

## Two new geobarometers for garnet amphibolites, with applications to southeastern Vermont

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### ABSTRACT

Two new geobarometers for the assemblage garnet + hornblende + plagioclase + quartz have been calibrated on the basis of the equilibrium

6 Anorthite + 3 Tremolite = 2 Grossular + 1 Pyrope + 3 Tschermakite + 6 Quartz  
and its Fe end-member equivalent.

Data representing 37 natural samples that equilibrated at conditions of 2.5 to 13 kbar and 500 to 800 °C were fitted to the general equation

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

by using a weighted least-squares method. Multiple correlation coefficients are high (0.98 and 0.97).

Lines of constant  $K_{eq}$  have extremely shallow slopes in  $P$ - $T$  space (–2 to +8 bars per degree), suggesting that pressures may be deduced precisely, even where temperatures are only poorly constrained. Typical analytical errors and temperature imprecisions propagate to very small errors in pressure (about  $\pm 500$  bars). Caution is advised in applying the barometers outside the range of calibrant-mineral compositions.

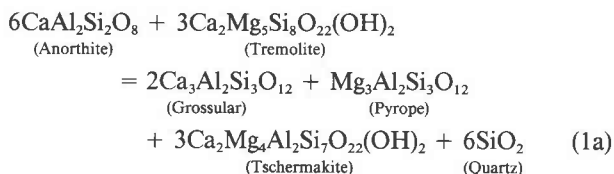
Application of the calibrations to samples from southeastern Vermont near the Stratford, Chester, and Athens domes documents relatively high pressure metamorphism (7 to 10 kbar) for these structures.

### INTRODUCTION

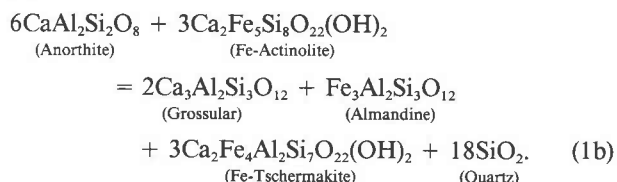
Although the assemblage garnet + hornblende + plagioclase + quartz is widespread in amphibolite- and granulite-facies terranes, few barometers have been calibrated that involve only the components of these minerals. Kohn and Spear (1989) have empirically calibrated barometers for this assemblage that involve pargasite exchange in amphibole. Although these barometers generally predict pressures that are consistent with other barometers and with phase equilibria, uncertainty in natural mineral composition and lack of internal consistency typically lead to imprecisions of  $\pm 1$  to  $\pm 2$  kbar. Consequently, we have continued exploration of the calibration of other barometers involving components of garnet, hornblende, plagioclase, and quartz so that pressure estimates may be made that are more internally consistent and that better correspond to pressures estimated using other barometers on natural rocks. In this effort, a larger data set has been compiled from the literature (Oliver, 1977; Glassley and Sorensen, 1980; Krogh, 1980; Jandhan et al., 1982; Spear, 1982; Ghent et al., 1983; Selverstone et al., 1984; Stoddard, 1985; Ghent and Stout, 1986; Spear and Rumble, 1986; Tella and Eade, 1986; Labotka, 1987; Thompson and Leclair, 1987), and many new data have been collected by us.

### TECHNIQUE

The reactions chosen for calibration are



and



The technique used for calibrating these reactions is identical to that employed by Kohn and Spear (1989). Briefly, it involves fitting the natural data to the general equation

$$-RT \ln K_{eq} = A - TB + PC \quad (2)$$

where  $A$ ,  $B$ , and  $C$  are fit parameters, and

$$K_{\text{eq}} = \frac{(a_{\text{Grs}})^2(a_{\text{Prp}})(a_{\text{Tsch}})^3(a_{\text{Qtz}})^6}{(a_{\text{An}})^6(a_{\text{Tr}})^3} \quad (\text{Reaction 1a})$$

$$K_{\text{eq}} = \frac{(a_{\text{Grs}})^2(a_{\text{Alm}})(a_{\text{Fe-Tsch}})^3(a_{\text{Qtz}})^6}{(a_{\text{An}})^6(a_{\text{Fe-Act}})^3}, \quad (\text{Reaction 1b})$$

where  $a_{\text{Grs}}$ ,  $a_{\text{Prp}}$ , and  $a_{\text{Alm}}$  are the activities of grossular, pyrope, and almandine, respectively, in garnet;  $a_{\text{Tsch}}$ ,  $a_{\text{Tr}}$ ,  $a_{\text{Fe-Tsch}}$ , and  $a_{\text{Fe-Act}}$  are the activities of tschermakite, tremolite, ferro-tschermakite, and ferro-actinolite, respectively, in amphibole;  $a_{\text{An}}$  is the activity of anorthite in plagioclase; and  $a_{\text{Qtz}}$  is the activity of  $\text{SiO}_2$  in quartz [mineral abbreviations used in this paper are after Kretz (1983)]. The approach used ignores nonideal mixing in amphibole, heat capacities, and changes of volume with pressure and temperature.

