American Mineralogist, Volume 92, pages 491–502, 2007

The barometer tremolite + tschermakite + 2 albite = 2 pargasite + 8 quartz: Constraints from experimental data at unit silica activity, with application to garnet-free natural assemblages

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ABSTRACT

Garnet is notably absent in mafic to felsic lithologies, in low-*P* metamorphic terranes, and in Mg-rich bulk compositions in high-*P* regionally metamorphosed terranes. In the absence of garnet, existing mineral barometers cannot be applied for estimating metamorphic pressure. A new garnet-free, hornblende-plagioclase barometer has been formulated based on the reaction tremolite + tschermakite + 2 albite = 2 pargasite + 8 quartz. The intra- and cross-site mixing parameters for hornblende were retrieved exclusively from experimental data in the *P-T* window 1–15 kbar and 650–950 °C, after screening the available data for the presence of quartz. A linear least-squares fit to the coexisting hornblende and plagioclase composition in the experiments yields the following barometric expressions:

$$P_1(\text{kbar}) = [-9.326 + 0.01462\text{T (K)} + \text{R}T\ln K_{\text{ideal}} - 98.698X^{\text{A}}_{\text{Na}} - 33.213X^{\text{A}}_{\text{K}} - 20.338X^{\text{M4}}_{\text{Na}} - 39.101X^{\text{M13}}_{\text{Fe}^{2+}} + 100.392X^{\text{M2}}_{\text{Al}} + 131.03X^{\text{M2}}_{\text{Fe}^{2+}} + 82.479X^{\text{M2}}_{\text{Fe}^{3+}} - 118.653X^{\text{T1}}_{\text{Al}} - 2\text{R}T\ln\gamma_{\text{Ab}}]/(-\Delta V)$$

and

$$P_2(\text{kbar}) = [-1.869 + 0.0076\text{T (K)} + \text{R}T\ln K_{\text{ideal}} - 102.692X^{\text{A}}_{\text{Na}} - 35.251X^{\text{A}}_{\text{K}} - 15.969X^{\text{M4}}_{\text{Na}} - 40.499X^{\text{M13}}_{\text{Fe}^{2+}} + 93.069X^{\text{M2}}_{\text{Al}} + 130.750X^{\text{M2}}_{\text{Fe}^{2+}} + 74.226X^{\text{M2}}_{\text{Fe}^{3+}} - 104.402X^{\text{T1}}_{\text{Al}} - 2\text{R}T\ln\gamma_{\text{Ab}}]/(-\Delta V)$$

where

$$K_{\text{ideal}} = \left[\frac{16(X^{A}_{\text{Na}})(X^{\text{T1}}_{\text{Al}})}{(X^{A}_{\square})(X^{\text{T1}}_{\text{Si}})(X_{\text{Ab}})}\right]^2.$$

X^{j}_{i} denotes the mole fraction of cation *i* in site *j* of amphibole, X_{Ab} and γ_{Ab} are the mole fraction and activity coefficient of albite in plagioclase, respectively, and ΔV is the volume change for the reaction. In the expression for P_2, the first two terms in the numerator on the right-hand side corresponding to $\Delta H°$ and $\Delta S°$, respectively, were adopted from an internally consistent thermodynamic database. In the expression for P_1, the first term on the right-hand side of the numerator, $\Delta\hat{H}$ (–9.326 kJ) = $\Delta H°$ + a_9, where a_9 is a mixing parameter, and the second term $\Delta S°$ = 0.01462 kJ/K, were retrieved by a linear least-squares fit to the experimental data. The formulations reproduced experimental *P* values within 2 kbar for 83% of the experimental runs. The cumulative precision (1σ) of pressure estimated using the formulations varied between 800 and 2000 bars for errors propagated due to uncertainties in *P-T*, volume, and thermometric estimate, and inaccuracies in estimated composition of phases. In natural assemblages spanning a pressure range of 2.5 to 12.5 kbar, the quartz–hornblende–plagioclase barometers yielded pressure within 2 kbar of the *P*-value recommended by the authors, and is consistent with the stable Al_2SiO_5 polymorph in associated metapelites.

Keywords: Thermobarometry, hornblende, plagioclase, quartz, thermodynamics, mixing parameters of hornblende, experimental petrology, mafic rocks, silica-saturated, metamorphic petrology

INTRODUCTION

Quantitative pressure estimation is based on reactions characterized by large volume changes. More often than not, garnet plays a key role in most barometric formulations because reactions with garnet are characterized by a large volume change, and garnet-bearing assemblages are common in medium- to high-grade metamorphic rocks. Only a few barometers exist for garnet-absent mineral assemblages (cf. Spear 1993, p. 518–519; Winter 2001, p. 558–559). The problem of estimating metamorphic pressure in garnet-free assemblages is especially acute for medium- to high-grade metabasic rocks in which garnet is

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absent in low-*P* regionally metamorphosed terranes or in contact metamorphic aureoles (Loomis 1966; Russ-Nabelek 1989; Shive et al. 1991), or because garnet does not form in intermediate- to high-pressure metamorphic terranes due to the Mg-rich nature of the rocks or due to quartz-saturation. These limitations in nature underscore the need to formulate a garnet-free barometer that can be applied to mafic, intermediate, and felsic rocks of wide-ranging composition for quantitative pressure estimation.

In garnet-free mafic to felsic lithologies, the hornblende-plagioclase thermometers of Spear (1980, 1981a) and Holland and Blundy (1994) provide useful tools for estimating temperature. However, mineralogical barometers for such assemblages are lacking. The barometers proposed by Hammarstrom and Zen (1986), Johnson and Rutherford (1989), and Anderson and Smith (1995) were calibrated empirically and designed to estimate pressure in igneous rocks. Dale et al. (2000) presented three garnet-bearing geobarometers based on the reactions (mineral abbreviations from Kretz 1983):

3Ts + 2Prp + 4 Grs + 12 Qtz = 3Tr + 12 An;
3Prg + 2Grs + Prp + 18 Qtz = 3Tr + 6An + 3Ab;
3Gln + 4Grs + 2Prp + 12Qtz = 3Tr + 6An + 6Ab.

The first two reactions were also modeled by Mäder et al. (1994). Dale et al. (2000, their Table 1) retrieved the site-mixing parameters in hornblende components for the reactions from a natural data set. In the data set, mineral compositions after Glassley and Sorensen (1980) and Stoddard (1985) are from assemblages that do not contain quartz. Because quartz/hornblende molar ratios vary between 4 and 6 in the reactions of Dale et al. (2000), silica undersaturation is expected to influence the magnitude of the retrieved mixing parameters. However, Dale et al. (2000) ignored the experimental data on coexisting hornblende, plagioclase, and garnet in quartz-bearing systems (Conrad et al. 1988: run 330B; Sen and Dunn 1994; Patino-Douce and Beard 1995; Ernst and Liu 1998). In contrast, as regards the thermometric equilibrium edenite + 4 quartz = tremolite + albite (quartz/hornblende molar ratio = 4), Holland and Blundy (1994) retrieved hornblende mixing parameters from a set of 61 experimental data and 215 natural data (Holland and Blundy 1994; their Table A1). Although the authors justifiably omitted the silica-undersaturated experimental charges in the regression analysis, the analytical data of natural assemblages without silica were adopted (e.g., Glassley and Sorensen 1980; Stoddard 1985; Russ-Nabelek 1989, samples: 83-15, 83-19A, 83-16 in their Table 1). As a result, the magnitudes of the retrieved parameters may have been influenced by the data.

Equilibrium *P* or *T* conditions for an assemblage can be estimated from the convergence of multiple reactions rather than reliance on a single reaction, using globally constrained thermodynamic data sets such as those of Berman (1988 1991) or Holland and Powell (1998). The multi-equilibra approach is not different from the single-reaction approach to estimating *P* or *T* because, in essence, both approaches require well-constrained thermodynamic data sets and activity-composition (*a*-*X*) relations, and any one of the equilibria (single reaction) in the multiple-equilibria approach is necessarily as good or bad as the other. To ascertain whether an available multi-equilibrium approach is suited for thermobarometry in hornblende-bearing assemblages, two experimental runs [323A; T = 725 °C, P =

Table 1b. Standard state enthalpy and entropy data for end-member components in reaction A

Phase	*H* (kJ/mol)	*S* [J/(mol·K)]	Method	References
Tremolite	–12305.58	551.15	PE	Berman 1988; Mader et al. 1994
	–12303.00	548.90	C	Robie and Hemingway 1995
	–12306.93	549.21	PE	Gottschalk 1997
	–12309.72	550.00	PE	Holland and Powell 1998
	–12305.48	549.86	PE	Chernosky et al. 1998
	–12307.90	549.50	PE	Evans et al. 2000
Tschermakite	–12449.10	542.72	PE	Lieberman and Kamber 1991
	–12534.67	538.6	PE	Leger and Ferry 1991
	–12578.95	514.69	PE	Mäder and Berman 1992
	–12574.76	517.71	PE	Mäder et al. 1994
	–12534.40	542.50	PE	Jenkins 1994
	–12527.70	–	C	Smelik et al. 1994
	–12540.57	545.00	PE	Holland and Powell 1998
	–12528.30	556.50	PE	Najorka et al. 2002
Pargasite	–12726.68	589.20	PE	Mäder et al. 1994
	–12719.60	601.00	PE	Holland and Powell 1998
Albite	–3921.62	224.41	PE	Berman 1988
	–3934.60	210.10	PE	Holland and Powell 1998
Quartz	–910.70	41.46	PE	Berman 1988
	–910.88	41.50	PE	Holland and Powell 1998

Note: PE and C refer to phase equilibria and calorimetry study, respectively.

