved with these barometers.

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APPENDIX 1. CALCULATION OF MOLE FRACTIONS AND ASSIGNMENT OF SITE OCCUPANCIES

Garnet

$$X_{Prp} = Mg/(Mg + Fe + Mn + Ca)$$
$$X_{Alm} = Fe/(Mg + Fe + Mn + Ca)$$
$$X_{Sps} = Mn/(Mg + Fe + Mn + Ca)$$
$$X_{Grs} = Ca/(Mg + Fe + Mn + Ca)$$

Plagioclase

$$X_{An} = Ca/(Ca + Na + K)$$
$$X_{Ab} = Na/(Ca + Na + K)$$

Amphibole

$$^{T1}Si = Si - 4.0 \qquad\qquad ^{T1}Al = 8.0 - Si$$
$$^{M2}Al = Al + Si - 8.0 \qquad ^{M2}Ti = Ti$$
$$^{M2}Fe^{3+} = Fe^{3+} \text{ (if any)}$$
$$^{M2}Fe = [2 - (^{M2}Al + {}^{M2}Ti + {}^{M2}Fe^{3+})] \times Fe/(Fe + Mg)$$
$$^{M2}Mg = [2 - (^{M2}Al + {}^{M2}Ti + {}^{M2}Fe^{3+})]$$
$$\times Mg/(Fe + Mg)$$
$$^{A}Na = Si + Al + Ti + Fe^{3+} + Mg + Fe + Mn + Ca + Na - 15$$
$$^{A}\square = 1 - {}^{A}Na - K$$
$$= 16 - (Si + Al + Ti + Fe^{3+} + Mg + Fe + Mn + Ca + Na + K)$$

$$X_{T1_{Si}} = {}^{T2}Si/4.0 \qquad\qquad X_{T1_{Al}} = {}^{T1}Al/4.0$$
$$X_{M2_{Al}} = {}^{M2}Al/2.0 \qquad\qquad X_{M2_{Mg}} = {}^{M2}Mg/2.0$$
$$X_{M2_{Fe}} = {}^{M2}Fe/2.0 \qquad\qquad X_{A_{Na}} = {}^{A}Na$$
$$X_{A_{\square}} = {}^{A}\square$$