### ACTIVITY MODELS

#### Garnet and plagioclase

Although several garnet and plagioclase activity models were tested, the anorthite activity model presented in Hodges and Royden (1984) and the garnet-component activity models proposed by Hodges and Spear (1982) were found to be statistically most consistent with the data:

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

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

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

$$a_{\text{An}} = X_{\text{An}} \exp[(610.34/T) - 0.3837].$$

$X_{\text{Prp}}$ , etc., are the mole fractions of phase components in garnet and plagioclase as defined in Table 1,  $R$  is the gas constant in  $J/(\text{mol} \cdot \text{K})$ , and  $T$  is temperature in kelvins.  $\text{Fe}^{3+}$  in garnet was calculated for the samples of Glassley and Sorensen (1980), Ghent et al. (1983), and Labotka (1987) by using stoichiometric and charge-balance constraints.

#### Amphibole

Kohn and Spear (1989) found that amphibole activity models representing partial local charge balance best fit the natural calibration data. Several activity models for the amphibole components were tested, and the data were fit best by using the following empirical partial-local-charge-balance models:

$$a_{\text{Tsch}} = (256/27)(X_{\text{T1Al}})(X_{\text{T1Si}})^3[\text{Mg}/(\text{Fe} + \text{Mg})]$$

$$a_{\text{Tr}} = (X_{\text{T1Si}})^4[\text{Mg}/(\text{Fe} + \text{Mg})]^2$$

$$a_{\text{Fe-Tsch}} = (256/27)(X_{\text{T1Al}})(X_{\text{T1Si}})^3[\text{Fe}/(\text{Fe} + \text{Mg})]$$

$$a_{\text{Fe-Act}} = (X_{\text{T1Si}})^4[\text{Fe}/(\text{Fe} + \text{Mg})]^2,$$

where  $X_{\text{T1Al}}$ , etc., refer to the mole fraction of Al in the amphibole tetrahedral site that accepts both Si and Al (T1), and  $\text{Fe}/(\text{Fe} + \text{Mg})$  is the bulk Fe-Mg ratio of the amphibole. The factor 256/27 is necessary so that the activities of pure tschermakite and ferro-tschermakite equal 1. The effects of titanian tschermakite, edenite, and

TABLE 1. Calculation of mole fractions and assignment of site occupancies

<b>Garnet</b>	
$X_{\text{Prp}} = \text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn} + \text{Ca})$	
$X_{\text{Alm}} = \text{Fe}/(\text{Mg} + \text{Fe} + \text{Mn} + \text{Ca})$	
$X_{\text{Sps}} = \text{Mn}/(\text{Mg} + \text{Fe} + \text{Mn} + \text{Ca})$	
$X_{\text{Grs}} = \text{Ca}/(\text{Mg} + \text{Fe} + \text{Mn} + \text{Ca})$	
<b>Plagioclase</b>	
$X_{\text{An}} = \text{Ca}/(\text{Ca} + \text{Na} + \text{K})$	
<b>Amphibole</b>	
${}^{\text{T1}}\text{Si} = \text{Si} - 4.0$	${}^{\text{T1}}\text{Al} = 8.0 - \text{Si}$
$X_{\text{T1Si}} = {}^{\text{T1}}\text{Si}/4.0$	$X_{\text{T1Al}} = {}^{\text{T1}}\text{Al}/4.0$

potassium edenite substitutions on tetrahedral Al content were ignored because corrections for Ti in the M2 site and for Na and K in the alkali site resulted in poorer fits to the calibration data.  $\text{Fe}^{3+}$  in amphibole was calculated to a minimum value consistent with amphibole stoichiometry (typically all  $\text{Fe}^{2+}$ ) by using the method of Spear and Kimball (1984). Because correction of the amphibole activities for nonideality was not made for other amphibole components, the activity models are believed to be applicable only to amphiboles similar in composition to those of the calibrants.

### DATA SET

#### Sample selection

Samples were chosen for calibrating the equilibria on the basis of (1) the presence of (at least) the minerals garnet, hornblende amphibole, plagioclase, and quartz, (2) no significant evidence for retrogression, and (3) well-constrained temperatures and pressures.

A literature search produced eleven appropriate data sets (Oliver, 1977; Glassley and Sorensen, 1980; Krogh, 1980; Janardhan et al., 1982; Spear, 1982; Ghent et al., 1983; Selverstone et al., 1984; Ghent and Stout, 1986; Stoddard, 1985; Tella and Eade, 1986; Labotka, 1987; Thompson and Leclair, 1987). In addition, our previously unpublished microprobe data from Chilean and New Hampshire samples were also used and are presented in Table 2.

#### Calibrant pressures, temperatures, and compositions

Table 3 presents the pressures, temperatures, and calculated equilibrium constants used for calibrating the geobarometers. Pressures and temperatures for the calibrant samples were determined from a variety of mineral equilibria as described in the footnotes of Table 3. Mineral compositions were derived from electron-microprobe analyses and were considered to represent rim compositions.

### CALIBRATION

Equation 2 was fit to the data set using a weighted least-squares method. An explicit requirement of least-squares analysis is that the independent variables be free of error.