Table 1a. Chemical formula and site occupancy of cations for the amphibole end-members

		Site occupancy				
Phase	Chemical formula	A	M4	M13	M2	T1
Tremolite	$\square Ca_2Mg_5Si_8O_{22}(OH)_2$	$\square$	Ca_2	Mg_3	Mg_2	Si_4
Tschermackite	$\square Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$	$\square$	Ca_2	Mg_3	Al_2	Al_2Si_2
Pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	Na	Ca_2	Mg_3	MgAl	Al_2Si_2

Table 1c. ΔH and ΔS (1 bar) of the barometric reaction (A) at 25, 650, and 950 °C computed from available thermodynamic data sets

298 K, 1 bar		923 K, 1 bar		1223 K, 1 bar		Source data				
ΔS (kJ/K)	ΔH (kJ)	ΔS (kJ/K)	ΔH (kJ)	ΔS (kJ/K)	ΔH (kJ)	Tr	Ts	Prg	Ab	Qtz
0.0188	–6.75	0.0238	–3.26	0.0276	0.88	HP98	HP98	HP98	HP98	HP98
0.0073	–19.02	0.0123	–15.53	0.0161	–11.39	HP98	N02	HP98	HP98	HP98
–0.0076	–13.07	0.0074	–6.78	0.0098	–4.31	B88	M94	M94	B88	B88
–0.0059	–15.39	0.0091	–4.46	0.0114	–1.99	E00	M94	M94	B88	B88

Notes: The heat capacity has been calculated as $C_P = a + bT + cT^{-2} + dT^{-1/2}$ after Holland and Powell (1998) and $C_P = k_0 + k_1T^{-1/2} + k_2T^{-2} + k_3T^{-3}$ after Berman (1988). Acronyms: B88, Berman 1988; M94, Mäder et al. 1994; HP98, Holland and Powell 1998; E00, Evans et al. 2000; and N02, Najorka et al. 2002.

10 kbar, X_{H_2O} = 0.5] and [305A; T = 675 °C, P = 10 kbar, X_{H_2O} = 0.75] of Conrad et al. (1988) were considered. Hornblende, plagioclase, biotite, and quartz constitute the run products. The chemical data of the phases were recast using the AX program (Holland and Powell 1998), and the corresponding activities of the end-member components were used as input into the THERMOCALC program (Holland and Powell 1998) to calculate the *P-T* locations for the set of possible vapor-free reactions (Fig. 1). The *P-T* locations of the reactions are widely dispersed around the experimental *P-T* values. The discrepancy can be traced to uncertainties in constraining either the *a-X* relationships in hornblende and/or the end-member thermodynamic data of the reactions.

A pragmatic solution to the problem of estimating *P* (and *T*) conditions from hornblende-bearing assemblages, therefore, is to model a single equilibrium thermodynamically, on the basis of well-constrained experimental data, followed by a test of its applicability to natural assemblages. In this communication, a barometer involving hornblende, plagioclase, and quartz is formulated for metamorphic *P* estimation in natural assemblages. The formulation is based on the retrieval of thermodynamic parameters from existing experimental work, which were carefully scrutinized for silica-saturation. This was followed by a robust test of the applicability of the barometer to both experimental run products and well-constrained natural assemblages at unit silica activity.

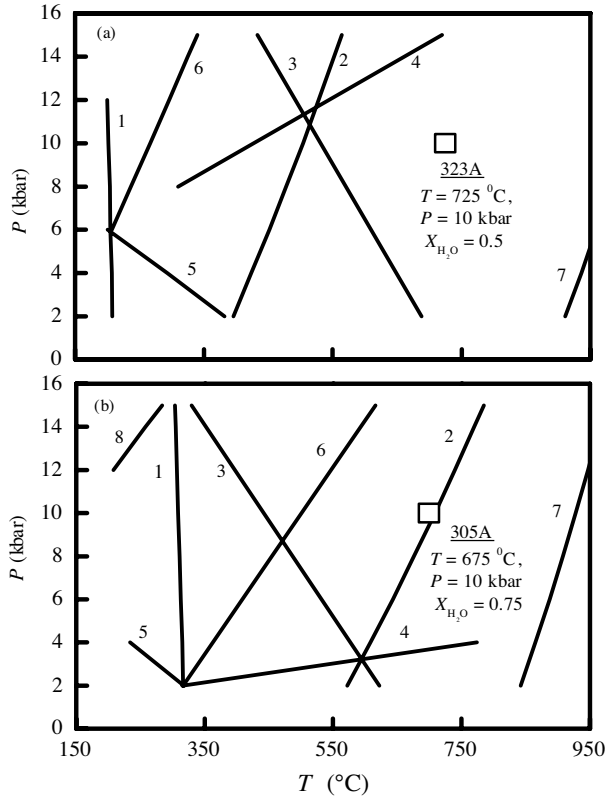

FIGURE 1. A comparison of the experimental *P-T* conditions (box), and the *P-T* locations of possible vapor-free reactions obtained using the THERMOCALC program of Holland and Powell (1998) for compositions of run products (**a**) 323A (*T* = 725 °C, *P* = 10 kbar) and (**b**) 305A (*T* = 675 °C, *P* = 10 kbar) in Conrad et al. (1988). The numbers keyed to the lines correspond to the reactions: (1) Tr + 2East = Ts + 2Phl; (2) Ts + 2Ab = Gl + 2An; (3) 2Prg + 8Qtz = Tr + Gl +2An; (4) 2Prg + 8Qtz = Tr + Ts + 2Ab; (5) Prg + Phl + 4Qtz = Tr + Ab + East; (6) Prg + East + 4Qtz = Ts + Ab + Phl; (7) Prg + Ab + East + 4Qtz = Gl + 2An + Phl; (8) 2Prg + 2East + 8Qtz = Ts + Gl + 2An + 2Phl. *P-T* location of reaction 8 lies beyond the *P-T* window in **a**. Mineral abbreviations are from Kretz (1983).

THEORETICAL CONSIDERATIONS

The barometric reaction modeled in this study is

$$\underset{\text{(Tr)}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{(Ts)}}{Ca_2Mg_3Al_4Si_6O_{22}(OH)_2} + \underset{\text{(Ab)}}{2NaAlSi_3O_8} = \underset{\text{(Prg)}}{2NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2} + \underset{\text{(Qtz)}}{8\ SiO_2} \quad \text{(A)}$$

For this reaction, the condition for equilibrium at *P* and *T* can be expressed as

$$\Delta G = 0 = \Delta H° - T\Delta S° + P\Delta V° + RT \ln K_{ideal} + RT \ln\gamma_{Amph} - 2RT \ln\gamma_{Ab} \quad (1)$$

where $\Delta H°$, $\Delta S°$, and $\Delta V°$ are the changes in enthalpy, entropy, and volume of the reaction, respectively, at the equilibrium *P* and *T* conditions. γ_{Amph} is the activity coefficient term for expressing the deviation from ideality arising from intra-site and cross-site mixing in amphibole (cf. Powell and Holland 1993), and γ_{Ab} is the activity coefficient of albite in plagioclase. K_{ideal} is expressed in the form

$$K_{ideal} = \frac{(X_{Prg})^2}{(X_{Ts})(X_{Tr})(X_{Ab})^2} \quad (2)$$

γ_{Ab} is expressed by Holland and Powell (1992) and Dale et al. (2000) as

$$R T \ln\gamma_{Ab} = W_{I\bar{1}}(1 - X_{Ab})^2 - \Delta W X_b^2 \quad (3a)$$

for the $I\bar{1}$ structural state in plagioclase, for which $X_{An} > X_b$, with $X_b = 0.12 + 0.00038T$ (K) and, for the $C\bar{1}$ structure

$$R T \ln\gamma_{Ab} = W_{C\bar{1}}(1 - X_{Ab})^2 \quad (3b)$$

where: $W_{I\bar{1}}$ = 10.0 kJ, $W_{C\bar{1}}$ = 1.0 kJ, and $\Delta W = W_{I\bar{1}} - W_{C\bar{1}}$.

The mole fraction terms for amphibole end-members tremolite (X_{Tr}), tschermakite (X_{Ts}), and pargasite (X_{Prg}) are calculated using the on-site mixing model (Powell 1978) on A, M13, M2, M4, and T1 sites. M13 represents equivalent M1 (two) and M3 (one) sites (Table 1a). The mixing parameters include Na-□ (vacancy) in the A-site, Mg-Al in the M2 site, and Al-Si in the T1 site (Table 1a). The mole fraction X_{Prg}, X_{Ts}, and X_{Tr} are expressed as:

$$X_{Prg} = 64(X^{A}_{Na})(X^{M4}_{Ca})^2(X^{M13}_{Mg})^3(X^{M2}_{Mg})(X^{M2}_{Al})(X^{T1}_{Al})^2(X^{T1}_{Si})^2$$

$$X_{Ts} = 16(X^{A}_{\square})(X^{M4}_{Ca})^2(X^{M13}_{Mg})^3(X^{M2}_{Al})^2(X^{T1}_{Al})^2(X^{T1}_{Si})^2,$$

and

$$X_{\mathrm{Tr}} = (X^{\mathrm{A}}_{\square})(X^{\mathrm{M4}}_{\mathrm{Ca}})^2(X^{\mathrm{M13}}_{\mathrm{Mg}})^3(X^{\mathrm{M2}}_{\mathrm{Mg}})^2(X^{\mathrm{T1}}_{\mathrm{Si}})^4. \quad (4)$$

The normalization factors (64 and 16) in Equation 4 make the mole fraction of end-member components equal to unity, and X^j_i denotes the mole fraction of cation i in site j of the amphibole.

