Contrib. Mineral. Petrol. 66, 113–117 (1978)

Contributions to
Mineralogy and
Petrology

Experimental Calibration of the Partitioning of Fe and Mg Between Biotite and Garnet

J.M. Ferry* and F.S. Spear

Geophysical Laboratory, 2801 Upton St., N.W., Washington, D.C. 20008, USA

Abstract. The cation exchange reaction $Fe_3Al_2Si_3O_{12}$ + $KMg_3AlSi_3O_{10}(OH)_2$ = $Mg_3Al_2Si_3O_{12}$ + $KFe_3AlSi_3O_{10}(OH)_2$ has been investigated by determining the partitioning of Fe and Mg between synthetic garnet, $(Fe, Mg)_3Al_2Si_3O_{12}$, and synthetic biotite, $K(Fe, Mg)_3AlSi_3O_{10}(OH)_2$. Experimental results at 2.07 *kbar* and 550°–800° C are consistent with $\ln [(Mg/Fe)\ \text{garnet}/(Mg/Fe)\ \text{biotite}] = -2109/T(°K) + 0.782$. The preferred estimates for $\Delta\bar{H}$ and $\Delta\bar{S}$ of the exchange reaction are 12,454 cal and 4.662 e.u., respectively. Mixtures of garnet and biotite in which the ratio garnet/biotite = 49/1 were used in the cation exchange experiments. Consequently the composition of garnet-biotite pairs could approach equilibrium values in the experiments with minimal change in garnet composition (few tenths of a mole percent). Equilibrium was demonstrated at each temperature by reversal of the exchange reaction. Numerical analysis of the experimental data yields a geothermometer for rocks containing biotite and garnet that are close to binary Fe—Mg compounds.

Introduction

One of the major goals of experimental petrologists is to provide methods that can be used to estimate the temperature at which minerals in rocks crystallize. Laboratory calibration of element partitioning between mineral phases is a particularily useful method because it is a temperature-dependent phenomenon that is independent of the activity of volatile components (e.g., CO_2 and H_2O) in the geologic environment. The fugacity of volatile components may determine the stability of a phase but not the partitioning of elements between phases. This report presents data on the partitioning of Fe^{2+} and Mg between garnet, $Fe_3Al_2Si_3O_{12}$ (*alm*)—$Mg_3Al_2Si_3O_{12}$ (*py*), and biotite, $KFe_3AlSi_3O_{10}(OH)_2$(*ann*)—$KMg_3AlSi_3O_{10}(OH)_2$ (*phl*). An experimental procedure is presented by which the determination of Fe—Mg partitioning between two phases can be achieved below 800° C. The procedure is significant because determination of Fe—Mg partitioning between phases below 800° C has in the past been unsuccessful (Medaris, 1969; Gunter, 1974).

Experimental Procedures

Garnets ($alm_{80}py_{20}$ and $alm_{90}py_{10}$) were synthesized dry in graphite capsules in a solid medium, high-pressure apparatus at 1100° C, 26 *kbar* (piston-out, no friction correction) for 18 h. Biotites ($ann_{25}phl_{75}$, $ann_{50}phl_{50}$, $ann_{75}phl_{25}$, and $ann_{100}phl_{00}$) were synthesized hydrothermally in $Ag_{70}Pd_{30}$ capsules in cold-seal pressure vessels at 750°–780° C, 2.07 *kbar*, at f_{O_2} defined by the iron-wustite buffer, for 124–206 h. Both minerals were prepared from appropriate mixtures of fayalite, γ-Al_2O_3, cristobalite, MgO, and crystalline $K_2Si_2O_5$, ground for one hour under acetone. Fayalite was synthesized from a mixture of cristobalite and Fisher reagent-grade Fe_2O_3 held at 1000° C, $\log_{10}f_{O_2} = -14$ in a one atmosphere CO—CO_2 gas-mixing furnace for 24 h. The mixture was quenched and crushed at six hour intervals. Cristobalite, γ-Al_2O_3, and MgO were synthesized by firing Fisher reagent-grade silicic acid, $Al(OH)_3$, and MgO, respectively, at 1400° C, one atmosphere, for 2 h. The $Al(OH)_3$ was heated gently over a Bunsen burner for 5 min before firing at 1400° C. The crystalline $K_2Si_2O_5$ was synthesized from Fisher reagent-grade K_2CO_3 and cristobalite by the method of Schairer and Bowen (1955).