TABLE 2. Composition data from samples from Chile, New Hampshire, and Vermont

	CD-301G	BP-3A	CD-303N	VI-1U	71-49H	D84-3F	K87-18	TM-650	N2	N1
<b>Garnet</b>										
SiO <sub>2</sub>	38.42	38.34	37.77	38.52	37.75	36.92	38.27	37.49	37.25	37.20
Al <sub>2</sub> O <sub>3</sub>	21.93	22.02	21.60	22.25	21.17	21.56	22.07	21.28	21.32	21.33
MgO	4.35	3.30	3.76	3.56	2.35	3.23	2.52	1.96	1.77	2.02
FeO	28.75	28.84	29.29	29.43	30.44	30.00	29.48	29.84	31.50	30.16
MnO	3.38	2.83	2.31	3.29	3.37	3.66	2.44	0.65	0.62	0.90
CaO	4.78	7.03	6.08	5.92	4.48	5.25	7.50	8.64	6.66	7.84
Total	101.63	102.37	100.80	102.98	99.56	100.61	102.30	99.86	99.11	99.45
Si	2.991	2.976	2.976	2.973	3.029	2.942	2.980	2.993	3.003	2.985
Al	2.013	2.015	2.007	2.025	2.003	2.025	2.026	2.003	2.026	2.018
Mg	0.505	0.382	0.441	0.410	0.281	0.383	0.293	0.233	0.213	0.242
Fe <sup>2+</sup>	1.872	1.872	1.930	1.900	2.043	1.999	1.920	1.992	2.124	2.024
Mn	0.223	0.186	0.154	0.215	0.229	0.247	0.161	0.044	0.042	0.061
Ca	0.399	0.585	0.513	0.490	0.385	0.448	0.626	0.739	0.575	0.674
Fe/(Fe + Mg)	0.788	0.831	0.814	0.823	0.879	0.839	0.868	0.895	0.909	0.893
Pyrope	0.168	0.126	0.145	0.136	0.096	0.124	0.098	0.077	0.072	0.081
Alman	0.624	0.619	0.635	0.630	0.695	0.650	0.640	0.662	0.719	0.674
Spess	0.074	0.061	0.051	0.071	0.078	0.080	0.054	0.015	0.014	0.020
Gross	0.133	0.193	0.169	0.163	0.131	0.146	0.209	0.246	0.195	0.225
<b>Plagioclase</b>										
An	34.5	26.8	30.2	33.9	59.8	70.2	14.3	30.2	18.0	19.0
Ab	65.3	72.7	69.6	65.8	39.9	29.6	84.7	69.6	81.8	80.7
Or	0.2	0.5	0.2	0.3	0.3	0.2	1.0	0.2	0.2	0.3
<b>Amphibole</b>										
SiO <sub>2</sub>	42.44	43.82	41.98	42.99	42.20	42.58	42.49	41.49	42.34	41.87
Al <sub>2</sub> O <sub>3</sub>	19.48	14.98	17.67	17.79	17.61	16.73	17.02	15.07	16.11	16.78
TiO <sub>2</sub>	0.42	0.70	0.52	0.63	0.30	0.37	0.47	0.70	0.41	0.34
MgO	8.94	9.03	9.09	9.17	7.01	8.47	8.59	7.40	7.57	7.07
FeO	13.99	16.84	14.23	13.94	17.37	14.68	15.97	18.55	17.70	17.42
MnO	0.30	0.26	0.10	0.19	0.29	0.25	0.18	0.07	0.05	0.07
CaO	10.66	11.25	11.27	11.01	11.05	10.99	11.45	11.07	10.30	10.39
Na <sub>2</sub> O	2.10	1.25	1.90	1.90	1.25	1.34	1.30	1.56	1.91	1.78
K <sub>2</sub> O	0.35	0.64	0.41	0.45	0.29	0.32	0.55	0.48	0.43	0.43
Total	98.68	98.75	97.09	98.07	97.38	95.73	98.02	96.39	96.82	96.17
Si	6.142	6.435	6.194	6.265	6.284	6.372	6.266	6.321	6.361	6.324
<sup>iv</sup> Al	1.858	1.565	1.806	1.735	1.716	1.628	1.734	1.679	1.639	1.676
<sup>vi</sup> Al	1.466	1.028	1.275	1.322	1.376	1.324	1.225	1.027	1.215	1.315
Ti	0.046	0.077	0.058	0.069	0.034	0.042	0.052	0.080	0.046	0.039
Mg	1.927	1.976	2.003	1.991	1.556	1.889	1.888	1.680	1.695	1.592
Fe <sup>2+</sup>	1.693	2.068	1.760	1.699	2.163	1.837	1.969	2.364	2.224	2.201
Mn	0.037	0.032	0.012	0.023	0.037	0.032	0.023	0.009	0.006	0.009
Sum oct	5.169	5.181	5.108	5.104	5.166	5.124	5.157	5.160	5.186	5.156
Ca	1.653	1.771	1.785	1.720	1.763	1.762	1.809	1.807	1.658	1.681
Na(M4)	0.178	0.048	0.107	0.176	0.071	0.114	0.034	0.033	0.156	0.163
Na(A)	0.410	0.307	0.439	0.362	0.290	0.275	0.338	0.429	0.401	0.359
K	0.064	0.120	0.078	0.084	0.055	0.061	0.103	0.094	0.082	0.082
Sum A	0.474	0.427	0.517	0.446	0.345	0.336	0.441	0.523	0.483	0.441
Fe/(Fe + Mg)	0.468	0.511	0.468	0.460	0.582	0.493	0.511	0.585	0.567	0.580

