

The thermodynamic properties of dumortierite $\text{Si}_3\text{B}[\text{Al}_{6.75}\square_{0.25}\text{O}_{17.25}(\text{OH})_{0.75}]$

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ABSTRACT

The heat capacities of dumortierite have been measured from 7 to 1000 K by quasi-adiabatic low-temperature and differential scanning calorimetry. The corrected calorimetric entropy at 298.15 K calculated from the experimental data is 330.2 ± 5.0 J/(mol·K) based upon the chemistry of the sample, average compositions proposed by Alexander et al. (1986), and correction to the structural formula given by Moore and Araki (1978). Moore and Araki (1978) have shown the Al(1) site to be disordered, and chemical analyses suggest that there is some Al substitution for Si. A minimum configurational entropy of 4.74 J/(mol·K) should be added to the corrected calorimetric entropy for third law calculations.

The enthalpy and Gibbs free energy of formation of dumortierite from the elements have been estimated from synthesis and decomposition data and are -9109 ± 20 and -8568 ± 20 kJ/mol, respectively, at 298.15 K and 1 bar.

INTRODUCTION

The presence of B in a geochemical system may have strong effects on phase stability in that system. B has been shown to disrupt partially the aluminosilicate network of melts in the haplogranite system, to increase H_2O solubility, to reduce the melt viscosity, and to reduce the liquidus and solidus temperatures in such melts (Pichavant, 1981, 1987). Melt depolymerization by dissolved B may lead to an increase in melt solubility of important or strategic elements such as Sn, W, U, Ta, Y, Nb, and Be that may be concentrated later in pegmatites or other deposits. London et al. (1989) and London (1986) have concluded that pegmatite formation is the result of crystallization from a volatile-rich, vapor-undersaturated melt. B_2O_3 in relation to other melt components has been shown to be strongly partitioned into the vapor phase associated with such melts (London et al., 1988) and to increase the Na and silicate solubility in the vapor phase (Pichavant, 1981). London et al. (1989) suggested that vapor saturation may interfere with pegmatite genesis. Consequently, an increased understanding of the chemistry of B in peraluminous systems and of B-bearing phases would provide a more complete picture of pegmatite genesis and of the localization of associated mineralization.

Knowledge of the thermodynamic properties of dumortierite together with those of the oxyborosilicates grandidierite, kornerupine, and tourmaline should help define late-stage changes in pegmatite formation and in regionally metamorphosed B-bearing aluminous rocks.

Dumortierite is a refractory aluminum oxyborosilicate that is found in acidic granulites, pegmatites, and hydrothermally altered tuffs (e.g., Wilson, 1929; Sabzehei, 1971; Schreyer et al., 1975; Vrána, 1979; Huijsmans et al., 1982; Applin and Hicks, 1987; Foit et al., 1989). The oxyborosilicates appear to crystallize after kyanite, andalusite, and sillimanite in the order given by Vrána (1979): grandidierite, kornerupine, dumortierite, and tourmaline. After tourmaline, dumortierite appears to be the most common of the oxyborosilicate minerals (Vrána, 1979) and differs from the other phases because it contains high Al_2O_3 and low MgO and FeO.

Unfortunately, very little is known about the thermodynamic properties of dumortierite and several other of these B-bearing phases. We report here heat capacities measured by quasi-adiabatic low-temperature calorimetry and differential scanning calorimetry for a natural sample of dumortierite, and we estimate the Gibbs free energy of formation and entropy for dumortierite.

EXPERIMENTAL METHODS

Low-temperature quasi-adiabatic calorimetry was performed on our dumortierite sample using the intermittent heating method. The apparatus and procedures are described elsewhere (Robie and Hemingway, 1972; Robie et al., 1976; Hemingway et al., 1984). The sample was sealed in the calorimeter under pure He gas at a pressure of 5 kPa. The sample represented 6.8% of the heat capacity of the sample plus calorimeter measured at 10 K, 11% at 50 K, 19% at 100 K, 32% at 200 K, and 39% at

TABLE 1. Experimental low-temperature molar heat capacities for natural dumortierite (molar mass = 565.937 g)