Substitution of Equation 4 into Equation 2 yields

$$K_{\mathrm{ideal}} = \frac{(64)^2(X^{\mathrm{A}}_{\mathrm{Na}})^2(X^{\mathrm{M4}}_{\mathrm{Ca}})^4(X^{\mathrm{M13}}_{\mathrm{Mg}})^6(X^{\mathrm{M2}}_{\mathrm{Mg}})^2(X^{\mathrm{M2}}_{\mathrm{Al}})^2(X^{\mathrm{T1}}_{\mathrm{Al}})^4(X^{\mathrm{T1}}_{\mathrm{Si}})^4}{16(X^{\mathrm{A}}_{\square})^2(X^{\mathrm{M4}}_{\mathrm{Ca}})^4(X^{\mathrm{M13}}_{\mathrm{Mg}})^6(X^{\mathrm{M2}}_{\mathrm{Mg}})^2(X^{\mathrm{M2}}_{\mathrm{Al}})^2(X^{\mathrm{T1}}_{\mathrm{Al}})^2(X^{\mathrm{T1}}_{\mathrm{Si}})^6(X_{\mathrm{Ab}})^2}$$
$$= \frac{256(X^{\mathrm{A}}_{\mathrm{Na}})^2(X^{\mathrm{T1}}_{\mathrm{Al}})^2}{(X^{\mathrm{A}}_{\square})^2(X^{\mathrm{T1}}_{\mathrm{Si}})^2(X_{\mathrm{Ab}})^2}$$
$$= \left[\frac{16(X^{\mathrm{A}}_{\mathrm{Na}})(X^{\mathrm{T1}}_{\mathrm{Al}})}{(X^{\mathrm{A}}_{\square})(X^{\mathrm{T1}}_{\mathrm{Si}})(X_{\mathrm{Ab}})}\right]$$

Hence,

$$\mathrm{R}T\ln K_{\mathrm{ideal}} = 2\mathrm{R}T\ln\left[\frac{16(X^{\mathrm{A}}_{\mathrm{Na}})(X^{\mathrm{T1}}_{\mathrm{Al}})}{(X^{\mathrm{A}}_{\square})(X^{\mathrm{T1}}_{\mathrm{Si}})(X_{\mathrm{Ab}})}\right]. \quad (5)$$

The non-ideal activity coefficient (γ_{Amph}) for amphibole end-members was formulated assuming symmetric within-site and Bragg-Williams cross-site mixing parameters (Holland and Blundy 1994). In the model barometric reaction A, the $Na^{A}_{2}Al^{T1}_{2}(\square^{A}_{-2}Si^{T1}_{-2})$ exchange vector relates the amphibole end-members on either side of the reaction. This implies that the non-ideality on sites other than A (alkali) and T1 (tetrahedral) cancel out, and therefore are ignored in the present formulation. The model thus considers the effect of within-site mixing on the A and T1 sites and cross-site mixing on A-M4, A-M13, A-M2, A-T1, M4-T1, M13-T1, and M2-T1 sites. The interaction-parameters arising out of mixing on these sites are listed in Table 2.

For the regular solution model, the general expression of the non-ideality arising from within-site mixing was given by Equation 4 of Holland and Blundy (1994)

$$\mathrm{R}T\ln\gamma_r = -n\sum_{i=1}\sum_{j>1} y_i y_j W_{ij} \quad (6)$$

where "r" represents the amphibole end-member, n is the site multiplicity, y_k is the normalized mole-fraction ($X_{k,\text{end-member}} - X_k$), and W_{ij} is the interaction between ions i and j within a single site. Thus, for end-member tremolite, the non-ideal activity due to mixing of Al and Si on T1 site can be written in terms of mole fractions $X^{\mathrm{T1}}_{\mathrm{Al}}$, $X^{\mathrm{T1}}_{\mathrm{Si}}$, and the interaction parameter W_{AlSi} as

$\mathrm{R}T\ln\gamma_{\mathrm{Tr}} = -4(-X^{\mathrm{T1}}_{\mathrm{Al}})(1 - X^{\mathrm{T1}}_{\mathrm{Si}})W_{\mathrm{AlSi}}$.

TABLE 2. Interaction parameters arising from within-site and cross-site mixing in amphibole

Within-site mixing		
Site		Mixing parameter
A	3 terms	W_{NaK}, $W_{\mathrm{Na}\square}$, $W_{\mathrm{K}\square}$
T1	1 term	W_{AlSi}
Cross-site mixing		
Site		Mixing parameter
A↔M4	2 terms	$W_{\square\mathrm{CaNaNa}}$, $W_{\square\mathrm{CaKNa}}$
A↔M13	1 terms	$W_{\square\mathrm{FeNaMg}}$
A↔M2	3 terms	$W_{\square\mathrm{MgNaAl}}$, $W_{\square\mathrm{MgNaFe^{3+}}}$, $W_{\square\mathrm{MgNaFe}}$
A↔T1	2 terms	$W_{\square\mathrm{SiNaAl}}$, $W_{\square\mathrm{SiKAl}}$
M4↔T1	1 term	W_{CaAlNaSi}
M13↔T1	1 term	W_{MgSiFeAl}
M2↔T1	3 terms	W_{MgSiAlAl}, W_{MgSiFeAl}, $W_{\mathrm{MgSiFe^{3+}Al}}$

The general non-ideality expression for end-member "p" arising due to cross-site mixing has the form

$$\mathrm{R}T\ln\gamma_p = \sum_{i\neq r}\sum_{j\neq s} y_{i1}y_{j2}W_{rsij}$$

(Holland and Blundy 1994; Eq. 6), (7)

where y_k is the normalized mole fraction and W_{rsij} is the interaction energy due to mixing of *r*-*i* on site 1 and *s*-*j* on site 2. The total number of independent interaction parameters is given as $(m\text{-}1)(n\text{-}1)$, with m ions on site 1 and n ions on site 2 (Powell 1977). Therefore, for cross-site mixing between A and T1, with Na-K-□ on A-site and Si-Al on T1-site, we have two independent interaction parameters, $W_{\square\mathrm{SiNaAl}}$ and $W_{\square\mathrm{SiKAl}}$. For end-member tremolite, the cross-site term according to Equation 7, will be

$$\mathrm{R}T\ln\gamma_{\mathrm{Tr}} = (-X^{\mathrm{A}}_{\mathrm{Na}})(-X^{\mathrm{T1}}_{\mathrm{Al}})\,W_{\square\mathrm{SiNaAl}} + (-X^{\mathrm{A}}_{\mathrm{K}})(-X^{\mathrm{T1}}_{\mathrm{Al}})\,W_{\square\mathrm{SiKAl}}.$$

The non-ideal activity of amphibole ($\mathrm{R}T\ln\gamma_{\mathrm{Amph}}$) for the barometric reaction A can be expressed as

$$\mathrm{R}T\ln\gamma_{\mathrm{Amph}} = 2\mathrm{R}T\ln\gamma_{\mathrm{Prg}} - \mathrm{R}T\ln\gamma_{\mathrm{Tr}} - \mathrm{R}T\ln\gamma_{\mathrm{Ts}}. \quad (8)$$

Considering two within-site and seven cross-site mixing (Table 2) for the end-members, Equation 8 can be expressed linearly in terms of 8 mole fraction terms (i.e., $X^{\mathrm{A}}_{\mathrm{Na}}$, $X^{\mathrm{A}}_{\mathrm{K}}$, $X^{\mathrm{M4}}_{\mathrm{Na}}$, $X^{\mathrm{M13}}_{\mathrm{Fe^{2+}}}$, $X^{\mathrm{M2}}_{\mathrm{Al}}$, $X^{\mathrm{M2}}_{\mathrm{Fe^{2+}}}$, $X^{\mathrm{M2}}_{\mathrm{Fe^{3+}}}$, and $X^{\mathrm{T1}}_{\mathrm{Al}}$) and one constant term. So, the non-ideal term finally reduces to

$$\mathrm{R}T\ln\gamma_{\mathrm{Amph}} = a_1X^{\mathrm{A}}_{\mathrm{Na}} + a_2X^{\mathrm{A}}_{K} + a_3X^{\mathrm{M4}}_{\mathrm{Na}} + a_4X^{\mathrm{M13}}_{\mathrm{Fe^{2+}}} + a_5X^{\mathrm{M2}}_{\mathrm{Al}} + a_6X^{\mathrm{M2}}_{\mathrm{Fe^{2+}}} + a_7X^{\mathrm{M2}}_{\mathrm{Fe^{3+}}} + a_8X^{\mathrm{T1}}_{\mathrm{Al}} + a_9 \quad (9)$$

where:

$$a_1 = -4W_{\mathrm{Na}\square} - W_{\square\mathrm{MgNaAl}} - 0.5W_{\square\mathrm{SiNaAl}}$$

$$a_2 = 2W_{\mathrm{NaK}} - 2W_{\mathrm{Na}\square} - 2W_{\mathrm{K}\square} + 0.5W_{\square\mathrm{SiKAl}}$$

$$a_3 = 0.5W_{\mathrm{CaAlNaSi}} - 2W_{\square\mathrm{CaNaNa}}$$

$$a_4 = 2W_{\square\mathrm{FeNaMg}} - 0.5W_{\mathrm{MgSiFeAl}}$$

$$a_5 = -0.5W_{\mathrm{MgSiAlAl}} - W_{\square\mathrm{MgNaAl}}$$

$$a_6 = -0.5W_{\mathrm{MgSiFeAl}} - 2W_{\square\mathrm{MgNaFe}}$$

$$a_7 = -0.5W_{\mathrm{MgSiFe^{3+}Al}} - 2W_{\square\mathrm{MgNaFe^{3+}}}$$

$$a_8 = -4W_{\mathrm{AlSi}} - 2W_{\square\mathrm{SiNaAl}}$$

and

$$a_9 = 2W_{\mathrm{Na}\square} + W_{\mathrm{AlSi}} + W_{\square\mathrm{SiNaAl}}$$

Incorporating Equations 5 and 9 into Equation 1 yields

$$\Delta G = 0 = \Delta H^\circ - T\Delta S^\circ + P\Delta V^\circ + 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right] + a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al} + a_9 - 2RT\ln\gamma_{Ab}. \quad (10)$$

The equation further reduces to

$$\Delta G = 0 = \Delta\hat{H} - T\Delta S^\circ + P\Delta V^\circ + 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right] + a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al} - 2RT\ln\gamma_{Ab} \quad (11)$$

where $\Delta\hat{H} = \Delta H^\circ + a_9$.

