Composition of synthetic tremolite-tschermakite solid solutions in amphibole + anorthiteand amphibole + zoisite-bearing assemblages

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ABSTRACT

The composition of synthetic amphiboles was investigated experimentally along the tremolitetschermakite join in the system CaO-MgO-Al₂O₃-SiO₂-H₂O-Br₂. Compositions of these amphiboles were studied within the phase assemblages: amphibole-anorthite-quartz-diopside (I), amphiboleanorthite-quartz-talc (II), amphibole-anorthite-quartz-enstatite (III), amphibole-anorthite-talcclinochlore (IV), amphibole-zoisite-talc-quartz (V), and amphibole-zoisite-talc-clinochlore (VI). Assemblages were synthesized from oxide-hydroxide mixtures in the presence of a CaBr₂-bearing solution between 600–800 °C and 200–2000 MPa. Solid phases were investigated using SEM, HRTEM, EMP, and XRD techniques. EMP data show that the amphiboles produced are solid solutions of the ternary system tremolite-tschermakite-cummingtonite. Enstatite, diopside, talc, and clinochlore showed small deviations from their respective end-member compositions due to incorporation of some Al.

The thermodynamic properties of the tschermakite end-member and the mixing properties along the tremolite-tschermakite join were extracted from corresponding exchange reactions of the unreversed synthesized phase assemblages I–VI. Various ideal mixing models were tested for Al-Mg and Al-Si substitution at octahedral M2 and M3 sites and at tetrahedral T1-sites. Best fits were obtained for a two-site coupled model, resulting in $\Delta_t H_{ts}^0 = -12528.3 \pm 11.7$ kJ/mol and $S_{ts}^0 = 556.5 \pm$ 12.0 J/(mol·K) for the tschermakite end-member. Similar calculations were carried out for magnesiohornblende, and values of $\Delta_t H_{Mghb}^0 = -12418.7 \pm 5.9$ kJ/mol and $S_{Mghb}^0 = 562.8 \pm 6.1$ J/(mol·K) were extracted. Calculated phase relations and amphibole compositions agree well with experimental data if the derived thermodynamic data of tschermakite and a two-site mixing model for Al incorporation in amphibole solid solutions are applied.

INTRODUCTION

In greenschist- to granulite-facies rocks, Al-bearing calcic amphiboles are common. They occur either in metabasites (e.g., Robinson et al. 1982), metamorphosed marls (e.g., Baker and Matthews 1994) or in calc-alkaline granitoids (e.g., Hammarstrom and Zen 1986; Hollister et al. 1987). In calc-alkaline granitoids, the Al content of amphibole commonly increases with depth. This has been used to derive an empirical "Al in hornblende" geobarometer (Hammarstrom and Zen 1986; Hollister et al. 1987; Johnson and Rutherford 1989; Thomas and Ernst 1990; Schmidt 1992). The Al content of amphibole, however, is not only a function of pressure and temperature but also depends on bulk composition as given by a particular mineral assemblage. This complicates using the Al content in amphibole as a simple petrogenetic indicator. Lèger and Ferry (1991), for example, demonstrated that calcic amphiboles at the same metamorphic grade have highly variable Al contents of 0.4 to 3.3 Al³⁺ apfu due to the presence of different Al-bearing minerals.

Because of its suitable ionic size ($^{IVI}AI^{3+} = 0.39$ Å, $^{VVI}AI^{3+} = 0.54$ Å; Shannon 1976) Al³⁺ enters various tetrahedral and oc-

tahedral sites in the amphibole structure. The octahedral M2 site and the tetrahedral T1 site are the most probable locations (Hawthorne 1983; Makino and Tomita 1989), but the M3 site (Oberti et al. 1995a; Welch and Knight 1999) and the T2 sites (Oberti et al. 1995b; Welch et al. 1998) have also been suggested for Al incorporation in pargasite. Jenkins et al. (1997) considered the incorporation of Al³⁺ at all octahedral (M1–M3) and tetrahedral sites (T1–T2). In synthetic amphiboles along the tremolite-tschermakite join, incorporation of octahedral Al³⁺ at M2 and M3 sites and of tetrahedral Al³⁺ at T1 sites has been discussed in recent studies (Hawthorne et al. 2000; Najorka and Gottschalk in preparation).

Using Al-free tremolite $(Ca_2Mg_5[Si_8O_{22}(OH)_2])$ as a reference, Al is incorporated as a coupled substitution represented by the tschermaks AlAl(SiMg)₋₁ exchange vector. The thermodynamic properties of Al-bearing amphibole, i.e., its Gibbs free energy, depend on the intracrystalline Al-distribution at the different tetrahedral and octahedral sites. It is clear that the Al concentrations in calcic amphiboles could be used more effectively in geothermobarometry if the thermodynamic properties of the amphibole end-members, their mixing properties and particularly the distribution of Al³⁺ between different crystallographic sites were better known.

There have been many experimental studies on the tschermaks substitution in amphibole, its respective phase equi-

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libria, and thermodynamic properties (e.g., Jasmund and Schäfer 1972; Jenkins 1981, 1994; Cao et al. 1986, Cho and Ernst 1991; Smelik et al. 1994; Hoschek 1995; Quirion and Jenkins 1998). However, except for the study of Cho and Ernst (1991), all work encountered the crucial difficulty that the synthesized amphiboles were mostly too small for accurate EMP analysis. Compositional information was often obtained on unpolished grain mounts using energy dispersive analysis (Cao et al. 1986; Jenkins 1983, 1988, 1994; Hoschek 1995; Quirion and Jenkins 1998) or from systematic variations of X-ray reflections (Jenkins 1981, 1983, 1988, 1994; Cho and Ernst 1991; Hoschek 1995). However, both methods are hampered by inherent difficulties. Uneven surfaces of unpolished grain mounts make absorption corrections for characteristic X-rays difficult, if not impossible. Consequently, such analyses are not sufficiently precise. Moreover, the system tremolite-tschermakite $(Ca_2Mg_5[Si_8O_{22}(OH)_2]-Ca_2Mg_3Al_2[Al_2Si_6O_{22}(OH)_2)]$ is not binary but ternary because the cummingtonite component $(Mg_2Mg_5[Si_8O_{22}(OH)_2])$ also varies up to 18 mol% (Najorka and Gottschalk in preparation). The shifts of X-ray reflections do not provide sufficiently precise chemical information if the exact amounts of X_{cum} are not considered. Figure 1 shows the location of the (310) reflection for X_{cum} of 0 and 0.10 (Najorka and Gottschalk in preparation). The XRD-calibration curves for X_{cum} used by Jenkins (1988), Cho and Ernst (1991), and Hoschek (1995) all coincide with the calculated line for a X_{cum} of 0.10 (Fig. 1). However, if X_{cum} is 0.05 instead of 0.10, the derived tschermakite content of amphibole (X_{ts}) is too low by 9 mol% if the above calibration curve is applied. It is clear that accurate compositions are indispensable for any correct thermodynamic evaluation.

With the use of chloride or bromide solutions it is possible to synthesize amphiboles large enough for electron microprobe analysis (Zimmermann et al. 1996; Gottschalk et al. 1998; Melzer et al. 1998). Using this experimental approach, a pre-



FIGURE 1. Variation of the $d_{(310)}$ – reflection with composition in ternary tremolite-tschermakite-cummingtonite amphiboles. Calibration lines of previous studies coincide with the calculated line for $X_{\text{cum}} = 0.1$ (Najorka and Gottschalk in preparation).

cise characterization of tremolite-tschermakite-(cummingtonite) solid solutions in the compositional range between $Tr_{100}Ts_0$ and $Tr_{45}Ts_{55}$ by EMP, IR, X-ray, and TEM methods will be presented in a forthcoming paper by Najorka and Gottschalk (in preparation).

In this study, large amphiboles along the tremolitetschermakite join have been synthesized in the presence of various Al-bearing phase assemblages at varying P and T. The following equilibria were investigated in detail:

1 tschermakite + 2 diopside + 2 quartz \leftrightarrow 1 tremolite + 2 anorthite (1)

1 tschermakite + 2 quartz \leftrightarrow 1 talc + 2 anorthite (2)

2 tschermakite + 2 quartz \leftrightarrow 4 anorthite + 3 enstatite + 2 H₂O (3)

5 tschermakite + 4 $H_2O \leftrightarrow 1$ tremolite + 8 anorthite + 2 clinochlore (4)

3 tremolite + 9 tschermakite +14 quartz + 8 $H_2O \leftrightarrow$ 12 zoisite + 14 talc (5)

5 tremolite + 43 tschermakite + 60 $H_2O \leftrightarrow 14$ clinochlore + 28 talc + 48 zoisite. (6)

Aluminum concentrations in amphibole solid solutions have been measured, and thermodynamic properties of the tschermakite end-member and mixing properties along the tremolite-tschermakite join are presented.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The experimental strategy follows the "synthesis-exchange technique" (Zimmermann et al. 1997; Melzer et al. 1998; Najorka et al. 1999) where synthesis and exchange reactions are combined in one experiment. Experiments were performed from 200 to 500 MPa and 600 to 850 °C in standard cold-seal hydrothermal vessels. H₂O and CO₂ were used as pressure media. Temperatures were measured inside the vessels with Ni-CrNi thermocouples placed close to the sample. The pressure was controlled with a calibrated strain gauge. The uncertainties in temperature and pressure are estimated to be less than ± 5 °C and ± 5 MPa. At the end of each run the samples were quenched isobarically to 300 °C within 3 minutes using compressed air. For runs at 1500 and 2000 MPa and 650 to 750 °C a piston-cylinder apparatus with NaCl assemblies was used. The estimated uncertainties of temperature and pressure are ±15 °C and ±50 MPa, respectively.

The starting materials were mixtures of analytical grade SiO₂, MgO, Al₂O₃, Ca(OH)₂, and aqueous CaBr₂-solution (≤ 2 molal). The solid/fluid ratio varied between 1.0 and 3.0. With respect to CaO, MgO, Al₂O₃, and SiO₂, the bulk compositions were chosen to lie within the subsystems amphibole-anorthitequartz-diopside (I), amphibole-anorthite-quartz-talc (II), amphibole-anorthite-quartz-enstatite (III), amphibole-anorthite-clinochlore-talc (IV), amphibole-zoisite-quartz-talc (V), amphibole-zoisite-clinochlore-talc (VI), and amphibole-zoisitekyanite-clinochlore (VII). The respective bulk compositions and the run conditions are listed in Table 1. The water content of the starting mixture $(X_{H_{2}O}^{\text{before}})$ was calculated from bulk compositions. The water content of the products $(X_{H_{2}O}^{after})$ was calculated from bulk composition minus the water content of OH-bearing phases. In Figure 2, the bulk compositions of the runs are presented as subtetrahedra in the CaO-MgO-SiO₂-Al₂O₃ tetrahedron.

