

Tremolite-richterite amphiboles: Synthesis, compositional and structural characterization, and thermochemistry

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ABSTRACT

The substitution $\text{NaNa}\square_{-1}\text{Ca}_{-1}$, which fills the A site, has been investigated in amphiboles close to the join tremolite-richterite $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2\text{-Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$. At 1123 K, compositions of amphiboles synthesized from bulk compositions on this binary are displaced towards magnesio-cummingtonite $[\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2]$, such that average compositions are better represented by the pseudobinary tremolite₉₂magnesio-cummingtonite₈-richterite. Major-element compositions and H₂O contents are close to theoretical values for eight samples synthesized along this join. Unit-cell parameters vary smoothly with composition, $a \sin \beta$ showing the greatest increase as Na fills the A site. High-resolution transmission electron microscopy demonstrates that the amphiboles are highly ordered, with only the tremolite-rich compositions containing any chain multiplicity faults.

Enthalpies of drop solution of the synthetic amphiboles (+quartz), measured in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 977 K, vary from 937 ± 13 kJ/mol for $\text{Tr}_{92}\text{Mc}_8$ to 1036 ± 7 kJ/mol for Ri_{100} and show a systematic asymmetric deviation from linearity, suggesting subregular solution behavior. Interaction parameters obtained from a third-order polynomial fitted to the drop-solution data are $W_{\text{Ri}} = -163 \pm 84$ kJ/mol and $W_{\text{Tr}} = 81 \pm 58$ kJ/mol. A proposed mixing model comprises random mixing of Na and Ca on the M4 site and of Na and vacancies on the A site, along the whole solid solution. The region of negative ΔH_{mix} at low richterite contents may arise from ordering of Na onto minimum-energy A-site positions and from interaction with M4 cations, decreasing towards richterite, with the resulting increasing disorder destabilizing richterite-rich compositions. Configurational entropy of mixing models requires W_{Ri} and W_{Tr} to be reduced if the whole solid solution is stable at the synthesis temperature of 1123 K, but not if richterite-rich compositions are metastable.

The similarity between ΔH_{mix} of tremolite-richterite and fluor-tremolite-fluor-edenite amphiboles (Graham and Navrotsky, 1986) suggests that the A site controls the mixing energetics of both solid solutions, with A-site positional ordering and interactions with other cations playing an important role. Because the richterite and edenite exchanges are the two most important A-site substitutions that occur in calcic amphiboles, the same factors will influence the stability of all amphiboles with any Na in the A site. Therefore, metamorphic calcic amphiboles with small A-site occupancies should be stabilized relative to compositions with zero or high A-site occupancies, and any natural amphiboles with high A-site occupancies must have crystallized at a high temperature and presumably cooled relatively fast, thereby preventing exsolution.

INTRODUCTION

Amphiboles are important H₂O-bearing minerals in a wide range of igneous and metamorphic rock types in the crust and mantle, where their compositions are often strongly dependent on the pressure and temperature of crystallization. Therefore, they have the potential to be

of considerable use in geothermobarometry, provided that compositions can be accurately determined and thermodynamic data are available. However, few natural amphiboles have simple compositions, making description and thermodynamic treatment difficult. Fortunately their description can often be simplified by treating compositions as sums of a single simple end-member, or “additive component,” and fractions of cation (and anion) substitutions, or “exchange vectors” (using the terminology

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of Thompson, 1981). Therefore, if thermodynamic properties are known for common additive components and exchange vectors, it should be possible to derive data for almost any complex amphibole composition.

The derivation of thermodynamic data for simple amphibole compositions has been the goal of many experimental studies over the last few decades, but the majority of these have been hindered by experimental difficulties, leading to discrepancies between data obtained in the different studies. For example, until recently, accurate chemical analysis of starting materials and experimental products was difficult because of fine grain size, and examination of fine structure and cation order-disorder was seldom undertaken, resulting in considerable uncertainty as to the value of using synthetic samples as analogues of well-ordered natural samples. Fortunately, modern analytical techniques have greatly facilitated sample characterization, which should therefore be a very important part of any experimental study on amphiboles. Some important techniques used for sample characterization in this, as well as previous, studies are as follows:

1. Electron microprobe analysis (EMPA) using back-scattered electron imaging, allowing the operator to image and analyze crystals of only a few micrometers in diameter.
2. Independent H₂O analysis: When an amphibole is analyzed by EMPA, it is usually assumed that there are two OH groups per formula unit, occupying the two structural O3 sites, and the analysis is normalized to 23 O atoms. But when H₂O is analyzed by an independent technique, it is not uncommon to find an excess (e.g., Kuroda et al., 1975; Maresch and Langer, 1976). This may have a significant effect on amphibole thermochemistry but would go undetected without analysis using a reliable technique such as H extraction by radio-frequency induction heating.
3. High-resolution transmission electron microscopy (HRTEM): The ideal amphibole structure consists of double chains of SiO₄ tetrahedra, 9 Å wide along y, and extending infinitely along z. However, this is simply an intermediate member of the continuous polysomatic biopyrribole series between single-chain pyroxenes and infinite-chain sheet silicates, and therefore it is not uncommon for amphiboles to incorporate chains of multiplicity where $m \neq 2$ (chain multiplicity faults, CMF), which may have a significant effect on the amphibole's thermodynamic properties.
4. Vibrational spectroscopy: Although EMPA provides a valuable means of characterizing the average chemical composition over a large number of unit cells, infrared and Raman spectroscopy can often be used to estimate site occupancies and to provide information on structural disorder and cation order-disorder. However, because a typical amphibole spectrum is very complex, to date only the O-H stretching region has been investigated in any great detail (e.g., Hawthorne, 1983). The amphiboles synthesized in this study have been investigated using vibrational spectroscopy, and the results will be presented in a separate paper (Pawley and McMillan, in preparation; see also McMillan and Pawley, 1990).

The most popular method for deriving thermodynamic data for minerals is through phase equilibrium experiments. However, this technique is only straightforward for compositions with univariant breakdown reactions involving other phases with known thermodynamic properties. Divariant reactions of amphiboles are common (e.g., the breakdown of tremolite, Graham et al., 1989), and amphibole reactions frequently also involve a melt (e.g., the high-temperature breakdown of richterite), hindering the use of phase equilibrium experiments to obtain accurate data for end-members. For these compositions it is necessary to derive thermodynamic data by a different method. High-temperature solution calorimetry (Navrotsky, 1977) is a useful method for obtaining enthalpy of formation data (ΔH_f°) through the measurement of enthalpy of solution (ΔH_{sol}), in an appropriate solvent, of pure natural or synthetic samples and component oxides. Also, the enthalpy of mixing (ΔH_{mix}) of a solid solution can be calculated from ΔH_{sol} of compositions along the solid solution, from which activity-composition relations may be derived. The application of oxide-melt solution calorimetry to hydrous phases is a fairly recent development, and therefore to date the only amphibole solid solution for which solution calorimetric data exist is the fluor-tremolite-fluor-edenite solid solution (Ca₂Mg₅Si₈O₂₂F₂-NaCa₂Mg₅Si₇AlO₂₂F₂), defined by the edenite exchange (NaAl□₁Si₋₁, where □ represents a vacancy in the A site of the amphibole structure) (Graham and Navrotsky, 1986). Experimental procedure applied in the present study will be discussed in some detail below.

Another substitution involving the A site that can occur in tremolite and other calciferous amphiboles is the richterite exchange, NaNa□₁Ca₋₁, defining the solid solution between tremolite and richterite [Na₂CaMg₅Si₈O₂₂(OH)₂]. Tremolite is one of the simplest end-member amphibole compositions and is not only a common component of amphiboles from a wide range of geological environments, but also one of the few compositions found naturally in almost pure form, and for which thermodynamic data exist (e.g., Jenkins et al., 1991; Welch and Pawley, 1991). Each cation site in the C2/m structure is occupied by one type of cation: the octahedral sites M1, M2, and M3 by Mg, the eightfold-coordinated M4 by Ca, and the tetrahedral sites T1 and T2 by Si. The large A-site cavity is empty. The exchange reaction NaNa□₁Ca₋₁ involves the simultaneous substitution of Na into the A site and Na into M4, such that in end-member richterite the A site is fully occupied by Na, and equal numbers of Ca and Na mix on M4.

