

## The enthalpy of formation and internally consistent thermodynamic data of Mg-staurolite

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### ABSTRACT

The enthalpies of drop solution in lead borate (2 PbO·B<sub>2</sub>O<sub>3</sub>) of four Mg-staurolite samples, synthesized at 720 °C and pressures between 2 and 5 GPa, were measured by high-temperature oxide-melt calorimetry at 702 °C. Staurolite compositions, determined by electron microprobe analysis, Karl-Fischer titration, and thermogravimetry, are: Mg<sub>3.71</sub>Al<sub>18.17</sub>Si<sub>7.60</sub>O<sub>44.31</sub>(OH)<sub>3.69</sub>, Mg<sub>3.87</sub>Al<sub>17.65</sub>Si<sub>7.75</sub>O<sub>43.68</sub>(OH)<sub>4.32</sub>, Mg<sub>3.66</sub>Al<sub>17.76</sub>Si<sub>7.68</sub>O<sub>43.31</sub>(OH)<sub>4.69</sub>, and Mg<sub>3.58</sub>Al<sub>18.05</sub>Si<sub>7.43</sub>O<sub>43.01</sub>(OH)<sub>4.99</sub>. The enthalpy of drop solution of the bulk samples (as well as the calculated values for the enthalpy of formation from the elements of Mg-staurolite) are strongly correlated to the H content of the samples. The enthalpy of formation from the elements is best described by the linear relation  $\Delta_f H_{298}^0$  (Mg-staurolite) = (-25357.58 + 87.35 *N*) kJ/mol, where *N* = number of H atoms per formula unit in Mg-staurolite. The enthalpy of drop solution of two partially dehydrated Mg-staurolite samples is in a good agreement with the linear relation. Phase-equilibrium data for Mg-staurolite (Fockenberg 1998) were recalculated using the stoichiometric formula Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>. Based on these mineral equilibria and the internally consistent data set of Berman (1988), a mathematical programming analysis of the thermodynamic data of Mg-staurolite gave  $\Delta_f H_{298}^0$  [Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>] = -25005.14 kJ/mol, and  $S_{298}^0$  [Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>] = 937.94 J/(K·mol). Thus, for the first time, reliable thermodynamic data for Mg-staurolite, based on experimental constraints, are provided.

### INTRODUCTION

Staurolite is a characteristic mineral of many medium-grade metapelitic rocks. In these rocks, staurolite is normally rich in Fe<sup>2+</sup> and shows a highly variable H content ranging at least from 2.7 to 4.2 atoms per formula unit (apfu) (Holdaway et al. 1986a, 1986b). According to Hawthorne et al. (1993a), the formula Fe<sub>3-4</sub>Al<sub>18</sub>Si<sub>8</sub>O<sub>48</sub>H<sub>2-4</sub> best describes most examples of naturally occurring Fe-rich staurolite. During the past two decades, staurolite in which substantial Mg replaces the Fe<sup>2+</sup> has been reported in high-pressure metamorphic rocks (e.g., Schreyer et al. 1984; Enami and Zang 1988; Gil Ibarra et al. 1991). Near end-member Mg-staurolite [up to Mg/(Mg + Fe) = 0.965] was described from the Dora-Maira massif in the western Alps (Simon et al. 1997; Simon and Chopin 2001). These staurolite samples, probably with a high H content, formed during ultra-high-pressure metamorphism at *T* ≈ 700 °C and *P* ≈ 3 GPa (Simon et al. 1997; Simon and Chopin 2001).

Parallel to the increasing number of discoveries of Mg-rich staurolite in nature, this high-pressure mineral has been in the focus of experimental research. Following pioneering studies of Schreyer (1968) and Schreyer and Seifert (1969), Fockenberg (1995, 1998) investigated the chemical variability of Mg-staurolite in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O as

a function of water pressure and delineated its *P-T* stability. Mg-staurolite is stable at pressures between 1.2 and 6.6 GPa and temperatures ranging from 608 to 918 °C. Generally, the H content increases with increasing pressure (Holdaway et al. 1995; Fockenberg 1995). A complete solid solution series of Fe- and Mg-bearing staurolite samples was synthesized by Lattard and Bubenik (1995), and the Fe-Mg exchange between staurolite and garnet was experimentally determined by Koch-Müller (1997).

Unfortunately, the interpretation of these experimental results suffers from the lack of reliable thermodynamic data for staurolite (cf., Fockenberg 1998). While significant progress was achieved by Holdaway et al. (1995) in deriving thermodynamic data for theoretical end-member Fe-staurolite with variable H content, for Mg-staurolite only a few estimated values of the enthalpy of formation or its standard entropy can be found in the literature (cf., Table 1). In order to verify these estimates and to improve the thermodynamic database of this high-pressure phase, we have done calorimetric experiments on several synthetic Mg-staurolite samples with variable H content. The results of these experiments serve as constraints for a mathematical programming (MAP) analysis based on the experimentally determined *P-T* stability of Mg-staurolite (Fockenberg 1998) and the internally consistent thermodynamic data set of Berman (1988, revised 1992).

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**TABLE 1.** Estimated thermochemical data of Mg-staurolite from the literature

Reference	Structural formula	$\Delta_f H_{298}^\circ$ (kJ/mol)	$S_{298}^\circ$ J/(K·mol)
Patrick and Chopin (1989)	$Mg_3Al_8Si_6O_{44}(OH)_4$	-25011.69	843.0
Holland and Powell (1990)	$Mg_4Al_{18}Si_{17.5}O_{46}(OH)_4$	-25118.49	890.0
Grevel and Fockenberg (1994)	$Mg_4Al_{18}Si_6O_{46}(OH)_2$	-25215.05	957.8
Massonne (1995)	$Mg_4Al_{18}Si_6O_{46}(OH)_2$	-25299.50	860.0
Massonne (1995)	$Mg_4Al_{18}Si_7O_{42}(OH)_6$	-24832.00	1060.0
Holland and Powell (1998)	$Mg_4Al_{18}Si_{17.5}O_{44}(OH)_4$	-25103.09	910.0

## EXPERIMENTAL TECHNIQUES

### Synthesis and characterization

Mg-staurolite samples were synthesized at 720 °C and pressures between 2 and 5 GPa in a piston-cylinder apparatus. A stoichiometric gel of composition 4 MgO:9 Al<sub>2</sub>O<sub>3</sub>:8 SiO<sub>2</sub> with excess H<sub>2</sub>O was used as starting material. In order to remove traces of hydrocarbons from the gel, it was heated at 700 °C for 24 h before it was placed into Au capsules. The materials used for the preparation of the gel and all other experimental details are identical to those described by Fockenberg (1995) with the exception of the synthesis temperature, which was lowered by 80 °C. These experimental conditions were chosen to see if the chemical variability of synthetic Mg-staurolite obtained at 720 °C and higher pressures is similar to the composition of the samples prepared at 800 °C by Fockenberg (1995) in the same pressure range.