RESULTS

Phase characterization

Synthesized products were characterized by optical microscopy, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), electron microprobe (EMP) analysis, and powder X-ray diffraction (XRD). Details of the analytical procedures are given by Najorka and Gottschalk (in preparation). The lattice constants and other structural parameters were refined using the *GSAS* software package for Rietveld refinement (Larson and Von Dreele 1987). The following algorithm was used during the refinement procedure: scale factor, background (real space correlation function), zero-point correction, phase fractions, lattice constants, Caglioti W, preferred orientation, atomic positions, Caglioti U+V, Lorentz LX+LY. Further details of the refinement procedure are described by Gottschalk et al. (1998).

SEM. Shapes of the synthesized crystals were subhedral or euhedral (Fig. 3). Amphibole produced needles or lath-shaped crystals in the size range of $1-20 \times 10-300 \mu m$. Talc usually occurred as distinct, leaf-like crystals (5 to 300 μm across) and smaller grains commonly had a pseudohexagonal shape. Anorthite formed euhedral platy crystals up to $50 \times 150 \mu m$. Quartz crystallized as euhedral prisms (<20 μm). Diopside, zoisite, enstatite, and forsterite crystallized as thin prisms with sizes in the range of $2-5 \times 10-50 \mu m$. In a few cases, the crystals were covered by amorphous quench SiO₂. However, because of the similar habit of amphibole, diopside, zoisite, enstatite, and forsterite, it was difficult to distinguish among these phases by

TABLE 1. Starting conditions of the runs

Run	Ca(OH) ₂	CaBr ₂	MgO	Al ₂ O ₃	SiO ₂	H ₂ O	CaBr ₂ -	X before	X after	Т	Р	time
	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	molality	H ₂ O	¹¹ H ₂ O	(°C)	(MPa)	(days)
					Bul	lk (I) amph-	an-di-qtz					
TS-3	3.94	1.19	5.18	0.77	13.93	51.26	0.11	0.99	0.99	750	200	60
TS-14	4.64	2.85	5.39	1.08	14.72	14.24	0.93	0.98	0.98	750	500	7
TS-20	3.70	2.85	4.35	0.75	11.65	14.28	0.94	0.98	0.98	800	200	1
15-34	4.63	3.41	5.33	1.23	14.22	17.06	0.94	0.98	0.98	600	500	14
18-35	4.67	3.45	5.21	1.35	14.23	17.27	0.94	0.98	0.98	700	200	1/
TS-36	4.68	3.42	5.21	1.34	14.09	17.13	0.94	0.98	0.98	600	200	16
15-38	9.37	3.50	10.41	2.68	27.55	17.51	0.88	0.98	0.98	600	350	14
TS-40	4.68	3.52	5.20	1.34	14.51	17.58	0.94	0.98	0.98	750	350	17
TS-47	1.43	1.29	1.71	0.45	5.53	3.64	1.62	0.97	0.97	850	350	19
TS-57	5.76	5.19	6.87	1.83	20.74	17.02	1.41	0.98	0.97	700	350	17
TS-58	5.75	5.18	6.86	1.83	20.76	17.04	1.41	0.98	0.97	650	500	18
TS-59	5.75	5.18	6.86	1.82	20.61	17.05	1.40	0.98	0.97	650	200	18
TS-60	5.76	5.19	6.87	x1.83	20.89	16.76	1.43	0.97	0.97	800	350	16
TS-69	8.08	10.92	4.43	6.46	20.72	25.09	2.02	0.96	0.96	700	500	12
					Bul	k (II) amph-	-an-ta-qtz					
TS-9	1.10	0.99	1.85	0.81	5.36	3.59	1.29	0.98	0.98	600	500	19
TS-13	1.10	1.00	1.85	0.81	5.38	3.54	1.31	0.98	0.98	650	350	19
TS-61	4.38	3.95	7.36	3.22	21.38	12.99	1.41	0.98	0.97	650	200	18
TS-62	4.38	3.95	7.36	3.21	21.36	13.00	1.40	0.98	0.97	650	500	18
TS-67	6.46	4.97	6.09	5.34	21.47	22.48	1.03	0.98	0.98	600	200	32
TS-68	8.48	9.65	6.36	8.76	25.65	30.20	1.50	0.97	0.97	700	500	12
TS-94	4.38	3.95	7.35	3.21	21.35	13.04	1.40	0.98	0.97	800	350	16
TS-95	4.38	3.95	7.35	3.21	21.34	12.95	1.41	0.98	0.97	700	350	17
					Bulk	(III) amph	an-en-atz					
Ts-87	6.41	5.84	13.30	5.49	31.58	19.88	1.36	0.98	0.98	800	200	14
TO 04	4 75	0.00	0.74	0.55	Bui	k (IV) ampn	-an-ta-cin	1.00	1 00	050	050	10
15-21	4.75	0.00	6.71	3.55	15.14	9.74	0.00	1.00	1.00	650	350	19
15-22	1.58	0.00	2.23	1.18	5.03	4.33	0.00	1.00	1.00	750	350	19
15-37	4.75	0.00	6.72	3.55	15.15	9.79	0.00	1.00	1.00	600	500	19
15-55	5.06	4.57	9.30	6.74	20.71	22.54	0.96	0.98	0.98	700	500	15
12-00	5.07	4.54	9.40	6.50	20.85	22.38	0.96	0.98	0.98	600	200	32
					Bul	k (V) amph	-zo-ta-qtz					
TS-71	1.44	1.30	1.93	1.37	6.41	6.00	1.02	0.98	0.98	750	1500	7
TS-72	1.42	1.29	1.98	1.25	6.32	6.00	1.02	0.98	0.98	650	2000	7
TS-76	1.43	1.31	1.95	1.32	6.23	7.01	0.89	0.98	0.98	650	1500	8
TS-88	1.34	1.25	2.22	1.03	6.61	5.99	0.99	0.98	0.98	700	2000	7
					Bull	k (VI) amph	-zo-ta-cln					
TS-85	1.51	1.40	2.25	1.84	5.32	6.06	1.09	0.98	0.98	700	1500	8
					D II.	(VII) om - h						
TS-84	1.27	1.19	2.08	2.64	5.03	6.04	0.94	0.98	0.98	700	1500	8
Note:	n _{H O}				2.00							-
, юле. Х _н	$_{20} = \frac{n_{20}}{n_{20} + n_{20}}$	-										



FIGURE 2. Phase assemblages I–VII plotted within the CMAStetrahedron with excess water. Bulk compositions were chosen to lie within the subtetrahedra of the phase assemblages I-VII. Abbreviations: an = anorthite, cln = clinochlore, di = diopside, en = enstatite, ky = kyanite, qtz = quartz, ta = talc, tr = tremolite, trts = tremolitetschermakite solid solutions, ts = tschermakite, and zo = zoisite. Dashed line: tremolite-tschermakite join. Note that a small amount of cummingtonite component in amphibole shifts the trts join slightly toward the MgO-apex.

SEM-imaging alone. Traces of remaining starting materials were not observed.

XRD. All experimental products were investigated by powder XRD. For each run product, a Rietveld refinement was performed that provided quantitative phase proportions of solids as well as their lattice parameters (Tables 2, 3, and 4). In the products of most runs, amphibole was the predominant phase. As predicted by the chosen bulk compositions, the intended divariant phase assemblages consisting of four solids and one fluid were observed in most cases. For runs at 200, 350, and 500 MPa, amphibole and anorthite were observed together with either quartz and diopside, quartz and talc, quartz and enstatite, or clinochlore and talc. At 1500 and 2000 MPa, amphibole and zoisite formed along with either quartz and talc, or clinochlore and talc. In runs TS-34, TS-36, TS-38, TS-58, and TS-59 (Table 1), which produced the phase assemblage amphibole-anorthite-diopside-quartz, talc was observed as an additional phase. In run TS-22, the assemblage amphibole-anorthite-clinochloretalc was expected; however, amphibole-anorthite-enstatiteforsterite formed instead. In the runs TS-47 and TS-84, no amphibole was produced.

Compositions of amphibole in the tremolite-tschermakitecummingtonite ternary were determined using the lattice pa-



FIGURE 3. SEM images of run products. (a) lath-shaped amphibole crystals $(20 \times 2-5 \ \mu\text{m})$ and leaf-like talc crystals $(4 \times 4 \ \mu\text{m})$ from run TS-88 (b) amphibole, talc, anorthite, and quartz crystals (run TS-68).

rameters a and β (Najorka and Gottschalk in preparation). The compositional dependence of the lattice parameters was crosschecked with measurements by EMP and FTIR. Results agree within error limits of either method (Najorka and Gottschalk in preparation; see also below). Lattice parameters for amphibole solid solutions and the derived compositions are listed in Tables 2 and 3. Refinement of the lattice parameters for anorthite, quartz, forsterite, and zoisite indicated that these were nearly pure end-member composition. Deviations from endmember lattice parameters were observed for talc, clinochlore, diopside, and enstatite due to the incorporation of Al-bearing components (Table 4), and these were used to determine the compositions of the respective phases. The extent of tschermaks substitution in ortho- and clinopyroxenes (Ca₋₁Si₋₁Al₂ and Mg₋₁Si₋₁Al₂, respectively) was estimated by applying the compositional dependence of the lattice parameters (Gasparik 1986; Danckwerth and Newton 1978; Table 2). The Al concentrations of talc and chlorite were determined using the calibrations by Hoschek (1995) and Baker and Holland (1996), respectively (Table 2). The determined Al concentrations correspond to 2 to 5 mol% Mg-tschermaks component in orthopyroxene, 0 to 8 mol% Ca-tschermaks component in clinopyroxene, 0 to 19 mol% tschermaks component in talc

(tats), and 5 to 34 mol% amesite component in chlorite.

EMP. The synthesized amphiboles were in many cases sufficiently large for reliable EMP analyses. Composition of amphiboles from 18 runs are presented in Table 5. The amphiboles are ternary solid solutions of tremolite, tschermakite, and cummingtonite. Bromine concentrations were found to be below the EMP detection limit (0.1 wt%). Analyses were normalized to 23 oxygen atoms and the cations were distributed according to the formula $AB_2C_5[T_8 O_{22}/(OH)_2]$, where A = vacant; B = Ca, Mg; C = Mg, Al; T = Al, Si. The total Al concentration was distributed equally (Altot/2) over the C and T sites assuming that the tschermaks substitution is obeyed. A single analysis was accepted if the total oxide sum was in the range of 91 to 99 wt%. Because of the small crystal size of the amphiboles in three runs (TS-9, TS-35, TS-57), the total oxide sum was commonly below 90 wt%, and a sum between 84-99 wt% was accepted here. T-site occupancies greater than 8 were calculated from several analyses. Such occupancies are unlikely and interpreted as an analytical artifact. Therefore, site occupancies were used as additional criteria and analyses were rejected if these deviations were larger than the 2σ analytical error. If these occupancies exceeded the nominal value by $\pm 1\%$ at the T sites, $\pm 3\%$ at the B and C sites, and $\pm 0.5\%$ for the total sum of 15 on all cation sites, the analysis was rejected.