Note: Sample locations as follows: Chile—CD-301G, lat 54°55'27"S, long 69°10'27"W; BP-3A, lat 54°45'49"S, long 69°35'45"W; CD-303N, lat 54°54'31"S, long 69°16'26"W; VI-1U, lat 54°54'47"S, long 69°14'24"W. New Hampshire—71-49H, lat 44°0'36"N, long 71°49'56"W; D84-3F, lat 43°54'20"N, long 72°7'24"W; Vermont—K87-18, lat 43°43'31"N, long 72°25'22"W; TM-650, lat 43°52'6"N, long 72°19'56"W; N-1 and N-2, lat 43°12'21"N, long 72°30'39"W.

In practice, this is seldom possible, but can be approximated by choosing the parameter with the largest error as the dependent variable. In the present calibrations, this parameter is pressure, and so the dependent variable *P* was regressed as a function of the independent variables *T* and ln *K<sub>eq</sub>*. Because the sum of the squares of the deviations between model and measured pressures is minimized, this procedure also results in the best possible barometers.

Weighting was assigned according to the assumed errors in thermobarometrically determined pressures. For most samples, the errors in Table 3 correspond to the range in estimated pressures after simultaneously solving for pres-

sure and temperature by using the equilibria listed in the footnotes. Errors for samples from Spear (1982) and Selverstone et al. (1984) were based on typical precisions for chemically well-characterized samples whose pressures have been determined using the garnet-plagioclase-kyanite-quartz and garnet-plagioclase-muscovite-biotite equilibria. The errors in pressure for samples SM-80-3, 41-16, and GM-78-31 were increased slightly because of minor questions concerning equilibrium mineral compositions.

The estimated *P*, *T*, and *K<sub>eq</sub>* for each sample were assumed to be uncorrelated. This assumption is justified because many of the pressure estimates for the samples

**TABLE 3.** Preferred pressures, temperatures, and calculated equilibrium constants for samples used in calibration

Sample no.	<i>P</i> (bars)	<i>T</i> (°C)	ln <i>K</i> <sub>eq</sub>	
			Fe	Mg
<b>Oliver (1977)<sup>1,2,3,4</sup></b>				
(1) 36511	13000 ± 2000	800	3.59	0.81
<b>Glassley and Sorensen (1980)<sup>1,2,3,4</sup></b>				
(2) 91141	7600 ± 1000	725	-2.04	-4.76
(3) 88589	6650 ± 750	710	-2.70	-5.43
<b>Krogh (1980)<sup>1,2,4</sup></b>				
(4) MA-1	12650 ± 1500	750	5.49	2.85
(5) KV-1	13100 ± 2000	800	4.18	1.54
(6) MA-2	11500 ± 1500	720	6.26	3.88
<b>Janardhan et al. (1982)<sup>1,2,4</sup></b>				
(7) 11-1C	6650 ± 1500	705	0.06	-4.26
(8) 4-1A	6250 ± 1500	675	0.69	-2.88
<b>Spear (1982)<sup>1,5</sup></b>				
(9) 73-20A	5250 ± 500	560	-2.94	-6.16
(10) 73-20C	5300 ± 500	575	-2.03	-5.55
(11) 73-28A	5500 ± 500	610	-2.42	-5.72
(12) 73-29D	5275 ± 500	570	-2.10	-5.70
(13) 73-30S	5000 ± 500	535	-2.32	-6.87
<b>Ghent et al. (1983)<sup>1,2,4,6</sup></b>				
(14) GM-78-10	7900 ± 1000	690	1.35	-2.38
(15) GM-78-14A	8000 ± 1000	685	2.30	-1.49
(16) GM-78-14B	7900 ± 1000	695	2.38	-1.46
(17) GM-78-31	10800 ± 1500	770	3.93	0.57
(18) GM-78-32	7850 ± 1000	670	1.82	-1.55
(19) SM-80-5	8750 ± 1000	760	1.06	-1.73
(20) SM-80-3	8300 ± 1500	750	0.82	-2.14
(21) 41-16	8900 ± 2000	760	1.91	-1.50
<b>Selverstone et al. (1984)<sup>7</sup></b>				
(22) Z3-N	8000 ± 500	540	0.57	-3.15
(23) FH-1M	7000 ± 500	550	-0.78	-4.77
(24) FH-1P	7500 ± 500	545	0.36	-3.99
(25) FH-1R	8500 ± 1000	530	2.77	-2.27
<b>Stoddard (1985)<sup>1,2,3,4</sup></b>				
(26) 74-C-248B	7100 ± 1500	670	-0.07	-3.37
<b>Tella and Eade (1986)<sup>1,2,4</sup></b>				
(27) EA-510-79	12000 ± 1500	750	6.73	3.66
(28) EA-346-80	12700 ± 1500	775	6.66	3.78
<b>Thompson and Leclair (1987)<sup>1,8</sup></b>				
(29) A-2	5000 ± 500	550	-2.32	-6.37
<b>Labotka (1987)<sup>9</sup></b>				
(30) MCD-350a	2750 ± 1000	610	-7.26	-10.63
(31) PML-225b	2750 ± 1000	590	-8.06	-11.50
<b>Our unpublished data, New Hampshire and southern Chile<sup>1,10</sup></b>				
(32) 71-49H <sup>6</sup>	3750 ± 500	520	-4.38	-8.82
(33) D84-3F <sup>8</sup>	4500 ± 500	550	-4.71	-9.11
(34) CD-301G <sup>8</sup>	7500 ± 500	575	0.42	-3.42
(35) BP-3A <sup>9</sup>	9000 ± 750	600	2.76	-1.20
(36) CD-303N <sup>11</sup>	7900 ± 500	565	2.33	-1.87
(37) VI-1U <sup>11</sup>	7500 ± 500	565	1.18	-3.30