Powder diffraction patterns of all run products were collected using an automated X-ray powder diffractometer (AXS GmbH, D500) with CuK $\alpha$  radiation; silicon (NIST, SRM 640,  $a = 5.43088$  Å) served as an internal standard. Unit-cell dimensions of Mg-staurolite were calculated by least-squares refinement of 27 to 31 reflections indexed in orthorhombic symmetry (Koch-Müller et al. 1998; cf. also Hawthorne et al. 1993b). Molar phase proportions of the samples were derived from Rietveld analysis (Philips X'Pert Plus software).

The water content of all samples was determined by coulometric Karl-Fischer titration (Johannes and Schreyer 1981) with an estimated relative uncertainty of  $\pm 5\%$ . Water contents were also determined by thermogravimetric measurements using a Netzsch STA 449C instrument. The relative uncertainty of the measurements is estimated to be less than 5%. About 10 to 15 mg of bulk sample were heated from room-temperature to 1300 °C at a constant rate of 10 °C/min under a dynamic Ar atmosphere (50 mL/min).

Electron-microprobe analyses (EPMA) were carried out using a CAMECA SX50 electron microprobe and the PAP cor-

rection procedure (Pouchou and Pichoir 1984). Beam current was 10 nA, accelerating voltage 15 kV, and counting time 20 s. Pyrope served as standard for MgK $\alpha$ , AlK $\alpha$ , and SiK $\alpha$  radiation.

### High-temperature oxide-melt solution calorimetry

The enthalpy of dissolution in lead borate (2 PbO·B<sub>2</sub>O<sub>3</sub>) at 702 °C was measured by high-temperature, drop-solution calorimetry using a Tian-Calvet type twin microcalorimeter (Navrotsky 1977, 1997). In order to purge the volatiles expelled from the solvent quantitatively, all experiments were done under a flowing Ar atmosphere (90 mL/min) (Navrotsky et al. 1994). Corundum,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, used for the calibration (Alfa Aesar, no. 38368, 99.997%), was heated at 1500 °C overnight to ensure complete conversion to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, to improve crystallinity, and to remove any traces of moisture.

## RESULTS

### Samples

Four different Mg-staurolite samples (K8, K6, K3, K14), which were pure white, were synthesized for calorimetric purposes (Table 2). Mean values of the unit-cell parameters  $a$  (16.543 Å),  $b$  (7.881 Å), and  $c$  (5.639 Å) of these samples prepared at 720 °C are, within uncertainties, identical to the values reported by Fockenberg (1995; synthesis temperature: 800 °C). No correlation between lattice parameters and either run pressure or chemical composition could be detected; a similar result was obtained by Fockenberg (1995).

The water content of all bulk samples as determined by Karl-Fischer titration and thermogravimetric analysis is listed in Table 3. The weight loss/differential thermal analysis (DTA) traces of all samples appear very similar (Fig. 1). Dehydration starts at about 400 °C and ends between 900 and 1000 °C. Therefore, the total weight loss and the weight difference between 400 and 1000 °C are separated in Table 3. The water content determined by both methods agrees well, except for sample K8, where the thermogravimetric weight loss is about 10% smaller than the water content determined by Karl-Fischer titration.

About 10 grains of each Mg-staurolite sample (grain size  $\approx 10$   $\mu$ m) were analyzed with the EMP to obtain an average chemical composition (Table 3). In samples K8 and K14, corundum and clinocllore, Mg<sub>5</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>8</sub>, are additional minor constituents, K6 contains only corundum as an impurity, and K3 contains a significant amount of yoderite, ideally Mg<sub>2</sub>Al<sub>6</sub>Si<sub>4</sub>O<sub>18</sub>(OH)<sub>2</sub>. Fockenberg and Schreyer (1991) were able

**TABLE 2.** Synthesis conditions and volumetric properties of the Mg-staurolite samples used for the calorimetric experiments

Sample no.	Synthesis conditions			Lattice parameters			
	$T$ (°C)	$P$ (GPa)	$t$ (h)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
K8	720	2.0	124	16.541 $\pm$ 0.002	7.879 $\pm$ 0.001	5.637 $\pm$ 0.001	734.6 $\pm$ 0.1
K6	720	3.0	100	16.544 $\pm$ 0.001	7.882 $\pm$ 0.001	5.642 $\pm$ 0.001	735.7 $\pm$ 0.1
K3	720	4.0	174	16.543 $\pm$ 0.005	7.885 $\pm$ 0.002	5.636 $\pm$ 0.002	735.1 $\pm$ 0.3
K14	720	5.0	233	16.542 $\pm$ 0.002	7.879 $\pm$ 0.001	5.640 $\pm$ 0.001	735.0 $\pm$ 0.1
K5	720	5.0	95	16.545 $\pm$ 0.002	7.879 $\pm$ 0.001	5.641 $\pm$ 0.001	735.3 $\pm$ 0.1
K5 (dehyd.)*	720	5.0	95	16.576 $\pm$ 0.004	7.885 $\pm$ 0.002	5.631 $\pm$ 0.001	736.0 $\pm$ 0.2
A42†	750	4.0	45	16.576 $\pm$ 0.004	7.884 $\pm$ 0.002	5.627 $\pm$ 0.001	735.4 $\pm$ 0.3

\* Dehydrated at 650 °C, 12 h.