Compositions of pyroxene from runs TS-20, TS-36, TS-47, TS-69, and TS-87 were also obtained by EMP. Amounts of Al of up to 0.12 apfu in diopside and 0.04 apfu in enstatite were observed (Table 6). Because of the small size of the pyroxene crystals, the total oxide sum was in many cases below 100 wt%. Therefore, single analyses with a total oxide sum as low as 90 wt% were accepted. The analyses were calculated on the basis of six oxygen atoms according to the pyroxene formula XY [T₂ O₆] with X = Ca, Mg; Y = Mg, Al; T = Al, Si. The total Al content (Al^{tot}) was distributed equally (Al^{tot}/2) over the X and

TABLE 2. Phase proportions of the runs and compositions of amphiboles along with Al-bearing minor phases determined by EMP and XRD

Run	Т	Р	time	Phase proportions (wt%)	Group				Amphibole	
(°C)	(MPa)	(days)				χ_{ts}^{EMP}	$\chi^{\text{EMP}}_{\text{cum}}$	$\mathcal{X}_{\mathrm{tr}}^{\mathrm{EMP}}$	$\mathcal{X}_{ ext{ts}}^{ ext{XRD}}$	$\mathcal{X}_{ ext{cum}}^{ ext{XRD}}$
(I) amph	-di-qtz-an									
TS-36	600	200	16	12 amph, 40 di, 6 qtz, 13 an, 29 ta	(iii)				0.22	0.03
TS-38	600	350	14	36 amph, 30 di, 7 qtz, 7 an, 19 ta	(iii)				0.30	0.04
TS-34	600	500	14	1 amph, 49 di, 6 qtz, 11 an, 33 ta	(iii)					
TS-59	650	200	18	46 amph, 19 di, 16 qtz, 10 an, 9 ta	(iii)				0.19	0.07
TS-58	650	500	18	49 amph, 20 di, 19 qtz, 5 an, 7 ta	(iii)				0.22	0.05
TS-35	700	200	17	75 amph, 10 di, 4 qtz, 11 an	(i)	0.14	0.00	0.86	0.15	0.04
TS-57	700	350	17	73 amph, 2 di, 15 qtz, 10 an	(i)	0.18	0.00	0.82	0.16	0.05
TS-69	700	500	12	41 amph, 10 di, 10 qtz, 40 an	(i)				0.26	0.03
TS-3	750	200	60	93 amph, 1 di, 4 qtz, 2 an	(i)				0.14	0.04
TS-40	750	350	17	66 amph, 18 di, 6 qtz, 10 an	(i)				0.19	0.05
TS-14	750	500	7	78 amph, 15 di, 4 qtz, 3 an	(i)				0.23	0.08
TS-20	800	200	7	68 amph, 20 di, 6 qtz, 6 an	(i)	0.12	0.03	0.85	0.11	0.03
TS-60	800	350	16	84 amph, 1 di, 9 qtz, 5 an	(i)				0.19	0.06
TS-47	850	350	19	60 dio, 40 fo, melt	(ii)					
(II) ampł	n-qtz-an-ta									
TS-67	600	200	32	44 amph, 10 qtz, 34 an, 11 ta	(i)	0.23	0.00	0.77	0.18	0.03
TS-9	600	500	19	50 amph, 13 qtz, 17 an, 20 ta	(i)	0.26	0.04	0.70	0.24	0.05
TS-61	650	200	18	49 amph, 12 qtz, 19 an, 20 ta	(i)	0.23	0.01	0.76	0.19	0.05
TS-13	650	350	19	48 amph, 15 qtz, 17 an, 20 ta	(i)	0.24	0.00	0.75	0.22	0.05
TS-62	650	500	18	50 amph, 13 qtz, 16 an, 21 ta	(i)	0.26	0.01	0.73	0.25	0.06
TS-95	700	350	17	48 amph, 13 qtz, 19 an, 20 ta	(i)	0.24	0.01	0.75	0.23	0.06
TS-68	700	500	12	45 amph, 8 qtz, 43 an, 3 ta	(i)	0.29	0.05	0.66	0.33	0.07
TS-94	800	350	16	63 amph, 10 qtz, 22 an, 5 ta	(i)				0.23	0.11
(III) amp	h-qtz-an-en	ı								
TS-87	800	200	14	35 amph, 3 qtz, 25 an, 37 en	(i)	0.14	0.13	0.73	0.16	0.10
(IV) amp	h-an-ta-cln									
TS-66	600	200	32	25 amph, 33 an, 22 ta, 20 cln	(i)				0.31	0.04
TS-21	650	350	19	74 amph, 13 an, 8 ta, 6 cln	(i)	0.30	0.03	0.68	0.29	0.05
TS-37	600	500	19	76 amph, 13 an, 5 ta, 6 cln	(i)	0.36	0.02	0.62	0.33	0.05
TS-55	700	500	15	41 amph, 26 an, 20 ta, 12 cln	(i)	0.37	0.03	0.60	0.36	0.06
TS-22	750	350	19	70 amph, 19 an, 8 en, 4 fo	(i)	0.28	0.08	0.08	0.33	0.09
(V) ampl	h-zo-ta-qtz									
TS-76	650	1500	8	16 amph, 36 zo, 42 ta, 6 qtz	(i)	0.24	0.10	0.65	0.24	0.06
TS-72	650	2000	7	12 amph, 33 zo, 42 ta, 10 qtz	(i)	0.21	0.04	0.75	0.19	0.04
TS-71	750	1500	7	25 amph, 28 zo, 40 ta, 7 qtz	(i)				0.32	0.08
TS-88	700	2000	7	37 amph, 22 zo, 32 ta, 8 qtz	(i)				0.23	0.05
(VI) amp	h-zo-ta-cln									
TS-85	700	1500	8	8 amph, 40 zo, 42 ta, 10 cln	(i)	0.34	0.07	0.59	0.33	0.05
(VII) amr	oh-zo-ky-cl	n								
TS-84	700	1500	8	43 ta, 30 zo, 14 cln, 13 cor	(i)					
Note: (I)	to (VII) den	ote the res	spective b	pulk compositions explained in text. Pha	ise propor	tions of the	e runs were r	efined using	the Rietveld	method.

T sites assuming that tschermaks substitution is obeyed.

Anorthite, quartz, forsterite, and zoisite had end-member compositions. The talc and chlorite crystals were too small (<1 μ m) to obtain reasonable EMP analyses. The results from EMP and XRD measurements show that amphibole, orthopyroxene, clinopyroxene, talc, and chlorite were solid solutions of two or more end-members. The compositions of the amphiboles from many runs were obtained by EMP and XRD and the results generally agree (Table 2). In a few runs, amphiboles were too small for accurate EMP analyses and totals were unacceptably low. In addition, cummingtonite contents as obtained by EMP are of low accuracy (Gottschalk et al. 1999). However, reasonable lattice parameters were obtained for all phases in mineral mixtures, even if the total amount of a particular phase was as low as 5 wt%. Furthermore, precise relationships between lattice parameters and composition in the tremolite-tschermakitecummingtonite ternary do exist (Najorka and Gottschalk in preparation). This relationship also holds for pyroxene com-

TABLE 2. continued

positions, where similar results from EMP and XRD analysis were obtained (Table 2). For talc and chlorite solid solutions, only compositions from XRD were available. In the following, all compositional details rely on data obtained by XRD.

Compositions of amphiboles in P-T-X-space

Stability fields of the fluid-saturated assemblages amphibole-anorthite-quartz-diopside, amphibole-anorthite-quartz-talc, amphibole-anorthite-quartz-enstatite, amphibole-anorthiteclinochlore-talc, amphibole-zoisite-quartz-talc, amphibolezoisite-clinochlore-talc, and amphibole-zoisite-kyanite-clinochlore have been calculated for the respective bulk compositions I to VII using VERTEX (Connolly 1990) assuming $a_{H_{2O}} = X_{H_{2O}}$ (values from Table 1; Figs. 4a–4d). Thermodynamic properties for mineral end-members are from the internally consistent data set of Gottschalk (1997). Activities of diopside in clinopyroxene, enstatite in orthopyroxene, clinochlore in chlorite, and talc in talc-tats solid solutions were calculated with compositions from

	Clinopyroxene					Orthopyro	xene		Та	ιlc	Chlorite		
X_{tr}^{XRD}	$\chi^{\rm EMP}_{\rm Cats}$	χ_{di}^{EMP}	χ_{Cats}^{XRD}	X_{di}^{XRD}	χ_{Mqts}^{EMP}	$X_{en}^{\sf EMP}$	X_{Mgts}^{XRD}	X_{en}^{XRD}	$\chi_{\rm tats}^{\rm XRD}$	X_{ta}^{XRD}	χ_{ames}^{XRD}	χ_{cln}^{XRD}	
0.74	0.06	0.94	0.03	0.97					0.00	1.00			
0.65			0.06	0.94					0.04	0.96			
	0.05	0.95							0.09	0.91			
0 74	0.00	0.00	0.07	0 93					0.00	1 00			
0.74			0.07	0.00					0.00	0.06			
0.75			0.00	0.32					0.04	0.30			
0.00			0.05	0.97									
0.00	0.05	0.05	0.00	0.07									
0.71	0.05	0.95	0.03	0.97									
0.82													
0.76			0.01	0.99									
0.69			0.04	0.96									
0.86	0.03	0.97	0.00	1.00									
0.75													
	0.06	0.94											
0.79									0.00	1.00			
0.71									0.02	0.98			
0.76									0.00	1.00			
0.73									0.00	1 00			
0.69									0.02	0.98			
0.00									0.02	0.00			
0.60									0.02	0.00			
0.00													
0.00													
0.75					0.02	0.08	0.02	0.08					
0.75					0.02	0.30	0.02	0.30					
0.65									0.00	1 00	0.05	0 05	
0.00									0.00	0.03	0.00	0.00	
0.05									0.07	0.93	0.07	0.93	
0.02									0.19	0.01	0.00	0.94	
0.58							0.05	0.05	0.01	0.99	0.09	0.91	
0.58							0.05	0.95					
0.60									0.06	0.04			
0.09									0.00	0.94			
0.77									0.03	0.97			
0.61									0.09	0.91			
0.72									0.00	1.00			
0.63									0.05	0.95	0.16	0.84	
									0.10	0.00	0.24	0.66	
									0.12	0.00	0.34	00.0	
$X_{ts} = AI^{tot}/4$	4 = AI™²/2 in	i amphibole;	X _{cum} = Mg ^{M4}	/2 in amphil	$OOIE; X_{Cats} =$	AI [™] /2 = Al ^{™1}	in diopside;	$X_{Mots} = AI^{tot}/2$	2 = Al™' in er	istatite: X_{tats}	= AI ¹⁰¹ /2 = AI ¹	"° in talc;	

Table 2 and mixing models explained below. In Figures 4a–d, the measured X_{ts} values are plotted into the calculated stability fields along with X_{ts} isopleths that were calculated using an ideal two-site coupled model for Al incorporation into amphibole (see also discussion below).