Rearranging the equation with known terms to the left hand side, the expression used in the regression analysis to determine the ten unknown parameters ($\Delta\hat{H}$, ΔS°, and a_1 to a_8) takes the form of

$$2RT\ln\gamma_{Ab} - P\Delta V^\circ - 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right] = \Delta\hat{H} - T\Delta S^\circ + a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al}$$

or,

$$Y = \Delta\hat{H} - T\Delta S^\circ + a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al} \quad (12)$$

where $Y = 2RT\ln\gamma_{Ab} - P\Delta V^\circ - 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right]$.

In the regression analysis, the compositions of the co-existing hornblende and plagioclase were obtained from 42 silica-saturated experimental runs (discussed later). The mole fraction terms are explained in Table 3.

Alternatively, ΔH° and ΔS° in Equation 10 may be used as inputs from existing thermodynamic databases. These parameters, therefore, may be associated with the other known parameters in Equation 10, and the relevant expression after rearranging the terms takes the following form

$$2RT\ln\gamma_{Ab} - P\Delta V^\circ - 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right] - \Delta H^\circ + T\Delta S^\circ = a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al} + a_9$$

or,

$$Z = a_1X^{A}_{Na} + a_2X^{A}_{K} + a_3X^{M4}_{Na} + a_4X^{M13}_{Fe^{2+}} + a_5X^{M2}_{Al} + a_6X^{M2}_{Fe^{2+}} + a_7X^{M2}_{Fe^{3+}} + a_8X^{T1}_{Al} + a_9 \quad (13)$$

where, $Z = 2RT\ln\gamma_{Ab} - P\Delta V^\circ - 2RT\ln\left[\frac{16X^{A}_{Na}X^{T1}_{Al}}{X^{A}_{\square}X^{T1}_{Si}X_{Ab}}\right] - \Delta H^\circ + T\Delta S^\circ$.

The ΔV° of reaction 13 was calculated after the formulations of Holland et al. (1996), Pawley et al. (1996), and Holland and Powell (1998), using the thermodynamic dataset of Holland and Powell (1998). The volume expression incorporating κ_{298} (bulk modulus) and a° (thermal expansion) for each phase is

$$V_{P,T} = V_{1,T}\left[1 - \frac{4P}{\kappa_T + 4P}\right]^{1/4} \quad (14)$$

$\kappa_T = \kappa_{298}\,[1 - 1.5\times10^{-4}(T - 298)]$ and

$$V_{1,T} = \left\{V_{1,298}\left[1 + a^\circ(T - 298) - 20a^\circ\left(\sqrt{T} - \sqrt{298}\right)\right]\right\}.$$

The constants κ_{298} and a° for the phases were obtained from Table 5 of Holland and Powell (1998).

THE GEOBAROMETER: CHOICE OF EXPERIMENTAL DATA SET AND DATA RETRIEVAL

In reaction A, the stoichiometric proportion of quartz is high. It was felt imperative, therefore, to ascertain if the activity of quartz, a_{SiO_2}, in the experimental runs approximated unity. A large data set exists for coexisting compositions of hornblende and plagioclase for dehydration, melting, and crystallization experiments performed with mafic and felsic starting materials (Table 4[1]). The experimental data set can be divided into two categories: (1) Experiments with quartz in the starting assemblage or in the run products; and (2) Melting/crystallization experiments performed with quartz-undersaturated mafic starting compositions, in which hornblende and plagioclase coexist with felsic melts (rhyolite to tonalite in composition, Table 4[1]). Since the presence of quartz

TABLE 3. Scheme for calculation of mole fraction terms (Eq. 12) in amphibole

X^{A}_{Na} = Na in A-site
X^{A}_{K} = K in A-site
X^{M4}_{Na} = 1/2(Na in M4/B-site)
$X^{M13}_{Fe^{2+}} = r = Fe^{2+}/(Fe^{2+} + Mg)$ in amphibole
X^{M2}_{Al} = 1/2(Al in M2-site)
$X^{M2}_{Fe^{3+}}$ = 1/2(Fe^{3+} in M2-site)
$X^{M2}_{Fe^{2+}} = (1 - X^{M2}_{Fe^{3+}} - X^{M2}_{Al} - X^{M2}_{Ti}) \cdot r$
X^{T1}_{Al} = 1/4(8-Si)
X^{T1}_{Si} = 1/4(Si-4)
$X^{A}_{\square}$ = 1 – ΣA-site

Notes: Amphibole analyses were recast (following average Fe^{3+} estimation of Leake et al. 1997) into eight tetrahedral (4T1 and 4T2), five octahedral (C-site in Leake et al. 1997, that includes 3 M13 sites and 2 M2 sites), two cubic (B-site in Leake et al. 1997, or the M4 site) and one Alkali (A) site.

[1] Deposit item AM-07-012, Tables 4, 8, and 9 and Appendix 1 and Appendix 2. (A large data set for coexisting compositions of hornblende and plagioclase for dehydration, melting, and crystallization experiments performed with mafic and felsic starting materials; the difference between P_1 and P_2 values; and estimated pressures in quartz-bearing natural assemblages, respectively.) Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 5. Structural formula of amphiboles (recast following Leake et al. 1997) and X_{Ab} in coexisting plagioclase in the 42 experimental runs chosen for retrieval calculations

Ref. no.	Exp. run no.	Si	Al	Ti	ΣT	Al	Ti	Fe^{3+}	Cr	Mg	Fe^{2+}	Mn	ΣC	Fe^{2+}	Mn	Ca	Na	ΣB	Na	K	ΣA	X_{Ab}
PB1	1093-2/1H	6.91	1.09	0.00	8.00	0.21	0.17	0.28	0.00	2.80	1.54	0.00	5.00	0.01	0.07	1.79	0.13	2.00	0.25	0.13	0.38	0.60
PB2	1093-12/1H	6.79	1.21	0.00	8.00	0.26	0.20	0.21	0.00	2.56	1.77	0.01	5.00	0.00	0.06	1.85	0.09	2.00	0.29	0.14	0.43	0.60
PB3	1093-17/1H	6.71	1.29	0.00	8.00	0.14	0.22	0.34	0.00	2.97	1.33	0.00	5.00	0.04	0.06	1.78	0.12	2.00	0.36	0.13	0.49	0.58
PB4	1093-34/1H	6.81	1.19	0.00	8.00	0.28	0.23	0.30	0.00	2.71	1.48	0.00	5.00	0.02	0.07	1.75	0.16	2.00	0.19	0.13	0.32	0.56
PB5	292-15/1H	6.86	1.14	0.00	8.00	0.15	0.13	0.42	0.00	2.78	1.51	0.00	5.00	0.00	0.06	1.86	0.08	2.00	0.24	0.15	0.39	0.60
PB6	292-34/1H	6.71	1.29	0.00	8.00	0.09	0.22	0.36	0.00	2.88	1.44	0.00	5.00	0.05	0.05	1.79	0.11	2.00	0.37	0.13	0.50	0.59
PB7	APD584/PC	6.78	1.22	0.00	8.00	0.19	0.23	0.26	0.00	2.72	1.58	0.03	5.00	0.00	0.06	1.86	0.07	2.00	0.26	0.14	0.40	0.58
PB8	APD554/PC	6.83	1.17	0.00	8.00	0.05	0.16	0.62	0.00	2.98	1.19	0.01	5.00	0.00	0.07	1.84	0.08	2.00	0.15	0.13	0.28	0.56
PB9	APD511/PC	6.39	1.61	0.00	8.00	0.40	0.26	0.42	0.00	2.65	1.26	0.00	5.00	0.08	0.04	1.64	0.24	2.00	0.36	0.14	0.51	0.51
PB10	APD588/PC	6.70	1.30	0.00	8.00	0.21	0.23	0.30	0.00	2.76	1.50	0.00	5.00	0.04	0.05	1.78	0.13	2.00	0.33	0.13	0.46	0.60
PB11	547/PC	6.80	1.20	0.00	8.00	0.68	0.19	0.18	0.00	2.89	1.07	0.00	5.00	0.02	0.03	1.51	0.44	2.00	0.27	0.14	0.41	0.60
PB12	571PCc	6.63	1.37	0.00	8.00	0.31	0.24	0.32	0.00	3.18	0.95	0.00	5.00	0.06	0.04	1.72	0.19	2.00	0.29	0.17	0.46	0.44
PB13	552/PCc	6.34	1.66	0.00	8.00	0.47	0.26	0.58	0.00	2.73	0.96	0.00	5.00	0.15	0.05	1.52	0.29	2.00	0.19	0.20	0.39	0.46
PB14	570/PCc	6.21	1.79	0.00	8.00	0.86	0.27	0.28	0.00	2.44	1.16	0.00	5.00	0.04	0.03	1.55	0.37	2.00	0.21	0.27	0.48	0.55
S1	T2-119A	7.27	0.73	0.00	8.00	0.28	0.04	0.41	0.00	3.93	0.34	0.00	5.00	0.11	0.02	1.68	0.19	2.00	0.13	0.02	0.15	0.51
S2	T2-124A	7.20	0.80	0.00	8.00	0.10	0.05	0.50	0.00	4.32	0.03	0.00	5.00	0.27	0.06	1.57	0.10	2.00	0.17	0.02	0.19	0.50
S3	T2-45B	7.23	0.77	0.00	8.00	0.23	0.05	0.41	0.00	4.29	0.02	0.00	5.00	0.40	0.05	1.39	0.16	2.00	0.16	0.02	0.18	0.56
S4	T2-R44	6.92	1.08	0.00	8.00	0.32	0.15	0.38	0.00	4.05	0.12	0.00	5.00	0.26	0.06	1.39	0.29	2.00	0.33	0.05	0.39	0.58
S5	T2-125A	7.13	0.87	0.00	8.00	0.24	0.08	0.45	0.00	3.89	0.34	0.00	5.00	0.12	0.05	1.63	0.20	2.00	0.18	0.04	0.21	0.50
S6	T2-44A	7.12	0.88	0.00	8.00	0.39	0.06	0.39	0.00	3.67	0.49	0.00	5.00	0.06	0.05	1.65	0.24	2.00	0.19	0.02	0.21	0.43
S7	T2-126A	6.91	1.09	0.00	8.00	0.37	0.07	0.55	0.00	3.56	0.45	0.00	5.00	0.11	0.05	1.63	0.21	2.00	0.20	0.04	0.23	0.56
EL1	900/1.0	6.09	1.91	0.00	8.00	0.54	0.29	0.46	0.00	2.26	1.45	0.00	5.00	0.10	0.03	1.68	0.18	2.00	0.49	0.02	0.51	0.44
EL2	800/1.0	6.23	1.77	0.00	8.00	0.68	0.21	0.32	0.00	2.15	1.64	0.00	5.00	0.06	0.03	1.73	0.18	2.00	0.51	0.02	0.53	0.44
EL3	800/1.2	6.27	1.73	0.00	8.00	0.85	0.19	0.33	0.00	2.03	1.61	0.00	5.00	0.06	0.03	1.68	0.22	2.00	0.36	0.03	0.39	0.45
EL4	750/1.0	6.64	1.36	0.00	8.00	0.69	0.15	0.15	0.00	2.16	1.85	0.00	5.00	0.01	0.03	1.78	0.17	2.00	0.37	0.03	0.39	0.55
EL5	700/0.8	6.56	1.44	0.00	8.00	0.66	0.13	0.20	0.00	2.15	1.86	0.00	5.00	0.03	0.03	1.84	0.10	2.00	0.39	0.03	0.42	0.47
EL6	700/1.0	6.47	1.53	0.00	8.00	0.72	0.14	0.15	0.00	2.11	1.88	0.00	5.00	0.02	0.02	1.86	0.10	2.00	0.45	0.03	0.48	0.61
SD1	B1	6.40	1.60	0.00	8.00	0.57	0.17	0.24	0.00	2.30	1.72	0.00	5.00	0.04	0.03	1.85	0.08	2.00	0.38	0.15	0.53	0.45
SD2	B3	6.38	1.62	0.00	8.00	0.53	0.16	0.35	0.00	2.36	1.60	0.00	5.00	0.05	0.03	1.81	0.10	2.00	0.37	0.15	0.52	0.46
CNW1	624A	6.63	1.37	0.00	8.00	0.72	0.20	0.36	0.00	2.22	1.49	0.00	5.00	0.28	0.03	1.38	0.31	2.00	0.12	0.08	0.20	0.57
CNW2	323A	6.66	1.34	0.00	8.00	0.56	0.12	0.59	0.00	1.90	1.83	0.00	5.00	0.21	0.05	1.42	0.32	2.00	0.20	0.08	0.27	0.65
CNW3	321A	6.56	1.44	0.00	8.00	0.60	0.16	0.50	0.00	1.94	1.80	0.00	5.00	0.10	0.04	1.58	0.28	2.00	0.16	0.13	0.30	0.64
CNW4	305A	6.41	1.59	0.00	8.00	0.84	0.13	0.35	0.00	2.02	1.66	0.00	5.00	0.07	0.03	1.72	0.18	2.00	0.26	0.06	0.32	0.62
CNW5	310A	6.40	1.60	0.00	8.00	0.95	0.13	0.23	0.00	1.85	1.84	0.00	5.00	0.03	0.03	1.71	0.23	2.00	0.23	0.15	0.38	0.63
P1	R8A	6.56	1.44	0.00	8.00	0.91	0.01	0.24	0.00	2.09	1.75	0.00	5.00	0.06	0.01	1.75	0.18	2.00	0.45	0.01	0.46	0.75
P2	R5A	6.87	1.13	0.00	8.00	0.74	0.00	0.29	0.00	2.37	1.60	0.00	5.00	0.01	0.08	1.68	0.24	2.00	0.30	0.03	0.33	0.80
P3	R11	6.78	1.22	0.00	8.00	0.97	0.00	0.26	0.00	2.43	1.34	0.00	5.00	0.07	0.00	1.56	0.37	2.00	0.35	0.00	0.35	0.82
JR1	80	6.27	1.73	0.00	8.00	0.42	0.23	0.32	0.00	1.89	2.15	0.00	5.00	0.05	0.05	1.80	0.11	2.00	0.43	0.21	0.64	0.62
H1	PG-750	6.53	1.47	0.00	8.00	0.55	0.15	0.08	0.00	1.79	2.42	0.00	5.00	0.02	0.00	1.81	0.17	2.00	0.60	0.09	0.70	0.48
H2	1921-700	7.00	1.00	0.00	8.00	0.22	0.14	0.11	0.00	2.90	1.64	0.00	5.00	0.03	0.00	1.92	0.05	2.00	0.37	0.09	0.46	0.44
H3	1921-HM725	6.86	1.14	0.00	8.00	0.44	0.13	0.13	0.00	3.09	1.21	0.00	5.00	0.04	0.00	1.83	0.14	2.00	0.35	0.09	0.44	0.39
H4	1921-HM825	6.72	1.28	0.00	8.00	0.54	0.15	0.18	0.00	3.00	1.13	0.00	5.00	0.05	0.00	1.77	0.17	2.00	0.35	0.08	0.43	0.20