T (K)	Heat capacity [J/(mol·K)]	T (K)	Heat capacity [J/(mol·K)]	T (K)	Heat capacity [J/(mol·K)]
Series 1		Series 2		Series 3	
300.22	443.3	46.83	15.89	176.83	256.3
305.06	447.9	52.23	21.13	181.47	264.8
310.36	454.0	58.14	28.10	186.10	273.6
315.71	459.7	Series 3		190.73	282.2
321.12	465.6	63.67	35.66	195.37	290.7
326.51	470.8	68.56	42.90	200.03	298.7
331.90	476.6	73.03	49.88	Series 4	
337.27	483.8	77.88	57.88	205.28	308.0
342.63	488.3	83.27	67.22	211.03	317.6
Series 2		88.61	77.22	216.64	326.7
7.93	0.3041	94.00	87.54	222.37	335.9
9.06	0.1995	99.31	98.07	228.04	344.6
10.18	0.1518	104.54	108.6	233.84	353.5
11.40	0.2041	109.69	119.2	239.72	362.2
12.81	0.2361	114.76	129.6	245.65	370.7
14.34	0.3323	119.77	140.0	251.63	379.1
16.00	0.4767	124.73	150.6	257.66	387.5
17.81	0.6925	129.62	160.9	263.71	396.0
19.81	0.9792	134.48	170.9	269.80	404.4
22.02	1.313	139.29	180.9	275.90	412.2
24.48	1.844	144.06	191.0	281.97	420.0
27.22	2.612	148.80	201.2	288.02	428.0
30.30	3.787	153.52	210.5	294.04	435.4
33.74	5.661	158.22	219.7	300.04	442.4
37.62	7.838	162.90	229.1	306.03	448.6
41.98	11.63	167.55	238.0	312.00	455.1
		172.20	247.2	317.94	463.1

300 K. The sample used for the low-temperature heat-capacity measurements was 23.5378 g, in the form of a coarse powder ($-200 + 325$ mesh).

High-temperature heat capacities were measured by differential scanning calorimetry (DSC). The apparatus and procedures are described elsewhere (Hemingway et al., 1981). The DSC sample was 28.69 mg in the same form.

Sample description

A deep blue cube of about 3 in. on a side was donated for the study by Brian Beck (Harding Lawson Associates, Phoenix, Arizona). The material was collected in the Indian Pass area of southeastern California, approximately 30 miles from Yuma, Arizona. Examination of a thin section of this material showed that the material was approximately 30 vol% dumortierite needles intermixed with quartz, muscovite, and magnetite. The dumortierite needles were purified with magnetic separation, using a Franz magnetic separator, and heavy liquids. No phase other than dumortierite was seen in the cleaned sample. The sample chemistry was determined by microprobe analysis (in weight percent) as SiO₂ 29.3, Al₂O₃ 62.8, CaO 0.01, Na 0.01, MgO 0.01, FeO 0.55, B₂O₅ 5.0, and TiO₂ 1.36. B was assumed to occupy fully the B site in accordance with the findings of Alexander et al. (1986). This assumption is supported by preliminary analyses of the dumortierite using two microprobes and two sets of B reference standards. The B analyses are considered preliminary because we have not fully developed standards that are appropriate or correction terms for the

observed counts, and we suspect that there may be some interference in the analysis for B using the two crystals we have examined, depending upon the sample chemistry. Further work in this area is in progress. OH was assumed to be equivalent to that selected by Alexander et al. (1986).

The formula for dumortierite, Si₃B[Al_{6.75}□_{0.25}-O_{17.25}(OH)_{0.75}], was taken as the ideal composition based upon the study of Moore and Araki (1978). The ideal molar mass is 565.937 g, based upon the 1975 atomic weights.

EXPERIMENTAL RESULTS

Heat capacities measured at low temperatures by adiabatic calorimetry are listed in Table 1. Low-temperature heat capacities were smoothed using a cubic spline routine. Heat-capacity data for temperatures less than 20 K were used to estimate a Debye θ for dumortierite of 780 K. The experimental and smoothed values for temperatures less than 25 K were plotted as C_p/T vs. T^2 and used with the estimated Debye θ to extrapolate the heat capacity to 0 K. A small Schottky anomaly at <10 K was observed and attributed to the presence of a minor concentration of Fe in the structure. Smoothed values of the heat capacity and the derived thermodynamic functions are given in Table 2. The heat-capacity results are reported for the molar mass of 565.937 g that are calculated from the specific heat measured for the natural sample. The experimental results listed in Tables 1 and 2 are based upon heat capacities for the natural sample that have not been corrected for impurity phases or deviations from the selected chemical formula.