Bulk composition amphibole-anorthite-quartz-diopside (I). Fourteen runs were performed at 200–500 MPa and 600–850 °C. Amphibole coexisting with anorthite-quartz-diopside was observed in eight runs at 700, 750, and 800 °C (filled circles in Fig. 4a). $X_{\rm ts}$ in amphibole is strongly pressure dependent and

 TABLE 3. Refined lattice constants of synthetic amphiboles of the tremolite-tschermakite-cummingtonite ternary

Run	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
TS-3	9.8066(7)	18.0400(13)	5.2763(3)	104.76(1)
TS-9	9.7942(12)	18.0160(18)	5.2818(4)	104.83(1)
TS-13	9.7958(14)	18.0191(23)	5.2825(5)	104.81(2)
TS-14	9.7858(12)	18.0281(20)	5.2790(5)	104.76(1)
TS-20	9.8138(4)	18.0516(5)	5.2798(1)	104.76(1)
TS-21	9.7889(8)	18.0125(13)	5.2841(28)	104.88(1)
TS-22	9.7729(7)	18.0093(13)	5.2823(3)	104.82(1)
TS-35	9.8054(15)	18.0450(26)	5.2774(6)	104.77(2)
TS-36	9.802(11)	17.9732(26)	5.2984(8)	104.86(18)
TS-37	9.7863(6)	17.9930(9)	5.2846(2)	104.92(1)
TS-38	9.7869(45)	17.9746(90)	5.2754(28)	104.89(7)
TS-40	9.8009(15)	18.0449(31)	5.2790(7)	104.80(2)
TS-55	9.7803(10)	18.0063(0)	5.2851(0)	104.92(0)
TS-57	9.8041(13)	18.0437(20)	5.2797(4)	104.77(1)
TS-58	9.7950(20)	18.0312(30)	5.2804(7)	104.81(2)
TS-59	9.7936(40)	18.0403(83)	5.2823(19)	104.74(6)
TS-60	9.7964(9)	18.0300(10)	5.2777(2)	104.77(1)
TS-61	9.7993(12)	18.0270(24)	5.2797(5)	104.79(1)
TS-62	9.7903(14)	18.0136(21)	5.2832(4)	104.82(2)
TS-66	9.7932(19)	18.0205(32)	5.2847(6)	104.94(2)
TS-67	9.8094(15)	18.0322(26)	5.2822(6)	104.84(2)
TS-68	9.7811(11)	18.0005(17)	5.2819(4)	104.88(1)
TS-69	9.8015(13)	18.0264(20)	5.2807(5)	104.91(2)
TS-71	9.7822(5)	18.0119(7)	5.2816(1)	104.84(1)
TS-72	9.8017(32)	18.0190(40)	5.2818(7)	104.81(3)
TS-76	9.7889(23)	18.0152(31)	5.2839(6)	104.81(2)
TS-85	9.7876(30)	18.0036(30)	5.2843(2)	104.88(1)
TS-87	9.7861(8)	18.0376(11)	5.2783(3)	104.75(1)
TS-88	9.7925(16)	18.0160(17)	5.2856(3)	104.83(1)
TS-94	9.7732(16)	18.0175(23)	5.2812(5)	104.66(2)
TS-95	9.7908(14)	18.0222(27)	5.2807(6)	104.79(2)

TABLE 4. Refined lattice constants of Al-bearing phases

increases from 0.11–0.15 at 200 MPa to 0.23–0.26 at 500 MPa. In experiments between 600–650 °C, talc occurred as an additional phase (open squares in Fig. 4a). In talc-bearing runs, X_{ts} in amphiboles is significantly higher and ranges from 0.19 to 0.30. Obviously, there is a metastable phase in this assemblage (discussed below) and, therefore, X_{ts} values of the talc-bearing assemblages were omitted in Figure 4a. No amphibole formed in run TS-47 (850 °C, 350 MPa) where only diopside, forsterite, and melt were detected.

Bulk composition amphibole-anorthite-quartz-talc (II). Eight runs were performed at 200–500 MPa and 600–800 °C. This phase assemblage was produced in all runs (filled circles in Fig. 4b). The tschermakite component in amphibole is strongly pressure dependent and increases from 0.18 at 200 MPa to 0.24–0.33 at 500 MPa.

Bulk composition amphibole-anorthite-quartz-enstatite (III). One experiment was conducted at 200 MPa and 800 °C. This phase assemblage was produced and X_{ts} of the amphibole was 0.16 (filled square in Fig. 4b).

Bulk composition amphibole-anorthite-clinochlore-talc (IV). Five runs were carried out at 200–500 MPa and 600–750 °C. At 600 to 700 °C, this assemblage was actually produced (filled circles in Fig. 4c). $X_{\rm ts}$ in amphibole increased with pressure and temperature from 0.29 (650 °C, 350 MPa) to 0.36 (700 °C, 500 MPa). At 750 °C and 350 MPa, clinochlore was not stable and, as predicted by VERTEX, the assemblage amphibole-anorthite-enstatite-forsterite was observed instead (square in Fig. 4c).

Bulk composition amphibole-zoisite-talc-quartz (V). Four runs were performed at 1500–2000 MPa and 650–750 °C. The phase assemblage amphibole-zoisite-talc-quartz formed in every case (Fig. 4d), despite the fact that at 1500 MPa and 750 °C, calculations by VERTEX predict the presence of kyanite instead of talc. X_{ts} in amphibole varies with temperature and pressure. The lowest (0.19) and the highest (0.32) X_{ts} were observed at 650 °C, 2000 MPa and 750 °C, 1500 MPa, respectively.

Bulk composition amphibole-zoisite-talc-clinochlore (VI). One run, using bulk composition VI in the amphibole-

			-	-							
Run	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β(°)	Run	<i>a</i> (Å)	<i>b</i> (Å)	<i>C</i> (Å)	α (°)	β (°)	γ (°)
enstatite					talc						
TS-22	18.2241(57)	8.7765(58)	5.1763(23)		TS-9	5.2936(10)	9.1647(8)	9.4882(31)	90.54(2)	99.96(2)	90.00(1)
TS-87	18.2262(9)	8.8036(6)	5.1791(2)		TS-13	5.2955(20)	9.1649(14)	9.4943(40)	90.57(3)	99.89(5)	89.98(2)
diopside					TS-21	5.2948(33)	9.1670(31)	9.4645(61)	90.76(5)	99.69(7)	90.00(3)
TS-14	9.7565(32)	8.9122(25)	5.2656(13)	106.09(2)	TS-34	5.2979(10)	9.1633(15)	9.4763(32)	90.22(2)	100.29(2)	89.96(1)
TS-20	9.7463(7)	8.9217(7)	5.2544(3)	105.95(1)	TS-36	5.2921(22)	9.1642(15)	9.5076(31)	90.41(3)	100.07(3)	90.03(3)
TS-34	9.7431(12)	8.9084(10)	5.2596(5)	106.00(1)	TS-37	5.3095(44)	9.1619(36)	9.4106(86)	90.47(8)	99.39(8)	90.03(6)
TS-35	9.7663(67)	8.9127(47)	5.2669(10)	105.99(3)	TS-38	5.2736(22)	9.1627(34)	9.4899 (39)	90.40(4)	100.27(4)	89.68(3)
TS-36	9.7569(15)	8.9147(16)	5.2601(7)	106.00(1)	TS-55	5.2923(9)	9.1619(10)	9.4984(42)	89.98(2)	100.24(3)	89.85(2)
TS-38	9.7483(26)	8.9061(24)	5.2652(8)	106.03(2)	TS-58	5.2834(70)	9.1652(79)	9.485(11)	90.79(10)	100.04(10)	90.11(7)
TS-40	9.7617(29)	8.9190(26)	5.2675(8)	106.01(2)	TS-59	5.2891(35)	9.1631(38)	9.4843(68)	90.64(7)	99.42(8)	90.09(4)
TS-58	9.7395(36)	8.9033(25)	5.2659(10)	105.99(3)	TS-61	5.2930(22)	9.1622(15)	9.4862(33)	90.67(3)	99.61(5)	90.01(2)
TS-59	9.7393(26)	8.9036(21)	5.2646(8)	106.00(2)	TS-62	5.2946(23)	9.1650(15)	9.4889(42)	90.54(3)	100.06(5)	90.00(2)
TS-69	9.7424(34)	8.9133(26)	5.2576(18)	105.92(3)	TS-66	5.2965(9)	9.1688(11)	9.4926(33)	90.56(2)	99.85(3)	89.96(1)
clinochlor	e				TS-67	5.3052(33)	9.1643(33)	9.5039(46)	90.65(5)	100.06(7)	89.88(4)
TS-21	5.3207(15)	9.2139(32)	14.3756(86)	96.85(4)	TS-71	5.2955(7)	9.1663(6)	9.4689(19)	90.56(1)	100.06(2)	90.01(1)
TS-37	5.3207(16)	9.2088(28)	14.3781(77)	96.79(3)	TS-72	5.3004(8)	9.1639(7)	9.4828(15)	90.30(1)	99.87(2)	90.11(1)
TS-55	5.3181(5)	9.2112(16)	14.3705(42)	96.95(2)	TS-76	5.2933(7)	9.1651(6)	9.4772(16)	90.43(1)	99.99(2)	90.01(1)
TS-66	5.3188(3)	9.2139(16)	14.3793(48)	96.90(2)	TS-84	5.2919(6)	9.1668(5)	9.4639(15)	90.32(1)	100.24(2)	90.03(1)
TS-84	5.3133(3)	9.1998(10)	14.3068(33)	96.93(1)	TS-85	5.2929(4)	9.1656(5)	9.4816(24)	90.41(1)	100.04(1)	90.01(1)
TS-85	5.3141(4)	9.1981(11)	14.3513(99)	96.89(3)	TS-88	5.2955(7)	9.1672(5)	9.4933(23)	90.51(1)	99.92(2)	90.01(1)
					TS-95	5.2942(23)	9.1628(16)	9.4862(34)	90.56(3)	99.88(5)	90.00(2)