Notes: Structural formula of amphiboles (recast following Leake et al. 1997) and X_{Ab} in coexisting plagioclase in the 42 experimental runs chosen for retrieval calculations. References: PB, Patino–Douce and Beard (1995); S, Spear (1981b); EL, Ernst and Liu (1998); SD, Sen and Dunn (1994); CNW, Conrad et al. (1988); P, Poli (1993); JR, Johnson and Rutherford (1989); CW, Carroll and Wyllie (1989, 1990); BS, Blundy and Sparks (1992); RD, Rutherford and Devine (1988); RSCD, Rutherford et al. (1985); H, Helz (1973, 1976); RW, Rapp and Watson (1995); and LC, Lopez and Castro (2001).

constrains a_{SiO_2} to be equal to unity, the first set of experiments was used for the retrieval calculation.

Different schemes have been proposed for recalculating Fe^{3+} in amphibole from electron-probe microanalytical data. In the present study, amphibole compositions in the experimental runs were recast following the scheme outlined by Leake et al. (1997). Computed Fe^{3+} in the experimental amphiboles corresponds to the average estimate of Leake et al. (1997). The compositions of co-existing plagioclase are provided in Table 5. The f_{O_2} conditions of experimental runs vary widely (Table 4[1]). Since f_{O_2} conditions are known to influence the $Fe^{2+}/(Fe^{2+} + Mg)$ ratio in amphiboles (cf. Spear 1981a), Fe^{2+}, Mg, and other cations are likely to be redistributed in the different crystallographic sites in amphiboles via coupled substitutions to accommodate Fe^{3+}. Therefore, if the energetics of intra-site and cross-site cation interactions are adequately constrained (as attempted in this study), the incorporation of f_{O_2} as an explicit variable is arguably not essential for the barometer equation, although the problem of how much Fe^{3+} is present remains speculative.

The correlation matrix between the site fraction terms (Eq. 12) is shown in Table 6. The site fraction terms in (Eq. 12) are poorly correlated (Table 6), except for $X^{A}_{Na} - X^{A}_{\square}$ and $X^{T1}_{Al} - X^{T1}_{Si}$. By implication, the a terms in Equation 12 vary independently of each other. The standard-state enthalpy and entropy values of end-member components, especially those of tschermakite, pargasite, and albite, vary widely (Table 1b). This is reflected in the differences in ΔS and ΔH values (Table 1c) computed for reaction A using the updated internally consistent thermodynamic databases. In view of the discrepancy, the regression analysis on the 42 experimental runs (Tables 4[1] and 5) was done in two different ways, viz.: (1) Equation 12 was adopted to retrieve $\Delta\hat{H} = \Delta H° + a_9$), $\Delta S°$, and a_1 *to* a_8 using experimental P, T, and X terms as inputs; and (2) Equation 13 was adopted to retrieve a_1 to a_9 using $\Delta H°$ and $\Delta S°$ as inputs from the data sets of Berman (1988) and Mäder et al. (1994) on one hand, and Holland and Powell (1998) on the other.

In the first step, the ten unknown parameters including $\Delta\hat{H}$ and $\Delta S°$ in the right-hand side of Equation 12 were retrieved following a linear least-squares fit to the experimental data set (Table 5). Ideally, the regression would be more robust if

TABLE 6. Correlation matrix of the mole fraction terms (Eq. 12) in amphibole and X_{Ab} in co-existing plagioclase for the experimental data used in the regression analysis

	X^{A}_{Na}	X^{A}_{K}	X^{M4}_{Na}	X^{M13}_{Fe2+}	X^{M2}_{Al}	X^{M2}_{Fe2+}	X^{M2}_{Fe3+}	X^{T1}_{Al}	X^{T1}_{Si}	$X^{A}_{\square}$	X_{Ab}
X^{A}_{Na}	1.000										
X^{A}_{K}	–0.095	1.000									
X^{M4}_{Na}	–0.281	–0.015	1.000								
X^{M13}_{Fe2+}	0.529	0.213	–0.104	1.000							
X^{M2}_{Al}	0.235	–0.190	0.528	0.509	1.000						
X^{M2}_{Fe2+}	0.598	0.291	–0.484	0.786	–0.005	1.000					
X^{M2}_{Fe3+}	–0.586	–0.009	0.148	–0.402	–0.341	–0.562	1.000				
X^{T1}_{Al}	0.506	0.354	0.093	0.703	0.552	0.319	–0.137	1.000			
X^{T1}_{Si}	–0.506	–0.354	–0.093	–0.703	–0.552	–0.319	0.137	–1.000	1.000		
$X^{A}_{\square}$	–0.863	–0.421	0.263	–0.590	–0.117	–0.692	0.539	–0.641	0.641	1.000	
X_{Ab}	–0.119	–0.053	0.220	0.240	0.214	0.139	0.046	–0.091	0.091	0.135	1.000

the number of equations (runs) was more and fewer unknowns (coefficients) were to be retrieved. But due to the unavoidable limitation of adequate experimental work for the theoretical model adopted, the present study possibly represents a somewhat under-determined system. The regression data are summarized in column 1 of Table 7. The retrieved parameters were then fed back into Equation 12, and pressures (P_{com}) recalculated at the experimental temperature for the composition of coexisting Hbl and Pl in the experimental runs. Seven of the 42 data points (17%) lie outside 2 kbar uncertainty (Fig. 2a). The aberrant plots include PB 2, 10, and 11 (Patino-Douce and Beard 1995), S6 (Spear 1981b), EL 6 (Ernst and Liu 1998), and H2 and H4 (Helz 1973, 1976).