Heat capacities measured at superambient temperatures by DSC are listed in Table 3. High-temperature heat capacities were combined with heat capacities measured at temperatures greater than 280 K by adiabatic calorimetry and with estimates of the heat capacity at temperatures greater than 1000 K. The data were fitted to an equation of the form suggested by Haas and Fisher (1976). The heat-capacity equation $C_p = 1438.612 - 0.24273T + 4.8835 \times 10^{-5}T^2 - 1.68183 \times 10^4T^{-0.5} + 3.8604 \times 10^6T^{-2}$ fits the data with an average deviation of 0.33%. The equation is valid from 280 to 1800 K.

The entropy at 298.15 K calculated for the natural dumortierite sample (Table 2) was corrected to the chemical composition proposed by Moore and Araki (1978) by addition or subtraction of the entropies for the proportionate differences in the oxide totals reported in the chemical analysis and based upon the chemistry for dumortierite samples given by Alexander et al. (1986). The corrections result in additions of entropy for the deficiencies in SiO₂ and OH and subtractions of entropy for the contributions of CaO, FeO, MgO, TiO₂, and excess Al₂O₃ present in the natural sample. The entropy estimated from this procedure is 330.2 ± 5 J/(mol·K) at 298.15 K and 1 bar. For third law calculations, a contribution for configurational entropy (discussed below) must be added to the corrected value.

TABLE 2. Molar thermodynamic properties of natural dumortierite (molar mass = 565.937 g)

T (K)	Heat capacity C _p	Entropy S _p ^o - S _g ^o	Enthalpy	Gibbs
			function (H _p ^o - H _g ^o)/T	function -(G _p ^o - H _g ^o)/T
J/(mol·K)				
5	0.015	0.005	0.003	0.002
10	0.121	0.040	0.030	0.010
15	0.408	0.136	0.102	0.034
20	1.006	0.320	0.189	0.130
25	1.976	0.635	0.438	0.198
30	3.655	1.129	0.821	0.308
35	6.312	1.889	1.412	0.476
40	9.802	2.937	2.222	0.715
45	14.20	4.348	3.311	1.037
50	18.82	6.077	4.625	1.453
60	30.55	10.49	7.920	2.573
70	45.10	16.27	12.17	4.101
80	61.51	23.34	17.29	6.051
90	79.82	31.63	23.20	8.422
100	99.44	41.04	29.84	11.20
110	119.8	51.47	37.09	14.38
120	140.6	62.78	44.84	17.94
130	161.6	74.87	53.02	21.85
140	182.5	87.61	61.52	26.09
150	203.3	100.9	70.28	30.63
160	223.4	114.7	79.23	35.45
170	243.0	128.8	88.28	40.53
180	262.2	143.2	97.41	45.83
190	280.8	157.9	106.6	51.34
200	298.7	172.8	115.7	57.04
210	315.8	187.8	124.9	62.91
220	332.1	202.8	133.9	68.93
230	347.7	218.0	142.9	75.08
240	362.6	233.1	151.7	81.35
250	376.9	248.2	160.4	87.72
260	390.9	263.2	169.0	94.18
270	404.5	278.2	177.5	100.7
280	417.6	293.2	185.9	107.3
290	430.2	308.1	194.1	114.0
300	442.2	322.8	202.1	120.7
310	453.5	337.5	210.1	127.5
320	464.4	352.1	217.8	134.3
330	475.2	366.6	225.5	141.1
340	485.8	380.9	233.0	147.9
273.15	408.7	282.9	180.2	102.8
298.15	440.0	320.1	200.7	119.5

Note: The results have not been corrected for deviations of the sample chemistry from the structural formula of Moore and Araki (1978).