Richterite-rich amphiboles are rare in nature, requiring unusually Na-rich and Al-poor bulk compositions. However, small amounts of the richterite exchange are common in natural metamorphic amphiboles. Although not

TABLE 1. Mineral abbreviations used in this paper

Am	Amphibole	
Cpx	Clinopyroxene	
Di	Diopside	CaMgSi ₂ O ₆
En	Enstatite	Mg ₂ Si ₂ O ₆
Mc	Magnesian-cummingtonite	Mg ₇ Si ₈ O ₂₂ (OH) ₂
Opx	Orthopyroxene	
Qz	Quartz	SiO ₂
Ri	Richterite	Na ₂ CaMg ₅ Si ₈ O ₂₂ (OH) ₂
Tr	Tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂

always apparent from the examination of compositional analyses, which are often recast in terms of the additive component tremolite and exchange vectors NaAlSi₋₁ (edenite exchange) and NaSiCa₋₁Al₋₁ (plagioclase exchange), both of these exchanges typically increase with increasing metamorphic grade in amphiboles in basaltic rocks metamorphosed in the greenschist to amphibolite facies (Robinson et al., 1982). Therefore, because



the richterite component must also increase with metamorphic grade. A study of the richterite substitution should therefore complement the similar investigation of the edenite substitution between fluor-tremolite and fluor-edenite (Graham and Navrotsky, 1986), because a comparison of results should clarify the nature of the energetics of A-site substitutions, site-splitting and disorder on the A site, and the energetic importance of interactions between A-site cations and other crystallographic sites for the stabilization of amphiboles with full A sites.

This study was therefore begun with the intention of doing solution calorimetry on several synthetic compositions along the solid solution from Ri towards Tr (amphibole and other mineral abbreviations are listed in Table 1), after first carefully characterizing samples to ensure that they were stoichiometric and well ordered. A well-characterized sample of almost-pure natural tremolite would be used instead of the synthetic end-member, as all previous attempts to synthesize tremolite had failed to produce the pure end-member. In those studies, amphiboles coexisted with Di ± Qz (e.g., Boyd, 1959; Jenkins, 1983, 1987) and must therefore have been nonstoichiometric. We also found this to be the case for amphiboles synthesized in this study from several bulk compositions along the Ri-Tr join. Therefore, to eliminate Di impurities from experimental products, we modified slightly the bulk compositions studied, such that they lay along the pseudobinary join Ri-Tr₉₂Mc₈. This join is considered to be close enough to the ideal binary for measured thermodynamic properties to be applicable to the binary. We also saturated our bulk compositions in SiO₂, in an attempt to prevent dissolution of the tremolite component of the amphiboles in the coexisting fluid (which is explained in more detail below).

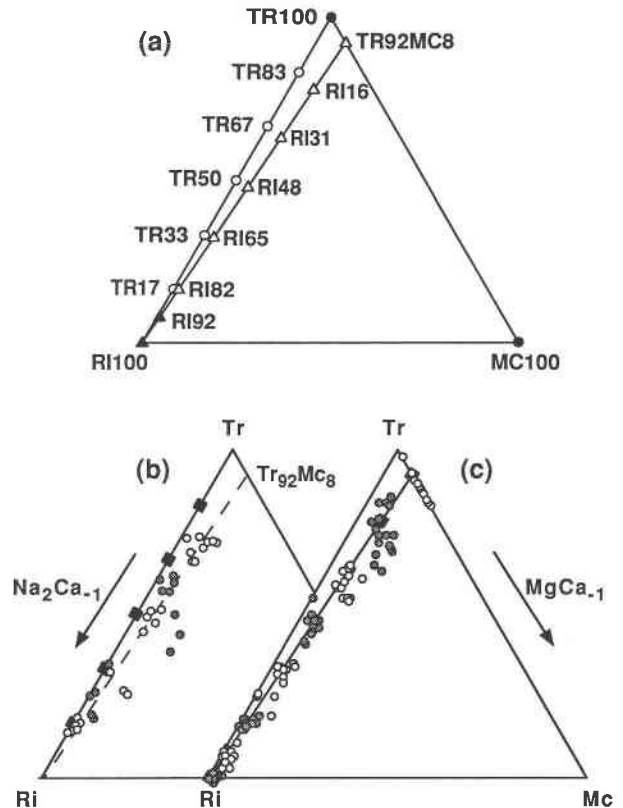


Fig. 1. (a) Compositions of gels and gel mixes used as starting materials in this study, in terms of Tr, Ri, and Mc components: filled triangles = gels used in synthesis of Tr₉₂Mc₈-Ri₁₀₀ amphiboles; open triangles = gel mixes used in synthesis of Tr₉₂Mc₈-Ri₁₀₀ amphiboles; open circles = gels used only in initial attempts to synthesize Tr₁₀₀-Ri₁₀₀ amphiboles; filled circles = gels used in mixes only. (b) Compositions determined by EMPA of amphiboles synthesized from bulk compositions (shown by filled squares) on the Ri₁₀₀-Tr₁₀₀ binary. Analyses for each bulk composition are shown by alternating groups of open and filled circles. Broken line is the join Ri-Tr₉₂Mc₈. (c) Compositions determined by EMPA of amphiboles synthesized from bulk compositions (+ Qz) on the Tr₉₂Mc₈-Ri₁₀₀ pseudobinary.

EXPERIMENTAL CONDITIONS

Compositions of starting materials are plotted in terms of Tr, Ri, and Mc components in Figure 1a. Compositions along the Tr-Ri join (Tr₁₀₀, Tr₈₃, Tr₆₇, Tr₅₀, Tr₃₃, Tr₁₇, and Ri₁₀₀), one composition on the join Tr₉₂Mc₈-Ri₁₀₀ (Ri₉₂), and end-member Mc (Mc₁₀₀) were prepared as gels following the method of Biggar and O'Hara (1969). The other compositions on the Tr₉₂Mc₈-Ri₁₀₀ join (Tr₉₂Mc₈, Ri₁₆, Ri₃₁, Ri₄₈, Ri₆₅, and Ri₈₂) were made by mixing accurately weighed amounts of gels Tr₁₀₀ to Tr₁₇ with appropriate amounts of gel Mc₁₀₀ and grinding under acetone for 15 min. Silica gel was also carefully weighed and mixed with these compositions, in increasing amounts toward Tr₉₂Mc₈. No SiO₂ was added to Ri₁₀₀ and Ri₉₂; Ri₈₂ already contained an excess of 0.4 wt% SiO₂ [re-

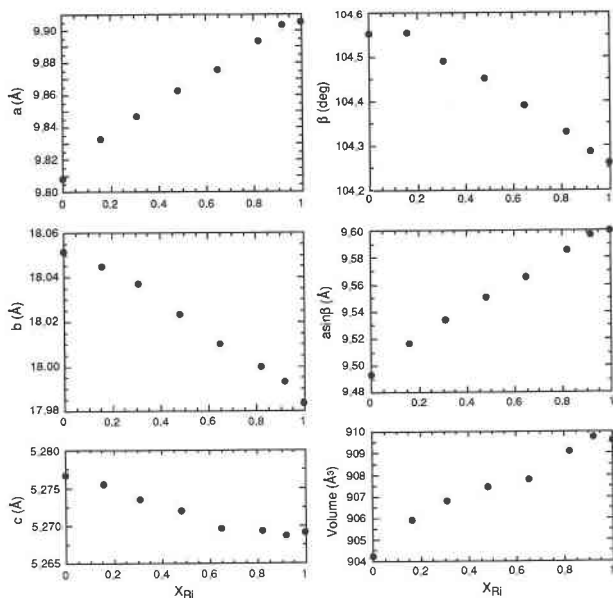


Fig. 2. Unit-cell parameters of synthetic $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ amphiboles.

vealed by X-ray fluorescence (XRF) analysis of the gels; 2 wt% SiO_2 was added to Ri_{65} , 5 wt% to Ri_{48} , 9 wt% to Ri_{31} and Ri_{16} , and 10 wt% to $\text{Tr}_{92}\text{Mc}_8$. XRF analysis of the gels suggested that oxide contents were within $\pm 1\%$ of ideal values, and EMPA of fused samples of the gel mixes indicated that CaO , MgO , and SiO_2 were within $\pm 0.1\text{--}0.2$ wt% of assumed values (Na was not analyzed because of its rapid loss under the electron beam).

Experiments were conducted at 2 kbar in externally heated cold-seal pressure vessels and at 6 kbar in internally heated pressure vessels. Operation and calibration of these vessels are described by Welch and Pawley (1991). Cold-seal vessels have the advantage over internally heated pressure vessels in accommodating larger sample sizes, but the increased pressure afforded by the latter was found to enhance reaction kinetics in the tremolite-rich samples. For each experiment, 250–700 mg of sample was sealed in an annealed Pt capsule 4 mm in diameter with 0.5–30.0 wt% H_2O . Weight loss on puncturing capsules at the conclusion of an experiment confirmed the presence of excess H_2O during the experiment.