Synthetic products were >99% biotite or garnet, as estimated optically. Powder X-ray diffraction patterns of synthetic products contained only biotite or garnet peaks. The composition of synthetic $alm_{80}py_{20}$ was checked by a four-element chemical analysis with the automated MAC electron microprobe at the Geophysical Laboratory on a flat, polished specimen using various natural silicate minerals as standards, and its composition was found to be as planned within the error of measurement ($\pm 0.01\ X_{alm}$). The intended composition of $alm_{90}py_{10}$ was verified by a partial chemical analysis by electron microprobe for Fe and Mg using synthetic $alm_{80}py_{20}$ as a standard. Approximately ten analyses were made of

---

* *Present address:* Department of Geology, Arizona State University, Tempe, Arizona 85281, USA

0010-7999/78/0066/0113/$01.00

Table 1. Unit cell parameters and refractive indices of synthetic biotites, $K(Fe, Mg)_3AlSi_3O_{10}(OH)_2$

Composition	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	d_{331}^{bar} (calc)	n_γ
$ann_{00}phl_{100}$	5.3138(8)	9.204(1)	10.311(2)	99.86(2)	469.9(2)	1.5340	–
$ann_{25}phl_{75}$	5.341(4)	9.236(5)	10.315(5)	99.93(6)	501.2(5)	1.5412	–
$ann_{50}phl_{50}$	5.361(2)	9.288(3)	10.330(4)	99.91(5)	506.7(4)	1.5478	–
$ann_{75}phl_{25}$	5.382(1)	9.309(5)	10.337(2)	100.13(3)	509.9(3)	1.5532	1.659(3)
$ann_{100}phl_{00}$	5.391(3)	9.337(4)	10.324(6)	100.02(6)	511.8(5)	1.5562	1.684(3)

Figures in parentheses represent the standard deviation in terms of least units cited for the value to their immediate left; these were calculated by the program used to refine the parameters and represent precision only.

garnets $alm_{90}py_{10}$ and $alm_{80}py_{20}$, randomly spaced over the sample mounts, and no chemical zonation was observed in the synthetic garnets (within ±0.01 X_{alm}).

The unit cell dimensions of biotites synthesized in this study are listed in Table 1; in addition, refractive index data were collected for some of the synthetic biotites. The unit cell dimensions for synthetic biotites were calculated by refining powder patterns obtained with an X-ray diffractometer, CuK_α radiation, a silicon internal standard (National Bureau of Standards, SRM 640), and the computer program LCLSQ written by Burnham (1962). Refractive index, n, was measured at 25° C using sodium light ($\lambda = 589$ nm).

The unit cell dimensions and refractive indices of biotites listed in Table 1 agree very well (in most cases within experimental error) with the values listed for corresponding biotite compositions in Hewitt and Wones (1975), with the exception of the biotite with composition $ann_{100}phl_{00}$. The discrepancy between the unit cell dimensions of $ann_{100}phl_{00}$ from this study and those of Hewitt and Wones may be explained by the presence of a small amount (approximately 6%) of Al in the octahedral sites of our biotite synthesized from the $ann_{100}phl_{00}$ mix. The consistency between the results of this study in Table 1 and the results of Hewitt and Wones (1975) is a strong argument that the synthetic biotites of intermediate Fe–Mg composition had compositions as planned. Further evidence for this conclusion is presented in Figure 1. Synthetic biotites were dispersed on flat, polished diamond surfaces, and the intensities of background-corrected X-ray peaks for Fe and Mg, I_{Fe} and I_{Mg}, respectively, were measured. For $ann_{25}phl_{75}$, $ann_{50}phl_{50}$; and $ann_{75}phl_{25}$, measured I_{Fe}/I_{Mg} is a linear function, passing through (0,0), of C_{Fe}/C_{Mg}, where C_i is the weight fraction of element i. The internal consistency of the I_{Fe}/I_{Mg} vs. C_{Fe}/C_{Mg} data would be a necessary consequence of synthetic biotites having compositions as planned.