	. 00111	JUSILION	3 01 3yi	1010312	eu amp		30110 30	Julion	5 110111		easurer	nemo						
Run	TS-9	TS-13	TS-20	TS-21	TS-22	TS-35	TS-37	TS-55	TS-57	7 TS-61	TS-62	TS-67	TS-68	TS-72	TS-76	TS-85	TS-87	TS-95
No. of	9	18	20	11	9	3	10	15	1	11	6	9	9	7	2	15	10	13
analyses																		
CaO	12 38	13 16	13.05	13.07	12 35	12 85	13 23	13 21	12 04	13 36	13 36	13 75	12 84	13 10	11 70	12 52	12 04	13 16
MaO	20.69	20.99	23 22	20.84	21 79	21 44	20.73	21 09	19.38	21.81	21.58	22 16	21 65	22 43	21 41	21 22	24 30	21 46
Al ₂ O ₃	5.94	5.77	2.83	7.20	6.91	3.15	8.83	9.04	3.80	5.75	6.45	5.64	7.21	5.25	5.81	8.34	3.44	5.68
SiO	51.62	53.33	56.46	53.76	53.48	52.06	53.21	53.08	49.37	54.56	53.88	55.66	53.80	55.37	53.12	52.87	57.53	53.48
Sum	90.63	93.25	95.56	94.87	94.53	89.49	96.00	96.42	84.59	95.48	95.25	97.21	95.51	96.15	92.04	94.95	97.31	93.78
							0	ماميط ط		n of the								
1020	1 00	0.40	0 40	1 02	1 62	0.64	20 Star		eviatio			0.54	0.62	0.07	1 40	1 09	0.66	0.60
	1.22	1 0/	1 / 2	0.82	1.03	1.09	0.82	1 1 2		1 31	0.32	1 32	1 52	1 66	0.22	1 / 2	1 17	0.00
	0.03	2 02	0.87	1 28	0.95	0.17	0.02	1 16	_	0.41	0.02	0.30	1.32	1.00	0.22	1 /0	0.41	0.00
	4 02	3 73	2 70	2 29	3 25	2 76	2 44	2.34	_	2 16	1 41	1 92	3 16	2 79	2 04	2.38	1.63	1.50
	4.02	0.70	2.70	2.20	0.25	2.70	2.77	2.04		2.10	1.41	1.52	0.10	2.75	2.04	2.00	1.00	1.00
						Amph	ibole c	ompos	ition b	ased on	23 O at	toms						
Ca ^{™₄}	1.93	2.00	1.93	1.95	1.84	2.04	1.95	1.94	2.01	1.98	1.99	2.00	1.90	1.93	1.79	1.86	1.74	1.99
Mg ^{M₄}	0.07	0.00	0.07	0.05	0.16	0.00	0.05	0.06	0.00	0.02	0.01	0.00	0.10	0.07	0.21	0.14	0.26	0.01
Mg ^{M1,2,3}	4.43	4.43	4.71	4.27	4.38	4.73	4.21	4.25	4.51	4.48	4.45	4.50	4.36	4.52	4.35	4.26	4.64	4.50
^{VI} AI	0.51	0.48	0.23	0.59	0.57	0.27	0.72	0.73	0.35	0.47	0.53	0.45	0.59	0.42	0.49	0.68	0.27	0.47
™AI	0.51	0.48	0.23	0.59	0.57	0.27	0.72	0.73	0.35	0.47	0.53	0.45	0.59	0.42	0.49	0.68	0.27	0.47
Si	7.52	7.56	7.80	7.48	7.46	7.70	7.32	7.28	7.71	7.55	7.48	7.57	7.44	7.60	7.59	7.35	7.77	7.54
X	0.26	0.24	0.12	0.30	0.28	0.14	0.36	0.37	0.18	0.23	0.26	0.23	0.29	0.21	0.24	0.34	0.14	0.24
ΛX_{te}	0.02	0.06	0.02	0.02	0.02	0.01	0.02	0.02	0.00	0.01	0.00	0.01	0.02	0.03	0.01	0.03	0.01	0.01
Xcum	0.04	0.00	0.03	0.03	0.08	0.00	0.02	0.03	0.00	0.01	0.01	0.00	0.05	0.04	0.10	0.07	0.13	0.01
\mathcal{X}_{tr}	0.71	0.75	0.85	0.68	0.64	0.86	0.62	0.60	0.82	0.76	0.73	0.77	0.66	0.75	0.65	0.59	0.73	0.75
5 M1 0	4.04	4 0 2	4.04	4 96	4.05	E 00	4 0 0	1 00	1 96	4.05	4 0.0	4 05	4 05	4 0 4	1 01	4.04	4.01	4.07
Σ IVI I -3 Σ T	4.94	9.04	4.94 9.02	9.07	4.95	7.00	9.04	9.01	4.00	4.95	4.90 9.01	4.95	4.95	4.94 9.02	4.04 0.00	4.94 9.02	9.05	9.01
∠ i Σ cations	1/ 07	1/ 06	1/ 07	1/ 03	1/ 07	15.02	1/ 06	1/ 00	1/ 0/	1/ 08	1/ 00	1/ 08	1/ 08	1/ 07	1/ 02	1/ 07	1/ 05	1/ 00
Z cations	14.97	MaM123	· VIAI: 57	T _ IVAI	1 97	10.02 (VAL	· VIAIV/	14.99 A. V	- Ma ^{M4}	/ 0	14.99	14.90	14.90	14.97	14.92	14.97	14.95	14.99
NULE. Z IV	n -o ≓ I	vig,_,o .	+ ∵Ai, 2	I = ∵AI	+ OI, A	ts = (∵AI	+ ∵Ai)/	+, ∧ _{cum}	– wy	12.								

BLE 5. Compositions of synthesized amphibole solid solutions from EMP measurements

zoisite-talc-clinochlore subsystem, was performed at 1500 MPa and 700 °C (TS-85). The assemblage amphibole-zoisite-talc-clinochlore formed and X_{1s} in amphibole is 0.33.

Bulk composition amphibole-zoisite-kyanite-clinochlore (VII). One run was performed at 700 °C and 1500 MPa with bulk composition VII in the amphibole-zoisite-kyanite-clinochlore subsystem. No amphibole formed and only the phases talc, zoisite, clinochlore, and corundum crystallized (TS-84).

DISCUSSION

Phase assemblages

In the five-component system, CaO-MgO-Al₂O₃-SiO₂-H₂O equilibrium assemblages of five phases are divariant. If fluid is present, stable divariant assemblages then consist of four solids, as identified by the label group i in Table 2. For any given pressure and temperature, the compositions of all phases are fixed even if the bulk chemistry varies within certain compositional limits. Such assemblages form subtetrahedra within the CaO-MgO-Al₂O₃-SiO₂ tetrahedron (Fig. 2) and have stability fields in the P-T plane (Fig. 4). An additional degree of freedom is introduced if only three solids are present. In this case, variations in bulk composition are accompanied by changes in the composition of one or more phases. Such threephase solid assemblages are represented by triangles within a tetrahedron. We found no amphibole-bearing, three-phase solid assemblages in our experiments. Obviously, the chosen bulk compositions did not allow for formation of higher-variance assemblages except in run TS-47, where at 850 °C and 350 MPa, diopside, forsterite, and melt were produced (group ii in Table 2). Equilibrium assemblages of five solids are univariant.

TABLE 6. Composition of Al-bearing ortho- and clinopyroxenes

TABLE 0. Compo		bourning o		лпорутокс	100
Run	TS-20	TS-36	TS-47	TS-69	TS-87
phase	di	di	di	di	en
no. of analyses	5	2	2	4	3
CaO	24.9	23.02	24.79	23.67	0.54
MgO	18.2	15.81	15.48	17.43	38.24
Al ₂ O ₃	1.27	2.59	2.56	2.49	1.19
SiO2	54.3	50.28	51.69	52.64	59.51
Sum	98.7	91.69	94.51	96.24	99.48
	2 o standaro	d deviation	of the mea	an	
∆CaO	1.37	1.11	0.66	2.28	0.14
∆MgO	1.19	2.99	1.25	2.09	0.05
ΔAl_2O_3	0.33	4.30	0.62	0.77	0.31
∆SiO₂	2.15	1.15	3.03	5.14	0.90
Pyrox	ene compo	sition base	ed on six C	atoms	
Ca ^{M2}	0.97	0.96	1.01	0.95	0.02
Mg ^{M2}	0.03	0.04	0.00	0.05	0.96
Mg ^{M1}	0.96	0.89	0.88	0.91	0.96
^{VI} ĂI	0.03	0.06	0.06	0.05	0.02
^{IV} AI	0.03	0.06	0.06	0.05	0.02
Si	1.98	1.97	1.97	1.96	2.00
X _{ts}	0.03	0.06	0.06	0.05	0.02
ΔX_{ts}	0.00	0.05	0.01	0.01	0.01
Xen	0.03	0.04	0.00	0.05	0.96
X _{di}	0.94	0.91	0.94	0.89	0.02
Σ M1-2	1.99	1.95	1.95	1.97	1.96
ΣΤ	2.01	2.03	2.03	2.02	2.02
Σcations	3.99	3.97	3.97	3.98	3.98
<i>Note:</i> Σ M1-2 = Ca – Mα ^{M2}	^{M2} + Mg ^{M1,2} -	+ ^{νι} ΑΙ; Σ Τ =	V Al + Si; X_{ts}	$= (^{IV}AI + ^{VI}A)$	I)/ 2; X _{en}

In Figure 2, such assemblages are represented by a distorted ditrigonal pyramid, where a triangle is common to two adjacent tetrahedra on which the respective starting bulk composition resides. In the P-T plane, these assemblages are stable along



amphibole (see below). (a) Assemblage amphibole-anorthite-diopsidequartz for bulk composition I with $a_{H_{20}} = 0.98$ (Table 1). Runs between 700 and 800 °C yielded the assemblage amphibole-anorthite-diopsidequartz (filled circles). In runs between 600–650 °C, talc occurred as an additional phase (open squares). At 850 °C and 350 MPa, diopside, forsterite, and melt formed (open circle). Note that exchange reaction 1 does not depend on $a_{H_{20}}$. (b) Assemblages amphibole-anorthite-talcquartz (filled circles) and amphibole-anorthite-enstatite-quartz (square, run TS-87) for bulk compositions II and III with $a_{H_{20}} = 0.97$ (Table 1). (c) Assemblages amphibole-anorthite-clinochlore-quartz (filled circles) and amphibole-anorthite-forsterite for bulk composition IV

with $a_{H_{2O}} = 0.99$ (Table 1). Square represents run TS-22 which produced the assemblage amphibole-anorthite-enstatite-forsterite, in agreement with the stability fields calculated by VERTEX. (d) Assemblage amphibole-zoisite-talc-quartz (filled circles) for bulk composition V with $a_{H_{2O}} = 0.98$ (Table 1).

-0.15-

500

1200

20

C

0.25

600

0.35°.

700

T (°C)

C×-0

800

the univariant curves of reactions denoted in Figures 4a–d. However, the presence of five solids (group iii in Table 2) in our experimental products does not necessarily mean that this actually constitutes a stable univariant assemblage because one of the phases may have formed metastably. If a stable amphibole-bearing univariant assemblage formed, compositions of amphibole solid solutions at the univariant boundaries must agree with the intersecting X_{ts} isopleths from the divariant field. If not, metastable formation of at least one phase is indicated.