ANALYSIS OF EXPERIMENTAL PRODUCTS

The detailed analysis of products involved use of the following techniques:

1. Optical microscopy and scanning electron microscopy (SEM): These techniques were used to search for trace amounts of nonamphibole phases and to observe crystal habit. Amphibole crystals were prismatic to acicular, $< 1 \mu\text{m}$ to tens of micrometers long and up to $20 \mu\text{m}$ wide.
2. EMPA: The Cameca Camebax electron microprobe at the University of Edinburgh, operated in the wave-

length-dispersive mode, was used to obtain chemical analyses of the synthetic amphiboles. Analyses were rejected if the oxide total was more than 2.5 wt% above or below the expected value (97.8–98.0 wt%).

3. X-ray diffraction (XRD): Powder XRD was used to identify impurities and also to observe changes in amphibole unit-cell parameters as a function of composition. A Guinier camera was used for this, with Si as an internal standard. On the basis of previous experience, errors in the cell parameters are assumed to be larger than those given by the refinement program (which are smaller than the symbols in Fig. 2).
4. H extraction: H_2O contents of the amphiboles were determined by H extraction using the facility at the Scottish Universities' Research and Reactor Centre at East Kilbride, Scotland. Radio-frequency induction heating under vacuum of dried samples results in decomposition and release of structural H_2O at ~ 1500 °C. This is reduced to H by passing over U at 750 °C, and its volume measured manometrically. Errors in measured wt% H_2O are inversely related to the total amount of H released. The calibration was checked by measuring the H_2O content of a sample of natural tremolite of known H_2O content (Graham et al., 1984).
5. High-resolution transmission electron microscopy: Amphibole fine structure was examined by HRTEM at the Department of Earth Sciences, University of Cambridge, England, using a Jeol JEM 100CX operated at 100 kV and fitted with a cartridge allowing a $\pm 10^\circ$ tilt about two orthogonal axes. A suspension of the sample in ethanol was deposited onto holey carbon film over a Cu grid 2 mm in diameter. Crystals were small enough that thin edges over holes in the film, essential for high-resolution imaging, were quite common. However, their acicular habit generally resulted in sedimentation with c in the plane of the C film, and, because crystals were typically flatter in the b direction than in a, with b also in this plane. Hence, while $\mathbf{b}^*\text{-c}^*$ images showing (0k0) fringes were easily obtained, $\mathbf{a}^*\text{-c}^*$ images were more difficult and $\mathbf{a}^*\text{-b}^*$ images virtually impossible to obtain. A 40- μm aperture allowed 5 (0k0) beams to form a $\mathbf{b}^*\text{-c}^*$ image, in which the 9- \AA repeat (0k0) fringes were resolvable at the typical 220 000 \times magnification. Two to five images of small crystals of each sample were obtained.

RESULTS OF EXPERIMENTS ON THE TREMOLITE-RICHTERITE BINARY

All experiment conditions and products are listed in Table 2. Optical examination and XRD revealed that the only bulk composition on the Tr-Ri binary that yielded $> 99\%$ amphibole was Ri_{100} . Experiments T-R 2(a) to T-R 2(e) contained predominantly amphibole, but also all contained Di in increasing proportions, Qz in increasing amounts from (b) to (e), and a trace of En in (e) and possibly in (d). EMP analyses of the amphiboles (Fig. 1b) show a significant scatter, indicating a degree of disequilibrium. This may have been reduced were longer exper-

TABLE 2. Results of synthesis experiments on the Ri_{100} - Tr_{100} binary and $Tr_{92}Mc_8$ - Ri_{100} pseudobinary

Exp.	Starting material	<i>P</i> (kbar)	<i>T</i> (°C)	H ₂ O content (wt%)	<i>t</i> (h)	Products*
T-R 2(a)	Tr ₁₇	2	850	3	160	Am, <u>Di</u>
T-R 2(b)	Tr ₃₃	2	850	3	160	Am, <u>Di</u> , <u>Qz</u>
T-R 2(c)	Tr ₅₀	2	850	3	160	Am, <u>Di</u> , <u>Qz</u>
T-R 2(d)	Tr ₆₇	2	850	3	160	Am, <u>Di</u> , <u>Qz</u> , <i>En?</i>
T-R 2(e)	Tr ₈₃	2	850	3	160	Am, <u>Di</u> , <u>Qz</u> , <i>En</i>
T-R 31	Tr ₉₂ Mc ₈ + Qz	6	850	27	160	Am, <u>Qz</u> , <u>Di</u> , <i>En</i>
T-R 33	Ri ₄₈ + Qz	2	850	12	165	Am, <u>Qz</u> , <i>Di</i>
T-R 34	Ri ₆₅ + Qz	2	850	9	165	Am, <u>Qz</u>
T-R 35	Ri ₁₆ + Qz	2	840	21	165	Am, <u>Qz</u> , <u>Di</u> , <i>En</i>
T-R 36	Ri ₈₂	2	850	3	166	Am, <u>Qz</u>
T-R 38(a)	T-R 31**	6	850	24	160	Am, <u>Qz</u>
T-R 38(b)	Tr ₉₂ Mc ₈ + Qz	6	850	22	160	Am, <u>Qz</u> , <u>Di</u> , <i>En</i>
T-R 39	Ri ₃₁ + Qz	2	850	15	160	Am, <u>Qz</u>
T-R 41	T-R 33**	2	850	13	188	Am, <u>Qz</u> , <i>Di</i>
T-R 42	T-R 35**	2	840	3	188	Am, <u>Qz</u> , <u>Di</u> , <i>En</i>
T-R 43	T-R 42**	6	850	17	161	Am, <u>Qz</u>
T-R 44	T-R 31 + T-R 38(b)**	6	850	24	165	Am, <u>Qz</u>
T-R 49	Ri ₉₂	2	850	3	162	Am, <i>Di</i> , <u>Qz</u>
T-R 55	Ri ₁₀₀	6.3–7.0	850	3	284	Am, <i>Di</i>
T-R 56	T-R 55**	6.3–7.0	850	0.5	159	Am, <i>Di</i>

* In order of decreasing abundance, with minor phases (~1%) underlined and trace phases (≤1%) italicized.

** Repeat experiments of products containing suspected metastable phases, which were ground under acetone for ~15 min before the synthesis was repeated. Quoted H₂O content is the wt% added to the repeated synthesis.

iment durations employed. However, it is evident that compositions are displaced from the Tr-Ri binary. The displacement increases towards Tr, such that the envelopes of compositions lie approximately on the straight line Ri- $Tr_{92}Mc_8$. $Tr_{92}Mc_8$ is close to the composition of the amphibole that Jenkins (1987) inferred to be stable for the tremolite bulk composition at 850 °C ($Tr_{90\pm3}Mc_{10\pm3}$). One of the exchange reactions involved in the displacement away from the binary is $MgCa_{-1}$, which occurs in the Tr component of the amphiboles through the reaction $Tr = Tr-Mc_{SS} + Di + Qz + H_2O$, thus accounting for the presence of Di + Qz in these samples. The presence of En in two samples suggests that the reaction $Tr = Di + En + Qz + H_2O$ is also occurring, the Qz perhaps dissolving in the fluid, as suggested by Jenkins (1987). This reaction reduces the Tr content of the amphiboles, shifting their compositions towards Ri and Mc. It was because of the observed deviations in amphibole composition from the bulk compositions and the resulting additional phases present that we mixed Mc gel with the original gels to make bulk compositions on the Ri- $Tr_{92}Mc_8$ pseudobinary and added extra SiO₂.

RESULTS OF EXPERIMENTS ON THE Ri_{100} - $Tr_{92}Mc_8$ PSEUDOBIARY

Optical examination

Synthesis conditions and results are listed in Table 2. The gel mixes, though initially assumed to be amorphous, in fact contained substantial pyroxene (Opx and Cpx), which had crystallized while sintering the gels during their preparation. Reaction of this pyroxene was slow in the Tr-rich samples but was enhanced by the presence of a large volume of fluid and by grinding incompletely re-

acted samples and rereacting with additional H₂O. The reaction was considered complete when either a pyroxene-free assemblage (Am + Qz) was obtained, or when additional cycles did not reduce the amount of pyroxene. For example, optical examination of samples T-R 33 and 41 (Ri₄₈ + Qz) suggested comparable amounts of Di in both; examination of T-R 55 and 56 (Ri₁₀₀) produced similar results. Therefore, these two bulk compositions cannot be stoichiometric. However, such small percentages of impurities (<1%) will have a negligible effect on the measured bulk properties (discussed in a later section). Examination by SEM of these samples revealed no additional impurities.

EMPA

Amphibole EMP analyses (Fig. 1c) show a scatter that exceeds analytical error and increases with increasing Tr content. Clearly the sluggish reaction kinetics associated with the persistence of metastable pyroxene have prevented compositional homogenization in the Tr-rich samples. Nevertheless, the envelopes of analyses are discrete, and the mean analyses are in close agreement with the theoretical values, suggesting that a complete solid solution exists at the synthesis temperature of 850 °C.

