

A calorimetric study of synthetic amphiboles along the tremolite-tschermakite join and the heats of formation of magnesiohornblende and tschermakite

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ABSTRACT

A suite of synthetic calcic amphiboles in the tremolite-tschermakite (Tr-Ts) series has been studied by high-temperature drop-solution calorimetry in molten $2\text{PbO} \cdot \text{B}_2\text{O}_3$. The pseudobinary join, which is shifted toward magnesiocummingtonite (Mc) by 10 mol%, extends from tremolite (Tr), $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2$, to magnesiohornblende (MgHb), $\text{Ca}_{1.8}\text{Mg}_{4.2}\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$, and represents the operation of one full Mg-Tschermak substitution, $^{[6]}\text{Mg},^{[4]}\text{Si} = ^{[6]}\text{Al},^{[4]}\text{Al}$, into the tremolite formula. Transmission electron microscope (TEM) examination of the amphiboles shows that all the samples contain a low concentration of (010) chain multiplicity faults (CMFs), suggesting that the increase of Al in the amphibole does not significantly increase or decrease the tendency of these defects to form. The calorimetric measurements indicate that the energy change associated with one full Mg-Tschermak substitution is quite small, on the order of -5 to -10 kJ/mol. Enthalpies of formation from the elements at 298.15 K and 1 bar have been calculated using the new calorimetric data for the magnesiohornblende (MgHb) and tschermakite (Ts) end-members. The values of ΔH_f° for MgHb and Ts are -12401.2 ± 10.6 and -12527.7 ± 16.4 kJ/mol, respectively. The entropy of MgHb, at 298.15 K and 1 bar, has also been calculated using four different site-mixing activity models involving the octahedral (M2) and tetrahedral (T1) sites and the experimental phase-equilibrium data of Jenkins (1994). Two of the models, the two-site and four-site coupled models, are essentially indistinguishable and gave the most consistent values for S_{MgHb}° , 575.1 ± 3.9 and 575.6 ± 3.9 J/(mol·K), respectively.

INTRODUCTION

The general form of the Tschermak cation exchange can be expressed as $^{[6]}\text{M},^{[4]}\text{Si} = ^{[6]}\text{Al},^{[4]}\text{Al}$, where M normally refers to a divalent cation such as Fe, Mg, or Ca. This exchange is of fundamental importance in many silicate solid solutions, including the pyroxenes, amphiboles, micas, chlorites, and melilites. In amphiboles, this coupled substitution is of primary importance in two solid-solution series, the orthorhombic ferromagnesian series and the monoclinic calcic series. Recent transmission analytical electron microscope (TEM-AEM) studies have shown that this substitution dominates during exsolution reactions between anthophyllite and gedrite in the ferromagnesian series (Smelik and Veblen, 1993) and between actinolite and hornblende in the calcic series (Smelik et al., 1991).

Any attempt to relate amphibole composition to a specific P and T or to an exchange reaction in P - T space requires accurate thermodynamic data for certain end-member amphibole compositions. For calcic amphiboles, these data have generally come from phase-equilibrium studies (e.g., Welch and Pawley, 1991; Léger and Ferry, 1991; Jenkins, 1994). Thermodynamic data for a large number of rock-forming minerals, including amphiboles, are tabulated in various thermodynamic data bases (Robie et al., 1979; Helgeson et al., 1978; Berman, 1988; Holland and Powell, 1990).

In this paper we present results from a calorimetric study of synthetic amphiboles in the tremolite-tschermakite (Tr-Ts) series $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2\text{-Ca}_2\text{Mg}_3\text{Al}_4\text{Si}_6\text{O}_{22}(\text{OH})_2]$. The primary goals of the study are to (1) investigate the energy change associated with the Mg-Tschermak exchange in calcic amphibole and (2) determine independently the

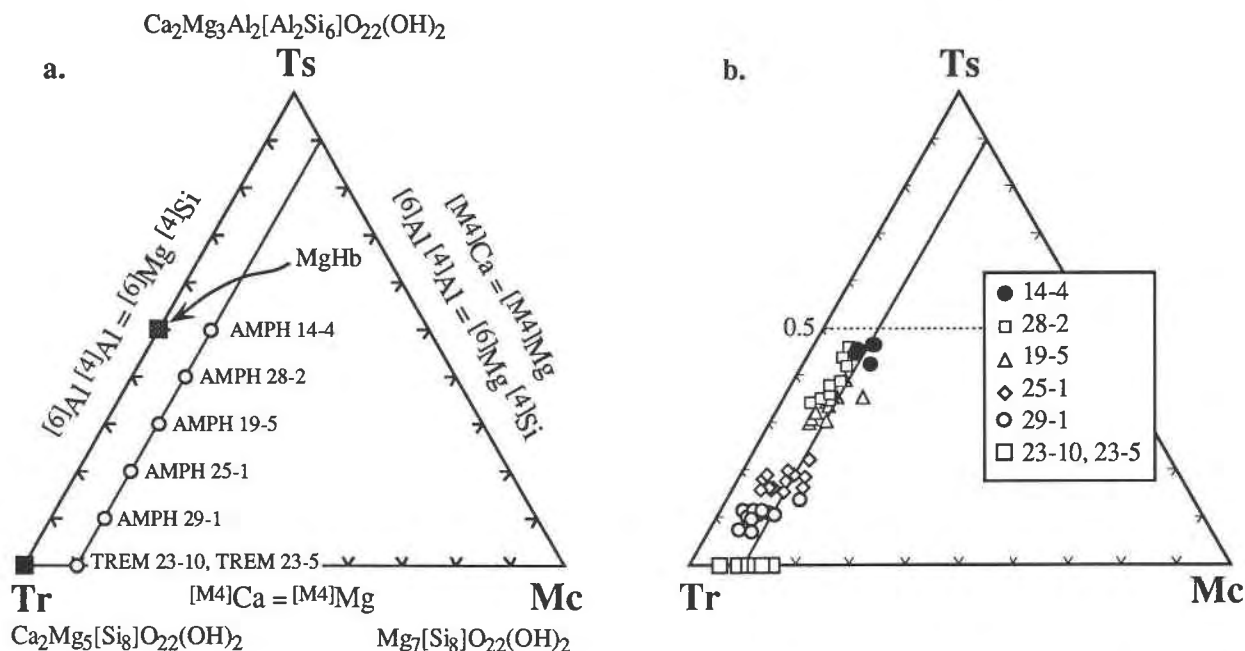


Fig. 1. (a) Plot of tremolite-tschermakite-magnesiocummingtonite (Tr-Ts-Mc) showing starting compositions for amphibole synthesis, made at intervals of 10 mol% along a pseudobinary join shifted toward the Mc apex by 10 mol% (circles). The solubility limit for Al in tremolite is near the MgHb end-member. (b) Representative electron microprobe analyses of the synthetic amphiboles. The dashed line at 0.5 Ts represents the operation of one full Mg-Tschermak substitution, i.e., the Al content of magnesiohornblende.

heats of formation for the amphibole end-members magnesiohornblende (MgHb), $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$, and tschermakite, and compare these results with those from phase-equilibrium studies. By incorporating thermochemical data from Berman (1988) and Holland and Powell (1990) in our analysis, the results presented here should be compatible with those internally consistent data sets.