In the next step, the seven aberrant data were excluded from the linear least-squares fit. The retrieved parameters (column 2 of Table 7) for the set of 35 data substituted into Equation 12, and the computed pressures (P_{com}) were compared with the experimental values (P_{exp}) for 42 sets of experimental data (Fig. 2b). 71% of the experimental data lies within ±1.5 kbar error limit. The exclusion of the aberrant data set (columns 1 vs. 2, Table 7) led to substantial decrease in the standard deviation (~4.4 to 2.2) and increase in R^2 (~0.93 to 0.98). Exclusion of the aberrant data is potentially justified in as much as "real" data sets are typically non-Gaussian (Hubber 1981; Powell 1985) and the "outliers" considerably influence the linear least-squares fit (Powell 1985). The regressed data in column 2 of Table 7 were preferred for the following reasons: (1) the standard errors of the retrieved parameters are smaller, and less than one-third of the magnitude of the respective parameter required for statistical analysis; (2) the residual sum of squares (0.98) of the regression analysis is higher; and (3) the number of experimental P values that lie within 1.5 kbar of the computed pressure is higher (71%).

TABLE 7. Regression statistics of the linear least-square fit discussed in text

	Column 1	Column 2	Column 3	Column 4
Multiple R	0.965	0.992	0.991	0.984
R Squared	0.932	0.983	0.982	0.968
Standard error	4.431	2.231	2.269	2.787
Observation	42	35	35	35
$\Delta H + a_9$ (kJ)	–9.952 (17.606)	–9.326 (9.288)	–	–
ΔS (kJ/K)	–0.017 (0.015)	–0.0146 (0.009)	–	–
a_1 (kJ)	–96.312 (18.765)	–98.698 (9.983)	–102.692 (9.816)	–110.128 (12.045)
a_2 (kJ)	–33.772 (25.821)	–33.213 (13.471)	–35.251 (13.680)	–35.634 (16.799)
a_3 (kJ)	–9.101 (32.221)	–20.338 (17.456)	–15.969 (16.801)	5.822 (20.632)
a_4 (kJ)	–16.152 (42.443)	–39.101 (21.898)	–40.499 (20.399)	–55.813 (27.506)
a_5 (kJ)	87.034 (25.376)	100.392 (13.002)	93.069 (11.825)	76.251 (14.522)
a_6 (kJ)	97.882 (75.547)	131.030 (38.798)	130.750 (40.781)	150.642 (50.080)
a_7 (kJ)	75.515 (28.614)	82.479 (14.737)	74.226 (14.641)	65.917 (17.980)
a_8 (kJ)	–124.441 (50.373)	–118.653 (26.481)	–104.402 (21.802)	–57.587 (26.774)
a_9 (kJ)	–	–	13.523 (6.310)	25.048 (7.749)

Notes: Values within parenthesis are 1σ uncertainty in the respective retrieved parameters. Note the statistical parameters, e.g., R-square and standard errors, refer explicitly to the regression itself and not to the individual data points.

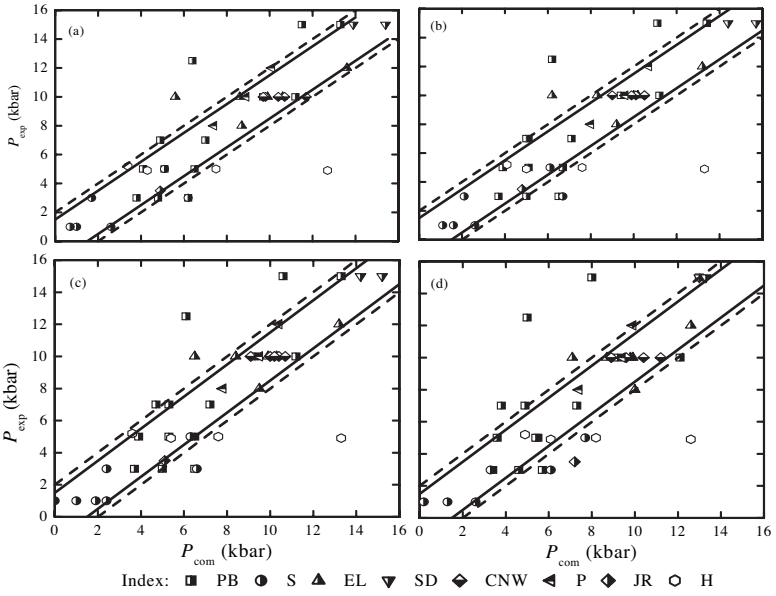

FIGURE 2. Experimentally determined P values (P_{exp}) plotted against computed pressures (P_{com}) estimated using the regressed parameters in column 1, Table 7 (**a**); column 2, Table 7 (**b**); column 3, Table 7 (**c**); column 4, Table 7 (**d**). ΔV is calculated from Equation 14 at the experimental P and T. Continuous and broken lines demarcate the 1.5 and 2 kbar limits respectively. Note that the same set of experimental runs, used in the regression analyses, were fed back in the barometric formulations (Eqs. 15 and 16) to estimate the pressure (P_{com}). Acronyms: PB, Patino-Douce and Beard (1995); S, Spear (1981b); EL, Ernst and Liu (1998); SD, Sen and Dunn (1994); CNW, Conrad et al. (1988); P, Poli (1993); JR, Johnson and Rutherford (1989); and H, Helz (1973 1976).

Another set of regression analysis was performed to determine a_1 to a_9 (Eq. 13), based on the data set of 35 experimental runs by adopting $\Delta H°$ and $\Delta S°$ from the internally consistent thermodynamic databases of Berman (1988) and Mäder et al. (1994) on the one hand and Holland and Powell (1998) on the other. The retrieved parameters listed in columns 3 and 4 (Table 7), respectively, were fed back into Equation 13 to compute the pressure at the experimental temperature for the compositions of co-existing hornblende and plagioclase. Between the two sets of standard-state thermodynamic data, the Berman (1988) and Mäder et al. (1994) databases generate a statistically superior fit (Table 7) to linear least-squares (higher R^2, lower standard error) reflected in the higher percentage of data points within the 2 kbar limit (Figs. 2c and 2d), e.g., ca. 83% using the database of Berman (1988) and Mäder et al. (1994), relative to ca. 76% computed using the database of Holland and Powell (1998). Consequently, the a_1 to a_9 parameters (column 3, Table 7) retrieved using $\Delta H°$ and $\Delta S°$ as input from Berman (1988) and Mäder et al. (1994) were preferred to those determined (column 4, Table 7) using $\Delta H°$ and $\Delta S°$ of Holland and Powell (1998). The magnitudes of a_1 to a_8 and $\Delta S°$ in column 3 (Table 7) are in excellent agreement with those retrieved (column 2, Table 7) from Equation 12 without using standard-state ΔH and ΔS as inputs from existing thermodynamic databases. Based on the results of the regression analyses, the following two barometric equations are proposed for reaction A.

$$P_1(\text{kbar}) = [-9.326 + 0.01462\text{T (K)} + R\mathit{T}\ln K_{\text{ideal}} - 98.698X^{\text{A}}_{\text{Na}} - 33.213X^{\text{A}}_{\text{K}} - 20.338X^{\text{M4}}_{\text{Na}} - 39.101X^{\text{M13}}_{\text{Fe}^{2+}} + 100.392X^{\text{M2}}_{\text{Al}} + 131.03X^{\text{M2}}_{\text{Fe}^{2+}} 82.479X^{\text{M2}}_{\text{Fe}^{3+}} - 118.653X^{\text{T1}}_{\text{Al}} - 2R\mathit{T}\ln\gamma_{\text{Ab}}]/(-\Delta V) \quad (15)$$

and

$$P_2(\text{kbar}) = [-1.869 + 0.0076\text{T (K)} + R\mathit{T}\ln K_{\text{ideal}} - 102.692X^{\text{A}}_{\text{Na}} - 35.251X^{\text{A}}_{\text{K}} - 15.969X^{\text{M4}}_{\text{Na}} - 40.499X^{\text{M13}}_{\text{Fe}^{2+}} + 93.069X^{\text{M2}}_{\text{Al}} + 130.750X^{\text{M2}}_{\text{Fe}^{2+}} + 74.226X^{\text{M2}}_{\text{Fe}^{3+}} - 104.402X^{\text{T1}}_{\text{Al}} - 2R\mathit{T}\ln\gamma_{\text{Ab}}]/(-\Delta V) \quad (16)$$

P_1 is formulated based on retrieved values of $\Delta\hat{H}° = \Delta H° + a_9$, $\Delta S°$, and a_1 *to* a_8 in column 2 (Table 7); whereas P_2 is formulated based on retrieved values of a_1 *to* a_8 (column 3, Table 7), with $\Delta H°$ and $\Delta S°$ used as input from Berman (1988) and Mäder et al. (1994). The difference between P_1 and P_2 values for experimental runs is less than 500 bars (Table 8[1]). Figure 3 shows the *P-T* loci of the barometric formulation P_2 (Eq. 16) for $R\ln K_{\text{ideal}}$ values between 0.01 and 0.03, neglecting the effects of non-ideality arising from intra- and cross-site mixing terms. For the P_1 barometer (Eq. 15), the *P-T* locations cannot be shown, because the non-ideal activity term (a_9) cannot be separated from the enthalpy ($\Delta H°$) term in the retrieved $\Delta\hat{H}$ parameter. But given the close correspondence between retrieved parameters in columns 2 and 3 of Table 7, the *P-T* loci of the two barometers are expected to be similar.