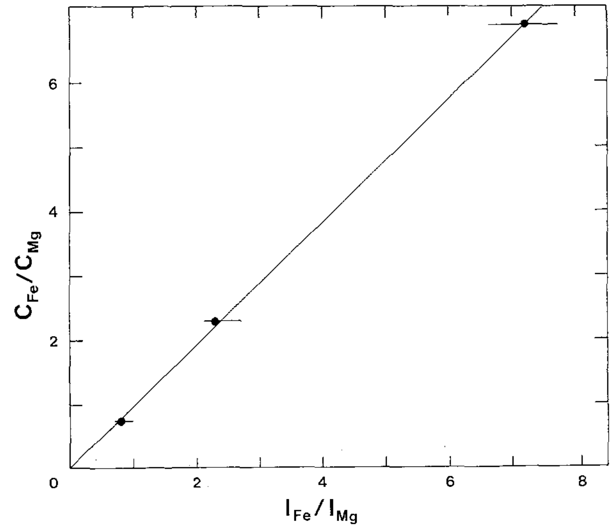

Fig. 1. Measured relation between I_{Fe}/I_{Mg} and C_{Fe}/C_{Mg} for synthetic biotites ($ann_{25}phl_{75}$, $ann_{50}phl_{50}$, $ann_{75}phl_{25}$). Circles and light horizontal lines are the average and range, respectively, of the population. The C_i and I_i are defined in the text. Operating conditions are 15 kv, 50 na; 100 second counting times. Grains in the size range 3–8 microns were analyzed

The Fe–Mg partitioning experiments consisted of combination of garnet with biotite in a mixture in which molar garnet/biotite = 98/2 (on a 12 oxygen atom basis). This mixture was ground under acetone to an average particle size of approximately one micron, sealed with H_2O in $Ag_{70}Pd_{30}$ capsules, and held at temperatures of 550°–800° C and 2.07 *kbar* for 3–9 weeks. Temperature was measured by unsheathed chromel-alumel thermocouples, newly prepared from unoxidized wire before each experiment and calibrated *in situ* (1 atm pressure) against the melting point of NaCl (800.4° C). Temperature in each experiment was maintained within a ±3° C cycle by a Honeywell-Brown controller. Reported temperatures are believed to be accurate to ±6°. Pressure was measured with a bourdon tube gauge calibrated against a factory-calibrated Heise gauge. Reported pressures are believed to be accurate to ±50 bars. The fugacity of oxygen was controlled in the partitioning experiments by the graphite-methane buffer (Eugster and Skippen, 1967). The high H_2O content of the experimental samples (Table 2), intended to facilitate reaction, apparently did not significantly change the bulk composition of the solids because garnet composition remained unchanged, within uncertainty of electron microprobe analysis, after the experiments. The refractive index of the garnet after the experiments was ~1.82, the value appropriate for $alm_{90}py_{10}$ (Chinner et al., 1960), and hydrogarnet, therefore, could not have formed during the partitioning experiments (H.S. Yoder, 1977, personal commun.). At the conclusion of the experiments, the capsules were opened and the contents were dispersed on flat, polished diamond surfaces. The compositions of biotite grains were subsequently determined by electron microprobe using a linear relation between I_{Fe}/I_{Mg} and C_{Fe}/C_{Mg} (Fig. 1 is a sample calibration curve). Five to fifteen grains in a population of unknowns were analyzed and their compositions averaged. This method was developed by White (1964) and has been successfully exploited by Eugster et al. (1972) and Spear (1976). Repeated analysis of synthetic biotites of known compositions, with the procedures described above, indicated that measured biotite compositions are accurate to ±0.01 X_{ann}.

Equilibrium was demonstrated at each temperature by placing two capsules in the same pressure vessel: one capsule contained garnet and a biotite more magnesian and the other capsule garnet and a biotite more iron-rich than the composition of the biotite in equilibrium with the garnet at a given

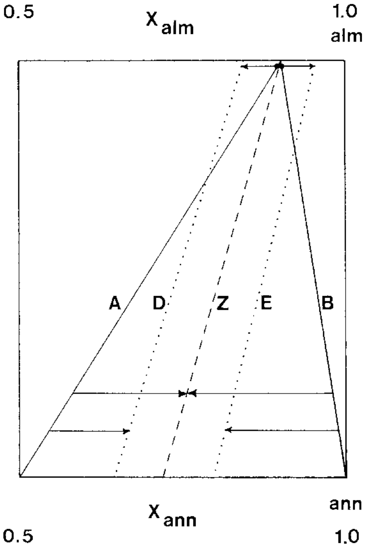

Fig. 2. Compositions of coexisting biotites and garnets at some arbitrary temperature and pressure. Tie lines D, E, and Z are equilibrium tie lines. All tie lines are explained further in the text