EXPERIMENTAL METHODS

Amphibole synthesis

All amphiboles were synthesized from mixtures of reagent grade CaCO_3 , MgO , and Al_2O_3 ; SiO_2 was prepared from desiccated silicic acid. Previous experimental work by Jenkins (1988) and Cho and Ernst (1991) has shown that the solubility limit of Al in tremolite approaches the magnesium hornblende end-member composition, $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$, which is equivalent to one full Mg-Tschermak substitution into the tremolite formula. For the synthesis of amphiboles for calorimetry, we purposely chose a join parallel to the true join of tremolite and magnesiohornblende, offset by 10 mol% magnesiocummingtonite (Mc), to obtain the purest amphibole yields possible. The magnesium-cummingtonite component is reflected by a constant substitution of 0.2 Mg for Ca in the M4 site across the entire join (Fig. 1a). We chose to offset the join on the basis of findings of previous workers, who reported a 5–10% enrichment of Mg in the M4 site in their attempts to synthesize end-member tremolite

(Jenkins, 1987; Graham et al., 1989; Pawley et al., 1993). Therefore, the amphiboles were synthesized at 10 mol% increments along the join $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Ca}_{1.8}\text{Mg}_{4.2}\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$. Electron microprobe (EMP) analysis of the amphiboles (discussed below) and previous work on similar compositions by Jenkins (1994) indicate that the compositional offset is preserved along the join. Approximately 1 wt% quartz was mixed into each experiment to compensate for the loss of silica to the ambient fluid during hydrothermal treatment (Jenkins, 1987). Syntheses were performed by loading a stoichiometric oxide-carbonate mixture into a Pt capsule sealed at one end, heating it with a butane torch to drive off CO_2 from CaCO_3 , and then sealing the other end after adding 25–30 wt% H_2O .

Syntheses below 10 kbar were performed in internally heated vessels using Ar as the pressure medium. Pressures were measured with both a PPI bourdon-tube and Harwood manganin resistance-coil gauges, the latter being factory calibrated against a dead-weight piston gauge. Pressure measurements are believed to be accurate to ± 50 bars. Temperatures were measured with two chromel-alumel thermocouples calibrated against the freezing point of NaCl and are believed accurate to ± 1 K. Syntheses above 10 kbar were carried out in a piston-cylinder press $\frac{1}{2}$ in. in diameter using NaCl as the pressure medium. The syntheses were performed in a hot piston-out fashion by pressurizing the assemblage to about 2 kbar below the desired pressure and then using the thermal expansion of the assemblage to reach the desired pressure. Pressure

TABLE 1. Details of amphibole synthesis

Sample	Composition	T (K)	P (kbar)	t (h)	Synthesis products*
TREM 23-10	Ca _{1.8} Mg _{5.2} Si ₈ O ₂₂ (OH) ₂	1133(10)	5.20(70)	239	amph, trace cpx, and trace opx
TREM 23-5	Ca _{1.8} Mg _{5.2} Si ₈ O ₂₂ (OH) ₂	1111(17)	6.10(10)	188	amph and trace cpx
AMPH 29-1	Ca _{1.8} Mg _{5.0} Al _{0.4} Si _{7.6} O ₂₂ (OH) ₂	1137(5)	6.35(5)	237	amph
AMPH 25-1	Ca _{1.8} Mg _{4.8} Al _{0.8} Si _{7.6} O ₂₂ (OH) ₂	1148(10)	6.00(5)	109	amph
AMPH 19-5	Ca _{1.8} Mg _{4.6} Al _{1.2} Si _{7.4} O ₂₂ (OH) ₂	1134(5)	13.0(3)	120	amph, trace opx, and trace qtz
AMPH 28-2	Ca _{1.8} Mg _{4.4} Al _{1.6} Si _{7.2} O ₂₂ (OH) ₂	1115(5)	12.9(3)	147	amph
AMPH 14-4	Ca _{1.8} Mg _{4.2} Al _{2.0} Si _{7.0} O ₂₂ (OH) ₂	1096(5)	12.0(5)	70	amph, cor (1.6 wt%)**, and trace opx

Note: the error ranges for *P*-*T* conditions (shown in parentheses) take into account small *P* and *T* fluctuations during the course of the experiment.

* Amph = amphibole; cor = corundum; opx = orthopyroxene; cpx = clinopyroxene; qtz = quartz; trace = below detection limit on powder XRD (about 1.0 wt%).

** Amount determined by Rietveld modal analysis.

transmission to the sample was calibrated by the reaction albite = jadeite + quartz at 873 K to a precision of ± 250 bars, and it was found that virtually no correction was required to obtain the accepted value of 16.25 kbar (Johannes et al., 1971; Holland, 1980). Temperatures were measured with chromel-alumel thermocouples newly made for each experiment and have an estimated uncertainty of ± 5 K. The synthesis conditions for the amphiboles are summarized in Table 1.

Amphibole characterization

Optical examination. All experimental products were examined with the petrographic microscope using an oil of refractive index 1.60, which matches n_α of the amphibole, to identify the presence of other phases. Only trace amounts (<1%) of impurities were detected for some samples (Table 1).

Electron microprobe. The synthetic amphiboles were analyzed using the Cameca SX-50 fully automated electron microprobe (EMP) at the Princeton Materials Institute, in wavelength-dispersive mode, operated at 15 keV and 20 nA. The beam diameter was typically 1 μm . Mineral standards for Mg, Ca, Si, and Al were MgO, CaSiO₃, and Al₂SiO₅. Analytical corrections were made using the PAP version of the $\phi(\rho Z)$ method (Pouchou and Pichoir, 1985). Performing quantitative EMP analysis on extremely fine-grained synthetic amphibole, typically occurring as $5 \times 20 \mu\text{m}$ laths, can be problematic. We have prepared our samples using conventional epoxy-mounting and polishing techniques (e.g., Graham et al., 1989; Raudsepp et al., 1991). The technique satisfies the requirement for a flat, polished surface but introduces the possibility that if the grain is thin, the analysis may be contaminated by other grains below it. For further discussion of this technique and grain-dispersal techniques, see Jenkins (1994).

Only the largest grains were analyzed, and even then we were never absolutely certain that the excitation volume of the beam was totally within the amphibole crystal. When it was not, the result usually was low analytical totals. An analysis was considered acceptable when the analytical sum was between 95 and 99%, and reasonable

amphibole stoichiometry was achieved when the analysis was normalized to 23 O atoms. Representative EMP analyses are plotted on the Tr-Ts-Mc triangle in Figure 1b for comparison with the end-member compositions (Fig. 1a). Despite the scatter in the probe data, most of the synthetic compositions cluster well along the offset Tr-Ts join. The most Al-rich one, AMPH 14-4, does not match the composition of the MgHb end-member. Optical examination of this sample indicated the presence of unreacted corundum from the original oxide mix in the experiment products (Table 1). The amount of corundum was quantifiable by Rietveld modal analysis, as discussed below.

X-ray diffraction. All synthetic amphiboles were subject to Rietveld structure refinement. Step-scans were made of each sample on a Scintag XDS-2000 powder diffractometer operated in the vertical θ - θ configuration using Cu radiation and a Si(Li) solid-state detector. The step increment for all amphiboles except sample TREM 23-10 was $0.1^\circ 2\theta$ for counting times of 1 s (500–1000 counts on the maximum peaks), using a 2-mm primary slit and a 0.3-mm receiving slit. For TREM 23-10 the conditions were changed to a step size of $0.04^\circ 2\theta$, 5-s counting time, primary slit of 0.5 mm, and a receiving slit of 0.02 mm. Rietveld refinements were performed using the program DBWS-9006 (Young, 1993) yielding R_{Bragg} values of about 0.08.

For AMPH 14-4, containing a small amount of corundum, a Rietveld modal analysis was performed following the method of Bish (1988) and Bish and Post (1993). The modal analysis indicates about 1.6 wt% corundum. Since the initial oxide mix for this composition contained 12.6 wt% Al₂O₃, it appears that only 11.0 wt% went into the amphibole, which equates to 1.74 total Al cations or 43.5 mol% tschermakite (0.87 X_{Ts}). This result agrees very well with the compositions measured for AMPH 14-4 by EMP (10.38–11.68 wt% Al₂O₃, Fig. 1b), which are shifted slightly toward the Tr apex.