The majority of the runs yielded four solids plus fluid (group i) with phase assemblages produced corresponding to the chosen bulk compositions and amphibole solid solutions of the tremolite-tschermakite-cummingtonite ternary. Within each phase assemblage, X_{ts} of the amphibole systematically varied with pressure and temperature and the compositional scatter was low. At a given pressure and temperature, different bulk compositions produced different four-phase solid assemblages with varying amphibole compositions. This finding is in line with chemographic considerations because, in this case, adjacent subtetrahedra are not allowed to intersect (Fig. 2). At 500 MPa and 700 °C, for example, three different assemblages were produced: amphibole-anorthite-quartz-diopside from bulk composition I; amphibole-anorthite-quartz-talc from bulk composition II; and amphibole-anorthite-clinochlore-talc from bulk composition IV, with amphibole solid solutions having X_{1s} -values of 0.26, 0.33, and 0.36, respectively. Increasing X_{ts} in amphiboles from assemblages I, II, and IV is consistent because the corresponding subtetrahedra for these assemblages do not intersect. For any other compositional sequence, the subtetrahedra would overlap at the corner that is represented by the amphibole composition along the trts-join (Fig. 2) and, if present, would indicate inconsistency. Similarly, at 500 MPa and 700 °C, X_{cum} of 0.07 in amphiboles from assemblage II and of 0.06 from assemblage IV were higher than that of 0.03 from assemblage I, again indicating internal consistency. Also, the cummingtonite component within each assemblage increased with temperature, as predicted by Gottschalk et al. (1999).

These observations indicate that the assemblages and phase compositions of group i experiments are consistent with equilibrium having been reached. Although oxides and hydroxides were used as starting materials and no reversed runs were conducted, three observations argue for equilibrium. First, the compositional scatter of the solid solutions is low. Second, the synthesized amphiboles are well ordered with low chain multiplicity fault concentrations (Najorka and Gottschalk in preparation). Third, phase relations and compositions of solid solutions are consistent. This result holds with the exception of the three runs, TS-94, TS-71, and TS-84. Run TS-94, conducted with bulk composition II at 800 °C and 350 MPa, should have produced amphibole-quartz-anorthite-talc, and it did. However, calculations by VERTEX predict the stability of enstatite instead of talc at these conditions (Fig. 4b). The calculated reaction boundary is only lower by 18 °C at 350 MPa, which is probably within the error limits of the calculation scheme. Thus, amphibole-quartz-anorthite-talc is considered to be the stable assemblage. Run TS-71, conducted with bulk composition V at 750 °C and 1500 MPa, should have produced amphibole-zoisite-talc-quartz, and it also did. VERTEX predicts the stability of kyanite instead of talc, which is unstable above 650 °C (Fig 4d). It is well known that kyanite is notoriously hard to nucleate (e.g., Goldsmith 1982) and, because of that, the stability field of amphibole-zoisite-talc-quartz is believed to have extended metastably to higher temperatures. Nucleation problems of kyanite probably also caused formation of corundum in run TS-84 and prevented formation of amphibole. We have, therefore, no information on amphibole from the experiment using bulk composition VII.

Five experiments at 600 to 650 °C and 200 to 500 MPa (TS-34, TS-36, TS-38, TS-58, TS-59) using bulk composition I produced talc in addition to the expected four solid assemblage amphibole-anorthite-quartz-diopside (group iii in Table 2). In these runs, X_{ts} in amphiboles is significantly higher than indicated for the four-phase solid assemblage amphibole-anorthite-quartz-diopside (Table 2, Fig. 4a). Measured X_{ts} in amphiboles from 0.19 to 0.30 from the five-phase solid assemblage would fit somewhat better into the compositional pattern of the assemblage amphibole-anorthite-quartz-talc. According to the arguments given above, one of the observed phases is metastable. This is probably talc, which might have nucleated rapidly during heating at lower temperatures and failed to decompose between 600 and 650 °C, but did at temperatures above 650 °C. In any case, the five-phase solid assemblage does not represent an univariant assemblage and results from these runs are excluded from further considerations.

Comparison with earlier results

Amphiboles along the tremolite-tschermakite join have been synthesized and studied experimentally by Jasmund and Schäfer (1972), Oba (1978), Cao et al. (1986), Cho and Ernst (1991), Jenkins (1981, 1983, 1988, 1994), Smelik et al. (1994), Hoschek (1995), Jenkins et al. (1997), and Najorka and Gottschalk (in preparation). The synthesis of pure end-member tschermakite was claimed by Oba (1978); however, our recalculation of his lattice constants using the compositional dependence of the a and β lattice parameters (Najorka and Gottschalk in preparation) results in a maximum X_{ts} of 0.55, far from the assumed composition of the tschermakite end-member. This finding is in accordance with an experimental study by Jenkins (1988), where a maximum X_{ts} of about 0.50 was determined. Limited tremolite-tschermakite solid solutions of up to roughly magnesiohornblende ($X_{ts} = 0.50$) were also observed in experimental studies by Jasmund and Schäfer (1972), Cho and Ernst (1991), Smelik et al. (1994), Jenkins et al. (1997), Hoschek (1995), and Najorka and Gottschalk (in preparation). The highest X_{ts} of up to 0.60 in tremolite-tschermakite solid solutions was reported by Cho and Ernst (1991) at 1250 MPa and 900 °C.

It is not yet understood if structural or thermodynamic restrictions are responsible for the limited incorporation of the tschermakite component into tremolite. Measured Al-concentrations for different assemblages at varying bulk compositions show that X_{ts} does not exceed 0.36 at our experimental *P-T* conditions, and calculated X_{ts} -isopleths reveal that X_{ts} is always lower than 0.5 over the entire *P-T* range (Figs. 4a–d). This result suggests that Al-rich tremolite-tschermakite solid solutions are thermodynamically unstable with respect to other phase assemblages. This is also seen in the CMAS(H)-tetrahedron (Fig. 2). We found, for example, that at 700 °C and 500 MPa, bulk composition IV produced amphibole-anorthiteclinochlore-talc with X_{ts} of 0.36 (TS-55; Fig. 4c). If, at identical *P*-*T* conditions, the bulk composition is shifted toward the Al₂O₃ apex, the Al-concentration in amphibole is buffered to some extent by anorthite-clinochlore-talc at relatively low X_{ts} (Fig. 2, IV). If, on the other hand, the P-T conditions are changed to 750 °C and 350 MPa for an identical bulk composition, the new assemblage amphibole-anorthite-enstatite-forsterite becomes stable (TS-22; Figs. 4c and 5). Again, X_{ts} in amphibole is buffered by anorthite-enstatite-forsterite at somewhat lower values within narrow compositional limits. It can be shown that for common bulk compositions, large stability ranges of four-phase solid assemblages exist in P-T-space, which preclude tremolite-tschermakite solid solutions with high tschermakite contents.

Our measured Al-concentrations in amphiboles from the assemblage amphibole-anorthite-quartz-diopside I show distinct differences compared to the results of Jenkins (1994) who investigated the same assemblage between 600-800 °C and 200-700 MPa. Both studies agree insofar as a significant pressure dependence of the Al isopleths in amphibole was detected. However, a comparison of the average pressure dependency (Fig. 6) shows that the pressure effect in our study is much more pronounced. Jenkins (1994) observed an average increase of 0.018 X_{ts} per 100 MPa, whereas our study shows that the pressure increases $0.036 X_{ts}$ per 100 MPa. Differences in both experimental and analytical techniques between our study and that of Jenkins (1994) could explain these discrepancies. In contrast to the runs of Jenkins, we carried out un-reversed runs and one may speculate that the amphibole compositions were in disequilibrium. However, a small compositional scatter and well-ordered amphibole structures indicate that equilibrium conditions were achieved in our experiments. On the other hand,



FIGURE 5. Phase assemblage amphibole-anorthite-enstatiteforsterite produced by bulk composition IV plotted within the CMAStetrahedron with excess water (see also Fig. 4c)



FIGURE 6. Average pressure dependency of amphibole composition from the assemblage amphibole-anorthite-quartz-diopside. Dashed line = this study (un-reversed runs). Dotted line = Jenkins (1994) (reversed runs).

EDS analyses of unpolished grain mounts were used by Jenkins (1994). The precision of this analytical technique is rather low, because uneven surfaces falsify the absorption correction of the characteristic X-rays. At present, it remains unclear whether the un-reversed experimental approach or analytical artifacts of the EDS technique are responsible for the discrepancies observed in amphibole compositions.

Al concentrations in amphiboles produced with bulk composition IV show overall agreement with the results of Cao et al. (1986) on the three-phase solid assemblage amphibole-anorthite-clinochlore (without talc) and on the four-phase solid assemblage amphibole-anorthite-enstatite-forsterite. For the former assemblage, Cao et al. (1986) detected X_{ts} to about 0.40 at 720 °C/1000 MPa using a few EMP measurements of unpolished grain mounts, and in our experiments X_{ts} was 0.29 at 650 °C/350 MPa, and 0.37 at 700 °C/500 MPa. For the latter assemblage, Cao et al. found $X_{ts} = 0.20$ at 795 °C/200 MPa whereas our value is 0.33 at 750 °C/350 MPa. Given the relatively large compositional scatter in our experiments (see Fig. 4c), a similar *P-T-X* dependence of the Al concentrations in amphibole for bulk composition IV is indicated.

THERMODYNAMIC EVALUATION

Thermodynamic properties of tschermakite and magnesiohornblende

For the experimentally observed assemblages I–VI, the corresponding reactions are given by Equations 1–6. Using these reactions, the experimental results are used to extract the thermodynamic properties of the tschermakite end-member and the mixing properties of the tremolite-tschermakite-cummingtonite solid solutions. The equilibrium of each reaction at a given *P* and T is expressed as:

$$\Delta G_r = 0 = \sum_{i}^{k} \mathbf{v}_i \left(G_i^0 + \mathbf{R}T \ln a_i^0 \right) + \mathbf{v}_{\mathbf{H}_2 \mathbf{O}} \mathbf{R}T \ln f_{\mathbf{H}_2 \mathbf{O}}^0$$
(7)

in which G_i^0 is the molar standard Gibbs free energy of the pure phase *i*, n_i its stoichiometric coefficient, *a* its activity, and $f_{\rm H2O}^0$ the fugacity of pure H₂O. Introducing the standard Gibbs free energy of tschermakite, G_{15}^0 , explicitly

$$\sum_{i}^{k} \mathbf{v}_{i} G_{i}^{0} = \sum_{j \neq \mathrm{ts}}^{k-1} \mathbf{v}_{j} G_{j}^{0} + \mathbf{v}_{\mathrm{ts}} G_{\mathrm{ts}}^{0}$$
(8)

and rearranging, Equation 7 becomes:

$$-\mathbf{v}_{ts}G_{ts}^{0} = \sum_{j\neq ts}^{k-1} \mathbf{v}_{j}G_{j}^{0} + \sum_{i}^{k} \mathbf{v}_{i}RT \ln a_{i}^{0} + \mathbf{v}_{H_{2}0}RT \ln f_{H_{2}0}^{0}.$$
 (9)

The standard state of the activity for pure solids is unity at *P* and *T* of interest and the standard state for water is a hypothetical ideal gas at 0.1 MPa and *T* of interest. Considering the reference conditions T^0 and P^0 at 298 K and 0.1 MPa, and introducing the temperature and pressure dependence for G_i^0 , the apparent Gibbs free energy $(\Delta_t H_i^0 - TS_i^0)$ instead of G_i^0 , and the definition of the equilibrium constant *K*, Equation 9 becomes:

$$\Delta_{i}H_{ts}^{0} - TS_{ts}^{0} = -\frac{1}{v_{ts}} \left(\sum_{j\neq ts}^{k-1} v_{j} \left(\Delta_{j}H_{j}^{0} - TS_{j}^{0} \right) + RT \ln K_{(P,T)} - \int_{T}^{T} \int_{T}^{T} \frac{\Delta c_{P}^{0}}{T} dT dT + \int_{P}^{P} \Delta V_{solids}^{0} dP \right).$$
(10)

If the right hand side of Equation 10 is evaluated for Equations 1–6 at various *P*-*T* conditions and plotted against temperature, one obtains a straight line where the enthalpy of formation from the elements ($\Delta_{\rm f} H_{\rm is}^0$) and the negative of the third law entropy ($S_{\rm is}^0$) of tschermakite is determined from the intercept and slope, respectively.