† Dehydrated at 700 °C, 12 h.

**TABLE 3.** Determination of water content and results of EPM analyses

Sample no.	No. of EPMA	Composition* (wt%)	Formula† (O = 48)	Water content (wt%)	Impurities	
K8	6	Al <sub>2</sub> O <sub>3</sub>	58.56 ± 0.59	Al	17.76 ± 0.12	2.73 (KF) 2.37 (TG) 2.51 (TG 400) traces of corundum and clinochlore
		SiO <sub>2</sub>	29.83 ± 0.41	Si	7.68 ± 0.09	
		MgO	9.53 ± 0.22	Mg	3.66 ± 0.08	
		H <sub>2</sub> O	2.73	H	4.69	
		Sum	100.65			
K6	11	SiO <sub>2</sub>	57.57 ± 0.89	Al	17.65 ± 0.15	2.49 (KF) 2.41 (TG) 2.26 (TG 400) corundum, 4.1 wt% = 40 mol%
		Al <sub>2</sub> O <sub>3</sub>	29.81 ± 0.40	Si	7.75 ± 0.10	
		MgO	9.97 ± 0.21	Mg	3.87 ± 0.08	
		H <sub>2</sub> O	2.49	H	4.32	
		Sum	99.84			
K3	10	Al <sub>2</sub> O <sub>3</sub>	59.27 ± 0.53	Al	18.17 ± 0.10	2.13 (KF) 2.44 (TG) 2.11 (TG 400) yoderite (Mg <sub>2</sub> Al <sub>6</sub> Si <sub>4</sub> O <sub>18</sub> (OH) <sub>2</sub> ) 10.2 wt% = 22 mol%
		SiO <sub>2</sub>	29.21 ± 0.34	Si	7.60 ± 0.07	
		MgO	9.58 ± 0.19	Mg	3.71 ± 0.07	
		H <sub>2</sub> O	2.13	H	3.69	
		Sum	100.19			
K14	22	Al <sub>2</sub> O <sub>3</sub>	59.02 ± 0.63	Al	18.05 ± 0.15	2.88 (KF) 2.77 (TG) 2.61 (TG 400) corundum, 1.5 wt% = 19 mol% clinochlore, 0.7 wt% = 2 mol%
		SiO <sub>2</sub>	28.62 ± 0.60	Si	7.43 ± 0.12	
		MgO	9.27 ± 0.15	Mg	3.58 ± 0.06	
		H <sub>2</sub> O	2.88	H	4.99	
		Sum	99.79			
K5	7	Al <sub>2</sub> O <sub>3</sub>	56.64 ± 0.72	Al	17.43 ± 0.12	2.76 (KF) n.d. (TG) n.d. (TG 400) corundum, 0.7 wt% = 10 mol% clinochlore, 0.4 wt% = 1 mol% unidentified Si-Al-Mg-Na-Ca phase
		SiO <sub>2</sub>	29.99 ± 0.30	Si	7.83 ± 0.08	
		MgO	9.70 ± 0.21	Mg	3.78 ± 0.08	
		H <sub>2</sub> O	2.76	H	4.81	
		Sum	99.09			
K5 (dehyd.)	7	Al <sub>2</sub> O <sub>3</sub>	56.64 ± 0.72	Al	17.86 ± 0.12	n.d. (KF) 1.44 (TG) 1.11 (TG 400) corundum, 0.7 wt% = 10 mol% unidentified dehydration products of clinochlore unidenti- fied Si-Al-Mg-Na-Ca phase
		SiO <sub>2</sub>	29.99 ± 0.30	Si	8.03 ± 0.08	
		MgO	9.70 ± 0.21	Mg	3.87 ± 0.08	
		H <sub>2</sub> O	1.44	H	2.57	
		Sum	97.77			
A42	17	Al <sub>2</sub> O <sub>3</sub>	56.65 ± 0.76	Al	18.48 ± 0.16	0.12 (KF) n.d. (TG) n.d. (TG 400) corundum, 1.6 wt% = 20 mol% traces of pyrope
		SiO <sub>2</sub>	29.36 ± 0.58	Si	8.13 ± 0.12	
		MgO	9.50 ± 0.16	Mg	3.92 ± 0.07	
		H <sub>2</sub> O	0.12	H	0.22	
		Sum	95.63			

Notes: The first value given for the water content was obtained by Karl-Fischer titration (KF), the other two values describe the weight loss in a thermogravimetric experiment in total (TG) and after heating to 400 °C (TG 400) respectively (cf. Fig. 1). (n.d. = not determined.)

\* Errors are one standard deviation.

† Errors propagated from the errors in composition.

to synthesize yoderite only in the presence of Fe<sub>2</sub>O<sub>3</sub> and concluded, therefore, that Fe-free yoderite does not exist. The upper pressure stability of Fe-bearing yoderite of idealized stoichiometry Mg<sub>2</sub>Al<sub>5.6</sub>Fe<sub>0.4</sub>Si<sub>4</sub>O<sub>18</sub>(OH)<sub>2</sub> was obtained experimentally by Fockenberg and Schreyer (1994) at 2.5 GPa. Therefore, it might be possible that yoderite in sample K3, synthesized at 4 GPa, has grown metastably, and at least traces of Fe in the MgO (FLUKA, Switzerland, >99.8%) used for preparing the gel, which was used as starting material for our syntheses, were present (cf., Fockenberg 1995), promoting the formation of yoderite.

The structural formulae of Mg-staurolite were calculated from the mean values of the EMP analyses and the respective water content obtained by Karl-Fischer titration (cf., Table 3) on the basis of 48 O atoms. The substitution mechanisms in Mg-staurolite in relation to pressure suggested by Fockenberg (1995) cannot be confirmed by the experiments in this study. The analyses show relatively large scatter, and sample K3 seems to be an outlier possibly due to the presence of yoderite. In

comparison to Mg-staurolites synthesized at 800 °C (Fockenberg 1995), the H content in all other samples obtained in our study is greater than 4 apfu, suggesting an increase of H content with increasing pressure and decreasing temperature, a tendency already expected for naturally occurring staurolite by Holdaway et al. (1995). As in the study of Fockenberg (1995), the Mg content increases with pressure up to 3 GPa and then decreases with pressure thereafter. In contrast to Fockenberg (1995), the Si content is always below 8 apfu. Aluminum shows no correlation with pressure.