The refined unit-cell parameters for the synthetic amphiboles are summarized in Table 2 and plotted against the composition in Figure 2. We used two batches of Tr₉₀Mc₁₀ tremolite (TREM 23-5 and TREM 23-10) in

TABLE 2. Crystallographic data for synthetic tremolite-tschermakite amphiboles

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
TREM 23-5	9.807(2)	18.054(3)	5.276(1)	104.56(1)	904.2(2)
TREM 23-10	9.815(1)	18.058(1)	5.279(1)	104.58(1)	905.49(9)
AMPH 29-1	9.801(1)	18.042(2)	5.279(1)	104.68(1)	902.9(2)
AMPH 25-1	9.784(1)	18.027(2)	5.280(1)	104.74(6)	900.6(2)
AMPH 19-5	9.771(1)	18.013(2)	5.284(1)	104.80(1)	899.2(2)
AMPH 28-2	9.767(1)	17.994(2)	5.288(1)	104.90(1)	898.0(2)
AMPH 14-4	9.769(1)	17.995(2)	5.287(1)	104.91(1)	898.2(2)

Note: the numbers in parentheses indicate the error in the last decimal place.

this study and we were surprised to find that their refined unit-cell volumes differ by about 1.3 Å³. We initially thought that this might be due to different instrumental conditions for the data collections, but we rejected this hypothesis on the basis of data for corundum refinements (multiple scans at different conditions), which indicate no systematic variation in cell parameters as a function of scanning condition. However, there does appear to be as much as 0.1% variation in the unit-cell volumes from multiple scans, which could account for the 1.3-Å³ difference between TREM 23-5 and TREM 23-10. On the basis of that, the EMP results, and the TEM results, we do not feel that the higher cell volume for TREM 23-10 indicates something fundamentally different about the sample; it is simply on the high side of statistical variations for volume determinations.

All the unit-cell parameters vary linearly as a function of composition (Fig. 2). These trends suggest a complete solid solution across the join at the temperatures of formation (1093–1148 K). The linear decrease in cell volume with increasing Al content is consistent with other studies in the Tr-Ts system (Jenkins, 1988, 1994), and agrees well with the trends observed for the Mg-Tschemak substitution in the pyroxene system along the join of diopside and Ca-Tschemak (Newton et al., 1977) and in the mica system along the phlogopite-eastonite join (Circone et al., 1991). Extrapolation of a least-squares regression line through the volume data ($R^2 = 0.96$) yields a cell volume for the hypothetical Ts end-member (with 10 mol% Mc) of 888.3 Å³, which agrees well with the study of Jenkins (1994, 888 ± 2 Å³). This cell volume should be regarded as a minimum volume for tschemakite, since there is no correction for the approximately 10 mol% Mg in the M4 site.

Transmission electron microscopy. The synthetic amphiboles were also examined with a Philips CM20-ST transmission electron microscope (TEM) operated at 200 keV. The samples were gently ground and dispersed in anhydrous alcohol. A drop of each suspension was then applied to a 3.0-mm Ni grid with a holey carbon support film.

The primary purpose of the TEM examination was to determine the nature and concentration of defects in the amphiboles. Previous high-resolution TEM (HRTEM) work by Maresch and Czank (1988), Graham et al. (1989),

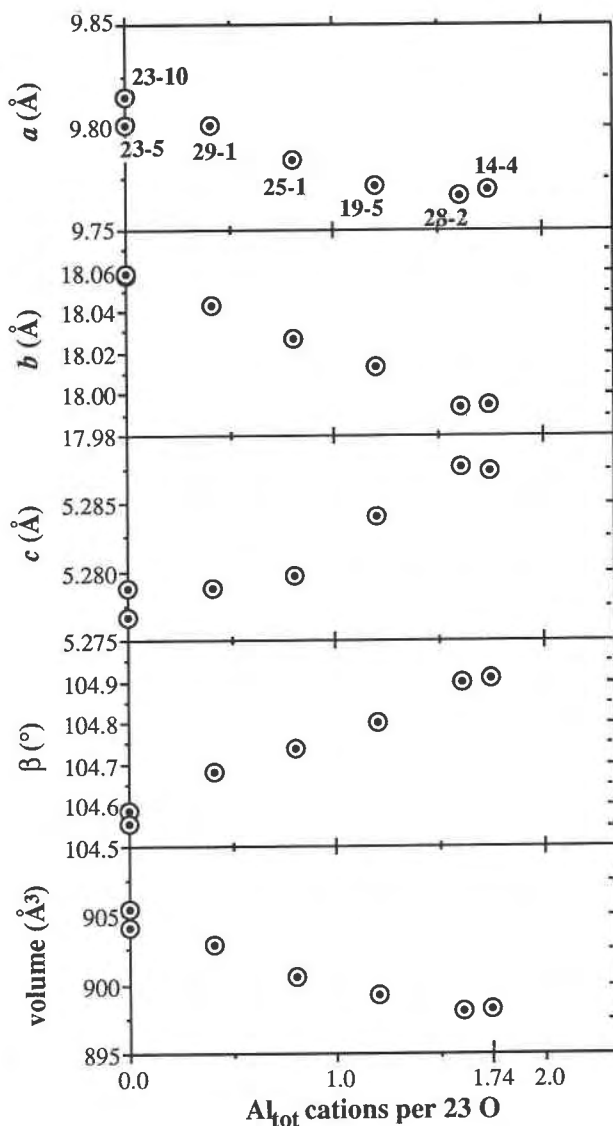


Fig. 2. Unit-cell parameters for synthetic tremolite-tschemakite amphiboles (with 10 mol% Mc) vs. total Al content. All cell parameters show nearly linear trends with composition, suggesting a complete solid solution at the synthesis conditions.

Maresch et al. (1990), and Ahn et al. (1991) has shown varying degrees of defect concentration in synthetic amphiboles. The dominant defect type is the chain-multiplicity fault (CMF), which occurs parallel to (010) of the amphibole structure. These planar faults can be either the single-chain variety, which are essentially unit-cell slabs of pyroxene structure, or the multiple-chain variety (>2), which increases the proportion of the mica-like slab of the amphibole structure. Characterization of these faults is important for two reasons. First, if the defect concentration is high enough, it can significantly shift the amphibole stoichiometry from the expected value. Second, a highly defective structure may not be energetically sim-

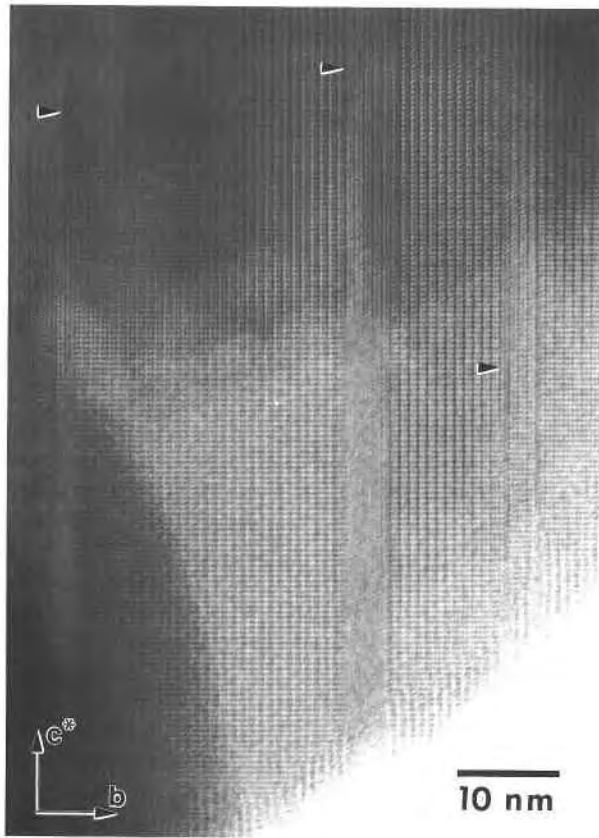


Fig. 3. High-resolution TEM (HRTEM) image of Al-free sample TREM 23-10 taken down $[100]$. The (020) fringes are clearly visible, running from top to bottom in the image. Planar defects are indicated by arrows. These defects are single-chain faults and represent narrow slabs of diopside-like material. Triple-chain faults were also observed.

ilar to one poor in defects, even if the composition is nearly identical.