<sup>1</sup> Testimated using the garnet-hornblende geothermometer (Graham and Powell, 1984).

<sup>2</sup> Testimated using garnet-clinopyroxene geothermometer (Ellis and Green, 1979).

<sup>3</sup> *P* estimated using the garnet-plagioclase-orthopyroxene-quartz geobarometers of Bohlen et al. (1983b), Newton and Perkins (1982), and Powell and Holland (1988).

<sup>4</sup> *P* calculated using garnet-plagioclase-clinopyroxene-quartz equilibrium (Newton and Perkins, 1982; Powell and Holland, 1988).

<sup>5</sup> *P* estimated at *T* using *P*-*T* path of Spear and Rumble (1986).

<sup>6</sup> *P* based on aluminosilicate phase diagram of Holdaway (1971).

<sup>7</sup> Pressures and temperatures calculated using intersection of the *P*-*T* path of Selverstone et al. (1984) and the garnet-plagioclase-kyanite-quartz or garnet-plagioclase-white mica-quartz (FH-1R only) equilibria of Koziol (1989) and Hodges and Crowley (1985).

<sup>8</sup> *P* estimated at *T* using garnet-plagioclase-muscovite-biotite barometers of Hodges and Crowley (1985) and Powell and Holland (1988) and

were essentially independent of temperature, and many of the mole fractions used to calculate the equilibrium constants were not those used to estimate pressure and temperature. General quality of fit was evaluated on the basis of the magnitude of the multiple correlation coefficient (*r*), and the statistical validity of a three-parameter regression model was assessed using *F*-test criteria.

Each regression results in values of 1/*C*, *A*/*C*, *B*/*C*, and their respective errors, which are reported in Table 4. Values for *C*, *A*, and *B* were derived from the inverse of 1/*C* and by dividing *A*/*C* and *B*/*C* by 1/*C*; this leads to the following calibrations (*P* in bars and *T* in kelvins):

$$P_{Mg} = [79507 + T(29.14 + 8.3144 \ln K_{eq})]/10.988$$

$$P_{Fe} = [35327 + T(56.09 + 8.3144 \ln K_{eq})]/11.906.$$

Figure 1 is a plot of predicted pressure versus measured pressure and shows the fit of the barometers to the data. As can be seen, both barometers fit nearly all the data within the estimated error bars. For a given sample, the differences between model and measured pressure are nearly identical for both barometers, and so we have no preference for either end-member calibration.

## DISCUSSION

### Analytical evaluation of barometer sensitivity

A characteristic of good barometers is their insensitivity both to estimated temperatures and to analytical errors. Figure 2 shows a pressure-temperature diagram contoured with lines of constant ln *K*<sub>eq</sub> for both reactions, with calibrant data for reference. Slopes of the isopleths of ln *K*<sub>eq</sub> are quite shallow; at 600 °C and 5 to 10 kbar, they vary from -2 to +3 bars per degree (Mg) and from +1 to +8 bars per degree (Fe). This extreme insensitivity to temperature represents a significant advantage over many other equilibria that are typically used as barometers. For example, a typical error in temperature of ±25 °C results in an error in pressure of only about ±50 to ±200 bars for the new equilibria, but an error of ±500 bars for the commonly applied garnet-plagioclase-kyanite-quartz barometer (Koziol, 1989).

The sensitivity of the equilibria to analytical uncertainties may be estimated by propagating electron-microprobe counting-statistics errors. Errors may be propagated for any function *Z*(*x*<sub>1</sub>, *x*<sub>2</sub>, etc.) by using a standard error-propagation equation:

$$\sigma_z^2 = \sum_i \sum_j (\partial Z / \partial x_i) (\partial Z / \partial x_j) \sigma_i \sigma_j \Omega_{ij} \quad (4)$$

garnet-plagioclase-white mica-quartz barometer of Hodges and Crowley (1985).

<sup>9</sup> *P* estimated on the basis of presence of andalusite and overburden estimates (Labotka, 1981).

<sup>10</sup> *T* estimated using the garnet-biotite thermometer (Ferry and Spear, 1978; Hodges and Spear, 1982).

<sup>11</sup> *P* estimated using the GRIPS barometer of Bohlen and Liotta (1986).