Two samples, K5 and A42, were used for comparison purposes (Tables 2 and 3). Run-product K5 contained an unidentified impurity consisting of about 78 wt% SiO<sub>2</sub>, 4 wt% Al<sub>2</sub>O<sub>3</sub>, and approximately 1 wt% MgO. Additionally, Na and Ca were detected in this phase using the energy dispersive system of the electron microprobe. This impurity suggests leakage in the capsule during synthesis, and was the reason why sample K5 was used only for comparison purposes. Sample A42 remained from earlier research on Mg-staurolite (Fockenberg 1995,

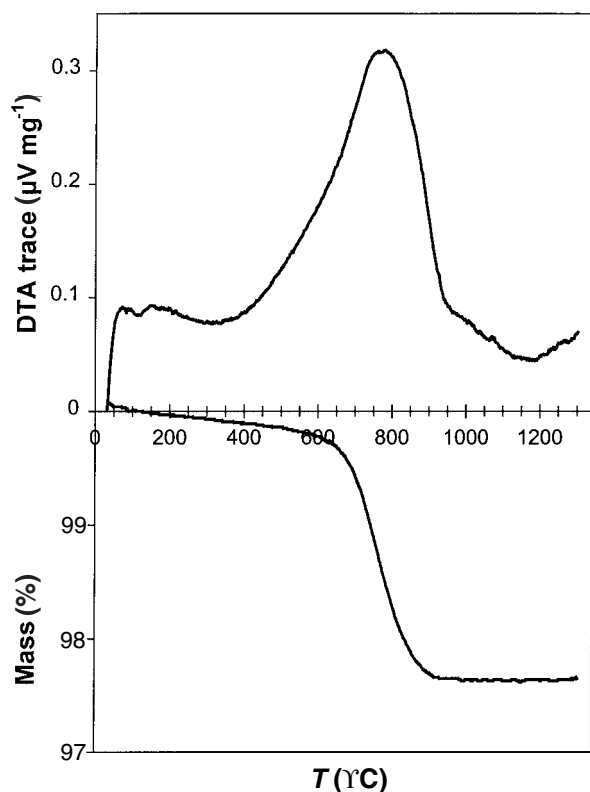


FIGURE 1. Weight loss (bottom) and DTA trace (top) of Mg-staurolite sample K6. Dehydration starts at about 400 °C and ends between 900 and 1000 °C. DTA maximum is at 762 °C.

1998). Both samples were tempered overnight in a furnace at 650 and 700 °C, respectively. Due to this heat treatment sample K5 lost about 50% of its water, and sample A42 was almost dehydrated. Nevertheless, after the heat treatment, no additional phase was observed in the X-ray diffraction patterns of both samples (detection limit  $\approx$  2 wt%) and the lattice parameters of the dehydrated Mg-staurolites are not significantly different from other samples.<sup>1</sup>

### Enthalpy of formation

The calibration and drop-solution experiments on corundum and Mg-staurolite samples K8, K6, K3, and K14, were done using pellets weighing 4.8 to 5.2 mg. Sample K5 and the dehydrated samples K5 (dehyd.) and A42 were later measured in order to check the previous results. The reaction curves for all experiments showed a good return to the baseline indicating proper equipment performance and reproducible sample

dissolution. Results are listed in Table 4. The amounts of impurities found in each sample and the electron microprobe analyses (Table 3) were used to determine the molecular weight of the bulk samples (Table 4).

To calculate the enthalpy of formation of the bulk Mg-staurolite sample (including the impurities) from the constituent solids plus water ( $\Delta_f H^{\text{cycle}}$ ) by means of a thermodynamic cycle, the heats of drop solution of its component oxides, corundum, and quartz, need to be known. Brucite,  $\text{Mg}(\text{OH})_2$ , rather than  $\text{MgO}$ , was used as the Mg reference material because the handling of  $\text{MgO}$  in calorimetric experiments is more difficult due to its hygroscopic behavior. The heats of drop solution of corundum, quartz, and brucite were obtained by Grevel et al. (2001). They are given in Table 4 as well. In addition, the impurities in the different samples had to be taken into account to calculate the enthalpy of formation of pure Mg-staurolite. The thermodynamic cycle listed in Table 5 (as an example) was used to calculate the enthalpy of sample K6; the cycles used for the other samples are similar (for the molar composition of the samples, see Table 3).

The resulting enthalpies of formation from the constituent solids plus water ( $\Delta_f H^{\text{cycle}}$ ) of the different Mg-staurolite samples are listed in Table 6. The values range from  $-46.9 \pm 18.1$  kJ/mol, obtained for the most H-rich sample K14, to  $+36.2 \pm 8.0$  kJ/mol (sample A42, almost dehydrated). The calculations of the enthalpy of formation from the oxides ( $\Delta_f H^{\text{oxides}}$ ) and from the elements ( $\Delta_f H_{298}^0$ ) of Mg-staurolite were based separately on the thermodynamic databases of Robie and Hemingway (1995), Berman (1988), and Holland and Powell (1998) (Table 6). Therefore, the values of enthalpies of formation from the elements of brucite, corundum, quartz, water, periclase, and clinocllore were taken from the respective databases as well. The value for  $\Delta_f H_{298}^0(\text{yoderite}) = -10277.5$  kJ/mol (Fockenberg and Schreyer 1994) was used to correct the values obtained for K3. The  $\Delta H_f$  values for each sample vary only slightly with the choice of the thermodynamic database (cf., Table 6). On the other hand, there is a strong correlation between the H content of the respective samples and its energetic behavior. A linear fit to the  $\Delta_f H_{298}^0(\text{Mg-staurolite})$  values as a function of the number of H apfu obtained for samples K8, K6, K3, and K14 gave:

$$\Delta_f H_{298}^0(\text{Mg-staurolite}) = (-25357.58 + 87.35 N) \text{ kJ/mol (1)}$$

where  $N$  = number of H apfu in Mg-staurolite (Fig. 2).