Representative TEM images of the synthetic amphiboles are presented in Figures 3–5. Most of the images were taken down a $[u0w]$ zone, usually $[100]$ or $[101]$, so that the CMFs were parallel to the electron beam and easily visible. All the synthetic amphiboles were found to contain CMFs. Figures 3, 4, and 5 are HRTEM images of Al-free TREM 23-10, AMPH 25-1 (0.8 total Al), and AMPH 14-4 (1.74 total Al), respectively. The most commonly observed defect types for the amphiboles were single-chain errors (pyroxene material) and triple-chain faults. The most common observation was several planar defects scattered randomly throughout a given crystal. No examples of ordered polysomes of the biopyrbole series (e.g., clinojimthompsonite or chesterite) were observed. For the vast majority of crystals, the estimated volume percent of defective material was less than 5%. The TEM observations did indicate, however, that the tremolite compositions (TREM 23-5, TREM 23-10) had a slightly higher frequency and abundance of defects than the Al-

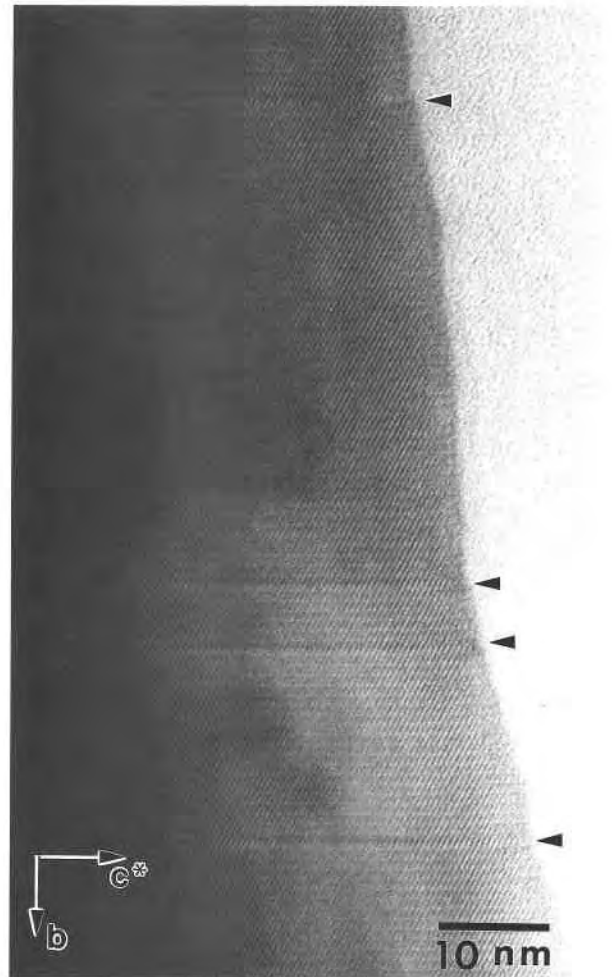


Fig. 4. HRTEM image of sample AMPH 25-1 with approximately 0.8 total Al cations pfu. This image, also taken down a , shows four individual triple-chain faults embedded in an otherwise perfect amphibole structure. This microstructure, consisting of several randomly scattered CMFs in a given crystal, was the most commonly observed one in the synthetic tremolite-tschemmakite amphiboles.

bearing samples, but they did not approach the defect concentration in synthetic end-member tremolite samples examined by Ahn et al. (1991). Pawley et al. (1993) also reported a relatively low CMF concentration in the Mg-enriched synthetic tremolite ($Tr_{92}Mc_8$) used in their calorimetric study. These authors further indicated that the increase of richterite component virtually eliminated the CMFs from the amphibole structure. The present results for tremolite-tschemmakite amphiboles indicate that the Mg-Tschemmak substitution does not appear to inhibit the formation of planar defects, as the richterite substitution does.

Maresch et al. (1990), in a HRTEM study of synthetic tremolite, found the defect character to vary with synthesis conditions. For synthesis conditions comparable with ours, they describe armored diopside relics, up to 10 nm

wide, on which the amphibole appears to nucleate. They also noted that CMFs are minor in both the diopside and tremolite. We have found no such diopside relics in our TEM examinations. Maresch et al. (1990) also studied synthetic anthophyllite-gedrite samples and found that there was a significant decrease of CMFs with only a slight increase of gedrite component into the anthophyllite. They were unable to determine whether the cause of this was due to the edenite substitution, the Tschermak substitution, or a combination of both. Even though our samples belong to the calcic, rather than the ferromagnesian series, the present TEM observations suggest that the edenite substitution may be largely responsible for the elimination of CMFs in synthetic orthorhombic amphiboles, rather than the Tschermak substitution.

As mentioned above, one major concern is whether the amphibole stoichiometry is significantly shifted as a result of the presence of defects. Simple calculations following the method of Veblen and Buseck (1979) show that even the most defective crystals in our study, with perhaps 10% defect concentration, do not cause a significant compositional shift in the amphibole. Furthermore, since in most crystals there was a combination of single-chain and triple-chain defects, any net compositional shift would be even smaller, since these defect types affect the stoichiometry in opposite directions.

Although the EMP results presented above (Fig. 1b) show good agreement with the chosen compositional join, the microprobe provides no information about compositional heterogeneity on the submicron scale. Therefore, we have examined several of the samples using analytical electron microscopy (AEM) to check the compositions of nondefective and defective amphibole areas. For these analyses, we used a probe size of about 10 nm. The analyses were collected with an EDAX Si(Li) detector with a fixed take-off angle of 25°. We were unable to detect any significant compositional differences between defective and nondefective areas using AEM. This is due in part to the poor precision of AEM, compared with EMP technique, and also to the fact that the small compositional differences that must exist in the defective areas are within a region <10 nm, which is the optimal resolution of the AEM system.

Drop-solution calorimetry

The calorimetric technique used in this study is based on the method described by Navrotsky (1977), employing a Calvet-type twin microcalorimeter. Two Pt crucibles, each containing 30 g of $2\text{PbO} \cdot \text{B}_2\text{O}_3$ solvent, are held at a constant temperature of 975 K in the calorimeter. Relative changes in heat flow within the calorimeter, from one sample chamber to the other, are measured by two thermopiles, connected in opposition. The samples are introduced into the solvent by dropping them from room temperature (~ 298 K) through a long, silica-glass tube, hence the term drop solution. The heat effect is a combination of the heat of solution of the amphibole in the lead borate and the heat effect from raising the temper-

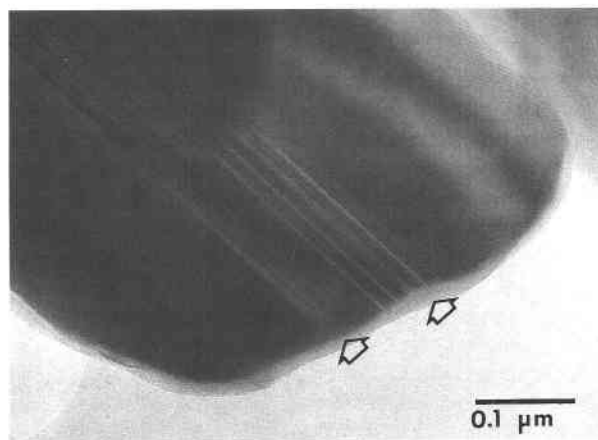


Fig. 5. Bright-field TEM image of sample AMPH 14-4 with about 1.74 Al pfu. The central part of the crystal (indicated by arrows) contains a considerable number of CMFs. This example represents the most extreme defect concentration observed, which still represents less than 5–10% of the total volume of the crystal. Similar defect concentrations were observed, though rarely, in all the synthetic amphiboles, regardless of the Al content.

ature of the sample from room temperature to the calorimeter temperature. This experiment differs from a regular-solution experiment, in which the sample is equilibrated at calorimeter temperature before dissolution. The calibration constant, relating microvolts to joules, was determined by the Pt-drop method (Navrotsky, 1977). Overall, the methodology is essentially identical to that used by Pawley et al. (1993) for tremolite-richterite amphiboles.