TABLE 3. Experimental superambient molar heat capacities for natural dumortierite (molar mass = 565.937 g)

T (K)	Heat capacity [J/(mol·K)]	T (K)	Heat capacity [J/(mol·K)]	T (K)	Heat capacity [J/(mol·K)]
Series 1		Series 2		Series 3	
338.9	481.0	500.0	593.6	661.0	654.7
349.0	491.6	510.0	597.5	671.1	658.5
359.1	501.1	520.1	602.1	681.1	658.6
369.1	510.1	530.2	607.6	691.2	664.5
379.2	518.2	540.2	611.3	700.3	667.5
389.3	526.2	550.3	616.6	Series 4	
399.3	534.7	560.4	620.5	750.6	677.4
409.4	541.9	570.4	626.1	Series 5	
419.5	549.0	580.5	629.9	750.6	676.9
429.5	555.9	590.6	637.2	Series 6	
439.6	561.3	599.6	640.8	800.9	690.2
449.6	567.2	Series 3		Series 7	
459.7	572.3	570.4	624.0	851.0	698.6
469.8	578.0	580.5	628.0	Series 8	
479.8	581.7	590.6	633.2	899.7	705.2
489.9	585.9	600.6	633.8	Series 9	
499.0	590.9	610.7	640.6	948.4	706.3
Series 2		620.8	644.0	Series 10	
469.8	579.8	630.8	645.9	948.4	704.8
479.8	584.3	640.9	647.8	Series 11	
489.9	589.7	651.0	651.4	988.4	707.1

kbar. The compositions of the dumortierite samples synthesized under the various temperature and pressure conditions showed little variation, each containing excess B, a small amount of OH, and a deficiency in Si compared with natural dumortierite (Alexander et al., 1986). Dumortierite, corundum, and a transparent glass were the products obtained at temperatures above about 900 °C. At lower temperatures (but above 10 kbar), dumortierite, corundum, and a brown, B-bearing material were the product phases. Dumortierite did not grow at temperatures greater than about 950 °C, 10 kbar and 1050 °C, 15 kbar. At such conditions, sillimanite, corundum, and glass were the product phases. At lower temperatures and pressures a brown, B-bearing phase, quartz, and corundum were the product phases. No chemical analysis was provided for the brown phase.

Some or all of the product phases in the experiments reported by Ono (1981) were metastable. Ono (1981) noted that the brown, B-bearing phase may be metastable with respect to dumortierite because equilibrium was not established in the experimental products as shown by the presence of quartz and corundum, which are presumed to be metastable with respect to sillimanite (e.g., Robie and Hemingway, 1984).

Further complicating our interpretation of the experimental results is the meager amount of information provided. Ono (1981) presented a table of representative experimental results and a figure on which representative results were plotted. These two data sets are, in part, different from each other, and neither is complete.

Based upon our analysis of the results presented by Ono (1981), we have selected two experiments at 1030 °C from which to estimate the stability of dumortierite. Dumortierite was a product in the higher pressure exper-

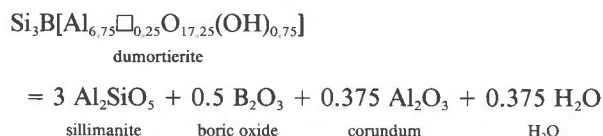
Free energy of formation

Neither phase-equilibrium measurements nor a calorimetrically determined enthalpy of formation that would allow an estimation of the free energy of formation of dumortierite are available. However, Ono (1981) studied the synthesis of dumortierite under various conditions of temperature and pressure. Ono's results may be used to estimate the free energy of dumortierite.

Ono (1981) used a mechanical mixture of SiO₂, Al₂O₃, and H₃BO₃ as starting material in synthesizing dumortierite. SiO₂ and Al₂O₃ were prepared from H₂SiO₃ and Al(OH)₃ at 1500 °C. Two mixtures were used, one stoichiometric for the formula Al₂O₃(BO₃)(SiO₄), and the other containing excess B with respect to this formula.

Ono (1981) grew dumortierite at temperatures between about 750 and 1050 °C at pressures between 10 and 20

iment (about 14 kbar), and sillimanite was present in the lower pressure experiment (13 kbar). The other components are assumed to be equivalent in state and present in the products. With the idealized formula for dumortierite given by Moore and Araki (1978) the reaction is



at 1030 °C and 13.5 kbar. Using the third law method (Robie, 1965), we estimate $\Delta_f H_{298}^0 = -26.4$ kJ and the enthalpy of formation of dumortierite to be -9103 kJ/mol at 298.15 K and 1 bar (ancillary data from Robie et al., 1979).

We made a second estimate of the enthalpy of formation of dumortierite from the reaction curve given by Ono (1981) limiting the stability of dumortierite. The estimate is derived by taking a point from the curve at 950 °C and 9.4 kbar and using the reaction products corundum, quartz, B₂O₃, and H₂O, based upon the results provided by Ono (1981) for his experiment 57. From these data, we estimate the enthalpy of formation of dumortierite to be -9115 kJ/mol at 298.15 K.