The linear relation between  $\Delta_f H_{298}^0(\text{Mg-staurolite})$  and the H content is supported by the results obtained for sample K5, and the dehydrated samples K5 (dehyd.) and A42 (Fig. 2). Additionally, estimated enthalpy values from the literature (cf., Table 1) are shown in Figure 2. The values of Massonne (1995) for the stoichiometric end-member  $\text{Mg}_4\text{Al}_{18}\text{Si}_8\text{O}_{46}(\text{OH})_2$  and Holland and Powell (1998), who used the formula  $\text{Mg}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{44}(\text{OH})_4$ , are significantly larger (in absolute terms) than the values obtained from Equation 1. The values reported by Grevel and Fockenberg (1994) for  $\text{Mg}_4\text{Al}_{18}\text{Si}_8\text{O}_{46}(\text{OH})_2$ , Patrick and Chopin (1989, pers. communication) based on the formula  $\text{Mg}_3\text{Al}_{18}\text{Si}_8\text{O}_{44}(\text{OH})_4$ , and Massonne (1995) for the H-rich formula  $\text{Mg}_4\text{Al}_{18}\text{Si}_7\text{O}_{42}(\text{OH})_6$  are in good agreement with our experimental results.

<sup>1</sup>The remains of the thermogravimetric analyses (max. temperature: 1300 °C) were investigated by XRD methods (Reinecke, personal communication). The XRD patterns still showed a significant amount of Mg-staurolite besides sapphirine. Additionally, some spinel could be detected.

**TABLE 4.** Results of drop-solution calorimetry ( $\Delta H_{ds}$ ); the calorimeter temperature used for the calculations was  $702 \pm 0.2$  °C

Sample	No. of measurements	$\Delta H_{ds}$ (J/g)*	Molecular weight of the bulk sample (g/mol)	$\Delta H_{ds}$ (kJ/mol)*	$\Delta H_{ds}$ (kJ/mol)* Values from the literature
K8	9	1116.5 ± 14.0	1556.46	1737.8 ± 21.8†	
K6	7	1116.9 ± 8.3	983.47	1098.4 ± 8.1	
K3	7	1085.2 ± 10.1	1366.43	1482.9 ± 13.8	
K14	7	1136.2 ± 12.0	1268.40	1441.2 ± 15.2	
K5	5	1117.9 ± 20.6	1404.78	1570.4 ± 28.9	
K5 (dehyd.)	4	1041.0 ± 13.0	1427.86	1486.5 ± 18.6	
A42	6	989.6 ± 22.2	1289.17	1275.7 ± 28.6	
Corundum, Al <sub>2</sub> O <sub>3</sub>	12	1055.5 ± 12.3	101.961	107.6 ± 1.39‡	107.9 ± 1.0§
Quartz, SiO <sub>2</sub>	14	655.9 ± 6.2	60.084	39.4 ± 0.4‡	39.1 ± 0.3§
Brucite, Mg(OH) <sub>2</sub>	32	2474.7 ± 12.1	58.319	144.3 ± 0.7‡	144.1 ± 3.6
Water, H <sub>2</sub> O			18.0152		69.0#

\* Reported uncertainties are two standard deviations of the mean.

† Impurities not taken into account for calculations.

‡ Measurements initially reported by Grevel et al. (2001).

§ Kiseleva et al. (1996).

|| Navrotsky et al. (1994).

# Calculated from Robie and Hemingway (1995).

**TABLE 5.** Thermodynamic cycle used to calculate the enthalpy of formation from the constituent solids plus water of Mg-staurolite sample K6 ( $\Delta_f H^{cycle}$ )\*

Reaction	Enthalpy of Reaction
$X_{MgSt} Mg_{a_1} Al_{b_1} Si_{c_1} H_{d_1} O_{48 cr, 298} + X_{Cr} Al_2 O_{3 cr, 298}$	$\rightarrow [X_{MgSt} a_1] MgO_{soln, 973} + [X_{MgSt} b_1 + 2 X_{Cr}]/2 Al_2 O_{3 soln, 973}$ $+ [X_{MgSt} c_1] SiO_{2 soln, 973} + [X_{MgSt} d_1]/2 H_2 O_{g, 973}$
$[X_{MgSt} a_1] Mg(OH)_{2 cr, 298}$	$\rightarrow [X_{MgSt} a_1] [MgO_{soln, 973} + H_2 O_{g, 973}]$
$[X_{MgSt} b_1 + 2 X_{Cr}]/2 Al_2 O_{3 cr, 298}$	$\rightarrow [X_{MgSt} b_1 + 2 X_{Cr}]/2 Al_2 O_{3 soln, 973}$
$[X_{MgSt} c_1] SiO_{2 cr, 298}$	$\rightarrow [X_{MgSt} c_1] SiO_{2 soln, 973}$
$\{[X_{MgSt} d_1]/2 - [X_{MgSt} a_1]\} H_2 O_{g, 973}$	$\rightarrow \{[X_{MgSt} d_1]/2 - [X_{MgSt} a_1]\} H_2 O_{l, 298}$
$[X_{MgSt} a_1] Mg(OH)_{2 cr, 298} + [X_{MgSt} b_1 + 2 X_{Cr}]/2 Al_2 O_{3 cr, 298} + [X_{MgSt} c_1] SiO_{2 cr, 298} + \{[X_{MgSt} d_1]/2 - [X_{MgSt} a_1]\} H_2 O_{l, 298}$	$\rightarrow X_{MgSt} Mg_{a_1} Al_{b_1} Si_{c_1} H_{d_1} O_{48 cr, 298} + X_{Cr} Al_2 O_{3 cr, 298}$
	$-\Delta H_{ds}$ (Mg-staurolite sample) $+ [X_{MgSt} a_1] \Delta H_{ds}$ (brucite) $+ [X_{MgSt} b_1 + 2 X_{Cr}]/2 \Delta H_{ds}$ (corundum) $+ [X_{MgSt} c_1] \Delta H_{ds}$ (quartz) $\{[X_{MgSt} d_1]/2 - [X_{MgSt} a_1]\} \Delta H$ (water)
	$-\Delta H_{ds}$ (Mg-staurolite sample) $+ [X_{MgSt} a_1] \Delta H_{ds}$ (brucite) $+ [X_{MgSt} b_1 + 2 X_{Cr}]/2 \Delta H_{ds}$ (corundum) $+ [X_{MgSt} c_1] \Delta H_{ds}$ (quartz) + $\{[X_{MgSt} d_1]/2 - [X_{MgSt} a_1]\} \Delta H$ (water) = $\Delta_f H^{cycle}$ (Mg-staurolite sample)