Unit-cell parameters

Unit-cell parameters are plotted as a function of composition in Figure 2. The trends of increasing *a* and decreasing *b*, *c* and β from $Tr_{92}Mc_8$ to Ri₁₀₀ are consistent with previously observed differences between fluor-tremolite (Cameron and Gibbs, 1973) and fluor-richterite (Cameron et al., 1983). The large increase in *a* and decrease in β is primarily a result of the substitution of Na

TABLE 3. H₂O contents of synthetic Tr₉₂Mc₈-Ri₁₀₀ amphiboles (+quartz) determined by H extraction

Sample	Mass (mg)	$\mu\text{mol H}$ in sample	wt% H ₂ O in sample	Ideal wt% H ₂ O
Tr ₉₂ Mc ₈	35.7	43.9	2.22 ± 0.12	2.01
Ri ₁₆	35.5	38.6	1.96 ± 0.13	2.02
Ri ₃₁	35.8	36.8	1.85 ± 0.14	2.02
Ri ₄₈	35.7	39.4	1.99 ± 0.13	2.10
Ri ₆₅	38.0	44.0	2.09 ± 0.11	2.16
Ri ₈₂	35.9	42.4	2.25 ± 0.11	2.20
Ri ₁₀₀	35.8	42.4	2.14 ± 0.12	2.20

Note: Uncertainties on H₂O contents were derived from 95% confidence brackets on measured $\mu\text{mol H}$.

into the empty A site, though β also decreases as Na substitutes for Ca on M4 (Papike et al., 1969).

All parameters show a slight deviation from ideality: a , b , and β have a positive deviation, and c has a negative deviation. The deviation in a is the main cause of a positive ΔV_{mix} in Tr-rich compositions. A positive ΔV_{mix} is not uncommon in mineral solid solutions (e.g., fluor-tremolite-fluor-edenite, Graham and Navrotsky, 1986). However, in the present study, because we expect that the real uncertainties in the cell parameters are considerably greater than those given in the cell refinement program, we consider it reasonable to approximate the data by a straight line, corresponding to a zero ΔV_{mix} , and implying no pressure effect on activity-composition relations. The continuous variation in cell parameters with composition is a further indication of complete solid solution at the synthesis temperature.

H₂O determination

H₂O contents of the synthetic Ri₁₀₀-Tr₉₂Mc₈ amphiboles are given in Table 3. Most are ideal within the 95% confidence brackets on the H extraction technique, suggesting that they do not contain any excess H₂O.

HRTEM

CMFs were clearly visible in HRTEM images, but the image quality was not sufficient to determine whether they consisted of single or multiple chains. CMF density was fairly uniform among samples of the same bulk composition. Low densities for all samples indicated that they are all highly ordered. The Tr-rich compositions contain a few CMFs (Fig. 3a is typical of Tr₉₂Mc₈), which decrease in abundance toward Ri₁₀₀, which is apparently CMF-free (Fig. 3b). In a^*c^* images ($h00$) fringes were occasionally observed, and their regular spacing indicates that there are no stacking (chain-arrangement) faults. Electron diffraction patterns are sharp, with no streaking of reciprocal lattice points. The similarity of the patterns of all of the samples confirms that the lattice spacings vary smoothly along the join Ri₁₀₀-Tr₉₂Mc₈.

Synthetic amphiboles typically contain more CMFs than their natural counterparts (e.g., Maresch and Czank, 1983, 1988). However, it has been observed that alkali-rich amphiboles may be less susceptible to CMFs than other

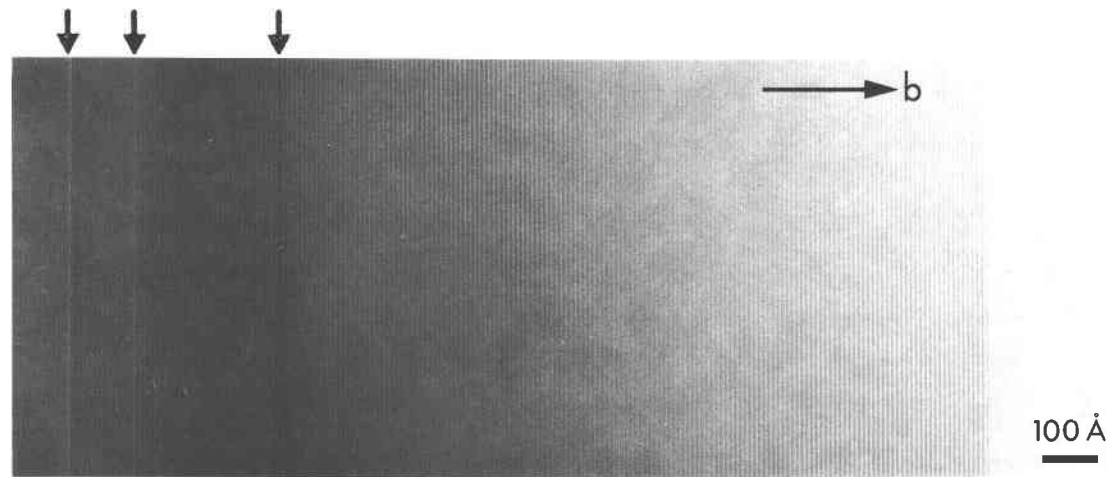
compositions (e.g., Koons, 1982; Maresch and Czank, 1983). The composition in this study (Ri₁₀₀) that contains the fewest defects is also the most alkali-rich. However, it is interesting that, even in the Na-free end-member Tr₉₂Mc₈, the number of visible CMFs is less than in published images of other synthetic amphiboles, e.g., manganese magnesium amphiboles (Maresch and Czank, 1988), and tremolite synthesized from the bulk compositions Ca₂Mg₅Si₈O₂₂(OH)₂ and Ca_{1.8}Mg_{5.2}Si₈O₂₂(OH)₂ (Maresch and Czank, 1988; Ahn et al., 1991). Maresch and Czank (1988) suggested that silica activity plays an important role in determining the frequency of CMFs in synthetic amphiboles, such that higher silica activity leads to fewer CMFs. This could account for the greater degree of order of Tr₉₂Mc₈, synthesized with 10 wt% excess Qz, than of synthetic tremolite. Furthermore, as the tremolite synthesized from its own bulk composition coexists with diopside, it is also more likely to contain single-chain CMFs of diopside composition. In common with the increase in compositional variation, the increase in CMF density along the join Ri₁₀₀-Tr₉₂Mc₈ is considered to be related to the synthesis kinetics, with the most Tr-rich amphiboles still containing a minor component of pyroxene in the form of CMFs.