Neither of the estimated values of the enthalpy of formation may be regarded as superior. Therefore, we accept the average of these values, -9109 kJ/mol, and assign an uncertainty of at least ± 20 kJ/mol.

The calorimetric entropy used in third law calculations must be adjusted for appropriate configurational contributions before the free energy of dumortierite can be estimated. Moore and Araki (1978) have concluded that Al and vacancies are disordered in the face-sharing chain [location Al(1)] of the dumortierite structure. Alexander et al. (1986) have verified the vacancy model proposed by Moore and Araki (1978) but have assigned a greater occupancy to the Al(1) site. Alexander et al. (1986) have further noted that all of the dumortierite samples they studied were silica-deficient, requiring Al substitution in the Si sites. Silica deficiency was also noted by Ono (1981) for synthetic dumortierite. Because of the many simplifying assumptions that are necessary to calculate the enthalpy of formation of dumortierite, we have chosen to follow the simplified structural model proposed by Moore and Araki (1978). Using that model, we estimate a configurational entropy of 4.74 J for dumortierite, which must be considered a minimum value. Combining our estimated values for the enthalpy of formation and the entropy corrected for disorder, we estimate -8568 ± 20 kJ/mol for the Gibbs free energy of formation of dumortierite from the elements at 298.15 K and 1 bar.

The Gibbs free energy of dumortierite may also be estimated from thermal decomposition data. Using a deep blue sample from Clip, Arizona, Bowen and Wyckoff (1926) used a combination of X-ray analysis and optical microscopy to study the thermal decomposition of dumortierite. The authors observed a change in color (to

white) after a few seconds of heating at 800 °C. After 4.5 h at 800 °C, the authors noted turbidity and suggested that some decomposition may have occurred. Assuming the initial products of dumortierite decomposition to be corundum, quartz, gaseous B₂O₃, and gaseous H₂O (by analogy with the experimental results of Ono, 1981), we estimate the Gibbs free energy of formation of dumortierite to be greater than (more positive than) or equal to -7090 kJ/mol at 800 °C. This value compares poorly with -7159 ± 20 kJ/mol, calculated at the same temperature from the enthalpy of formation estimated from the data of Ono (1981), the heat-capacity equation for dumortierite reported herein, and ancillary thermodynamic data from Robie et al. (1979). The value calculated for 800 °C from the decomposition data would underestimate the stability of dumortierite if the changes observed by Bowen and Wyckoff (1926) do not represent the onset of decomposition. Bowen and Wyckoff (1926) found stronger evidence suggesting dumortierite decomposition in studies conducted at 950 °C. The Gibbs free energy of dumortierite is estimated to be greater than or equal to -6971 kJ/mol at 950 °C and should overestimate the stability of dumortierite, assuming dumortierite to be unstable at 950 °C with respect to the products listed above. This value compares favorably with -6881 kJ/mol, derived from the data of Ono (1981), for the Gibbs free energy at 950 °C.

The decomposition experiment of Bowen and Wyckoff (1926) provides only an estimate of the maximum stability of dumortierite at 1 bar, because dumortierite was not grown at 1 bar in these experiments. Our estimate that the initiation of the decomposition process occurred at or below 950 °C is based upon the observation of the development of turbidity in dumortierite as seen by optical microscopy (Bowen and Wyckoff, 1926). The color change observed at the same temperature may reflect oxidation of Fe²⁺ to Fe³⁺ and loss of the charge transfer among Fe²⁺, Fe³⁺, and Ti⁴⁺ rather than dumortierite decomposition. Bowen and Wyckoff (1926) studied the decomposition reaction at higher temperatures where the kinetics of the reaction allowed short heating intervals to be employed. Work was not undertaken by Bowen and Wyckoff (1926) to delineate the lowest temperature at which decomposition began.

The synthesis studies of Ono (1981) showed that most experimental products were metastable. In such experiments, reaction rates are important. The appearance of sillimanite as a product phase in some of the reactions indicates that the reaction rate for sillimanite formation was rapid enough for sillimanite to form within the time frame of the experiment. Lack of sillimanite formation, together with formation of dumortierite, does not prove dumortierite stability with respect to sillimanite in those experiments. Such experiments simply show that the formation of dumortierite is faster than the formation of sillimanite. The reactions in which sillimanite forms do limit the stability predicted for dumortierite and provide an estimate of its maximum stability.