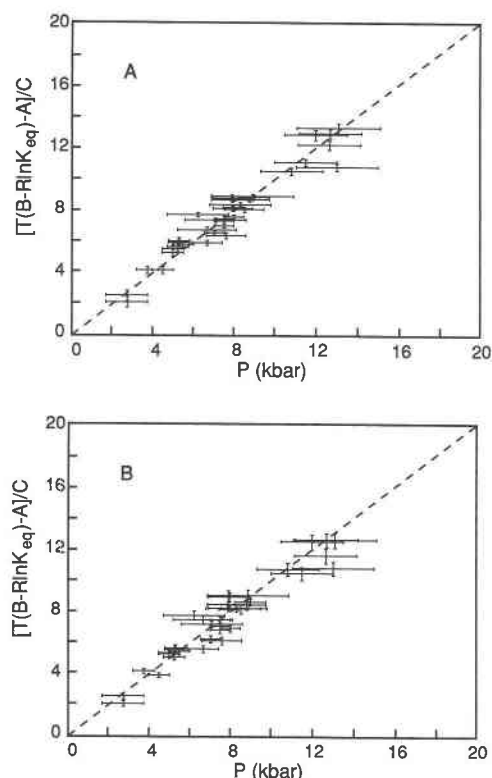


Fig. 1. Predicted pressure vs. measured pressure plot of calibrant data. (A) Mg end-member reaction; (B) Fe end-member reaction. Dashed line from (0,0) to (20,20) is the theoretically perfect fit of model to data. Note that deviation of predicted pressure from measured pressure for any one sample is similar for the two calibrations.

(+ higher-order terms), where  $\sigma_{ij}$  = error in  $x_{ij}$ , etc., and  $\Omega_{ij}$  = correlation between  $x_i$  and  $x_j$ . Application of Equation 4 requires knowing the magnitude of the errors in chemical composition and the correlation among mineral components and site occupancies involved in the equilibrium-constant expressions.

Kohn and Spear (manuscript in review) have presented results of a study of microprobe analyses that were collected over a period of two years on a single natural mineral standard. This study indicates that the range in measured concentration of any one element as determined

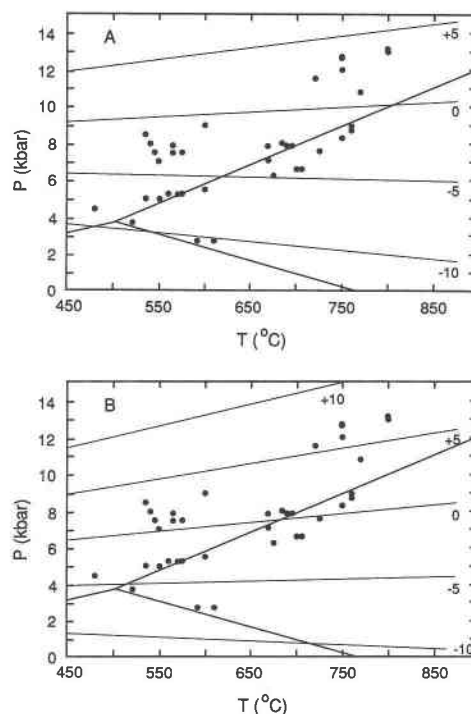


Fig. 2.  $P$ - $T$  diagram with isopleths of  $K_{eq}$  for (A) the Mg reaction and (B) the Fe reaction. Aluminosilicate phase diagram is after Holdaway (1971). Positions of calibration samples are plotted for reference (dots). Numbers to the right of and beneath isopleths are values of  $\ln K_{eq}$ .

from the multiple analyses is about two to three times the individual counting-statistics error for that element. This increase simply represents the effects of different standardizations and different operators collecting data on different days. Therefore, the magnitude of the errors in composition measurements may generally be assumed to be approximately 2.5 times the counting-statistics error of any one analysis. For example, if the counting-statistics error for MgO were 1%, the total analytical error in MgO would be assigned as 2.5%. Corresponding errors and correlation coefficients among different mineral components may be derived quite easily as described by Kohn and Spear (manuscript in review).

The resulting propagated errors are the expected range

TABLE 4. Regressed values for fit parameters  $A/C$ ,  $B/C$ , and  $1/C$ ; associated errors ( $1\sigma$ ); and correlation matrices

	Regressed values					
	$A/C$ (bars)	$B/C$ (bars/deg)	$1/C$ (bars/J)	$r$		
Mg reaction	$-7236 \pm 1392$	$2.652 \pm 1.506$	$-0.0910 \pm 0.0054$	0.975		
Fe reaction	$-2967 \pm 1401$	$4.711 \pm 1.616$	$-0.0840 \pm 0.0056$	0.968		
Correlation matrices						
	Mg		Fe			
$A/C$	1.000	0.9923	0.6159	1.000	0.9974	0.4889
$B/C$	0.9923	1.000	0.5288	0.9974	1.000	0.4722
$1/C$	0.6159	0.5288	1.000	0.4889	0.4722	1.000