Recent work by Navrotsky et al. (1994) has addressed the problem of the evolution of volatiles during calorimetric experiments on hydrous phases and carbonates. They found that performing calorimetric experiments under a flowing gas atmosphere resulted in a negligible enthalpy of interaction between the evolved H_2O or CO_2 and the solvent, suggesting that very little, if any, of the volatile remains dissolved in the solvent. Under flowing gas conditions, they were able to obtain reproducible results, with excellent base-line behavior, for several hydrous silicates and carbonates. The present drop-solution experiments were performed in the same manner, under an atmosphere of flowing Ar at 30–50 mL/min.

For TREM 23-5, the sample was prepared for calorimetry in two ways. The first series of drops employed the use of small silica-glass capsules, in which 6–12 mg of amphibole powder was placed. This technique, described by Burnley et al. (1992), was developed to overcome dissolution problems that commonly occur with Mg-rich compounds. Of course, using the capsules introduces the need for an additional calibration constant, and ultimately increases the likelihood of additional errors in the measurements. The results of these first experiments showed significant scatter (a little over 2% of the total

TABLE 3. Enthalpies of drop solution for synthetic tremolite-tschermakite amphiboles with 10 mol% Mc

Sample	TREM 23-5	TREM 23-10	AMPH 29-1	AMPH 25-1	AMPH 19-5	AMPH 28-2	AMPH 14-4
Al _{tot}	0.0	0.0	0.4	0.8	1.2	1.6	1.74
$\Delta H_{\text{drop sol}}^{\text{meas}}$ (kJ/mol)	931.7	946.2	936.4	937.9	928.5	938.4	933.9
	937.2*	948.6	945.6	939.5	935.1	949.2	941.1
	973.5*	952.3	948.2	967.4	936.6	950.2	946.7
	975.5	952.6	953.4	967.6	949.7	953.8	949.0
	977.0	956.8	953.7	968.5	949.8	957.1	950.2
	986.4*	959.2	955.9	978.8	959.2	961.3	951.4
		966.9	967.2		970.4	967.1	952.8
Mean	963.5	954.6	951.5	959.9	950.9	955.8	947.4
Std Err**	18.8	5.3	7.2	13.9	12.4	7.2	4.8

* These values for TREM 23-5 were obtained using SiO₂ glass capsules; the remaining TREM 23-5 values and all other values were obtained using pellets.

** The standard error equals $2\sigma/\sqrt{N}$.

heat effect) and showed some evidence of slow dissolution; therefore the capsule technique was abandoned.

A second batch of experiments for TREM 23-5, and all the remaining calorimetric experiments, were performed using pressed pellets of the amphiboles, which have been shown to dissolve well in molten 2PbO·B₂O₃ (Pawley et al., 1993). The pellets were about 3 mm in diameter and weighed from 10 to 20 mg. Each sample was carefully weighed before it was dropped into the calorimeter. The calorimetric peak normally returned to base line in 30–50 minutes, indicating complete, and rapid, dissolution.

RESULTS

The enthalpies of drop-solution for synthetic tremolite-tschermakite amphiboles (in kJ/mol) are given in Table 3. Six to eight enthalpy measurements were made for each composition. For sample TREM 23-5, the mean value for the enthalpy of drop solution, $\Delta H_{\text{drop sol}}$, includes experiments performed with capsules and with pellets. The uncertainty for this sample, given as 2 sd of the mean, is rather high, about 2% of the total heat effect, and may contain errors due to problems with the silica-glass capsules. We unfortunately exhausted the material before we could complete a full series of pellet drops for this sample.

For the other tremolite sample and the remaining amphibole compositions, the uncertainties are in the 0.5–1.5% range, expressed as 5–13 kJ/mol, which agree well with the magnitude of uncertainties encountered in the Pt-calibration experiments. The magnitude of the heat effect is in the 950 kJ/mol range for these amphiboles, and it becomes immediately obvious by examining the mean values of $\Delta H_{\text{drop sol}}$ as a function of Al content that there appears to be only a small energetic difference of about –10 kJ/mol or less between the Al-free and Al-rich compositions (Table 3). This small reduction in the enthalpy of solution is consistent with the effect that the Tschermak substitution has on the enthalpy of solution of akermanite (Charlu et al., 1981) and diopside (Newton et al., 1977). It also agrees with the initial effect of the Tschermak substitution in phlogopite (Circione and Na-

vrotsky, 1992), but the nonlinear trend of the mica data extrapolate to a slightly higher $\Delta H_{\text{drop sol}}$ for end-member eastonite.

DISCUSSION

$\Delta H_{\text{drop sol}}$ for MgHb and Ts

One of the primary goals of this study is to obtain, from calorimetric data, values for the enthalpies of formation from the elements for the amphibole end-members magnesiohornblende and tschermakite at 298.15 K. In order to extract this information we first need values for $\Delta H_{\text{drop sol}}$ for these compositions. The mean values for $\Delta H_{\text{drop sol}}$ from Table 3 are plotted against the Al content of the amphibole in Figure 6. Unlike Graham and Navrotsky (1986) and Pawley et al. (1993), we had only compositions for the Tr-rich half of the full Tr-Ts join, from Tr to MgHb, because more Al-rich compositions could not be synthesized. The lack of calorimetric data for $X_{\text{Ts}} > 0.5$ and the almost constant $\Delta H_{\text{drop sol}}$ for $0 < X_{\text{Ts}} < 0.5$ preclude a definite statement about enthalpies of mixing along the Tr-Ts join. The present data do not justify anything more than a least-squares regression through the data (Fig. 6).

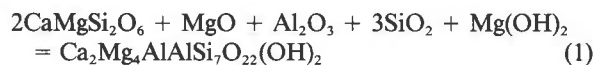
Because of the large and variable uncertainties, the linear regression was performed by weighting each $\Delta H_{\text{drop sol}}$ by the inverse of its uncertainty squared (e.g., Bevington and Robinson, 1992, p. 106). The equation for the line is $\Delta H_{\text{drop sol}} = 955.0 (\pm 4.4) - 3.0 (\pm 3.6)\text{Al}_{\text{tot}}$. The straight line fit is rather poor, with a low *R* value (0.563). Because the energy change associated with the Mg-Tschermak substitution is quite small, we feel the least-squares regression line is the best approach for extracting $\Delta H_{\text{drop sol}}$ values for the end-member MgHb and for a tentative extrapolation to Ts. The question still remains, however, whether the measured enthalpy values for the compositions with 10 mol% Mc can be used to represent true Tr-Ts amphiboles.

To check the possible effect of the 10 mol% Mc component, a series of drop-solution experiments was performed on a sample of very pure natural tremolite, kindly provided by Colin Graham. This tremolite was used by Graham et al. (1984) in a study of H isotopic exchange

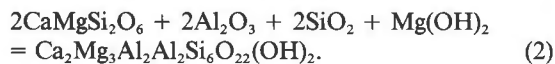
between amphibole and H_2O . It was also used in a phase-equilibrium study of the tremolite breakdown reaction $\text{tremolite} = 2 \text{ diopside} + 1.5 \text{ enstatite} + \beta \text{ quartz} + H_2O$ by Welch and Pawley (1991). These authors reported an average composition for this tremolite of $Ca_{1.98}Fe_{0.05}Mg_{5.06}Al_{0.01}Si_{7.95}O_{22}(OH)_2$, on the basis of 31 EMP analyses. This tremolite was also used by Pawley et al. (1993) in a calorimetric study of synthetic amphiboles along the tremolite-richterite join. The mean value of $\Delta H_{\text{drop sol}}$ for this sample was 959.6 ± 11.2 kJ/mol (8 drops), which compares well with the results of Pawley et al. (1993, 958.0 kJ/mol). These enthalpy values are in general agreement with our measured values for the Mc-substituted tremolite shown in Table 3. On the basis of this result, we conclude that the small amount of Mg in the M4 site has a minimal effect on the enthalpies of solution, and therefore we may calculate values of $\Delta H_{\text{drop sol}}$ for MgHb and Ts using the equation above. The results are 949.0 ± 8.5 and 943.0 ± 15.1 kJ/mol, respectively.