DROP-SOLUTION CALORIMETRY

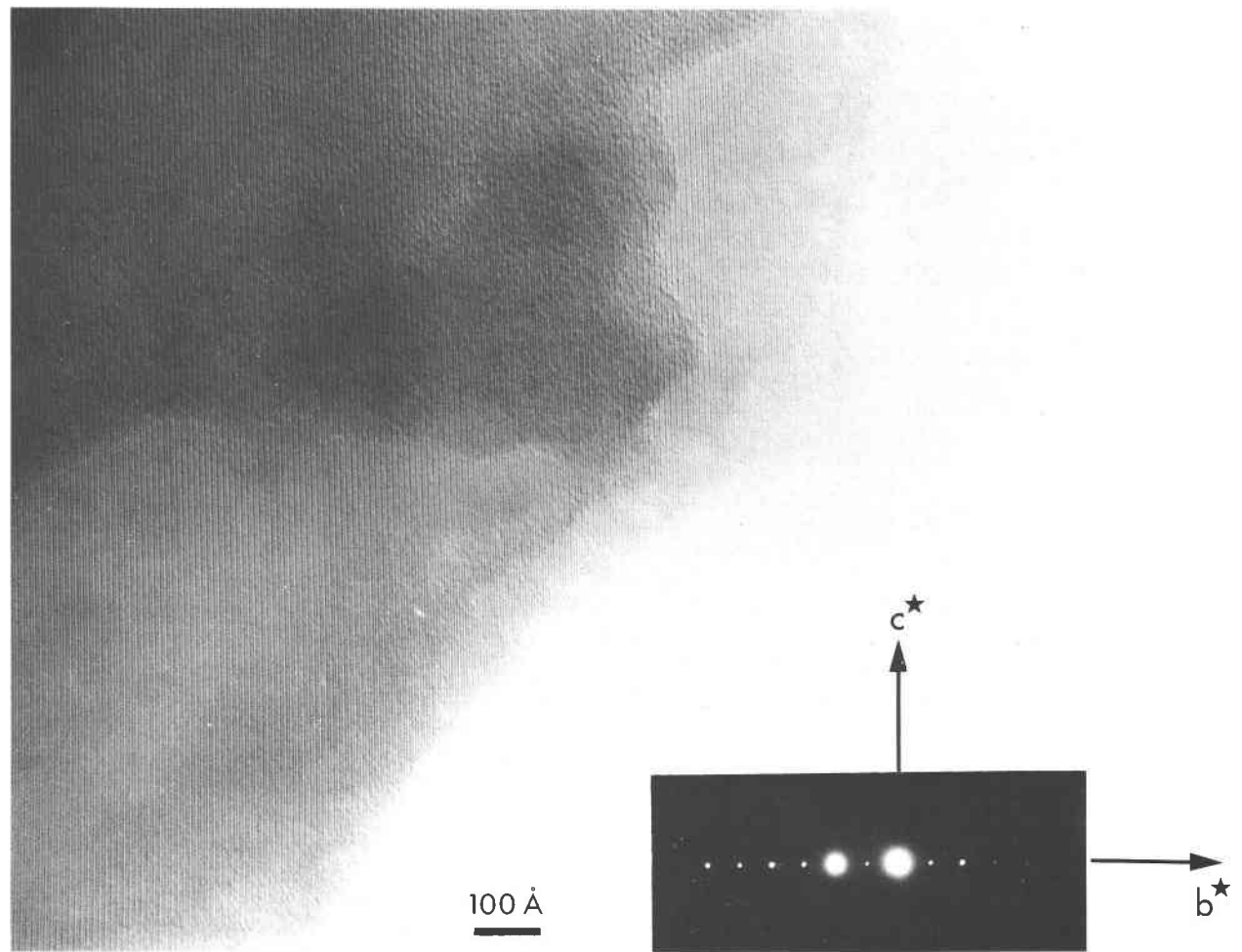
Technique

Enthalpies of solution of synthetic Tr₉₂Mc₈-Ri₁₀₀ amphiboles were measured in a Calvet-type twin microcalorimeter at Princeton University. The experimental technique is based on that described by Navrotsky (1977). There are two identical sample chambers, kept at a constant and uniform temperature of 977 K. Two thermopiles, connected in opposition, allow measurement of changes in heat flow in one chamber relative to the other. In both chambers a Pt crucible contains 30 g of lead borate solvent (2PbO·B₂O₃). A long vertical glass tube above the crucible allows samples to be dropped from room temperature into the molten solvent, where they dissolve. The integrated thermopile output is proportional to the combined heat effect of heating the sample and the dissolution reaction. This experiment is called a drop-solution experiment to distinguish it from a solution experiment, in which the sample is preequilibrated at calorimeter temperature before dissolution. We did not adopt the latter procedure because we had some evidence of possible energetic and structural changes of Ri-rich samples held at 977 K for several hours.

In any experiment on a hydrous mineral, the final state of H₂O evolved during dissolution is an important question that must be addressed. Previous studies on Mg(OH)₂, Ca(OH)₂, and micas along the phlogopite-eastonite join (Clemens et al., 1987; Circone and Navrotsky, 1992) showed that reasonably successful solution calorimetry could be performed in a static air atmosphere and appeared to show that H₂O interacted exothermically with molten 2PbO·B₂O₃ near 973 K. However, more recent work (Rapp and Navrotsky, 1990) suggests that not all of



(a)



(b)

Fig. 3. (a) HRTEM image of $(0k0)$ fringes in synthetic $\text{Tr}_{72}\text{Mc}_8$. CMFs are indicated by arrows. (b) HRTEM image of $(0k0)$ fringes in synthetic Ri_{100} . No CMFs are visible. Inset is an electron diffraction pattern.

TABLE 4. Drop-solution enthalpies of synthetic $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ amphiboles

Sample	ΔH_{drop} (kJ/mol)			Mean	$(2s/\sqrt{N})$
$\text{Tr}_{92}\text{Mc}_8$	916.3	924.4	934.3	937.4	12.7
	940.4	954.3	954.6		
	953.5	960.2	963.3		
Ri_{16}	963.4	969.8	976.8	971.7	10.7
	990.6	996.3			
	968.5	979.8	980.0		
Ri_{31}	981.6	994.8	998.9	984.8	10.0
	968.0	984.8	987.1		
	992.5	998.4	1002.9		
Ri_{48}	1009.4	1010.6	1020.0	997.1	10.6
	976.4	979.5	995.7		
	1000.0	1001.5	1005.8		
Ri_{65}	1017.3	1020.8	1022.4	1013.3	5.5
	1003.3	1011.3	1011.7		
	1013.5	1015.9	1024.0		
Ri_{82}	1010.1	1019.8	1020.2	1021.3	5.6
	1020.5	1027.3	1029.8		
	1022.1	1030.6	1036.1		
Ri_{100}	1038.1	1043.5	1045.5	1036.0	7.0

the H_2O remains dissolved in the solvent under static air conditions and that a more reproducible final state, in which no H_2O is dissolved (and its enthalpy of interaction with the solvent is zero or close to zero), can be achieved under a flow of gas of a few cubic meters per second. Ar gas was used in the present study.

Each calorimetric experiment consisted of the drop of an accurately weighed pressed pellet, ~ 5 mm in diameter and weighing 10–12 mg, down the silica-glass tube into the Pt crucible containing $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solvent. The calorimetric peak returned to base line in 25–30 min, indicative of rapid dissolution, and no abnormalities were seen. Calibration, as in previous studies, was by the Pt-drop method (Navrotsky 1977).

Results

For each composition, 6–9 measurements of enthalpies of drop solution (ΔH_{drop}) were made. These were corrected for the presence of quartz in the samples using the following enthalpies for quartz: $\Delta H_{\text{sol}} = -3.863$ kJ/mol (Navrotsky, personal communication) and $H_{977} - H_{295} = 41.976$ kJ/mol (calculated using C_p data of Berman, 1988). Corrected enthalpies of drop-solution of the synthetic $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ amphiboles are given in Table 4. Note that the magnitude of ΔH_{drop} is near 1000 kJ/mol, and the reported uncertainties (2 standard deviations of the mean) are near ± 10 kJ/mol, representing about 1% of the total heat effect and a reproducibility as good as that seen in Pt-drop calibrations. Nevertheless, because of the large molecular weight of amphiboles, the uncertainties on the thermodynamic mixing properties are relatively large. This inherent limitation on solution calorimetry of amphiboles and similar phases has already been noted by Graham and Navrotsky (1986).

ENTHALPY OF MIXING

The enthalpy of mixing of the solid solution at room temperature (295 K) is given by

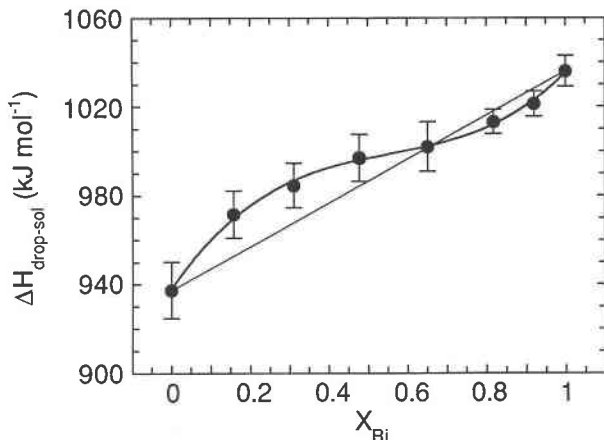


Fig. 4. Mean enthalpy of drop solution of synthetic $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ amphiboles, with $2s/\sqrt{N}$ error bars. Curve shows subregular solution fitted to the data; straight line represents ideal mixing.

$$\Delta H_{\text{mix}} = X\Delta H_{\text{drop, Ri}} + (1 - X)\Delta H_{\text{drop, Tr}_{92}\text{Mc}_8} - \Delta H_{\text{drop, ss}} \quad (1)$$

To simplify discussion of mixing properties, we will make three assumptions. First, we will assume dilute solution behavior in the solvent. Although not tested rigorously in this system, solution calorimetry on many other systems using lead borate solvent, including, most recently, phlogopite-eastonite (Circone and Navrotsky, 1992), has shown that the enthalpy of solution of a mechanical mixture of end-members does not differ from the weighted average of the end-member enthalpies, confirming this assumption and supporting the use of Equation 1 to obtain ΔH_{mix} . Second, we will assume that the enthalpy of mixing obtained for 295 K applies equally well to any high temperature, T . This implies that the heat capacity of the solid solution is the same as that of an appropriate average of end-member heat capacities in the range 295 K to T . This reasonable assumption is supported by the absence of any anomalous behavior in vibrational spectra along the solid solution (Pawley and McMillan, in preparation). Third, we will assume that the heat of mixing along the binary Tr-Ri join is the same as that along $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$. Lacking any evidence to the contrary, we consider this reasonable.