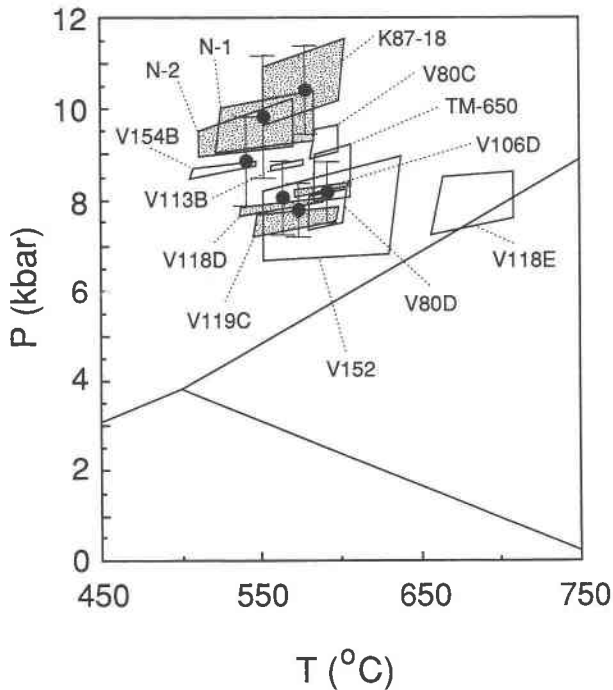


Fig. 3.  $P$  vs.  $T$  plot of the simultaneous solution of thermometers and newly calibrated barometers (boxes) for samples from southeastern Vermont. Boxes are stippled for those samples for which independent  $P$ - $T$  estimates (dots with error bars) are possible. Aluminosilicate phase diagram after Holdaway (1971) shown for reference.

in pressure for an assumed temperature that would be calculated if exactly the same spot were analyzed by different operators on different days. Thus, these errors could be taken to represent the internal consistency of pressure estimates made from data collected with similar standards at different electron-microprobe facilities. It must be noted that these propagated precisions will not estimate the true imprecision of pressure estimates for natural rocks. This is because natural variability in mineral compositions will always lead to a greater compositional uncertainty than indicated by counting-statistics errors derived from any one analysis.

We chose to propagate analytical errors for mineral compositions that represent approximate median values of the calibration data. Garnet was chosen as  $\text{Prp}_{15}\text{Alm}_{60}\text{Sps}_{05}\text{Gr}_{20}$ , plagioclase as  $\text{An}_{34.5}\text{Ab}_{64.5}\text{Or}_{1.0}$ , and hornblende as  $\text{Si}_{6.25}\text{Al}_{3.1}\text{Ti}_{0.05}\text{Mg}_{1.75}\text{Fe}_{2.0}\text{Mn}_{0.025}\text{Ca}_{1.8}\text{Na}_{0.45}\text{K}_{0.075}$ . The compositions were recalculated to weight percent oxides, analytical errors were assigned for all elements by assuming a uniform 40-s counting time and typical electron-microprobe operating conditions, and errors and correlation coefficients were calculated for each mineral component and element involved in the ideal part of the activity expressions of the barometers by using the technique described by Kohn and Spear (manuscript in review). The anorthite activity coefficient expression is independent of mineral composition, and the garnet activity coefficients are extremely insensitive to composition un-

TABLE 5. Compositional criteria

#### Amphibole

- Al: between 1.9 and 3.75 cations per 23 oxygens
- Ti: less than 0.275 cations
- Ca: greater than 1.5 cations
- Na: between 0.3 and 0.6 cations
- K: less than 0.4 cations
- Fe/(Fe + Mg): preferably between 0.4 and 0.6

#### Garnet

- Mn: less than 0.45 cations per 12 oxygens (i.e., <15% Sps)

#### Plagioclase

- Ca: greater than 0.15 and preferably less than 0.7 cations per 8 oxygens (i.e.,  $>\text{An}_{15}$  and  $<\text{An}_{70}$ )

certainties, so that ignoring their compositional dependencies introduces an uncertainty in the propagated error of less than 1%.

The propagated error in pressure at an assumed temperature of 900 K is between  $\pm 100$  and  $\pm 120$  bars, with nearly all the uncertainty stemming from errors in grossular and anorthite components. The approximate precisions of other barometers using the same composition errors and correlation coefficients (at 900 K) are  $\pm 110$  bars (garnet-rutile-sillimanite-ilmenite-quartz, Bohlen et al., 1983a);  $\pm 100$  bars (garnet-plagioclase-orthopyroxene-quartz, Bohlen et al., 1983b),  $\pm 90$  bars (garnet-plagioclase-kyanite-quartz, Koziol and Newton, 1988), and  $\pm 80$  bars (garnet-biotite-muscovite-sillimanite, Hodges and Crowley, 1985). Thus, the analytical precision of the newly calibrated barometers is similar to many other currently used barometers.

A final concern for the new barometers is the effect of the  $\text{Fe}^{3+}$  content in the amphibole on the estimated pressure. A 5% change in the  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio produces a corresponding change in pressure of less than 100 bars for the Fe end-member reaction and less than 50 bars for the Mg end-member. If all errors are considered together, including electron-microprobe counting-statistics errors, a  $\pm 25$  °C uncertainty in temperature, and a 5% error in amphibole  $\text{Fe}^{3+}$  content, then a total precision of less than  $\pm 400$  bars is derived.

#### Applications to southeastern Vermont

To demonstrate their use, the barometers were applied to a suite of samples from southeastern Vermont (Fig. 3). Most of the data (nine samples) have been described by Laird and Albee (1981). Three additional samples were analyzed by us, and compositions are presented in Table 2. All samples were collected from the flanks of domal structures and represent intermediate to lower tectonic levels.