TABLE 4. Estimated thermodynamic properties for dumortierite, $\text{Si}_3\text{B}[\text{Al}_{0.75}\square_{0.25}\text{O}_{17.25}(\text{OH})_{0.75}]$ (molar mass = 565.937 g)

T (K)	Heat capacity C_p°	Entropy S_T°	Enthalpy function ($H_T^\circ - H_{298}^\circ$)/T	Gibbs energy function ($G_T^\circ - H_{298}^\circ$)/T	Formation from elements	
					Enthalpy	Gibbs free energy
					(kJ/mol)	
298.15	440.0	334.9	0.000	334.9	-9109.0	-8568.1
300	442.1	337.7	2.720	334.9	-9109.1	-8564.7
400	532.5	478.2	124.68	353.5	-9112.5	-8382.6
500	592.8	603.9	212.66	391.2	-9111.0	-8200.3
600	634.7	715.9	279.70	436.2	-9106.6	-8018.5
700	664.8	816.1	332.68	483.4	-9100.8	-7837.6
800	687.1	906.4	375.66	530.8	-9094.5	-7657.6
900	703.9	988.4	411.23	577.1	-9088.1	-7478.3

1000	716.7	1063	441.17	622.0	-9154.4	-7294.5
1100	726.8	1132	466.70	665.3	-9146.8	-7109.0
1200	734.8	1196	488.72	706.9	-9138.4	-6924.1
1300	741.4	1255	507.91	746.8	-9130.4	-6739.8
1400	747.0	1310	524.79	785.1	-9122.5	-6556.4
1500	751.9	1362	539.77	821.8	-9113.6	-6373.3
1600	756.3	1410	553.17	857.1	-9106.2	-6190.9

1700	760.5	1456	565.24	891.0	-9249.3	-6007.8
1800	764.7	1500	576.21	923.6	-9239.0	-5817.3

Note: A contribution of 4.7 J/(mol·K) has been added to the entropy for disorder in Al/Si. The dashed lines signify transitions in the reference state elements Al and Si.

We recommend the enthalpy and Gibbs free energy of formation derived from the data of Ono (1981). We note, however, that the data available to date are only half reversals and synthesis experiments, and the values recommended here may be subject to significant modification. Our recommended values represent the best values we can estimate at present and are provided with the caveats discussed above. Carefully reversed equilibrium reactions or solution calorimetric measurements are required before the enthalpy and Gibbs free energy of formation can be accurately determined. Smoothed values of the thermodynamic properties of dumortierite are given for the temperature interval 298.15 to 1800 K in Table 4.

CONCLUSIONS

The corrected calorimetric entropy of dumortierite is 330.2 ± 0.6 J/(mol·K) at 298.15 K and 1 bar, based upon the average chemistry of dumortierite as given by Alexander et al. (1986) and corrected to the structural formula given by Moore and Araki (1978). Dumortierite is a complex aluminum oxyborosilicate showing vacancies and cation substitutions that result in a nonzero configurational entropy term. Using the simplified model for the dumortierite structure presented by Moore and Araki (1978), we estimate the minimum configurational entropy to be 4.74 J/(mol·K).

The enthalpy and free energy of formation of dumortierite have been estimated from the synthesis experiments of Ono (1981). These results are based upon a simplified structural model and metastable assemblages; therefore the values must be considered to be a first approximation and must be used with care. Decomposition data provided by Bowen and Wyckoff (1926) support the

selected enthalpy and free energy of formation values calculated from the data of Ono (1981). Carefully reversed equilibrium reactions or solution calorimetric measurements are required to improve these estimates.

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ERRATUM

Mixing properties of Ca-Mg-Fe-Mn garnets by R. G. Berman (v. 75, p. 328–344). Several applications of garnet mixing properties to natural assemblages containing biotite (particularly in Figs. 10 and 13) were reported erroneously to have been made with biotite solution model B of Indares and Martingole (1985). The actual $W_{\text{MgTi}}-W_{\text{FeTi}}$ and $W_{\text{MgAl}}-W_{\text{FeAl}}$ values used are 31.2 and 6.7 kJ per mole (12 O basis), respectively, the same values used by Indares and Martingole to describe nonideal mixing per octahedral site. The error reported here in no way affects the calibration of garnet solution properties as reported in this study.