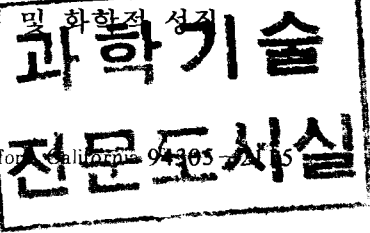


High-Pressure Synthesis and Chemistry of Amphibole Solid Solutions along the Join Tremolite-Tschermakite

투각섬석-처마카이트 각섬석 고용체의 고압합성 및 화학적 성질



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ABSTRACT: Calcic amphiboles along the tremolite (Tr)-tschermakite(Ts) join were synthesized using a piston-cylinder apparatus. At 750-850°C and 12-21 kb, amphibole+corundum coexist with zoisite(\pm talc, chlorite, and Mg-staurolite), but with anorthite(\pm chlorite, spinel, pyroxenes, and sapphirine) at lower P. At 900°C, amphibole+corundum+clinopyroxene(\pm anorthite, forsterite, sapphirine, and garnet) are stable over the P range 12-18 kb. These amphibole-bearing assemblages are replaced at high P by clinopyroxene+talc+chlorite+zoisite at 650-750°C, and at higher temperatures by garnet+clinopyroxene(\pm zoisite, orthopyroxene, and Mg-staurolite). Synthetic amphiboles with Ts>~45 mol % contain as much as 0.15 excess cations per formula unit(pfu) based on 23 oxygens(anhydrous formula), whereas less tschermakitic ones are deficient in cation occupancy by up to 0.18 pfu. This trend is attributed to the di/trioctahedral substitution in Ca-amphiboles. Compositions of synthetic amphiboles display systematic changes with P and T governed by coexisting mineral assemblages. The Ts content ($=[8-Si-Na]/2$) increases with increasing T ($\partial Ts/\partial T \sim 0.1 \text{ mol \% K}^{-1}$) in the range 750-850°C, but remains nearly constant at 850-900°C. Pressure dramatically affects the Ts content of Ca-amphiboles: it increases with P at 8-12 kb ($\partial Ts/\partial P = 2-3 \text{ mol \% kb}^{-1}$), but significantly decreases at 12-21 kb ($\partial Ts/\partial P = -2.5 \text{ mol \% kb}^{-1}$). Hence, the most tschermakitic amphiboles, containing 60 \pm 5 mol % Ts, or 1.2 \pm 0.1 tetrahedral Al, occur at 12 kb and 850-900°C. Compositions of Ca-amphiboles defined by a simple reaction, 3 Tr+2 zoisite+7 corundum+H₂O=5 Ts, are reversed and used to estimate thermodynamic parameters of tschermakite assuming ideal mixing of Tr-Ts solid solutions. Predicted standard molal entropy and enthalpy of tschermakite are: $S^{\circ} = 566.9 \pm 13.7 \text{ J mol}^{-1} \text{ K}^{-1}$ and $H^{\circ} = -12518.36 \pm 15.17 \text{ kJ mol}^{-1}$.