ΔH_f° for MgHb and Ts

The enthalpies of formation for MgHb and Ts may be calculated using a combination of the present calorimetric data and data from the literature. The thermodynamic cycle is based on the following equations for MgHb and Ts, respectively:



and



The data required for the calculations include enthalpies of formation from the elements and enthalpies of drop solution in lead borate at ~ 973 K for diopside, periclase, corundum, quartz, and brucite. For this paper we have chosen heat of formation values from two of the published internally consistent thermodynamic data sets, those of Holland and Powell (1990) and Berman (1988).

The heat of solution data for the reactant minerals available from the literature are summarized in Table 4. For quartz and diopside, both heats of drop solution and heats of solution in $2PbO \cdot B_2O_3$ have been reported, whereas for periclase and corundum only heats of solution are available, and for brucite only drop-solution experiments have been done. To calculate a heat of drop solution from solution data, it is only necessary to add the value of heat content, $H_{T_{\text{cal}}} - H_{298.15}$, for the mineral of interest. The value for $H_{T_{\text{cal}}} - H_{298.15}$ (T_{cal} = calorimeter temperature) varies depending upon which heat-capacity expression is chosen. To assess the extent of variability, we have calculated heats of drop solution for all five reactant minerals in Equations 1 and 2, using different published values for heats of solution and several heat-capacity expressions (Table 4), and have compared these with available measured values for $\Delta H_{\text{drop sol}}$.

For all the phases except quartz, the calculated values

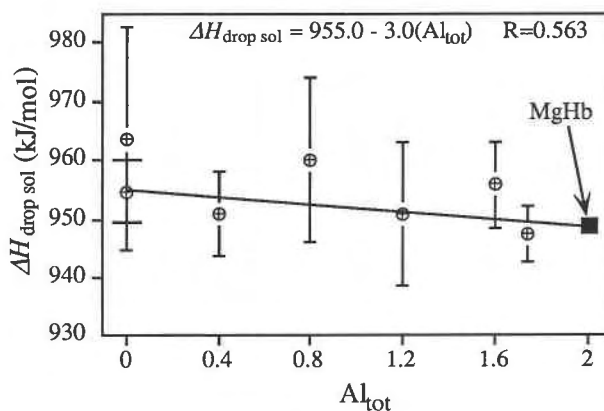


Fig. 6. Plot of $\Delta H_{\text{drop sol}}$ vs. Al_{tot} for synthetic tremolite-tschermakite amphiboles. A weighted least-squares regression line is fitted through the drop-solution data. The energy change associated with the Mg-Tschermak exchange, reflected by the heat of drop-solution data, is very small and negative, suggested by the slight negative slope of the line. The MgHb end-member is indicated by the solid square. Two points for synthetic tremolite ($Al_{\text{tot}} = 0$) are shown, TREM 23-5 and TREM 23-10, the latter having the smaller error.

for $\Delta H_{\text{drop sol}}$ show close agreement, independent of the heat-capacity expression chosen. The calculated values for quartz are complicated by the enthalpy of the α - β transition at 844 K. A summary of published values for $\Delta H_{\alpha-\beta}$, ranging from 0.335 to 1.21 kJ/mol, has been given by Ghiorso et al. (1979). Recently, Hemingway (1987) provided new heat-capacity data for quartz and reevaluated the literature in an attempt to resolve the published disparities in heat-capacity data in the 425–1025 K range. He concluded that all recent tabulations of thermodynamic data for quartz are low by about 1–2%. In light of these results, we have included in Table 4 calculations using the heat-capacity expression for quartz given by Hemingway (1987) and have incorporated his value for $\Delta H_{\alpha-\beta}$ (0.625 kJ/mol) in all the $H_{T_{\text{cal}}} - H_{298.15}$ calculations.

Because the variations in $\Delta H_{\text{drop sol}}^{\text{calc}}$ values are small, the errors resulting from differences in values from Table 4 are small, compared with the error in the heats of drop solution measured for the synthetic amphiboles. We have chosen the following values as the preferred values of $\Delta H_{\text{drop sol}}$ for the calculation of amphibole heats of formation: diopside and quartz, the values measured by Chai and Navrotsky (1993), 40.02 ± 0.22 and 237.4 ± 1.1 kJ/mol, respectively; periclase and corundum, the calculated values for $\Delta H_{\text{drop sol}}$ using the solution data of Navrotsky et al. (1994, 1986) combined with the heat-capacity expressions of Holland and Powell (1990), 36.51 and 107.63 kJ/mol, respectively; brucite, the measured value of Navrotsky et al. (1994), 144.1 ± 3.6 kJ/mol, which was obtained using the methodology employed for the synthetic amphiboles in this study.

Table 5 shows the calculated values of ΔH_f° for MgHb and Ts, using the preferred thermodynamic data for the reactant minerals from Table 4 and the ΔH_f° data for the

TABLE 4. Calorimetric data for silicates near 973 K from the literature

Mineral	$H_{T_{cal}} - H_{298}^*$				ΔH_{sol}^{meas}	$\Delta H_{drop\ sol}^{calc}$		
	R	B	H-P	H		R	B	H-P
Diopside	149.18	149.97	150.14		87.65 ± 1.05	236.83	237.62	237.79
					85.90 ± 1.05	235.08	235.87	236.04
					85.86 ± 1.55	235.04	236.00	235.83
					85.41 ± 1.47	234.59	235.38	235.55
Periclase	31.71	31.68	31.71		4.94 ± 0.33	36.65	36.62	36.65
					4.81 ± 0.58	36.52	36.49	36.52
					4.87 ± 0.62	36.58	36.55	36.58
					4.80 ± 1.00	36.51	36.48	36.51
Corundum	74.84	74.91	74.87		32.34 ± 0.33	107.18	107.25	107.21
					32.55 ± 0.46	107.39	107.46	107.42
					32.76 ± 0.33	107.60	107.67	107.63
Quartz	43.48	42.33	42.36	45.13	-5.15 ± 0.29	38.33	37.18	37.21
					-3.18 ± 0.42	40.30	39.15	39.18
					-4.23 ± 0.21	39.25	38.10	38.13
					-3.51 ± 0.18	39.97	38.82	38.85
Brucite	69.62	70.31	70.33					

Note: boldfaced values represent high and low values of $\Delta H_{drop\ sol}^{calc}$ for each mineral. Italicized values are the preferred values used in our calculations. Units of measure are kJ/mol.

* Heat-capacity expressions used: R = Robie et al. (1979); B = Berman (1988); H-P = Holland and Powell (1990); H = Hemingway (1987, for quartz only).

** Calorimetric experiments done at 986 K.

† Drop solution under static air conditions near 973 K.

‡ Drop solution under static air conditions near 977 K.

§ Drop solution under flowing Ar gas near 975 K.

reactant minerals from Holland and Powell (1990) and Berman (1988).

For magnesiohornblende, the calculated enthalpy of formation at 298.15 K is -12401.2 kJ/mol. For tschermakite, the calculated enthalpy of formation is -12527.7 kJ/mol. If the enthalpies for these amphiboles are calculated using the minimum and maximum thermodynamic values shown in Table 4, a range of about 25 kJ/mol (-12390.9 to -12419.5 and -12519.3 to -12543.5 kJ/mol, for MgHb and Ts, respectively) is obtained. This range can be largely attributed to variations in the quartz and diopside calorimetric data. The differences that result using the Berman (1988) ΔH_f^0 data are insignificant, shifting the values by a maximum of about 1 kJ/mol. It is difficult to determine accurately the error range associated with these calculations because some studies give uncertainties as 1 or 2 sd, whereas others give uncertainties as the standard deviation of the mean, and some studies give no errors at all. By taking the square root of the sum of the squares of all the reported errors for all the data used in the calculations (using the Holland and Powell ΔH_f^0 data), we obtain uncertainties of ±10.6 and ±16.4 kJ/mol for MgHb and Ts, respectively.