Notes:  $\Delta_f H^{Oxides}$  (Mg-staurolite) =  $\{ \Delta_f H^{cycle}$  (Mg-staurolite sample) +  $[X_{MgSt} a_1] \Delta_f H^{Oxides}$  (brucite)  $\} / X_{MgSt}$ . $\Delta_f H^{Oxides}$  (brucite) =  $\Delta_f H^{0_{298}}$  (brucite) -  $[\Delta_f H^{0_{298}}$  (periclase) +  $\Delta_f H^{0_{298}}$  (water)].\*  $X_{MgSt}$  and  $X_{Cr}$  are the molar fractions taken from Table 3, the atomic proportions  $a_1 - d_1$  of Mg-staurolite are listed in Table 3.**TABLE 6.** Enthalpies of formation of Mg-staurolite; three different sets of calculations were done based on three different thermodynamic databases\*: RH '95 (Robie and Hemingway 1995), B '88 (Berman 1988), HP '98 (Holland and Powell 1998); see text for further details

Sample no.	$\Delta_f H^{cycle}$ (kJ/mol)	$\Delta_f H^{Ox}$ (kJ/mol)			$\Delta_f H^{0_{298}}$ (kJ/mol)		
		RH '95	B '88	HP '98	RH '95	B '88	HP '98
K8	-42.3 ± 24.8	-178.0 ± 24.9	-183.5	-179.4 ± 24.8	-24922.2 ± 28.4	-24927.4	-24920.8 ± 26.0
K6	-31.0 ± 11.1	-194.8 ± 18.5	-200.6	-196.3 ± 18.5	-24982.7 ± 23.5	-24988.2	-24981.4 ± 20.3
K3	-11.6 ± 17.3	-140.4 ± 22.2	-146.8	-141.9 ± 22.1	-25039.5 ± 27.0	-25045.6	-25038.0 ± 23.7
K14	-46.9 ± 18.1	-188.3 ± 22.8	-194.0	-189.5 ± 22.7	-24941.0 ± 26.8	-24946.4	-24939.2 ± 24.1
K5	-34.7 ± 30.8	-177.0 ± 34.5	-182.9	-178.4 ± 34.5	-24877.8 ± 37.2	-24883.3	-24876.4 ± 35.3
K5 (dehyd.)	19.1 ± 21.5	-122.4 ± 24.0	-128.2	-123.9 ± 23.9	-25092.6 ± 27.8	-25098.1	-25091.2 ± 25.2
A42	36.2 ± 30.4	-100.0 ± 38.1	-105.9	-101.5 ± 38.1	-25372.2 ± 40.9	-25377.7	-25370.6 ± 39.0

\* The uncertainties were propagated from the values given by the different authors; no error was attributed to the heat content of H<sub>2</sub>O (cf., Table 4).

## MATHEMATICAL PROGRAMMING ANALYSIS

### Mg-staurolite stoichiometry

The  $P$ - $T$  stability of Mg-staurolite was delineated by experimental determination of reversal brackets for six mineral reactions (Fockenberg 1998). The stoichiometry of these reactions was based on the ideal Mg-staurolite end-member  $Mg_4Al_{18}Si_8O_{46}(OH)_2$ . However, the H content of naturally occurring staurolite and synthetic Mg-staurolite seems to be greater than 2 apfu (Holdaway et al. 1986a, 1986b; Simon et al. 1997; Simon and Chopin 2001; Fockenberg 1995). Most samples synthesized for this study contain between 4 and 5 H apfu. Therefore, even simple thermodynamic calculations on Mg-staurolite should be based on a formula with larger H con-

tent. Patrick and Chopin (1989; personal communication) suggested the formula  $Mg_3Al_{18}Si_8O_{44}(OH)_4$ , whereas Holland and Powell (1990, 1998) did thermodynamic calculations based on the Si-depleted formula  $Mg_4Al_{18}Si_{7.5}O_{44}(OH)_4$ . It must be noted that these substitutions by no means indicate that H is substituted for Mg in octahedral coordination or for Si in tetrahedral coordination, respectively—these Mg-staurolite formulae are only the simplified results of complicated substitution mechanisms involving vacancy ( $\square$ )—cation substitutions at several sites in the staurolite structure (Hawthorne et al. 1993c). Taking these complexities into account on the one hand, but to allow thermodynamic calculations based on a “relatively simple” stoichiometry on the other hand, we suggest a stoichiometrically balanced combination of the substitutions  $\square \leftrightarrow H$ ,