요약: 투각섬석(Tr)-처마카이트(Ts) 각섬석을 피스톤-실린더 고압실험장치를 사용하여 합성하였다. 750-850°C와 12-21kb에서는 각섬석+코런덤이 조이사이트(\pm 활석, 녹니석 및 Mg-심자석)와 공존하지만, 낮은 압력하에서는 회장석(\pm 녹니석, 스피넬, 휘석 및 사피린)과 나타난다. 이들 각섬석을 포함한 광물조합들은 650-750°C에서 단사휘석+활석+녹니석+조이사이트로 압력이 증가함에 따라 치환되고, 더 높은 온도에서는 석류석+단사휘석(\pm 조이사이트, 사방휘석 및 Mg-심자석)으로 치환된다. Ts>~45mol%인 합성각섬석의 경우 0.15만큼의 초과 양이온을 포함하는 반면(단위 화학식당 23개의 산소를 기준함), Ts가 적은 각섬석은 0.18양이온씩이나 결여된다. 합성 각섬석은 공생광물조합, 압력 및 온도에 따라서 체계적으로 변화한다. Ts의 양($=[8-Si-Na]/2$)은 750-850°C에서 온도가 증가함에 따라 증가되지만($\partial Ts/\partial T \sim 0.1 \text{ mol \% K}^{-1}$), 850-900°C에서는 거의 변화가 없이 일정하다. 압력은 각섬석의 Ts양에 크게 영향을 미친다: 8-12kb에서는 증가하지만($\partial Ts/\partial P = 2-3 \text{ mol \% kb}^{-1}$) 12-21kb에서는 크게 감소한다($\partial Ts/\partial P = -2.5 \text{ mol \% kb}^{-1}$). 그러므로 가장 Ts가 풍부한 각섬석은 60 \pm 5mol% Ts 즉 1.2 \pm 0.1 사면체 자리의 Al을 포함하며, 12kb와 850-900°C에서 산출된다. 3Tr+2조이사이트+7코런덤+H₂O=5Ts 반응식에 의해 지배되는 각섬석의 성분은 실험적으로 결정되었으며, Tr-Ts 고용체가 이상적 혼합이라는 가정하에, 처마카이트의 열역학적 값을 구하는 데 사용되었다. 예상되는 처마카이트의 표준 몰당엔트로피와 엔탈피는 $S^{\circ} = 566.9 \pm 13.7 \text{ J mol}^{-1} \text{ K}^{-1}$, 그리고 $H^{\circ} = -12518.36 \pm 15.17 \text{ kJ mol}^{-1}$ 이다.

INTRODUCTION

Experimental phase equilibrium studies of tschermakitic amphiboles have been carried out by several previous workers: Oba (1978) claimed the synthesis of end-member tschermakite at 10–24 kb and 750–850°C; Jenkins (1988), however, concluded that solid solution exists only in the composition range of Ts_{50} – Ts_{75} at 12 kb and 850°C, decreasing to Ts_{50} – Ts_{10} at 3 kb and 850°C. The earlier synthesis work on the Tr–Ts join by Jasmund and Schäfer (1972) also suggested a maximum limit of the Al solubility in amphiboles which amounts to 55 mol % Ts at pressures of 2 to 10 kb. As is common in synthesis experiments of amphiboles, extremely fine grain-size of run products hinders direct chemical analysis of tschermakitic amphiboles using the microprobe. Consequently, there are no reliable thermodynamic parameters for tschermakite and mixing properties of Tr–Ts solid solutions. This study adopts a simple model system, CaO – MgO – Al_2O_3 – SiO_2 – H_2O , to investigate P–T–X relationships along the join $Ca_2Mg_3Si_8O_{22}(OH)_2(Tr)$ – $Ca_2Mg_3Al_2^{IV}Al_2^{IV}Si_6O_{22}(OH)_2(Ts)$. Emphasis has been placed on determining compositions of Tr–Ts amphiboles synthesized with or without seed crystals of natural tremolite. Furthermore, the compositions of amphiboles coexisting with zoisite and corundum are reversed, and used to calculate thermodynamic parameters of tschermakite.

EXPERIMENTAL METHODS

All experiments were done using a conventional piston-cylinder apparatus. A 2.54-cm-diameter furnace assembly consisting of NaCl, pyrex, graphite, BN and MgO was used. Temperatures were measured with Pt_{100} – Pt_{90} – Rh_{10} thermocouples placed at the top of a capsule. Temperature uncertainty is within $\pm 10^\circ C$. Rapid quenching to room temperature was obtained by shutting off electric power to the furnace.

Five different starting mixtures ranging in their composition from Ts_{50} to Ts_{100} were prepared by combining gels and crystalline phases. Natural, analyzed F- and Cl-free, stoichiometric end-mem-

ber tremolite was employed as seed crystals in some experiments, which facilitated nucleation and growth of tschermakitic amphiboles. Experimental charges lacking tremolite seed crystals gave a fine-grained mixture of amphibole prisms typically less than 15 μm long, whereas those with seed tremolite generally produced newly grown tschermakitic amphibole crystals as well as tschermakitic rims around seed tremolite. The products of each experiment were examined with the petrographic microscope and immersion oils, X-ray diffractometer, and electron microprobe. One run product was also examined by Dr. J. H. Ahn using a high-resolution transmission electron microscope (HRTEM).