Comparison with values obtained from phase equilibrium

Our preferred values for the enthalpies of formation for MgHb and Ts are compared with values from the literature in Table 6. As far as we know, there have been

no previous studies, either phase-equilibrium or calorimetric, aimed at determining thermodynamic properties for the magnesiohornblende composition. Holland and Powell (1990), however, have derived a value of -12420.3 ± 12.7 kJ/mol for ΔH_f^0 of MgHb, for inclusion in their internally consistent thermodynamic data base (their Table 7, reliability level 2). Their value agrees closely with the value we calculate using the older quartz heat-capacity data but is somewhat more negative than our preferred ΔH_f^0 . This difference probably reflects Holland and Powell's (1990) use of the older heat-capacity expressions for quartz in their least-squares fitting process.

The enthalpy of formation for the end-member tschermakite composition has been derived in several phase-equilibrium studies, and the published values are compared with our preferred value in Table 6. Our results agree well with the results of the recent phase-equilibrium study of Jenkins (1994) and the study of Léger and Ferry (1991), which combines experimental data with natural mineral parageneses. The ΔH_f^0 reported by Chermak and Rimstidt (1989), obtained by summing the estimated polyhedral contributions for each oxide and hydroxide component, is significantly more negative than our preferred value, which corroborates that these authors admitted difficulties at predicting thermodynamic properties for calcium aluminum amphiboles and pyroxenes using the polyhedral approach. The value of Lieberman and Kamber (1991), derived by least-squares fitting to a combination of natural parageneses and experimental data, is considerably more positive than our value.

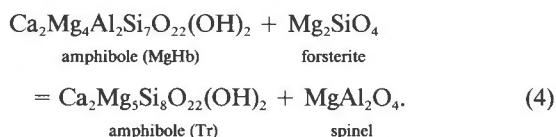
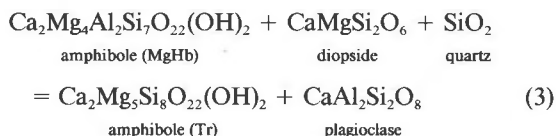
TABLE 4.—Continued

H	$\Delta H_{\text{drop sol}}^{\text{meas}}$	Reference
		Navrotsky and Coons (1976)**
		Newton et al. (1977)
		Kiseleva et al. (1979)
		Navrotsky et al. (1980)**
	237.40 ± 1.10	Chai and Navrotsky (1993)
		Charlu et al. (1975)
		Navrotsky and Coons (1976)**
		Davies and Navrotsky (1981)**
		Navrotsky et al. (1994)
		Charlu et al. (1975)
		Newton et al. (1980)
		Navrotsky et al. (1986)
39.98		Charlu et al. (1975)
41.95		Navrotsky and Coons (1976)**
40.90		Kiseleva et al. (1979)
41.62		Akaogi and Navrotsky (1984)
	40.02 ± 0.22	Chai and Navrotsky (1993)
	111.50 ± 1.59	Kiseleva and Ogorodova (1984)†
	120.04 ± 2.22	Clemens et al. (1987)†
	117.76 ± 1.54	Circone and Navrotsky (1992)‡
	144.10 ± 3.60	Navrotsky et al. (1994)§

Site-mixing models and entropy calculations

Jenkins (1994) examined experimentally two divariant reactions involving Al substitution in tremolitic amphibole to derive activity-composition relationships for amphiboles in the Tr-Ts pseudobinary system, as well as standard-state thermodynamic properties for end-member tschermakite. To complement Jenkins's study, we have used our ΔH_f^0 data, determined independently from calorimetry, combined with the experimental reversal data of Jenkins (1994), to derive the standard entropy for MgHb and test various site-mixing models for aluminum tremolites.

We have reformulated the divariant Reactions 2 and 3 studied by Jenkins (1994) in terms of the MgHb component, rather than the Ts component, to obtain the two reactions



Following the methodology of Jenkins (1994), at equilibrium we may write the following expression for the Gibbs free energy of reaction at P and T :

$$\Delta G_r = 0 = \Delta G_r^0 - \int_{T_0}^T \Delta S_r dT + \int_{P_0}^P \Delta V_r dP + RT \ln K_a \quad (5)$$

where ΔG_r^0 is the change in the Gibbs free energy of the

TABLE 5. Calculated enthalpies of formation for MgHb and Ts at 1 bar and 298.15 K using calorimetric data

Amphibole	Data base	Preferred value* (kJ/mol)
MgHb	H-P	-12401.2
	B	-12402.3
Ts	H-P	-12527.7
	B	-12528.7

Note: H-P = Holland and Powell (1990); B = Berman (1988).
* Calculated using preferred values of $\Delta H_{\text{drop sol}}^{\text{calc}}$ and $\Delta H_{\text{drop sol}}^{\text{meas}}$ from Table 4.

reaction at T_0 and P_0 (298.15 K, 1 bar), ΔS_r is the total entropy change of the reaction, and ΔV_r and K_a are the volume change and equilibrium constant for the reaction, respectively.

Because Reactions 3 and 4 involve only solids and conserve H_2O , and since no C_p data are available for MgHb, we will assume as a first approximation that $\Delta C_p = 0$ for both reactions and that ΔV_r (solids) is constant over the P - T range (1–8 kbar and 873–1073 K) of Jenkins's reversal experiments. These simplifications allow Equation 5 to be rewritten as

$$\Delta G_r = 0 = \Delta G_r^0 - \Delta S_r^0(T - T_0) + \Delta V_r(P - P_0) + RT \ln K_a \quad (6)$$

Noting that $\Delta G_r^0 = \Delta H_r^0 - T_0 \Delta S_r^0$ and substituting into Expression 6, we arrive at

$$\Delta G_r = 0 = \Delta H_r^0 - T \Delta S_r^0 + \Delta V_r(P - P_0) + RT \ln K_a \quad (7)$$

For Reactions 3 and 4, the entropy term in Equation 6, ΔS_r^0 , can be expanded as shown in Equation 8:

$$\Delta S_r^0 = \Delta S_{\text{others}}^0 - S_{\text{MgHb}}^0 \quad (8)$$

where $\Delta S_{\text{others}}^0$ is $S_{\text{Tr}}^0 + S_{\text{An}}^0 - S_{\text{Di}}^0 - S_{\text{Qtz}}^0$ for Reaction 3 and $S_{\text{Tr}}^0 + S_{\text{Sp}}^0 - S_{\text{Fo}}^0$ for Reaction 4. Substituting this into Equation 7 and rearranging gives the following expression for the entropy of MgHb at 298.15 K and 1 bar:

$$S_{\text{MgHb}}^0 = - \frac{\Delta H_r^0 - T \Delta S_{\text{others}}^0 + \Delta V_r(P - P_0) + RT \ln K_a}{T} \quad (9)$$

Using Equation 9, we can test various site-mixing models for MgHb to see which, if any, give constant values of S_{MgHb}^0 . The equilibrium constant, K_a , for Reaction 3 can be expanded as

$$K_a = \frac{(a_{\text{Tr}}^{\text{amph}})(a_{\text{An}}^{\text{plag}})}{(a_{\text{MgHb}}^{\text{amph}})(a_{\text{Di}}^{\text{px}})(a_{\text{Si}_2\text{O}_6}^{\text{qtz}})} \quad (10)$$

and for Reaction 4 as

$$K_a = \frac{(a_{\text{Tr}}^{\text{amph}})(a_{\text{MgAl}_2\text{O}_4}^{\text{spinel}})}{(a_{\text{MgHb}}^{\text{amph}})(a_{\text{Fo}}^{\text{olivine}})} \quad (11)$$

Electron microprobe analyses of plagioclase, diopside, quartz, forsterite, and spinel by Jenkins (1994) indicated that these phases are essentially pure. By accepting unit

TABLE 6. Comparison with ΔH_f° and S° values from the literature for MgHb and Ts

ΔH_f° kJ/mol	S° J/(mol·K)	References (methods)*
		MgHb
-12401.2 ± 10.6	575.3 ± 3.9	This study** (C)
-12420.29 ± 12.70	551.0	Holland and Powell (1990) (LS)
		Ts
-12527.7 ± 16.4	—	This study** (C)
-12534.4 ± 13.0	542.5 ± 12.7	Jenkins (1994)** (PE)
-12578.949	514.687	Mäder and Berman (1992) (PE)
-12449.094	542.72	Lieberman and Kamber (1991)† (LS, PE)
-12606.0 ± 36.0	—	Chermak and Rimstidt (1989)‡ (TH)
-12534.67	538.6	Léger and Ferry (1991) (PE)

* Methods: C = calorimetry; LS = least squares; PE = phase equilibrium; TH = theoretical.