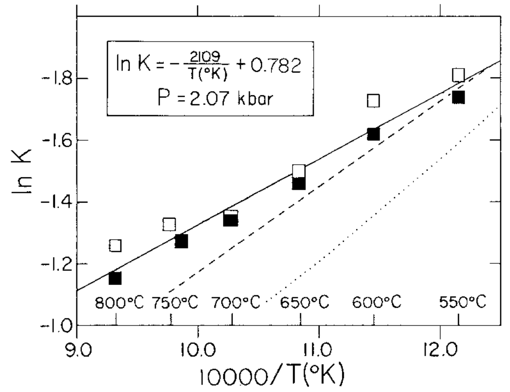

Fig. 3. Plot of $\ln K = \ln\{(\mathrm{Mg/Fe})_{\mathrm{garnet}}/(\mathrm{Mg/Fe})_{\mathrm{biotite}}$ vs. $1/T$(° K) for the data in Table 1A. The solid line is calculated from a least-squares fit to the data points (see inset). Size of boxes corresponds to ±5° uncertainty in temperature and ±0.01 uncertainty in X_{ann}. Dashed line is from Thompson (1975, Fig. 1 – B). Dotted line is from Goldman and Albee (1977, Equation (8))

temperature. In experiments with garnet $alm_{90}py_{10}$, the compositions of biotites at the end of the two different experiments did not differ by more than 0.04 mole fraction *ann.*

The advantage of the 98-2 garnet-biotite ratio in the experimental samples is that garnet, which is sluggish to react, does not have to change significantly in composition during the experiments. For example, two mixtures, $alm_{90}py_{10} + ann_{50}phl_{50}$ and $alm_{90}py_{10} + ann_{100}phl_{00}$ (solid circles on tie lines A and B, respectively, Fig. 2), have very nearly the same bulk composition. If the two mixtures are held at the arbitrary temperature and pressure of Figure 2, tie lines A and B will rotate to the equilibrium tie line, Z. Biotite composition in the two mixes changes considerably as equilibrium is approached, but the composition of garnet changes negligibly. In the 740° C experiment (Table 2) a garnet $alm_{90}py_{10}$ was mixed with $ann_{100}phl_{00}$. At the conclusion of the experiment, the measured composition of the biotite was $ann_{73}phl_{27}$, requiring, by mass balance, a change in the garnet composition of only +0.0055 mole fraction *alm.* The largest change in garnet composition occurred in the 740° C experiment; garnets in the other experiments changed even less, usually by about 0.002 mole fraction. This predicted small change in the garnet composition was verified experimentally by determining that the composition of the garnet from selected experiments remained unchanged within the uncertainty of electron microprobe analysis (±0.01 X_{alm}). This technique should be applicable to determination of element partitioning between any mineral pair provided at least one mineral (such as biotite in this study) is sufficiently reactive.

The narrow reversal brackets in Figure 3 indicate that biotite did not equilibrate with rims of garnets that were significantly different in composition from $alm_{90}py_{10}$. *If* biotite reacted only with garnet rims in the experiments, then the effective bulk composition of the biotite-garnet couple would lie along tie lines A or B (Fig. 2) but at garnet-biotite ratios less than 98-2. Starting tie lines A and B consequently would rotate, for example, to tie lines D and E, respectively, which differ greatly in biotite composition. Because starting tie lines A and B converged very nearly to the same tie line, Z, at each temperature investigated, biotite must have effectively equilibrated with the bulk of the garnet in the samples.

Results

Results of experiments with garnet, $alm_{90}py_{10}$, and biotite are presented in Table 2 and Figure 3. The data in Table 2 and Figure 3 are consistent with the expression (at 2.07 *kbar*):

$$\ln K = -2109/T(°\mathrm{K}) + 0.782, \qquad (1)$$

Table 2. Compositions of biotite equilibrated at various temperatures and 2.07 *kbar* with garnet $alm_{90}py_{10}$ or $alm_{80}py_{20}$. Garnet and biotite were mixed in a molar garnet/biotite = 98/2

Run #	T(°C) (±6°)	Starting Material (X_{ann})	Time (h)	Final X_{ann} (±0.01)	Number of Grains Analyzed	ln *K*
A. Experiments with garnet $alm_{90}py_{10}$						
112	799	1.00	551	0.750	8	−1.155
116	799	0.50	551	0.710	12	−1.258
89	738	1.00	316	0.730	4	−1.271
123	749	0.50	818[a]	0.695	12	−1.330
128	698	0.75	672	0.704	15	−1.342
125	698	0.50	1151[b]	0.690	10	−1.353
138	651	0.75	523	0.679	11	−1.459
135	651	0.50	1002[c]	0.661	11	−1.497
139	599	0.75	498	0.645	8	−1.623
137	599	0.50	1344[d]	0.608	4	−1.728
126	550	0.75	911	0.620	5	−1.741
118	550	0.50	911	0.587	3	−1.811
B. Experiments with garnet $alm_{80}py_{20}$						
153	697	0.75	869	0.574	15	−1.113
149	697	0.25	869	0.468	11	−1.486
152	601	0.50	869	0.500	6	−1.386
150	601	0.25	869	0.392	2	−1.806