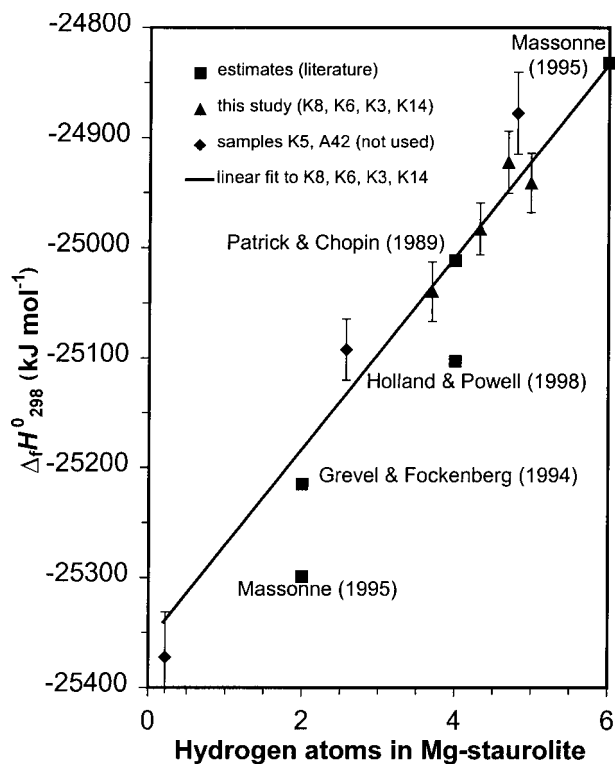


FIGURE 2. Enthalpy of formation from the elements (based on Robie and Hemingway, 1995; cf. Table 4) vs. H content of Mg-staurolite. The line denotes a linear fit to experimentally determined enthalpy values for K8, K6, K3, and K14.

$\text{Mg} + 2 \square \leftrightarrow \square + 2 \text{Mg}$ ,  $\text{Al} \leftrightarrow \text{Si}$ , and  $\text{Mg} \leftrightarrow \text{Al}$  (after Hawthorne et al. 1993c) in Mg-staurolite, resulting in the formula  $\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4$ . This simple stoichiometry is supported by all Mg-staurolite analyses obtained in this study (cf., Table 3).

### Optimization procedure

To check the consistency of Fockenberg's (1998) reversal brackets reported for Equilibria 2 to 7 (Table 7) with the enthalpy of formation of Mg-staurolite obtained in this study, we did a MAP analysis using an optimization technique similar to that described by Berman et al. (1986). The values of

$\Delta_f H_{298}^0[\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4] = -25008.2 \pm 30.0 \text{ kJ/mol}$  (Eq. 1), and  $S_{298}^0[\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4] = 957.83 \pm 50.00 \text{ J/(K}\cdot\text{mol)}$  (Grevel and Fockenberg 1994) served as initial constraints for the MAP analysis. Following Berman (1988), the  $P$ - $V$ - $T$  behavior of Mg-staurolite is described by the equation:

$$V(P,T) = V_{298}^0 \times [1 + a(T - T^0) + b(P - 1)], \quad (8)$$

where  $T^0 = 298.15 \text{ K}$ ,  $V_{298}^0 = 442.6 \text{ cm}^3/\text{mol}$ , and the parameters  $a$  and  $b$  were calculated from Grevel et al. (1997, 1998). The parameters  $\Delta_f H_{298}^0$ ,  $S_{298}^0$ ,  $a$ , and  $b$  were treated as variables during the MAP analysis. The coefficients of the  $C_p$  equation

$$C_p[\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4] = (2495.159 - 14616.11 \times T^{-0.5} - 66734070.0 \times T^{-2} + 9155096750.0 \times T^{-3}) \text{ J/(K}\cdot\text{mol)} \quad (T \text{ in K}) \quad (9)$$

were calculated according to Berman and Brown (1985) and kept constant for all calculations. Because the Berman (1988) data set does not contain thermodynamic properties for Mg-chloritoid, the database was augmented by the values listed in Table 8. To calculate the properties of water, the equation of state (EOS) proposed by Grevel and Chatterjee (1992) was used. Calculations of mineral equilibria based on this EOS are very similar to the Berman (1988) formalism at pressures <5 GPa (Theye et al. 1997). At higher pressures, the calculated temperature of equilibrium is approximately 30–40 °C lower if the EOS of Grevel and Chatterjee (1992) is used, well within the experimental uncertainties in this pressure-temperature range. Prior to calculating the phase-equilibrium constraints (Eqs. 2–7, Table 7, Fockenberg 1998), the  $P$ - $T$  coordinates of each half-bracket were adjusted away from the estimated position of equilibrium by an amount equal to the experimental uncertainties in pressure and temperature. For the mathematical proce-

TABLE 8. Thermodynamic data for Mg-staurolite and Mg-chloritoid\*

Phase	$\Delta_f H_{298}^0$ (kJ/mol)	$S_{298}^0$ [J/(K·mol)]	$V_{298}^0$ (cm <sup>3</sup> /mol)	$a \times 10^5$ (1/K)	$b \times 10^5$ (1/bar)
Mg-St	-25005.14	937.94	442.60†	2.014	-0.06029
Mg-Cld	-3557.53§	131.00§	68.75†‡	2.996	-0.07165‡

\* Notation after Berman (1988); heat capacity equations for Mg-staurolite and Mg-chloritoid derived after Berman and Brown (1985).  
† Holland and Powell (1998).  
‡ Grevel et al. (1997).  
§ modified after Holland and Powell (1998).  
|| Ivaldi et al. (1988).

TABLE 7. Recalculated stoichiometry of mineral equilibria (Fockenberg 1998) based on the Mg-staurolite formula  $\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4$ , phase abbreviations after Kretz (1983)