The mean values of ΔH_{drop} (Fig. 4) appear to deviate in a systematic fashion from a straight line joining the end-members. Because the deviation is systematic and also similar to that obtained for fluor-tremolite-fluor-edenite amphiboles by Graham and Navrotsky (1986), we suggest that, though an ideal-mixing straight line could be fitted through all of the error bars shown in Figure 4, a subregular solution model is justified. A third-order polynomial was fitted by least squares to all of the values of ΔH_{drop} : ΔH_{drop} (kJ/mol) = $937.99 + 260.11X - 406.17X^2 + 243.34X^3$, where $X = X_{\text{Ri}}$.

The value of ΔH_{mix} , obtained by subtracting this equa-

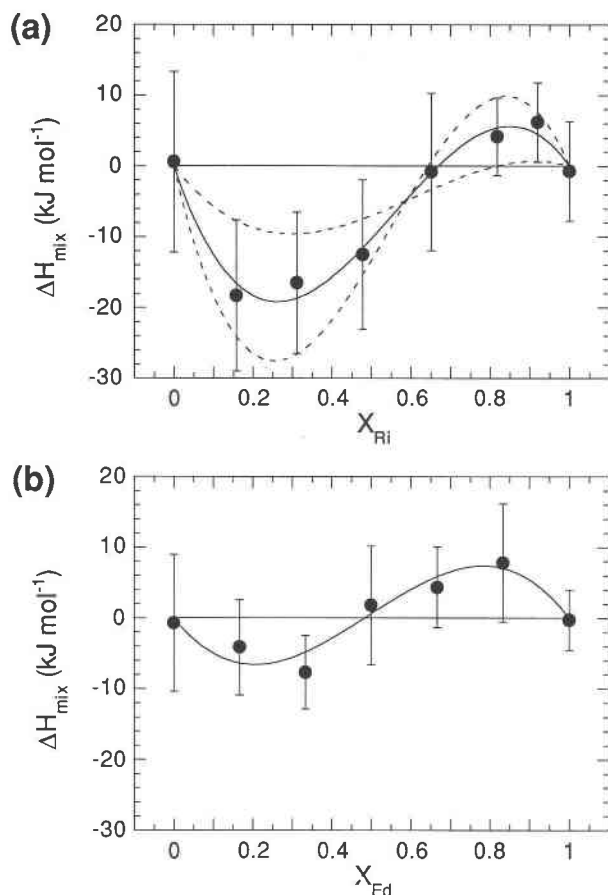


Fig. 5. (a) Enthalpy of mixing of synthetic $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ amphiboles, with calculated ΔH_{mix} curve. Broken curves were calculated for maximum and minimum values of W_{Ri} and W_{Tr} , as explained in the text. (b) Enthalpy of mixing of synthetic fluor-tremolite-fluor-edenite amphiboles (from Graham and Navrotsky, 1986).

tion from the straight line between calculated end-member ΔH_{drop} values, is shown in Figure 5a. The interaction parameters are $W_{\text{Ri}} = -162.82$ kJ/mol, $W_{\text{Tr}} = 80.52$ kJ/mol.

Uncertainties in these were obtained from the equation $\Delta H_{\text{mix}}/X_{\text{Tr}}X_{\text{Ri}} = W_{\text{Ri}} + X_{\text{Ri}}(W_{\text{Tr}} - W_{\text{Ri}})$ by plotting $\Delta H_{\text{mix}}/X_{\text{Tr}}X_{\text{Ri}}$ against X_{Ri} (Fig. 6) and using lines of maximum and minimum slope, which pass through all the error bars to give maximum and minimum values of W_{Ri} and W_{Tr} . Uncertainties are taken to be half of the difference between these values. Therefore, $W_{\text{Ri}} = -163 \pm 84$ kJ/mol, $W_{\text{Tr}} = 81 \pm 58$ kJ/mol.

Likely deviations in ΔH_{drop} values arising from the < 1 wt% diopside impurities in some of the samples and maximum deviation in quartz content from assumed values of 0.1 wt% are calculated to be ≤ 0.1 and $\leq 0.05\%$, respectively. These are much smaller than the above errors on the interaction parameters.

The enthalpy of mixing of the amphiboles implies that substituting Ri into Tr is initially significantly stabilizing, whereas substituting Tr into Ri is initially slightly desta-

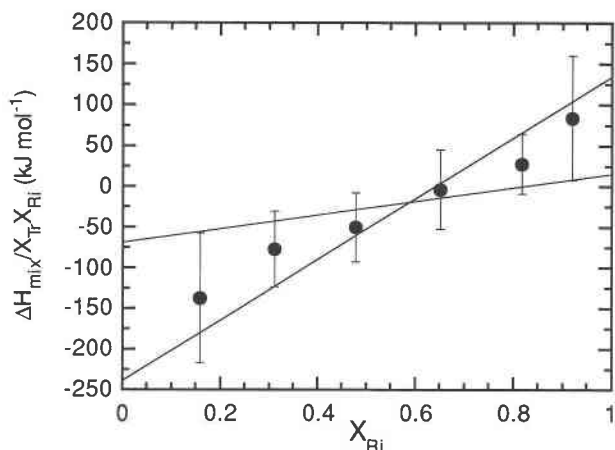


Fig. 6. Plot of $\Delta H_{\text{mix}}/X_{\text{Tr}}X_{\text{Ri}}$ against X_{Ri} , showing lines of maximum and minimum slope used to calculate uncertainties associated with W_{Ri} and W_{Tr} .

bilizing. This is analogous to the situation in fluor-tremolite-fluor-edenite, where $W_{\text{F-Tr}} = 74.73$ kJ/mol, $W_{\text{F-Ed}} = -70.12$ kJ/mol (Graham and Navrotsky, 1986; see also Fig. 5b), as discussed further below.

ENTROPY OF MIXING

In order to be able to calculate phase relations and to comment on the stability range of the Tr-Ri solid solution, the entropy of mixing, ΔS_{mix} , must be characterized. The ΔS_{mix} comprises a vibrational entropy term and a configurational entropy term (S_{cfg}). The vibrational term can be obtained by the measurement of heat capacities of end-members and solid solutions from 0 K to the temperature of interest. This was impractical in this study because there was insufficient sample for adiabatic calorimetry. Third-law entropies can also be estimated from vibrational spectra (e.g., Kieffer, 1985). However, to do so requires all infrared- and Raman-active vibrational modes to be determined, a task beyond the scope of this study. However, the observed relative insensitivity of vibrational frequencies to composition along the solid solution (McMillan and Pawley, 1990) implies little variation in this term, and hence probably a vibrational entropy of mixing close to zero. Therefore, only S_{cfg} needs to be considered in deriving a ΔS_{mix} model.

S_{cfg} results from mixing of different species on a single structural site and is given by the relationship

$$S_{\text{cfg}} = - \sum_j n_j R (\sum_i X_i^j \ln X_i^j) \quad (2)$$

where n_j is the number of sites, j , on which mixing occurs, X_i^j is the mole fraction of species i on site j , and the mixing on each site is assumed to be random. The simplest mixing model we can consider for Tr-Ri amphiboles comprises random Na-Ca mixing on M4 and Na-□ mixing on the A site. S_{cfg} arising from both of these are calculated below and shown by curves 1 and 2 in Figure 7.

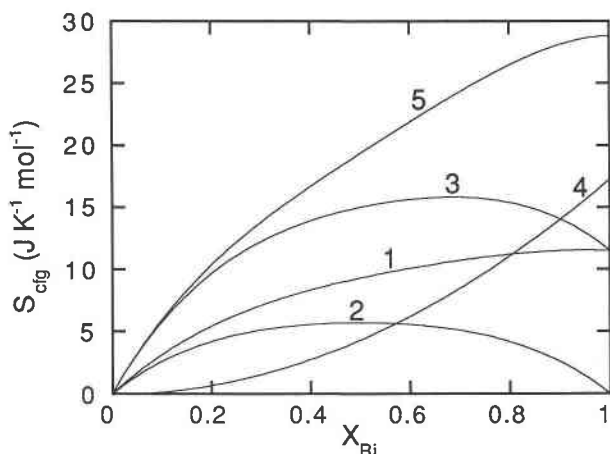


Fig. 7. Configurational entropy (S_{cfg}) of $\text{Tr}_{100}\text{-Ri}_{100}$ amphiboles calculated for various mixing models: 1 = Na-Ca mixing on M4; 2 = Na-□ mixing on the A site; 3 = 1 + 2; 4 = increasing A-site positional disorder toward Ri_{100} ; 5 = 1 + 2 + 4.