In the following, the right hand side of Equation 10 is assessed for each experimentally observed five-phase assemblage (four solids plus fluid). The required thermodynamic properties ($\Delta_t H_{j}^0, S_{p,i}^0, c_{p,j}^0, V_{j,solid}^0$) of all components are from Gottschalk (1997) except for tschermakite. For tschermakite, $c_{p,s}^0$ and V_{1s}^0 (268.5 cm³/mol) were taken from Holland and Powell (1998) and from Najorka and Gottschalk (in preparation), respectively, and the coefficients of thermal expansion and compression of tremolite (Gottschalk 1997) were used as a first approximation. The fugacity of pure water $f_{H_{20}}^0$ was calculated using the equation of state of Kerrick and Jacobs (1981).

The activities of all phases are required for the calculation of the equilibrium constant (Eq. 10). Because anorthite, forsterite, quartz, and zoisite have end-member compositions, their activities were treated as unity. Deviations from end-member composition were observed in diopside, enstatite, clinochlore, and talc due to incorporation of small amounts of Al (Table 2). Their activities were calculated assuming ideal mixing using compositions from Table 2 and compositional variables from Table 7. Because most experimental runs contained a bromidic solution, the activity of water was slightly reduced. Because of low molalities (Table 1), the activity of H₂O was approximated using Raoult's law ($a_{H_{2O}} = X_{H_{2O}}$).

The activities of tschermakite and tremolite in amphibole solid solutions depend both on site occupancies as well as the degree of short-range ordering. Consequently, the evaluation of their mixing properties is not straightforward. Aluminum substitution into amphibole has been discussed at length in the literature (Hawthorne 1983; Oberti et al. 1995a, 1995b; Jenkins et al. 1997; Welch et al. 1998; Welch and Knight 1999). Recent studies using NMR- and IR-spectroscopy indicate that, in tremo-lite-tschermakite solid solutions, Al occupies the octahedral M2 and M3 sites and the tetrahedral T1 sites (Hawthorne et al. 2000; Najorka and Gottschalk in preparation). Random distribution on these sites is restricted, however, if the rule of Al avoidance on adjacent T1 tetrahedra (Oberti et al. 1995b; Hawthorne 1997) and M2-, M3-octahedra (Hawthorne et al. 2000) is considered. Further restrictions are imposed by local charge balance, which requires that the tetrahedral substitution of Al for Si is accompanied by octahedral substitution of Al for Mg at the neighboring M2 or M3 sites.

The activities of the end-members tremolite and tschermakite are commonly expressed using ideal mixing models that consider substitution on the M2, M3, and T1 sites (e.g., Jenkins 1994; Smelik et al. 1994; Hoschek 1995; Quirion and Jenkins 1998). Local charge balance is assumed to exist to a certain extent in all but one of these ideal-mixing models. Difficulties arise, however, because the amounts of octahedral and tetrahedral sites per formula unit are not equal and the means by which charge is locally balanced are not unique. This adds a contribution to the configurational entropy term. For example, if Al is substituted at an M3 site, local charge can be balanced at four equivalent T1 sites above or below the octahedral band within the amphibole I-beam. Substitution of Al on M2 can be locally charge balanced at two equivalent T1 sites. On the other hand, incorporation of Al on a distinct T1 site can be charge balanced by either a coupled substitution on an M2 or M3 site.

The configurational entropies for various mixing models are shown in Figure 7 and the corresponding expressions for the respective activities are listed in Table 7. The highest entropies are calculated for models that neglect charge balance by assuming total random distribution at the M2 and T1 sites as shown for model f. In contrast to model f, model g (Holland and Powell 1998) considers random mixing at only two of the four T1 sites, which lowers the configurational entropy. Despite this decrease in configurational entropy, model g does not include local charge balance because the substitution of Al at the octahedral and tetrahedral sites is still independent in this case. From the mixing models shown in Table 7, only model c considers true charge balance by using clusters of Si_{T1}Mg_{M2}Si_{T1}, Si_{T1}Al_{M2}Al_{T1}, and Al_{T1}Al_{M2}Si_{T1}. However, because this model adds only a linear compositional term to model b, the resulting expressions for activities from models b and c are identical. The remaining constant after differentiation

$$\frac{\partial S^{con}}{\partial n_i} = -R \ln a_i^{con} \tag{11}$$

of model c is added to the entropy for the tschermakite endmember.

Neither of these models considers Al avoidance, however. On the other hand, the introduced error is probably low because the tremolite-tschermakite solid solutions are in the range between $tr_{100}ts_0$ and $tr_{40}ts_{60}$ and do not extend to compositions richer in Al. Assuming random distribution, even for the highest experimentally observed X_{ts} of about 0.60 (Cho and Ernst

Ideal mixing model	Compositional variable	Ston	<i>a</i> tr	a ts
(a) Al-Mg mixing at one M3-site charge coupled with Al-Si substitution at a "specific"T1-site (one-site coupled mode	$\begin{aligned} \mathcal{X}_{\text{ts}} &= \frac{\mathcal{X}_{\text{Al}}^{\text{M3}}}{2} \\ (\mathcal{X}_{\text{ts}} \leq 0.5) \end{aligned}$	$-\mathrm{R}(\mathcal{X}_{\mathrm{tr}}\ln\mathcal{X}_{\mathrm{tr}}+\mathcal{X}_{\mathrm{ts}}\ln\mathcal{X}_{\mathrm{ts}})$	$(1 - X_{ts})$	X _{ts}
(b) AI-Mg mixing at two M2-sites charge coupled with AI-Si substitution at two "specific" T1-sites (two-site coupled model)	$\mathcal{X}_{IS}=\mathcal{X}_{AI}^{M2}$	$-2R(X_{tr} \ln X_{tr} + X_{ts} \ln X_{ts})$	$(1 - X_{ts})^2$	$\chi^2_{ m ts}$
(c) Mixing of two charge coupled clusters of type Si _{T1} Mg _{M2} Si _{T1} (A), Al _{T1} Al _{M2} Si _{T1} (B), and Si _{T1} Al _{M2} Al _{T1} (C)	$\mathcal{X}_{is} = (1 - \mathcal{X}_{(A)})$ = $2\mathcal{X}_{(B)} = 2\mathcal{X}_{(C)}$	$-2R\left(X_{tt}\ln X_{tt} + X_{ts}\ln\frac{X_{ts}}{2}\right)$	$(1 - X_{ts})^2$	$\chi^2_{ m ts}$
(d) AI-Mg mixing at two M2 and with tetrahedral AI-Si substitution (three-site coupled model)	$X_{ts} = \frac{3}{2} X_{AI}^{M2} = \frac{3}{2} X_{AI}^{M3}$	$-3R\left[\left(\frac{1+2X_{tr}}{3}\right)\ln\left(\frac{1+2X_{tr}}{3}\right)+\frac{2}{3}X_{ts}\ln\frac{2}{3}X_{ts}\right]$	$(1 - \frac{3}{2}X_{ts})^3$	X_{ts}^2 (– 2 X_{ts})
(e) Al-Si mixing at four T1-sites charge coupled with a "specific" octahedral Al-Mg substitution (four-site coupled model)	$X_{ts} = X_{Al}^{M2}$	$-4R\left(\left(\frac{1+X_{tr}}{2}\right)\ln\left(\frac{1+X_{tr}}{2}\right)+\frac{X_{ts}}{2}\ln\frac{X_{ts}}{2}\right)$	$\left(1-\frac{X_{\rm ts}}{2}\right)^4$	$4X_{ts}^{2}\left(1-\frac{X_{ts}}{2}\right)^{2}$
(f) random mixing of AI-Mg at two M2-sites and four AI-Si-sites at four T1-sites (random mixing model)	$X_{\text{ts}} = X_{\text{Al}}^{\text{M2}} - R \left(2(X_{\text{tr}}) \right)$	$\ln X_{tr} + X_{ts} \ln X_{ts} + 4 \left(\left(\frac{1 + X_{tr}}{2} \right) \ln \left(\frac{1 + X_{tr}}{2} \right) + \frac{X_{ts}}{2} \ln \frac{X_{ts}}{2} \right) \right)$	$\left(1-X_{\rm ts}\right)^2 \left(1-\frac{X_{\rm ts}}{2}\right)^4$	$4X_{ts}^{4}\left(1-\frac{X_{ts}}{2}\right)$
(g) random mixing of Al-Mg at two M2-sites and four Al-Si-sites at two T1-sites (reduced random mixing model)	$\mathcal{X}_{\text{ts}} = \mathcal{X}_{\text{Al}}^{\text{M2}}$ -R $\left(2(X_{\text{tr}})\right)$	$\ln X_{tr} + X_{ts} \ln X_{ts} + 2\left(\left(\frac{1+X_{tr}}{2}\right) \ln\left(\frac{1+X_{tr}}{2}\right) + \frac{X_{ts}}{2} \ln\frac{X_{ts}}{2}\right)\right)$	$(1 - X_{\rm ts})^2 \left(1 - \frac{X_{\rm ts}}{2}\right)^2$	$2X_{ts}^{3}\left(1-\frac{X_{ts}}{2}\right)$
clinopyroxene random Al-Mg mixing at one M1-site and Al-Si at two T-sites	$X_{\text{Cats}} = X_{\text{Al}}^{\text{M1}} - R \left(X_{\text{di}} \ln X_{\text{di}} \right)$	$X_{\rm di} + X_{\rm Cats} \ln X_{\rm Cats} + 2\left(\left(\frac{1+X_{\rm di}}{2}\right)\ln\left(\frac{1+X_{\rm di}}{2}\right) + \frac{X_{\rm Cats}}{2}\ln\frac{X_{\rm Cats}}{2}\right)\right)$	$a_{\rm di} = \left(1 - X_{\rm Cats}\right) \left(1 - \frac{X}{2}\right)$	$\left(\frac{Cats}{2}\right)^2$
orthopyroxene random Al-Mg mixing at one M1-site and Al-Si at two T-sites	$X_{Mgts} = X_{Al}^{M1} - R \left(X_{en} \ln N \right)$	$X_{en} + X_{Mgs} \ln X_{Mgs} + 2 \left(\left(\frac{1 + X_{en}}{2} \right) \ln \left(\frac{1 + X_{en}}{2} \right) + \frac{X_{Mgs}}{2} \ln \frac{X_{Mgs}}{2} \right) \right)$	$a_{\rm en} = \left(1 - X_{\rm Mgts}\right) \left(1 - \frac{X}{2}\right)$	$\left(\frac{Mgts}{2}\right)^2$
talc random Al-Mg mixing at one M3-site and Al-Si at two T-sites	$X_{\text{tats}} = X_{\text{Al}}^{\text{M3}} - R \left(X_{\text{ta}} \ln X_{\text{tats}} \right)$	$X_{\text{ta}} + X_{\text{tats}} \ln X_{\text{tats}} + 2\left(\left(\frac{1+X_{\text{ta}}}{2}\right) \ln\left(\frac{1+X_{\text{ta}}}{2}\right) + \frac{X_{\text{tats}}}{2} \ln\frac{X_{\text{tats}}}{2}\right)\right)$	$a_{\rm tc} = \frac{(1 - X_{\rm tats})(2 - X_{\rm tats})}{4}$	<u>)</u> ²
clinochlore random Al-Mg mixing at one M1-site and Al-Si at two T2-sites	$X_{cin} = X_{Mg}^{M1} - R \left(X_{cin} \ln X_{cin} \right)$	$X_{\text{cin}} + X_{\text{ames}} \ln X_{\text{ames}} + 2 \left(\left(\frac{1 + X_{\text{cin}}}{2} \right) \ln \left(\frac{1 + X_{\text{cin}}}{2} \right) + \frac{X_{\text{ames}}}{2} \ln \frac{X_{\text{ames}}}{2} \right) \right)$	$a_{cin} = X_{cin}^2 (2 - X_{cin})$	