RESULTS

Seventy experiments were done at temperatures ranging from 650°C to 950°C and at pressures of 8 to 24 kb. Figure 1 summarizes various mineral assemblages synthesized at each experimental condition. Synthetic amphiboles occur with other phases in all amphibole-producing experiments. The identities and compositions of these extraneous phases vary with P, T, and bulk composition.

The phase compatibilities observed in synthesis experiments are largely divided into three amphibole-bearing assemblages as well as others lacking amphibole (Fig. 1). At 650–850°C and 8–12 kb, amphibole \pm corundum coexist with anorthite (\pm chlorite, talc, pyroxenes, spinel and sapphirine), but at pressures of 12–21 kb, amphibole + corundum coexist with zoisite (\pm talc, chlorite, kyanite and Mg-staurolite). At 900°C, amphibole + corundum + clinopyroxene (\pm anorthite, forsterite, sapphirine and garnet) are stable over the pressure range 12–18 kb. These amphibole-bearing assemblages are replaced at high pressure by clinopyroxene + talc + chlorite + zoisite at 650–750°C, and at higher temperatures by garnet + clinopyroxene (\pm zoisite, ortho-pyroxene and Mg-staurolite).

The stability range of phase assemblages containing Tr–Ts amphibole solid solutions is delineated as approximately defined by the dashed curves of Fig. 1. Taken in conjunction with the

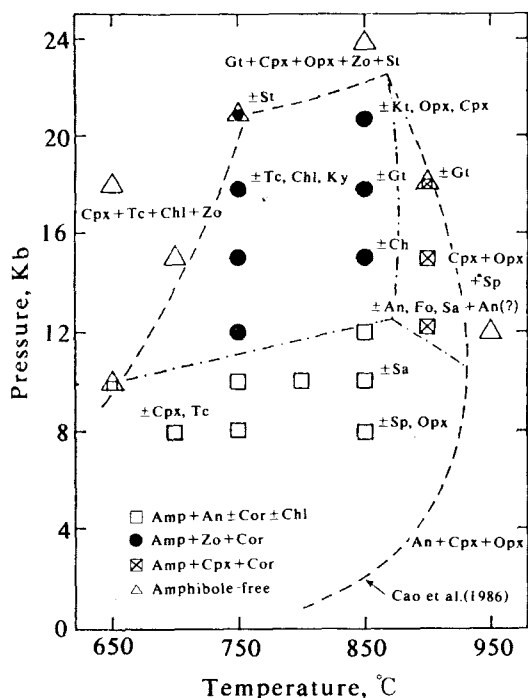


Fig. 1. P-T diagram illustrating various mineral assemblages synthesized at each experimental condition. Dashed curves approximately define P-T limits for the stability of phase assemblages containing tschermakitic amphiboles. The dot-dashed curves schematically show the boundaries between different amphibole-bearing assemblages. Various breakdown assemblages are also shown for each amphibole-absent P-T region. Abbreviations: Amp, amphibole; An, anorthite; Chl, chlorite; Cor, corundum; Cpx, clinopyroxene; Fo, forsterite; Gt, garnet; Ky, kyanite; Opx, orthopyroxene; Sa, sapphirine; Sp, spinel; St, Mg-staurolite; Tc, talc; Zo, zoisite.

experimental result of Cao et al. (1986) for the upper thermal stability limit of tschermakitic amphiboles at low pressures, it is evident that tschermakitic amphiboles synthesized from Ts_{50} to Ts_{100} bulk compositions are stable over a broad P-T range. They show a wedge-like stability field diminishing with increasing pressure. At pressures greater than 21–24 kb and temperatures of 750–850°C, tschermakitic amphiboles ultimately disappear.

AMPHIBOLE CHEMISTRY

Synthetic amphiboles are at least ternary solid solutions, and show wide compositional variations primarily due to three independent intracrystalline exchange components represented by the tschermakitic ($Al^{VI}Al^{IV}Mg_{-1}Si_{-1}$), sudoitic ($Al_2^{VI}\square^{VI}Mg_{-3} = Sud$, where \square denotes vacant site) and cummingtonitic ($CaMg_{-1} = Cum$) substitutions. Sudoitic substitution in amphibole is newly defined in this study by analogy with di/trioctahedral exchange in the six-fold coordinated sites of clinocllore ($Mg_5Al^{VI}Si_3Al^{IV}O_{10}(OH)_8$) – sudoite ($Mg_2\square^{VI}Al^{VI}_3Si_3Al^{IV}O_{10}(OH)_8$) solid solution.