[a] (316/502) = Sample run for 316 h, opened, ground under acetone for 1 h, reloaded, and run for an additional 502 h

[b] (479/672)

[c] (523/479)

[d] (846/498)

where $K = (\mathrm{Mg/Fe})_{\mathrm{garnet}}/(\mathrm{Mg/Fe})_{\mathrm{biotite}}$ (either on a weight or atomic metal basis) and the coefficients were determined by a linear least-squares fit of the ln *K* values vs. $1/T$ (Table 2A; data were unweighted in the regression). At equilibrium for the reaction

$$\mathrm{Fe_3Al_2Si_3O_{12} + KMg_3AlSi_3O_{10}(OH)_2 = KFe_3AlSi_3O_{10}(OH)_2 + Mg_3Al_2Si_3O_{12}}, \qquad (2)$$

$$\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} + P\Delta\bar{V} + 3RT\ln K = 0. \qquad (3)$$

If $\Delta\bar{H}$, $\Delta\bar{S}$, and $\Delta\bar{V}$ for reaction (2) are independent of pressure and temperature in the range of conditions experimentally investigated, by comparing Equations (1) and (3),

$$\Delta\bar{S} = 3R(0.782) = 4.662 \text{ e.u.}; \qquad (4)$$

$$\Delta\bar{H} + 2070\Delta\bar{V} = 3R(2109). \qquad (5)$$

For reaction (2), $\Delta\bar{V} = +0.057$ cal/bar (Robie et al., 1967), and

$$\Delta\bar{H} = 3R(2109) - 2070(0.057) = 12{,}454 \text{ cal}. \qquad (6)$$

The preferred estimates of $\Delta\bar{S}$ and $\Delta\bar{H}$ for reaction (2) are 4.662 e.u. and 12,454 cal. respectively. The experimental data in Table 1 are consistent (considering errors in measurement of T and K), however, with values of $\Delta\bar{S}$ in the range 0.143 − 9.227 e.u. and with values of $\Delta\bar{H}$ in the range 8166 − 16,784 cal. A polybaric, polythermal expression for Fe—Mg partitioning between biotite and garnet may be formulated by substituting values of $\Delta\bar{H}$, $\Delta\bar{S}$, and $\Delta\bar{V}$ (from Equations (4) and (6) above) into Equation (3):

$$12{,}454 - 4.662T(°\mathrm{K}) + 0.057P(\mathrm{bars}) + 3RT\ln K = 0. \qquad (7)$$

Experiments were conducted at 600° and 700° C, 2.07 *kbar*, with garnet $alm_{80}py_{20}$ starting material, to test the compositional dependence of ln *K* within the system *alm-py-ann-phl*. The brackets of ln*K* as a function of $1/T$ from experiments using $alm_{80}py_{20}$ are much larger than the brackets using $alm_{90}py_{10}$ (Table 2). The results of experiments with $alm_{80}py_{20}$, however, are consistent with Equation (1) and suggest that Fe and Mg mix ideally in biotite and garnet solid solutions at least in the composition interval $0.80 \leqq \mathrm{Fe/(Fe+Mg)} \leqq 1.00$.

Applications

Figure 3 and Equation (7) represent a geothermometer for rocks containing biotite and garnet that are close to binary Fe—Mg compounds. It is clear, from analyses of biotite and garnet of different compositions that crystallized at the same metamorphic grade, that *K* is also a function of Ca and Mn content of the garnet and the Ti and $\mathrm{Al^{VI}}$ content of the biotite (Dallmeyer, 1974; Saxena, 1969). Caution should be exercised in applying the data in Figure 3 to systems containing significant amounts of Ca, Mn, or Ti. The experiments of this study, nevertheless, demonstrate a procedure by which the dependence of *K* on Ca, Mn, and Ti in garnet and biotite could be experimentally determined.