Na-Ca mixing on M4

There are two M4 sites per formula unit, in Tr both occupied by Ca, and in Ri occupied by Ca and Na. The contribution to S_{cfg} from random mixing of Na and Ca on these sites is $S_{\text{cfg}} = -2R(X_{\text{Na}}^{\text{M4}} \ln X_{\text{Na}}^{\text{M4}} + X_{\text{Ca}}^{\text{M4}} \ln X_{\text{Ca}}^{\text{M4}})$ where $X_{\text{Na}}^{\text{M4}} = 1 - X_{\text{Ca}}^{\text{M4}} = 0.5 X_{\text{Ri}}$.

Na-□ mixing on the A site

There is one A site per formula unit, vacant in Tr and occupied by Na in Ri. Without A-site splitting, which is discussed below, random mixing on this one site contributes $S_{\text{cfg}} = -R(X_{\text{Na}}^{\text{A}} \ln X_{\text{Na}}^{\text{A}} + X_{\text{□}}^{\text{A}} \ln X_{\text{□}}^{\text{A}})$ where $X_{\text{Na}}^{\text{A}} = 1 - X_{\text{□}}^{\text{A}} = X_{\text{Ri}}$.

With the assumption that random mixing occurs on both M4 and the A site along the entire solid solution, their combined contribution to S_{cfg} is given by the sum of the above two contributions and is shown by curve 3 in Figure 7.

Such a simple mixing model, involving no site coupling or interactions, is consistent with the positive ΔH_{mix} at the Ri end of the solid solution, where mixing of cations of different sizes may increase structural strain energies. However, the negative ΔH_{mix} at the Tr end of the solid solution suggests additional stabilizing interactions. These might be related to order-disorder of Na on different A-site positions.

Positional disorder on the A site

Positional disorder on the A site has been recognized in synthetic and natural amphiboles since Papike et al. (1969) observed highly anisotropic electron density at the A site in an X-ray refinement of potassium richterite, which they interpreted as positional disorder about the $A(2/m) 2b$ position, mainly confined to the mirror plane $Am 4i$, but with residual density along the diad $A2 4g$. Hawthorne and Grundy (1978) proposed that the nature of the disorder is composition dependent, with Na or-

dering into $A2$ and K into Am , whereas Cameron et al. (1983) suggested that cation bond-strength requirements are important, and so Na occupies the general position, $8j$, and K $4i$. More recently, Docka et al. (1987), using model energy calculations, suggested that in richterite and edenite the most probable position for the A-site cation is $8j$, though a significant number will occupy $2b$, $4g$, and $4i$ positions. Their energy minimization calculations stabilize richterite relative to a structure in which all A-site cations are in the $2b$ position by about 100 kJ/mol. The magnitude of this stabilization energy suggests that variations in A-site positions along the Tr-Ri solid solution may be expected to have a significant effect on ΔH_{mix} . Below, we will therefore also calculate S_{cfg} for a model in which ordering of Na onto minimum energy positions and interaction with M4 cations stabilizes Tr-rich compositions, whereas with increasing Ri content, an increase in randomness of A-site positional occupancy causes a decrease in stabilization.

The contribution to S_{cfg} that would arise from complete A-site positional disorder along the whole solid solution is calculated by assuming that the A-site is split into eight positions of equal probability of occupancy [$2 \times A2$, $2 \times Am$, $4 \times A(2/m)$]. In each filled A site only one of these eight positions is occupied, and S_{cfg} is a maximum for equal occupancy of each position. Therefore, because the number of occupied A sites = X_{Ri} , X_{Ri} can be substituted for n_j in Equation 2, and $X_j' = 0.125$. For complete disorder, $S_{\text{cfg}} = -RX_{\text{Ri}} \ln 0.125$. This is shown as curve 4 in Figure 7, multiplied by X_{Ri} to take into account the fact that there is only complete disorder in end-member Ri; the disorder is assumed (for simplicity) to increase linearly from being fully ordered at $X_{\text{Ri}} = 0$ to fully disordered at $X_{\text{Ri}} = 1$.

A-site splitting should perhaps be considered as purely vibrational and not configurational, in which case the total S_{cfg} of Tr-Ri amphiboles is simply the sum of S_{cfg} arising from Na-Ca mixing on M4 and Na-□ mixing on the A site (curve 3 in Fig. 7). Adding the possible effect of increasing A-site disorder to this results in S_{cfg} curve 5 in Figure 7 (the sum of curves 1, 2, and 4). It is seen that, whether or not A-site splitting is important, along most of the solid solution S_{cfg} increases with increasing X_{Ri} , which is consistent with the observation from infrared and Raman spectra that cation disorder increases toward Ri (McMillan and Pawley, 1990). However, this increase in S_{cfg} continues all the way along the join only for the model involving increasing A-site positional disorder towards Ri. The ΔS_{mix} curves calculated relative to the straight line between the end-points for curves 4 and 5 are shown in Figure 8.

FREE ENERGY OF MIXING

For a solid solution to be stable, the free energy of mixing (ΔG_{mix}) must be less than zero for all intermediate compositions along the solid solution, and also there must be only one minimum in the ΔG_{mix} curve. Comparison of the mean ΔH_{mix} curve obtained in this study with both

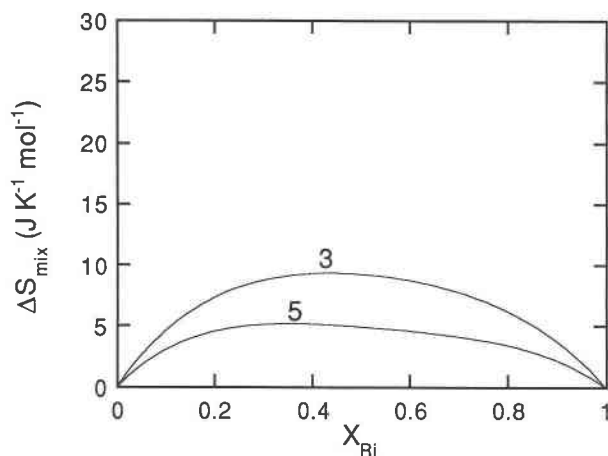


Fig. 8. Configurational entropy of mixing (ΔS_{mix}) of $\text{Tr}_{100}\text{-Ri}_{100}$ amphiboles calculated for the mixing models represented by curves 3 and 5 in Fig. 7.

models of ΔS_{mix} derived above (with and without A-site positional disorder) reveals that both of them are incompatible with complete stability at 850 °C. Therefore, either W_{Ri} and W_{Tr} are too high or the solid solution is metastable at 850 °C. Considering first our preferred S_{cfg} model incorporating A-site positional disorder and assuming stability of the solid solution, we calculate that a reduction of W_{Ri} and W_{Tr} by 70% of their errors, to $W_{\text{Ri}} = -104$ kJ/mol and $W_{\text{Tr}} = 40$ kJ/mol, allows ΔG_{mix} to be everywhere <0 . These values are well within the 95% confidence limits, and Figure 9 shows the resulting ΔG_{mix} as temperature decreases in 200° steps from 1000 °C. Because these interaction parameters are the maximum that allow the solid solution to be stable at 850 °C, at all lower temperatures there is a region of positive ΔG_{mix} , which expands with decreasing temperature. Low-temperature annealing experiments of Ri-rich compositions, followed by characterization by TEM and spectroscopy, would be instructive to test the prediction of a solvus in the solid solution at <850 °C. However, if the solid solution is metastable at 850 °C, the values of W_{Ri} and W_{Tr} are not necessarily too high. In this case we would expect annealing experiments at 850 °C to lead to unmixing, whereas annealing at some higher temperature would not. Using the mean values of W_{Tr} and W_{Ri} , we calculate that the solvus temperature, $T_{\text{solvus}} \approx 2300$ K.

In our model in which A-site positional disorder does not contribute to S_{cfg} , the higher values of ΔS_{mix} for intermediate compositions mean that W_{Tr} and W_{Ri} do not have to be reduced so far to allow the solid solution to be stable at 850 °C. Also, if the solid solution is metastable, then for the mean values of W_{Tr} and W_{Ri} , $T_{\text{solvus}} \approx 1350$ K.