Compositions of amphiboles synthesized at temperatures of 750, 850, and 900°C, respectively are shown in Fig. 2, which is a plot of Ts mol % versus (a) Sud mol % and (b) cation sum based on 23 oxygens pfu. A little wider scatter in Fig. 2b than Fig. 2a is apparent, because total cations for Ca-amphiboles from seeded experiments are generally greater by about 0.05 cations than those from unseeded experiments due to minor Na and Fe components from natural seed crystals. Also shown in Fig. 2 are electron microprobe analyses of synthetic tschermakitic amphiboles reported in the literature (Oba, 1978; Cao et al., 1986; Ellis and Thompson, 1986).

Fig. 2a suggests a positive correlation between Ts and Sud substitutions. The Sud substitution in the Tr-Ts solid solutions exhibits a significant variation, ranging from +18 to -15 mol %. Hence, the total number of cations in the amphibole also varies due to the nature of Sud substitution involving vacant octahedral sites. This relation (Fig. 2b) indicates a progressive increase in the cation sums of synthetic amphiboles with Ts content. Calcic amphiboles with $Ts > 45$ mol % may contain as much as 0.15 excess cations pfu, whereas less tschermakitic amphiboles are deficient in the cation occupancy by as much as 0.18 pfu. Thus, any normalization scheme for amphibole formula, assuming a cation sum equal to 15.0, may yield misleading results for estimating the Fe^{3+} content in amphiboles. It is also impor-

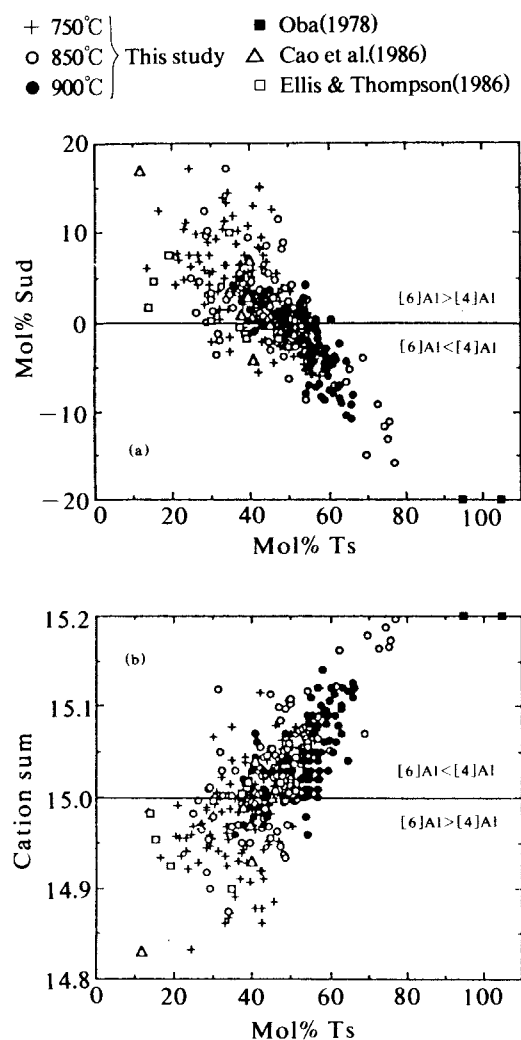


Fig. 2 Compositions of Ca-amphiboles synthesized at 750, 850, and 900°C, respectively, plotted in terms of mol % Ts versus (a) mol % Sud, and (b) cation sum. Typical uncertainties in mol % Ts or Sud, and cation sum of each spot analysis are 2 mol % Ts or Sud, and cation sum of each spot analysis are 2 mol % and 0.02 cations, respectively. The solid line denotes the ideal Tr-Ts solid solution ignoring the Sud component (i. e., $Al^{VI} = Al^{IV}$).

tant to note that the number of total cations may exceed 15.0 for Ts-rich solid solutions. These excess cations must be assigned to the A-site, because the I-beam structure is essentially close-packed. Consequently, a small number of Ca cations

(up to 0.15) apparently may occupy the A site of the amphibole structure, analogous to the occurrence of interlayer Ca cations in margarite.