TABLE 7. Configurational entropies and ideal mixing models of amphibole and ideal mixing models of Al-bearing phases

Note: X_{A1}^{M2} , X_{A1}^{M3} mole fractions of Al at M2 and M3 in amphibole; X_{A1}^{M1} mole fraction of Al at M1 in pyroxene; X_{A1}^{M3} mole fraction of Al at M3 in talc; X_{M1}^{M1} mole fraction of Mg at M1 in clinochlore.



FIGURE 7. Calculated configurational entropies vs. X_{ts} for the different mixing models a to g listed in Table 7.

1991), the probability of Al occupancy on adjacent tetrahedral or octahedral sites is still less than 9%. Consideration of Al avoidance or more complex mixing models, e.g., adding mixing at M3 to model c, would require the application of Monte-Carlo simulations or cluster variation methods (Vinograd and Putnis 1999).

Using the different activity models a to g from Table 7 and their contributions to the configurational entropy (Fig. 7), a series of $\Delta_{\rm f} H_{\rm is}^0$ and $S_{\rm is}^0$ values was derived (Table 8). The best fit to the experimental data (see r² values in Table 8) was achieved using the two-site coupled model b and the three-site coupled model d. Using the two-site coupled model b for tschermakite, $\Delta_{\rm f} H_{\rm is}^0 = -12528.3 \pm 11.7$ kJ/mol and $S_{\rm is}^0 = 556.5 \pm 12.0$ J/(mol·K) were derived (Fig. 8a). Model b is believed to represent the most robust mixing model for which a closed formulation exists.

Similar calculations were carried out using magnesiohornblende instead of tschermakite as the end-mem-

	Model a	Mode	el b	Model d	Model e	Model f	Model a
	one-site coupled	two-site coupled	including excess enthalpy term	three-site coupled	four-site coupled	random mixing	reduced random mixing
$\Delta_{\rm f} \mathcal{H}^{\rm 0}_{\rm ts}$ (kJ/mol)	-12521.2 ± 13.5	-12528.3 ± 11.7	-12528.7 ± 12.3	-12525.2 ± 12.4	-12523.8 ± 12.2	-12556.3 ± 16.7	-12542.3 ± 13.2
S⁰ _{ts} [J/(K·mo	585.1 ± 13.9)]	556.5 ± 12.0	555.3 ± 14.3	567.4 ± 12.0	570.5 ± 12.6	513.3 ± 17.2	534.9 ± 13.6
2 𝒴 ^{M2} _{Mg −AI} + 𝒴 ^{T1} _{Si−AI} (kJ/mol)	-	-1.2 ± 7.3	-	-	-	-	-
<u>r²</u>	0.9861	0.9884	0.9879	0.9882	0.9880	0.9727	0.9841

TABLE 8. Fits of $\Delta_{\rm f} \mathcal{H}_{\rm ts}^{\rm t}$ and $\mathcal{S}_{\rm ts}^{\rm t}$ for tschermakite and $2 \mathcal{W}_{\rm Mq-Al}^{\rm Mq} + \mathcal{W}_{\rm s+Al}^{\rm Tl}$ using different mixing models



FIGURE 8. Plot of $\Delta_{\rm f} H_{\rm ts}^0 - TS_{\rm ts}^0$ vs. temperature for exchange reactions 1 to 6 using compositional data from Table 2 and mixing models explained in the text. (a) tschermakite, (b) magnesiohornblende.

ber. The best fits were attained with two-site and three-site coupled models. For magnesiohornblende, values of $\Delta_{f} H_{Mehb}^{0} =$ $-12418.7 \pm 5.9 \text{ kJ/mol}$ and $S_{\text{Mghb}}^0 = 562.8 \pm 6.1 \text{ J/(mol \cdot K)}$ were extracted when the two-site coupled model was applied (Fig. 8b).

In addition to the configurational entropy, a term considering excess enthalpy and activity coefficients can be added to Equation 10 to the equilibrium constant $K_{(P,T)}$. Applying a twosite regular solution model for mixing model b, the excess enthalpy for the tremolite-tschermakite solid solution series is expressed by:

$$\begin{aligned} H^{\text{excess}} &= 2X_{\text{tr}}X_{\text{tr}}W_{\text{Mg-Al}}^{\text{M2}} + (1 + X_{\text{tr}})X_{\text{tr}}W_{\text{Si-Al}}^{\text{T1}} = X_{\text{tr}}X_{\text{tr}}\left(2W_{\text{Mg-Al}}^{\text{M2}} + W_{\text{Si-Al}}^{\text{T1}}\right) + X_{\text{tr}}W_{\text{Si-Al}}^{\text{T1}} \\ & (12) \\ RT\ln\gamma_{\text{tr}} &= X_{\text{ts}}^{2}\left(2W_{\text{Mg-Al}}^{\text{M2}} + W_{\text{Si-Al}}^{\text{T1}}\right) \\ \end{aligned}$$

$$RT \ln \gamma_{ts} = X_{tr}^2 \left(2W_{Mg-Al}^{M2} + W_{Si-Al}^{T1} \right) + W_{Si-Al}^{T1}.$$
(14)

The term for γ_{ts} involves a constant (W_{Si-Al}^{T1}) that cannot be distinguished from the parameter $\Delta_f H_{ts}^0$. Therefore, only a value for $2W_{Mg-A1}^{M2} + W_{Si-A1}^{T1}$ of -1.2 ± 7.3 kJ/mol was derived. The low value for $2W_{Mg-A1}^{M2} + W_{Si-A1}^{T1}$ indicates that an additional excess enthalpy term is not necessary to fit the data (see Table 8, columns 3 and 4). In conjunction with this excess enthalpy, the corresponding values for $\Delta_{\rm f} H_{\rm ts}^0$ and $S_{\rm ts}^0$ are -12528.7 ± 12 kJ/ mol and 555.3 \pm 14 J/(mol·K).

Compared with previously reported entropy and enthalpy values (Table 9), the entropy of tschermakite is about 3% higher

TABLE 9. Comparison of thermodynamic data of tschermakite and magnesiohornblende

$\Delta_{\rm f} H^0$ (kJ/mol)	S⁰ [J/(K·mol)]	References
	tschermak	kite
-12528.3 ± 11.7	556.5 ± 12.0	This study (two-site model)
-12540.57 ± 2.91	545.00	Holland and Powell (1998)
-12527.7 ± 16.4	-	Smelik et al. (1994)*
-12534.4 ± 13.0	542.5 ± 12.7	Jenkins (1994)
-12534.67	538.6	Leger and Ferry (1991)†
	magnesiohorn	blende
–12418.7 ± 5.9	562.8 ± 6.1	This study (two-site model)
-	575.4 ± 1.6	Quirion and Jenkins (1998)
-12401.2	575.3 ± 3.5	Smelik et al. (1994)*
–12420.29 ± 12.7	551.0	Holland and Powell (1990)
* Calorimetric study.		

than indicated in previous studies. Within error limits, the entropy is similar to the value from Holland and Powell (1998). Our derived enthalpy of tschermakite agrees with other studies, particularly with the calorimetrically measured value of Smelik et al. (1994).

Our value of the entropy of magnesiohornblende is between the reported values from other studies (Table 9). A significantly higher entropy and a lower enthalpy were suggested by Smelik et al. (1994). Quirion and Jenkins (1998) used Smelik's enthalpy data of magnesiohornblende and also derived a significantly higher entropy. The enthalpy of magnesiohornblende is in reasonable agreement with the value from Holland and Powell (1990).

Calculation of Al isoplethes

The derived thermodynamic data for tschermakite and the two-site coupled mixing model b for tremolite-tschermakite solid solutions were used for calculations of the *P*-*T* phase relations in the CMASH-system (Figs. 4a–d). For the assemblages amphibole-anorthite-quartz-diopside and amphibole-anorthite-quartz-talc, the resulting X_{ts} isopleths for Al incorporation in amphibole are nearly horizontal in the *P*-*T* plane (Figs. 4a and 4b) and provide excellent geobarometers. The X_{ts} isopleths in amphibole for the assemblage amphibole-anorthite-clinochlore-talc are both pressure and temperature dependent and show a negative slope in *P*-*T* plane, whereas for amphibole-anorthite-enstatite-forsterite, the slope is positive (Fig. 4c). The X_{ts} isopleths for the assemblage amphibole-zoisite-quartz-talc show only a slight pressure but a strong temperature dependence (Fig. 4d).

In general, the measured $X_{\rm ts}$ values in amphiboles are nicely reproduced by the calculated isopleths, at least within the stability fields of the assemblages amphibole-anorthite-quartz-diopside, amphibole-anorthite-quartz-talc, amphibole-anorthite-enstatiteforsterite, and amphibole-zoisite-quartz-talc. Less agreement exists for the assemblage amphibole-anorthite-clinochlore-talc where isopleths indicate somewhat enhanced incorporation of Al compared to the measured data. This difference is possibly due to the less certain thermodynamic properties of clinochlore in chlorite solid solutions. In general, the phase relations in the CMASH-system were calculated accurately with the proposed thermodynamic data of tschermakite and the two-site coupled mixing model. Observed small deviations between experimental and calculated Al concentrations are mostly due to the fact that ideal mixing was assumed along the tremolite-tschermakite join. At present, however, information about ordering of Al³⁺ between different sites, e.g., M2 and M3, in Al-bearing tremolite is insufficient to calibrate a more rigorous model.

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