COMPARISON WITH FLUOR-TREMOLITE-FLUOR-EDENITE AND IMPLICATIONS FOR NATURAL COMPOSITIONS

Fluor-tremolite-fluor-edenite is another amphibole solid solution defined by an A-site exchange, for which

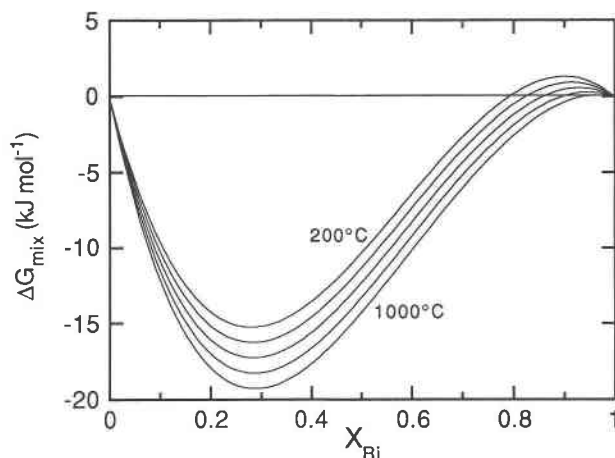


Fig. 9. Free energy of mixing (ΔG_{mix}) of $\text{Tr}_{100}\text{-Ri}_{100}$ amphiboles calculated using $W_{\text{Ri}} = -104$ kJ/mol, $W_{\text{Tr}} = 40$ kJ/mol, and assuming A-site positional disorder contributes to ΔS_{mix} .

Graham and Navrotsky (1986) obtained a ΔH_{mix} curve similar to that obtained in this study, with a positive interaction parameter for tremolite and a negative interaction parameter for the end-member with the A site filled. The similarity between ΔH_{mix} of the two solid solutions is striking and suggests that the A site controls the mixing energetics of both. Moreover, A-site positional ordering and interactions are suggested to be important in both solid solutions. In this study, A-site positional displacements and interactions with M4 cations may explain the negative ΔH_{mix} at low X_{Ri} , whereas Graham and Navrotsky (1986) interpret their negative ΔH_{mix} in Tr-rich compositions in terms of preferential ordering of Na into A2 sites and interaction with A1 in tetrahedral T1 sites. As these two exchanges are the only simple coupled substitutions involving A-site filling that can be written for calcic amphiboles, this potential for A-site cations to occupy more than one position and interact with other cations may be important for stabilizing all natural amphiboles with any small A-site occupancy.

The negative and positive regions of ΔG_{mix} for both synthetic solid solutions are consistent with compositions of natural amphiboles. For example, occupancy of the A site of metamorphic calcic amphiboles by Na lies in the range 0–0.4 and clusters around ~ 0.25 (Robinson et al., 1982), close to the minimum values of ΔG_{mix} . Also, the majority of amphiboles with high A-site occupancy are igneous (e.g., pargasitic hornblendes), and therefore presumably crystallized at sufficiently high temperatures for ΔG_{mix} to be reduced.

ESTIMATES OF ENTHALPY OF FORMATION OF TREMOLITE AND RICHTERITE

The enthalpy of drop-solution data may be used to derive estimates of enthalpies of formation of tremolite and richterite from the elements at 298 K by writing calorimetric cycles involving simple component minerals for which enthalpy of solution, enthalpy of formation,

TABLE 5. Enthalpies of solution and formation and heat contents of minerals used to calculate enthalpies of formation of tremolite and richterite

Mineral	ΔH_f^* (kJ/mol)	$H_{977}-H_{298.15}^{**}$ (kJ/mol)	ΔH_{sol}^\dagger (kJ/mol)	ΔH_{drop}^\ddagger (kJ/mol)	Source of ΔH_{sol} data
Diopside	-3200.6	150.5	85.4		Navrotsky et al. (1980)
Periclasé	-601.5	31.8	4.6		Navrotsky (pers. comm.)
β -quartz	-908.6	41.8	-3.9		Navrotsky (pers. comm.)
Low albite	-3935.1	186.7	84.8		Carpenter et al. (1985)
Corundum	-1675.7	75.2	33.0		Navrotsky (unpubl.)
Brucite	-925.9			134.5	Navrotsky (unpubl.)
Tremolite§				958.0	this study
Richterite				1036.0	this study

* The ΔH_f data from Berman (1988).

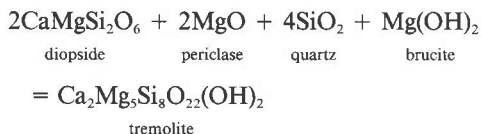
** $H_{977}-H_{298.15}$ data calculated using C_p coefficients given in Berman (1988).

† The ΔH_{sol} data measured in molten $2PbO \cdot B_2O_3$ near 973 K.

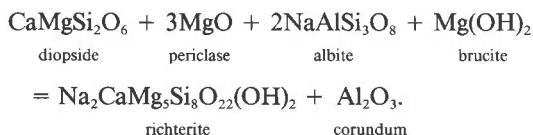
‡ The ΔH_{drop} data measured in molten $2PbO \cdot B_2O_3$ near 977 K under flowing Ar.

§ The tremolite is a natural sample from the Edinburgh University collection; its composition is given in Welch and Pawley (1991).

and heat capacity data exist. For tremolite and richterite we can write the following reactions:



and



Using the thermodynamic data given in Table 5, we calculate $\Delta H_f(\text{Tr}) = -12290.0$ kJ/mol, $\Delta H_f(\text{Ri}) = -12245.4$ kJ/mol. As noted in the legend to Table 5, the sample of tremolite used was not the synthetic $\text{Tr}_{92}\text{Mc}_8$ composition, but a natural sample. Its composition is close to ideal. We have not calculated any errors on the above values of ΔH_f , but we assume that they will be quite large, considering that we are combining data obtained in more than one laboratory and at more than one solvent temperature. We have also not attempted to calculate any phase equilibria using our data, as the large errors on ΔH_f would translate into large uncertainties in the pressure-temperature locations of reactions. However, the value for $\Delta H_f(\text{Tr})$ is in reasonable agreement with the value obtained from phase equilibrium experiments using both the same natural sample (-12299.48 ± 14.84 kJ/mol, Welch and Pawley, 1991) and synthetic tremolite (-12302.90 ± 7.05 kJ/mol, Jenkins et al., 1991).

CONCLUSIONS

1. At 2 kbar and 850 °C, bulk compositions along the $\text{Tr}_{100}\text{-Ri}_{100}$ binary yield amphiboles that coexist with diopside \pm quartz \pm enstatite. Their compositions are displaced off the ideal binary such that average compositions are better represented by the $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ pseudobinary.

2. At 2–6 kbar and 850 °C, bulk compositions along the join $\text{Tr}_{92}\text{Mc}_8\text{-Ri}_{100}$ (plus quartz) react completely to amphibole plus quartz in a single experiment or in two experiments with intermediate grinding.

3. EMPA and H extraction experiments demonstrate that the amphiboles are essentially stoichiometric, and contain no excess H_2O .

4. Powder XRD unit-cell refinements indicate that cell parameters vary smoothly with composition, and ΔV_{mix} is approximately linear. Therefore, there is negligible volume of mixing and hence no pressure effect on activity-composition relations.

5. All amphiboles are shown in HRTEM images to be structurally well ordered, with no CMFs in Ri_{100} and only a few in $\text{Tr}_{92}\text{Mc}_8$. Their use as analogues for well-ordered natural samples is therefore justified.

6. Enthalpies of drop solution vary from 937 ± 13 kJ/mol for $\text{Tr}_{92}\text{Mc}_8$ to 1036 ± 7 kJ/mol for Ri_{100} and can be fitted by a subregular solution model with $W_{\text{Ri}} = -163 \pm 84$ kJ/mol and $W_{\text{Tr}} = 81 \pm 58$ kJ/mol.

7. The mixing energetics are explained in terms of random mixing of Na and Ca on M4 and Na and vacancies on the A site along the whole solid solution, together with possible ordering of Na onto minimum-energy A-site positions in Tr-rich compositions and increasing disorder towards Ri.

8. For the whole solid solution to be stable at 850 °C, a configurational entropy of mixing model consistent with the above mixing properties requires W_{Ri} and W_{Tr} to be reduced by at least 70% of their errors, i.e., to -104 kJ/mol and 40 kJ/mol, respectively. However, Ri-rich compositions may be metastable.

9. The similarity in mixing energetics to those of the fluor-tremolite-fluor-edenite solid solution obtained by Graham and Navrotsky (1986) suggests that the energetics of substitutions involving the A site are important in determining the thermodynamic mixing behavior of natural amphiboles. A-site positional ordering and interaction with other cations might stabilize compositions with small A-site occupancies, and, because of the low-tem-

perature miscibility gap at high A-site occupancies, the only compositions stable in this region must crystallize at high temperatures.

10. A preliminary calculation of the enthalpies of formation from the elements at 298 K of an almost-pure natural tremolite and the synthetic richterite gives ΔH_f (Tr) = -12290.0 kJ/mol and ΔH_f (Ri) = -12245.4 kJ/mol.

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