The average X_{Cum} content of amphiboles in each experiment varies from 4 to 11 mol %. No systematic variation in Ca content is observed at low pressures (≤ 10 kb), or at a temperature of 750°C. However, at higher P and T, the Cum content generally increases with both P and T. In particular, at 900°C, the average X_{Cum} consistently increases with pressure ($\partial Cum / \partial P = 0.7 \text{ mol \% kb}^{-1}$). The increase in Cum content with increasing P can be accounted for by the volume reduction accompanying replacement of Ca by Mg.

Finally, stoichiometric deviation in synthetic amphiboles may be due partly to structural disorder producing single or multiple chains in conjunction with normal amphibole double chains. For example, Ca contents and cation sums may increase by the presence of single chains, but decrease by multiple chains in structurally disordered amphiboles. The amphibole compositions of this study do not fall along the join between talc and tschermakitic clinopyroxene including biopyroxenes. Structural disorder in synthetic amphiboles of this study are thus inferred to be very limited in extent. Independent evidence for limited structural disorder is obtained by examining the run product of an unseeded experiment at 10 kb and 751°C, using HRTEM. Except for the minor occurrence of triple chains, no structural disorder was found. Hence, the effect of structural disorder on Ca and Mg compositions of amphiboles is insignificant in tschermakitic amphiboles synthesized at high pressures in this study.

DISCUSSION

Compositions of tschermakitic amphiboles change systematically with P and T. Solid solution relationships are shown in Fig. 3 in terms of mol % Ts. The compositions of amphiboles were also reversed at seven different P and T, and are shown simultaneously at each experimental condition in Fig. 3. The Ts content first increases with increasing T ($\partial Ts / \partial T = \sim 0.1 \text{ mol \% K}^{-1}$) at 750–850°C, then remains nearly constant at 850–900

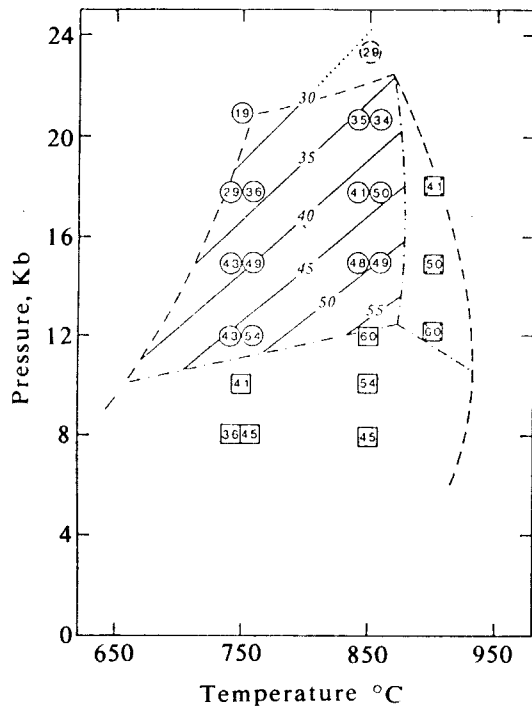
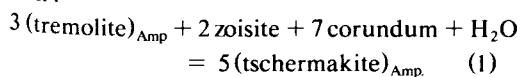


Fig. 3. $P_{\text{fluid}}-T$ diagram illustrating isopleths for the mol % Ts of Ca-amphiboles in various assemblages of run products. Isopleths in mol % Ts are calculated for the assemblage Amp+Zo+Cor+H₂O, assuming ideal mixing of Tr-Ts solution and the activity-composition relationship of $a_{\text{Ts}} = X_{\text{Ts}}$ (thin lines; dotted when isopleths are metastable).