The boxes of Figure 3 show the simultaneous solution of both barometers for each sample with the Fe-Mg exchange thermometers: garnet-hornblende (Graham and Powell, 1984), garnet-biotite (Hodges and Spear, 1982), and garnet-chlorite (Dickenson and Hewitt, 1986, with Hodges and Spear garnet-activity model). Boxes are stippled for those samples (K87-18, N-1, N-2, V106D, V118D, V119C) for which independent pressure estimates were possible. These additional pressures were cal-

culated by using the barometers garnet-plagioclase-muscovite-biotite (GPMB) (Hodges and Crowley, 1985; Powell and Holland, 1988) and garnet-rutile-ilmenite-plagioclase-quartz (GRIPS) (Bohlen and Liotta, 1986) and are shown by the dots with error bars. Error bars correspond to the maximum and minimum pressures consistent with simultaneous solution of the Fe-Mg thermometers and the GPMB and GRIPS barometers. As can be seen, the newly calibrated equilibria are in complete agreement with these estimates; mean pressures determined using the two independent barometers and our new calibrations are typically within a few hundred bars of each other. Crowley (1989) and Davidow (1989) have recently calculated the metamorphic *P-T* conditions near the Chester and Athens domes using thermobarometric techniques on pelitic schists. Their work generally indicates pressures of 7 to 9 kbar, again in excellent agreement with estimates made with our new barometers.

The large ranges in pressure for three samples described by Laird and Albee (V80C, V80D, and V152) are due to recalculations of Fe<sup>3+</sup> in garnet and estimation of andradite contents. The increase in the range in pressure for the four samples analyzed by us (K87-18, N-1, N-2, and TM-650) over the propagated analytical error for single analyses described above simply reflects compositional variation in the natural minerals; our experience analyzing 35 garnet amphibolites from New England and southern Chile indicates that precisions of  $\pm 500$  to  $\pm 750$  bars are typical.

Those samples that have only single analyses for garnet, plagioclase, and hornblende—and whose garnets apparently contain little or no Fe<sup>3+</sup> (V154B, V113B, V118D, V119C, V106D, and V119E)—have the smallest apparent variation in pressure. These small variations are representative of the similarity of pressure estimates made with the Fe and Mg calibrations. The difference in pressure between V80C and V80D, which were collected from the same outcrop, could represent either equilibration of the two rocks at different times during their *P-T* trajectory or analytical problems.

These pressures are some of the first to be calculated for rocks of southeastern Vermont and indicate that the peak metamorphism occurred at a higher pressure (7 to 10 kbar) than has been traditionally interpreted for the region (e.g., Rosenfeld, 1969, and Thompson et al., 1977). The consistency of the barometers calibrated in this paper with other commonly used barometers is taken as evidence of their general accuracy for determining pressures of amphibolite- to granulite-facies metamorphism.

### Compositional limits

Application of the geobarometers to samples with bulk compositions different from those of the calibrants may result in erroneous pressure estimates. We very strongly recommend that the user restrict application of the geobarometers to those samples that meet the garnet, plagioclase, and amphibole compositional criteria listed in Table 5.

Extensive speculation regarding the results of applying

the barometers outside the compositional limits of Table 5 is not warranted at present, given the limited number of data. However, initial applications to two suites of samples from western New Hampshire indicate somewhat higher predicted pressures for Mn-rich samples than for Mn-poor rocks. This result could represent either an inadequacy of the garnet or hornblende activity models for Mn-rich bulk compositions or closure of the Mn-rich rocks at higher pressures. Further research is under way to investigate these possibilities.

Certain trends in amphibole compositions that are unaccounted for in the present activity models may also result in inaccurate pressure estimates. For example, Fe-rich hornblendes often have elevated Al contents (e.g., Robinson et al., 1982), implying that predicted pressures may be too high when the barometers are applied to these compositions. It should also be noted that use 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

We have presented the empirical calibration of two new geobarometers that may be used to estimate pressures for the assemblage garnet + hornblende + plagioclase + quartz. These calibrations are internally very consistent and fit independent pressure estimates for 37 natural data quite precisely, as indicated by the high correlation coefficients of the regressions ( $>0.96$ ). Although pressures obtained from the new calibrations are generally similar to those calculated using the garnet-hornblende-plagioclase-quartz barometers of Kohn and Spear (1989), the internal consistency of the present calibrations is much better, and we consider the new barometers to be superior to the earlier calibrations.

The sensitivity of the barometers to analytical errors and to temperature uncertainties is quite small, and applications to samples from southeastern Vermont studied by us indicate precisions of  $\pm 500$  to  $\pm 1000$  bars. Similarly, our experience with many garnet amphibolites from New England and from southern Chile indicates that precisions of  $\pm 500$  to  $\pm 750$  bars are not atypical. At present, our understanding of garnet amphibolite compositional systematics is limited by the availability of data, and further refinements of garnet amphibolite barometry will require extensive study of natural rocks and/or experimentation. In the meantime, the present calibrations can be applied to a widespread rock type with a precision that rivals that of other empirical barometers.

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