Plots of ΔP_1 ($= P_{\text{exp}} - P_{1,\text{com}}$) against compositional parameters in hornblende (Figs. 4a–4d) show the computed pressures to be independent of hornblende composition. By implication, the retrieved *a-X* relationship in hornblende is adequately constrained within the compositional limits of the experimental run products. Pressures were also estimated for the 42 experimental run data (Fig. 5) from reaction A using the THERMOCALC program of Holland and Powell (1998) and the TWQ (ver. 1.02) program of Berman (1988). The input activities of the phases used for pressure determination using THERMOCALC were computed from the AX program (Holland and Powell 1998). For the TWQ program, site fractions in hornblende were calculated from the

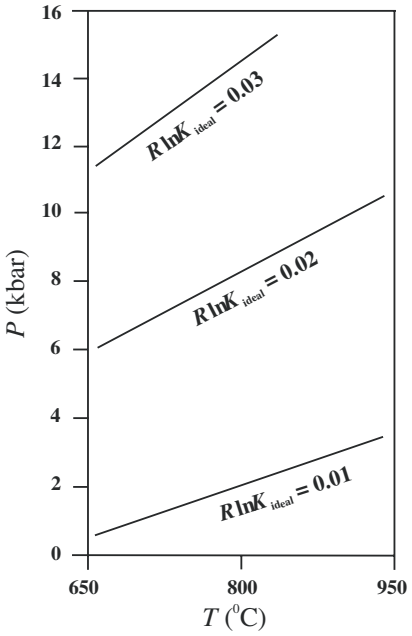

FIGURE 3. *P-T* locations of the proposed barometer P_2 (Eq. 16) for different $R\ln K_{\text{ideal}}$ values spanning the compositional limit of the phases in Table 5.

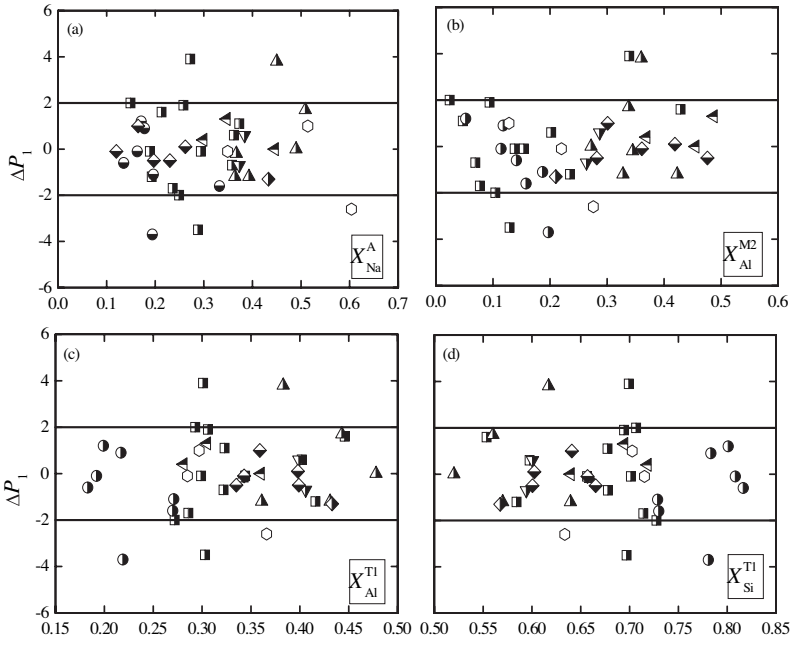

FIGURE 4. Variations of ΔP_1 ($= P_{\text{exp}} - P_{1,\text{com}}$) with compositional variables in amphiboles in experimental run products, e.g., (**a**) X^{A}_{Na}, (**b**) $X^{\text{M2}}_{\text{Al}}$, (**c**) $X^{\text{T1}}_{\text{Al}}$, and (**d**) $X^{\text{T1}}_{\text{Si}}$. Since the difference between computed pressures P_1 and P_2 is less than 500 bars, a plot ΔP_2 against the compositional variations is similar. Symbol style and abbreviations are identical to Figure 2.

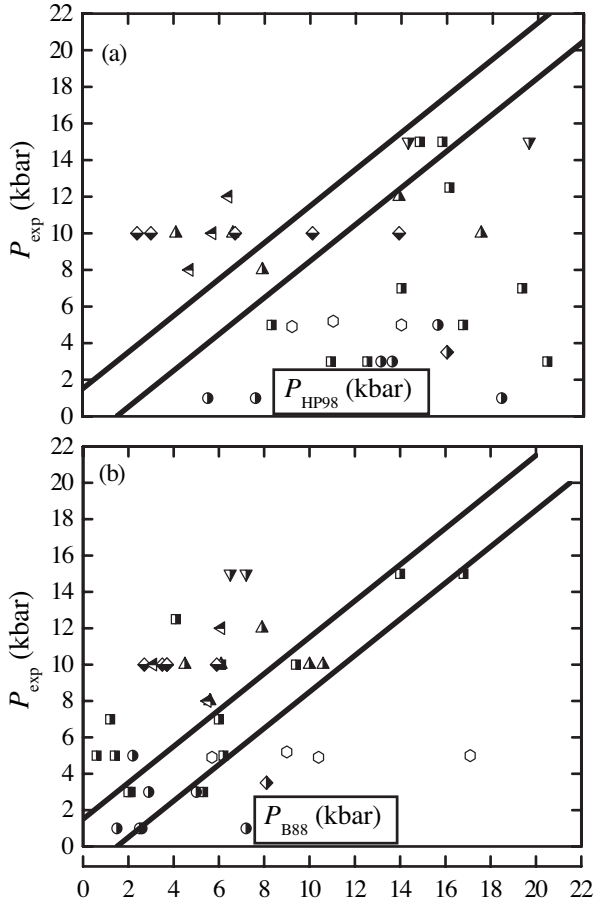

FIGURE 5. A comparison of experimentally determined P values (P_{exp}) with (**a**) pressures (P_{HP98}) estimated using the THERMOCALC program of Holland and Powell (1998), and (**b**) pressures (P_{B88}) estimated using the TWQ program of Berman (1988, v. 1.02).

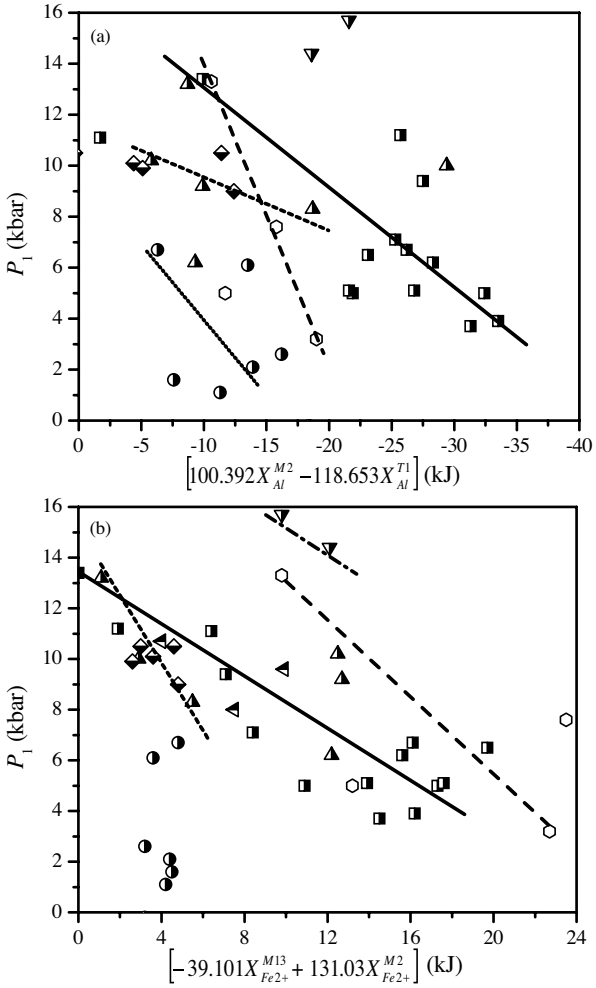

FIGURE 6. Variation of P_1 with (**a**) $[100.392X^{M2}_{Al} - 118.653X^{T1}_{Al}]$ and (**b**) $[-39.101X^{M13}_{Fe^{2+}} + 131.03X^{M2}_{Fe^{2+}}]$ (Eq. 15) for amphiboles in the 42 experimental runs. Symbols style and abbreviations are same as in Figure 2. Note the two terms are oppositely correlated with P_1. Each line corresponds to eye estimation fit to the compositional data for a set of experimental runs, e.g., PB (solid), S (dots), EL and CNW (short dash), SD (dash dot), and H (dash).

CMP module within TWQ, with amphibole properties from Mäder et al. (1994). The THERMOCALC program in most cases overestimates pressure relative to experimental pressures, with ca. 88% plotting outside the 2 kbar uncertainty, and only 12% within the uncertainty limit (Fig. 5a). On the other hand, the TWQ program generally underestimates experimental P values with ca. 67% lying outside the uncertainty limit (Fig. 5b). Based on the comparison, the present formulations (Eqs. 15 and 16) arguably provide significant improvement over available options for estimating pressure in quartz-bearing, garnet-free assemblages.

MECHANISTIC BASIS OF THE GEOBAROMETER

It is imperative to establish whether the retrieved parameters (Table 7) are sensitive to variations in pressure and thereby provide a mechanistic basis of the regression statistics from a petrologic view point. For the barometers to be petrologically significant, the coefficients and signs of the regressed parameters in the barometric equation should reflect pressure dependency established from petrologic considerations. For example, Al in M2 and T1 sites of amphibole is known to increase with increasing pressure (Laird and Albee 1981; Spear 1981a; Ernst and Liu 1998). Likewise, the pressure sensitivity of Al has been the basis for empirical barometry involving hornblende (Hammarstrom and Zen 1986; Johnson and Rutherford 1989; Anderson and Smith 1995). Also, higher-pressure amphiboles are expected to be richer in Mg compared to Fe^{2+}, as is the case with most ferromagnesian silicate minerals.