The partitioning of Fe and Mg between biotite and garnet has been calibrated in two studies by measuring the compositions of biotite and garnet from natural rock specimens for which temperatures of crystallization were estimated by independent means (Goldman and Albee, 1977: temperatures from $^{18}\mathrm{O}/^{16}\mathrm{O}$ fractionation between quartz and magnetite; Thompson, 1975: temperatures mainly from comparison of mineral assemblages with results of phase equilibrium experiments). Both calibrations assumed no pressure affect on Fe—Mg fractionation between biotite and garnet. The experimental results of this study and an extrapolation of them to lower temperatures agree with the calibration of Thompson (Fig. 3, dashed line) in the temperature range 400°–600° C and lie approximately 50° higher than the

Goldman and Albee calibration (dotted line). The agreement between the laboratory results of this study and the two calibrations based on natural samples suggests that Figure 3 and equation (7) may be a useful geothermometer without correction for components (up to ~0.2 (Ca+Mn)/(Ca+Mn+Fe+Mg) in garnet and up to ~0.15 $(Al^{VI}+Ti)/(Al^{VI}+Ti+Fe+Mg)$ in biotite) other than Fe and Mg. The geothermometer in Figure 3 has a maximum practical resolution of approximately ±50°, which corresponds to the error in temperature that results when ±0.01 errors in X_{ann}, X_{phl}, X_{alm}, and X_{py} are propagated through Equation (1).

Acknowledgements. The study was completed while both authors were postdoctoral fellows at the Geophysical Laboratory. A.A. Finnerty, R.K. Popp, D. Rumble, E.B. Watson, D.R. Wones and H.S. Yoder, Jr. assisted through discussion and critical review.

References

Burnham, C.W.: Lattice constant refinement. Carnegie Inst. Washington Yearbook **61**, 132–135 (1963)

Chinner, G.A., Boyd, F.R., England, J.L.: Physical properties of garnet solid solutions. Carnegie Inst. Washington Yearbook **59**, 76–78 (1960)

Dallmeyer, R.D.: The role of crystal structure in controlling the partitioning of Mg and Fe^{2+} between coexisting garnet and biotite. Am. Mineralogist **59**, 201–203 (1974)

Eugster, H.P., Albee, A.L., Bence, A.E., Thompson, J.B., Jr., Waldbaum, D.R.: The two-phase region and excess mixing properties of paragonite-muscovite crystalline solutions. J. Petrol. **13**, 147–179 (1972)

Eugster, H.P., Skippen, G.B.: Igneous and metamorphic reactions involving gas equilibria. In: Researches in geochemistry (P.H. Abelson, ed.), Vol. 2, pp. 377–396. New York: John Wiley 1967

Goldman, D.S., Albee, A.L.: Correlation of Mg/Fe partitioning between garnet and biotite with O^{18}/O^{16} partitioning between quartz and magnetite. Am. J. Sci. **277**, 750–761 (1977)

Gunter, A.E.: An experimental study of iron-magnesium exchange between biotite and clinopyroxene. Can. Mineralogist **12**, 258–261 (1974)

Hewitt, D.A., Wones, D.R.: Physical properties of some synthetic Fe—Mg—Al trioctahedral biotites. Am. Mineralogist **60**, 854–862 (1975)

Medaris, L.G.: Partitioning of Fe^{2+} and Mg^{2+} between coexisting synthetic olivine and orthopyroxene. Am. J. Sci. **267**, 945–968 (1969)

Robie, R.A., Bethke, P.M., Beardsley, K.M.: Selected x-ray crystallographic data, molar volumes, and densities of minerals and related substances. U.S. Geol. Surv. Bull. **1248** (1967)

Saxena, S.K.: Silicate solid solution and geothermometry: 3. Distribution of Fe and Mg between coexisting garnet and biotite. Contrib. Mineral. Petrol. **22**, 259–267 (1969)

Schairer, J.F., Bowen, N.L.: The system $K_2O—Al_2O_3—SiO_2$. Am. J. Sci. **253**, 681–746 (1955)

Spear, F.S.: Ca-amphibole composition as a function of temperature, fluid pressure, and oxygen fugacity in a basaltic system. Carnegie Inst. Washington Yearbook **75**, 775–779 (1976)

Thompson, A.B.: Mineral reactions in pelitic rocks: II. Calculation of some P—T—X(Fe—Mg) phase relations. Am. J. Sci. **276**, 425–454 (1975)

White, E.W.: Microprobe technique for the analysis of multiphase microcrystalline powders. Am. Mineralogist **49**, 196–197 (1964)

Received July 5, 1977/Accepted December 10, 1977