Reaction	Eq. no.
20 Mg-staurolite (Mg-St) + 16 H <sub>2</sub> O = 14 clinocllore (Chl) + 113 kyanite (Ky) + 53 corundum (Crn)	(2)
20 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> + 16 H <sub>2</sub> O = 14 Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub> + 113 Al <sub>2</sub> SiO <sub>5</sub> + 53 Al <sub>2</sub> O <sub>3</sub>	(2)
12 Mg-staurolite (Mg-St) = 14 talc (Tlc) + 37 kyanite (Ky) + 71 corundum (Crn) + 10 H <sub>2</sub> O	(3)
12 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> = 14 Mg <sub>5</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub> + 37 Al <sub>2</sub> SiO <sub>5</sub> + 71 Al <sub>2</sub> O <sub>3</sub> + 10 H <sub>2</sub> O	(3)
4 Mg-staurolite (Mg-St) = 14 enstatite (En) + 17 kyanite (Ky) + 19 corundum (Crn) + 8 H <sub>2</sub> O	(4)
4 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> = 14 MgSiO <sub>3</sub> + 17 Al <sub>2</sub> SiO <sub>5</sub> + 19 Al <sub>2</sub> O <sub>3</sub> + 8 H <sub>2</sub> O	(4)
12 Mg-staurolite (Mg-St) = 14 pyrope (Prp) + 51 kyanite (Ky) + 43 corundum (Crn) + 24 H <sub>2</sub> O	(5)
12 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> = 14 Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> + 51 Al <sub>2</sub> SiO <sub>5</sub> + 43 Al <sub>2</sub> O <sub>3</sub> + 24 H <sub>2</sub> O	(5)
4 Mg-staurolite (Mg-St) + 11 H <sub>2</sub> O = 14 Mg-chloritoid (Mg-Cld) + 17 kyanite (Ky) + 10 diaspro (Dsp)	(6)
4 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> + 11 H <sub>2</sub> O = 14 MgAl <sub>2</sub> SiO <sub>5</sub> (OH) <sub>2</sub> + 17 Al <sub>2</sub> SiO <sub>5</sub> + 10 AlO(OH)	(6)
4 Mg-staurolite (Mg-St) + 6 H <sub>2</sub> O = 14 Mg-chloritoid (Mg-Cld) + 17 kyanite (Ky) + 5 corundum (Crn)	(7)
4 Mg <sub>3.5</sub> Al <sub>18</sub> Si <sub>7.75</sub> O <sub>44</sub> (OH) <sub>4</sub> + 6 H <sub>2</sub> O = 14 MgAl <sub>2</sub> SiO <sub>5</sub> (OH) <sub>2</sub> + 17 Al <sub>2</sub> SiO <sub>5</sub> + 5 Al <sub>2</sub> O <sub>3</sub>	(7)

ture, FORTRAN routines of the NAG FORTRAN library (Numerical Algorithms Group Ltd., Oxford) were applied.

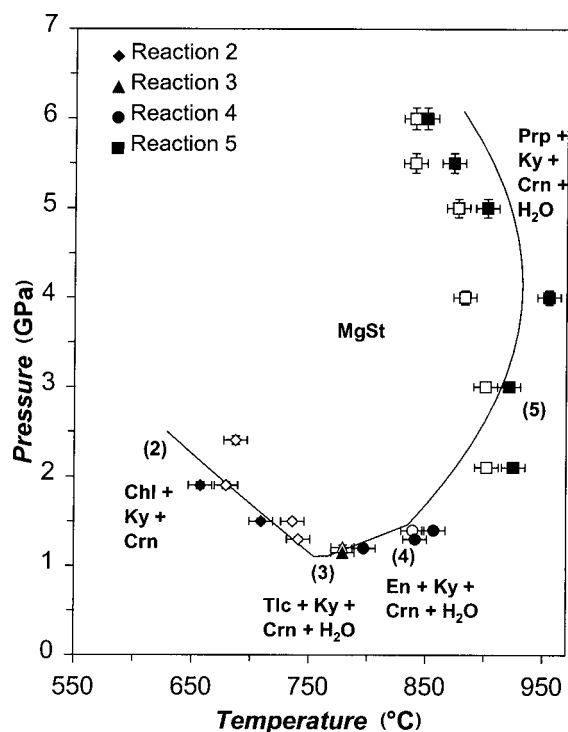
### Results of the MAP analysis

The refined enthalpy of formation of Mg-staurolite,  $\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4$ ,  $-25005.14$  kJ/mol, is very close to the experimentally determined value ( $-25008.2$  kJ/mol, Eq. 1). The resulting standard entropy,  $S_{298}^0$  [ $\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4$ ] is  $937.94$  J/(K·mol), well within the range of proposed values (cf., Table 1). The changes of the parameters  $a$  and  $b$  (Eq. 8) are almost negligible.

The calculated Equilibria 2–5 are compared to experimental reversals for these equilibria (Fockenberg 1998) in Figure 3. For the calculations, the Berman (1988) data were used, augmented by all data listed in Table 8. The Berman (1988) data, including the Mg-staurolite data, are consistent with most reversals of Fockenberg (1998). Only some reversals for Equation 5 are not compatible with the calculations, reflecting some deviations in the EOS for water.

Equilibria 6 and 7 are not included in Figure 3, because their position in  $P$ - $T$  space is strongly correlated with the stability field of diaspore.

2 diaspore (Dsp) = corundum (Crn) +  $\text{H}_2\text{O}$ , (Fockenberg et al. 1996) (10)



**FIGURE 3.** Pressure-temperature diagram showing Mg-staurolite reactions 2–5 (cf., Table 7) as calculated with the Berman (1988) data set augmented by the data listed in Table 8 (solid line). Experimental reversals of Fockenberg (1998) = open symbols Mg-staurolite growth; filled symbols Mg-staurolite breakdown. Error bars are  $\pm 2\%$  in pressure and temperature. Phase abbreviations after Kretz (1983)

Compared to the calculated position of Equation 10 using the Berman (1988) data set, the experimentally determined position of reaction 10 is shifted toward lower temperature. At 2.5 GPa, the experimental curve is about  $20$  °C lower than the calculated curve; at 5 GPa this difference is greater than  $100$  °C.

### CONCLUDING REMARKS

Based on the formula  $\text{Mg}_{3.5}\text{Al}_{18}\text{Si}_{7.75}\text{O}_{44}(\text{OH})_4$  with four H apfu, it is possible to obtain reliable thermodynamic data for Mg-staurolite. These data are compatible with the experimentally determined  $P$ - $T$ -stability field (Fockenberg 1998) and with the internally consistent thermodynamic database of Berman (1988). Consequently, the first thermobarometric estimates for high-pressure metamorphic rocks containing Mg-staurolite are now possible. If detailed information on the H content of naturally occurring Mg-rich staurolite is available, Equation 1 can be used to introduce appropriate activity models into the thermodynamic calculations. In order to calculate Equilibria 6, 7, and 10 consistently with all experimental data, a much more detailed MAP analysis of the Berman (1988) database including a refinement of the diaspore data is needed.

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