Since ΔV is negative in Equations 15 and 16, the denominator ($-\Delta V$) is positive; therefore, positive coefficients of mole fraction terms lead to higher P_1 and/or P_2 values. In the numerator, the term $[100.392X^{M2}_{Al} - 118.653X^{T1}_{Al}]$ expresses the pressure dependency of Al in amphibole, and the term $[-39.101X^{M13}_{Fe^{2+}} + 131.03X^{M2}_{Fe^{2+}}]$ broadly relates to Fe^{2+}/Mg ratio in hornblendes. For the range of hornblende compositions in the experimental runs used in regression analysis, the Al term increases and the Fe^{2+} term decreases with increasing P_1 (Fig. 6) as well as P_2. These variations are consistent with petrological considerations, and

therefore provide a mechanistic basis for the regressed coefficients. The only note of discord is the negative correlation between Na(M4) and P predicted by the barometer equations, e.g., available evidence (Laird and Albee 1981; Brown 1977) indicates amphiboles in high-P metamorphic rocks are richer in Na(M4) compared to amphiboles in low-P metamorphic terranes. The discordance may be traced to uncertainties in allocating small proportions of Na between A and M4 sites, and is reflected in the higher standard deviation associated with a_3 (Na in M4), i.e., 1σ error is greater than one third the magnitude of the parameter (Table 7). By implication, the parameter seems to be poorly constrained by the regression statistics. However, since the coefficients of X^{M4}_{Na} in the barometric equations are small and multiplied by small values of X^{M4}_{Na}, the net contribution of the term on the estimated P values is a small fraction of the 2 kbar uncertainty projected for the barometer equations.

Application to quartz-bearing natural assemblages

Recent research underscores the importance of determining errors associated with thermobarometric estimates (Anderson 1976; Hodges and Crowley 1985; Hodges and McKenna 1987; Giaramita and Day 1990; Kohn and Spear 1991a 1991b; Powell and Holland 1994; Todd 1998). The two most important sources of errors are uncertainties in temperature and mole fractions of end-member components, especially at extreme dilution (cf. Todd 1998). The scheme for calculating the precision of the proposed barometers is discussed in Appendix 1. The cumulative precision of the retrieved pressures estimated for two experimental runs, e.g., S5 (1 kbar, 701 °C) and PB9 (10 kbar, 925 °C) varied between 790 and 1910 bars; cf. Appendix Table 1c. For an uncertainty of 10% (cf. Kohn and Spear 1991b) in the $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio for hornblende, the deviation from the P_{com} values varied between 400 and 700 bars for the two experimental runs (Appendix 1).

For barometry in natural assemblages, computation of ΔV is not straightforward because ΔV is a function of both P and T (Eq. 16). At best, the temperature can be retrieved from Hbl-Pl pairs using existing thermometric formulations (e.g., Holland and Blundy 1994), and the ΔV calculated at an approximate pressure that may be gauged from mineral assemblages in associated rocks. Alternatively, the ΔV may be computed at a P-T value of 8 kbar and 800 °C, which lies midway between the experimental P-T range over which the barometers were calibrated. At this P-T, $\Delta V_{8kbar,800°C}$ computed to be –1.72433 KJ/kbar, and may be used in the denominator of Equations 15 and 16 for pressure estimation.

The retrieved parameters (Table 7) when fed back to the respective barometric formulations (Eqs. 15 and 16), pressure values for 83% of the experimental runs were reproduced within an uncertainty of 2 kbar (Fig. 2). The good correlation between computed and experimental pressure (Fig. 2) is to be expected since the computed pressures are derived using the experimental P values as input, and therefore, the correlation itself confers no predictive power to the solution model**.** Therefore, Equations 15 and 16 were applied to estimate pressures in quartz-bearing natural assemblages (Table 9[1]). The only means of crosschecking the retrieved pressure (P_{com}) is by comparing the retrieved P values with those recommended by the authors (P_{nat}). However, in most cases the rocks are of polymetamorphic origin, and due to the authors' emphasis elsewhere, the analytical data specific to the different equilibrium P-T events are not always available (Krogh 1980; Tella and Eade 1986). Despite the shortcomings, the computed and recommended P values for natural assemblages

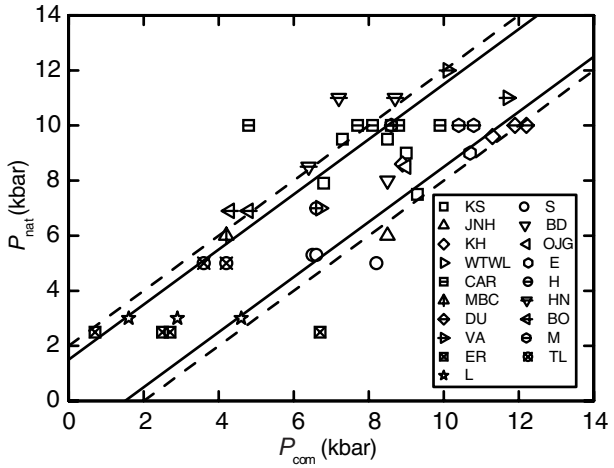

Figure 7. A comparison of computed pressure ($P_{1,com}$; Eq. 15), with those recommended by the respective authors for the dataset on naturally occurring hornblende-plagioclase pairs in quartz-bearing assemblage (P_{nat}). Continuous and broken lines demarcate the 1.5 and 2 kbar uncertainty limits, respectively. Acronyms: KS, Kohn and Spear (1989, 1990); S, Spear (1982); JNH, Janardhan et al. (1982); BD, Baker and Droop (1983); KH, Konzett and Hoinkes (1996); OJG, O'Beirne-Ryan et al. (1990); WTWL, Weaver et al. (1982); E, Encarnacion et al. (1995); CAR, Carney et al. (1991); H, Harley (1988); MBC, Mukherjee et al. (1986); HN: Hansen (1992); DU, Dufour (1985); BO, Burton and O'Nions (1990); VA, Valley et al. (2003); M, Miller et al. (1997); ER, Erdmer (1981); TL, Thompson and LeClair (1987); and L, Labotka (1981 1987).

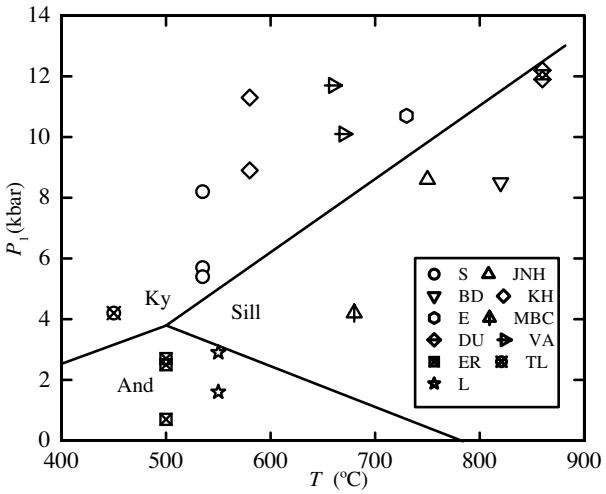

Figure 8. Pressures (P_1) computed for natural samples at the authors recommended temperature are shown in relation to the Al_2SiO_5 phase diagram. In any terrane, the computed pressure is compatible with the Al_2SiO_5 polymorph reported from the associated metapelite. Acronyms are same as in Figure 6.

Table 10. Compositional limits of amphibole for the proposed barometer

(Cation per 23 O atoms)	
$6.09 \le Si \le 7.27$	$0.90 \le Al \le 2.65$
$0.0 \le Ti \le 0.29$	$1.79 \le Mg \le 4.32$
$0.76 \le Fe \le 2.63$	$0.0 \le Mn \le 0.09$
$1.38 \le Ca \le 1.88$	$0.23 \le Na \le 0.77$
$0.0 \le K \le 0.27$	$1.73 \le Ca+Na+K \le 2.67$
$0.20 \le X_{Ab} \le 0.82$	

in the range 2.5 to 12.5 kbar (Fig. 7) are in good agreement; that is, 85% of the estimated pressures agree within 2 kbar of the recommended *P* values. Also, the mean pressures estimated for the terranes are consistent with the stable Al_2SiO_5 polymorph in metapelites associated with the quartz-bearing metabasites (Fig. 8). Appendix 2 provides a scheme for calculating pressures from the barometric equations.

Concluding remarks

Hornblende and plagioclase in equilibrium with quartz is a common assemblage in medium- to high-grade metabasic rocks, and intermediate to felsic lithologies in contact metamorphic aureoles and low- to high-*P* regional metamorphic terranes. The reaction tremolite + tschermakite + 2 albite = 2 pargasite + 8 quartz provides a convenient means to estimate pressure in such assemblages. Table 10 summarizes the compositional range of amphibole for which the barometer was formulated. Beyond this compositional limit, the barometer should be applied cautiously. Particularly, for low-Al amphiboles (greenschist- and epidote-amphibolite-facies rocks), and for high-Al amphiboles (metapelites and ultra-high pressure metamorphic rocks) the reliability of the estimated *P* values should be checked against other petrologic constraints.

Acknowledgments

The work was financially supported by the grant-in-aid (24/263/03 EMR II) from the CSIR (India) to A.B. We greatly appreciate the reviews by F.S. Spear and M. Hand on an earlier version of the manuscript. F.S. Spear's views on error propagation educated us in more ways than one. We are thankful to M. Hand for providing helpful suggestions as regards the role of silica-undersaturation in experimental runs and natural data sets. These suggestions greatly improved not only the content, but also the overall presentation, of the manuscript. We greatly acknowledge the critical reviews and helpful suggestions provided by the journal reviewers, T. Labotka and R.G. Berman. Associate Editor P. Dahl suggested many editorial and technical modifications that greatly improved the overall style of presentation. However, the authors are solely responsible for any possible errors, computational or otherwise, that may have unknowingly crept in.

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Manuscript received August 21 2005
Manuscript accepted October 16 2006
Manuscript handled by Peter Dahl