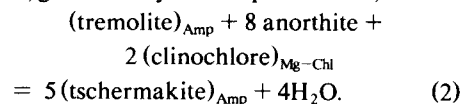
°C. Pressure dramatically affects the Ts content of Ca-amphiboles: it increases with P at 8–12 kb ($\partial\text{Ts}/\partial P = 2-3 \text{ mol \% kb}^{-1}$), but significantly decreases at 12–21 kb ($\partial\text{Ts}/\partial P = -2.5 \text{ mol \% kb}^{-1}$). Hence, the most tschermakitic amphibole, containing $60 \pm 5 \text{ mol \% Ts}$, occurs at 12 kb and 850–900°C. Such compositional variations are due to the change in mineral assemblages.

Compositions of Ca-amphiboles coexisting with corundum and zoisite at 12–21 kb and 750–850°C are defined by the simple degenerate reaction:



Six reversal experiments for reaction (1) were done at 750 and 850°C (Fig. 3), and used to estimate thermodynamic parameters of tschermakite assuming ideal mixing of Tr-Ts solid solutions. Various numbers of exchangeable cation sites were employed to fit the experimental brackets, in conjunction with thermodynamic data set of THERMOCALC (Holland and Powell, 1990). The most consistent result was obtained by a simple activity-composition relationship of $a_{\text{Ts}} = X_{\text{Ts}}$. Calculated isopleths have gentle positive P/T slope as shown in Fig. 3, and account for the observed decrease in Ts content with increasing pressure. Standard molal entropy and enthalpy of tschermakite are predicted from the linear programming method: $S^{\circ}_{\text{Ts}} = 566.9 \pm 13.7 \text{ J mol}^{-1} \text{ K}^{-1}$ and $H^{\circ}_{\text{Ts}} = -12518.36 \pm 15.17 \text{ kJ mol}^{-1}$. The latter value is greater than $532 \text{ J mol}^{-1} \text{ K}^{-1}$ estimated from the structural algorithm incorporating coordination number of Al. Apparent discrepancy in the entropy value is attributed to the cation disordering in synthetic tschermakitic amphiboles, because they are virtually free of structural disorders as revealed by the TEM study.

A similar trend of decreasing Ts content with increasing P is also evident at 900°C and $P > 12 \text{ kb}$. The exact reaction governing amphibole composition varies with P, because the observed mineral assemblages (+Amp+Cor) change from anorthite±sapphirine±forsterite to clinopyroxene±garnet. On the other hand, at low P and T, the Ts content increases systematically with both P and T, buffered by various anorthite-bearing assemblages (±Cor). For example, compositions of amphiboles coexisting with anorthite and chlorite define the maximum Ts solubility at a given P and T, governed by the simple reaction,



One reversal of this equilibrium has been obtained at 8 kb and 750°C (Fig. 3). In conjunction with my unpublished data on the Amp+An+Chl assemblage at low pressures, synthetic amphiboles increase in Ts content with both P and T, consistent with the negative P-T slope of reaction (2) calculated based on thermodynamic data

of Holland and Powell (1990).

CONCLUSIONS

Thermal stabilities of tschermakitic amphiboles have been determined at temperatures of 650–900°C for bulk compositions ranging from $T_{s_{50}}$ to $T_{s_{100}}$. These amphiboles show a wedge-like $P_{\text{fluid}}-T$ stability field, diminishing with increasing P ; amphibole-bearing associations are replaced by eclogitic analogue assemblages at $P > 18-24$ kb. The presence of octahedral vacancies (= dioctahedral component) in synthetic amphiboles is experimentally suggested, and delineated in terms of sudoitic substitution which shows a negative correlation with tschermakitic exchange. Compositions of tschermakitic amphiboles systematically change with P and T . In particular, the T_s contents of Ca-amphiboles coexisting with zoisite and corundum have been reversed at six different $P-T$ conditions; T_s solubility significantly decreases with increasing P ($\partial T_s / \partial P = -2.5$ mol % kb^{-1}) for the assemblage $\text{Amp} + \text{Zo} + \text{Cor} + \text{H}_2\text{O}$. The maximum Al-solubility of 1.2 ± 0.1 tetrahedral Al equivalent to 60 ± 5 mol % T_s occurs at 12 kb and 850–900°C.

Acknowledgement: Experimental and much of the analytical work on this project was done at UCLA, supported by NSF grant EAR 86-16624 to W. G. Ernst. HRTEM work kindly performed by Dr. Jung Ho Ahn, currently at Korea Ocean Research and Development Institute, is greatly appreciated.

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