** Using Holland and Powell (1990) data base; entropy is average of two-site and four-site activity-composition models.

† Using Berman (1988) data base.

‡ Calculated based on summation of polyhedral contributions with all OH as Mg(OH)₂.

activity for the pure solids at P and T of interest as the standard state, Equations 10 and 11 can be expressed in terms of amphibole activities only:

$$K_a = \frac{a_{\text{Ts}}^{\text{amph}}}{a_{\text{MgHb}}^{\text{amph}}} \quad (12)$$

Four mixing models will be considered here: (1) coupled substitution of octahedral and tetrahedral Al onto only one M2 site (one-site coupled model), (2) random mixing of Al on both M2 sites but not on the tetrahedral sites (two-site coupled model), (3) random mixing of Al and Si on the four T1 sites but not the M2 sites (four-site coupled model), and (4) complete random mixing of Al on the two M2 sites and Al and Si on the four T1 sites (random mixing model). These models represent idealized site-mixing configurations that serve as a starting point for the following calculations and are not meant to imply long-range ordering arrangements that would be inconsistent with amphibole crystallography or crystal chemistry. Ideal activity-composition models for these mixing schemes have been derived according to the procedure of Price (1985). The resultant expressions for K_a for the four mixing models are given below, with X defined as $X_{\text{Al}}^{\text{M2}}$ (mole fraction of Al on the M2 site):

(1) one-site coupled model:

$$K_a = \frac{(1 - 2X)}{2X}$$

(2) two-site coupled model:

$$K_a = \frac{(1 - X)^2}{4X(1 - X)}$$

(3) four-site coupled model:

$$K_a = \frac{(1 - x/2)^4}{25\%_{27}x/2(1 - x/2)^3}$$

(4) random mixing model:

$$K_a = \frac{(1 - X)^2(1 - x/2)^4}{102\%_{54}(X)^2(1 - X)(1 - x/2)^3}$$

The strategy here is to solve Equation 9 using the experimental reversal data for Reactions 3 and 4 of Jenkins (1994) to see which of the four site-mixing activity-composition models gives the most constant value for S_{MgHb}° . We have used the value for the ΔH_f° for MgHb from Table 6 and enthalpy of formation values for the other phases from Holland and Powell (1990), except for tremolite, which came from Jenkins et al. (1991), to calculate ΔH_f° . We used the entropies for diopside, tremolite, anorthite, quartz, forsterite, and spinel from Holland and Powell (1990) to calculate $\Delta S_{\text{others}}^\circ$. Using the cell volume for AMPH 28-2 (Table 2) and the planar extrapolation method described by Jenkins (1994), we obtain a volume of $270.8 \pm 0.1 \text{ cm}^3/\text{mol}$ ($899.16 \pm 0.33 \text{ \AA}^3$) for MgHb. Using the molar volumes from the Holland and Powell (1990) data set for all other phases, we calculate for ΔV_r a value of $+13.8 \text{ cm}^3$ ($+1.38 \text{ J/bar}$) for Reaction 3 and -1.98 cm^3 (-0.198 J/bar) for Reaction 4.

The results for the four site-mixing models are summarized in Table 7. The uncertainties reflect the propagation of all errors entering into the calculation of S_{MgHb}° by Equation 9. The mean values represent the weighted average $S_{\text{MgHb}}^\circ \pm 1 \text{ sd}$ of the mean. Although all activity-composition models examined provide a satisfactory range of constant entropy values, the two-site coupled and four-site coupled mixing models produce the least amount of scatter (smallest standard deviations). These two mixing models also yield nearly identical mean values for S_{MgHb}° . The average value of S_{MgHb}° from these two mixing models is listed in Table 6.

CONCLUSIONS

These results represent the first data on heat of formation from calorimetric measurements for calcic amphiboles approximately along the join between tremolite and tschermakite and allow the estimation of thermodynamic properties for the important amphibole end-member compositions, magnesiohornblende and tschermakite. The calorimetric data indicate that the energetic change associated with the Mg-Tschermak substitution (^{60}Mg , $^{40}\text{Si} = ^{60}\text{Al}$, ^{40}Al) is small. A weighted least-squares

TABLE 7. Calculated values of S_{MgHb}^0 values using different activity-composition models

PTX data point*	One-site coupled model	Two-site coupled model	Four-site coupled model	Random mixing model
Reaction 3				
1	571.44 ± 14.91	576.68 ± 14.90	577.84 ± 14.90	565.92 ± 15.19
2	570.55 ± 13.65	575.68 ± 13.62	576.79 ± 13.60	566.11 ± 14.16
3	570.97 ± 12.34	575.91 ± 12.30	576.95 ± 12.29	568.48 ± 12.73
4	572.56 ± 13.85	577.21 ± 13.82	578.13 ± 13.81	572.13 ± 14.07
5	572.02 ± 12.56	576.52 ± 12.53	577.37 ± 12.52	572.39 ± 12.82
6	573.38 ± 14.12	577.44 ± 14.11	578.11 ± 14.11	575.59 ± 14.17
7	572.02 ± 13.13	575.97 ± 13.00	576.61 ± 12.96	574.02 ± 13.58
Reaction 4				
8	575.37 ± 12.18	574.48 ± 12.05	573.89 ± 12.04	580.35 ± 12.13
9	570.62 ± 12.61	572.47 ± 12.60	572.46 ± 12.59	575.81 ± 12.63
10	571.53 ± 12.33	572.83 ± 12.30	572.68 ± 12.29	576.85 ± 12.35
11	570.25 ± 12.78	572.32 ± 12.75	572.37 ± 12.74	575.29 ± 12.82
Mean values				
	571.89 ± 3.94	575.09 ± 3.92	575.57 ± 3.92	573.38 ± 3.99

Note: units of measure for models are J/(mol · K).

* PTX data points are reversal experiments of Jenkins (1994).

linear regression through the calorimetric data suggests a slight decrease in $\Delta H_{\text{drop sol}}^{\text{meas}}$ with increasing Al content. This trend is also observed in other silicate systems in which the same substitution is operating, such as initially along the phlogopite-eastonite join (Circone and Navrotsky, 1992) and the join of diopside and Ca-Tschermak pyroxene (Newton et al., 1977). Because of the limited range of compositions available for this study (only the Al-poor half of the join), the data for the Al-rich end-member tschermakite were determined by linear extrapolation.

The thermodynamic data calculated from the measurements of the heat of drop solution and other calorimetric data from the literature agree well with previous values derived from phase-equilibrium studies. Our final preferred values for ΔH_f° for MgHb and Ts are -12401.2 ± 10.6 and -12527.7 ± 16.4 kJ/mol, respectively. Four ideal activity-composition relationships were tested using the calorimetric data. Although all four models gave satisfactory results, the two-site and four-site coupled models gave the least scattered values for S_{MgHb}^0 , 575.1 ± 3.9 and 575.6 ± 3.9 , respectively. These values are significantly higher than the one published value in Holland and Powell's (1990) data base.

Although these results are insufficient for the precise calculation of phase equilibria involving aluminous calcic amphiboles, they represent another step in the persistent effort to understand the activity-composition relationships in complex amphibole solid solutions. It is hoped that the results from this paper can be incorporated into the ever-evolving internally consistent thermodynamic data sets and provide some critical data needed for thermodynamic modeling of mineral reactions involving tschermakitic calcic amphiboles.

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