Experimental study on the tremolite-pargasite join at variable temperatures under 10 kbar

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Abstract. The join tremolite (Tr)-pargasite (Pa) was studied at temperatures between 800 and 1150°C under water vapour pressure of 10 kbar. The results show a continuous solid solution of amphibole between the composition $\text{Tr}_{80}\text{Pa}_{20}$ and Pa_{100} at 800°C and 10 kb. Pargasite melts incongruently and breaks down at high temperature to clinopyroxene + forsterite + spinel + L + V. A single phase amphibole with composition lying between $\text{Tr}_{80}\text{Pa}_{20}$ and nearly pure Pa, breaks down to amphibole of different composition plus other phases. The stability fields of amphibole spread toward higher temperature side with increasing pargasite content, and pargasite itself has the widest stability field. At subliquidus, the composition of amphibole coexisting with other phases becomes more pargasitic with increasing temperature.

The compositions of liquid, which are formed by partial melting of amphibole of $\text{Tr}_{40}\text{Pa}_{60}$ composition (Fo-normative) under water vapour pressure of 10 kbar, are alumina-rich and Qz-normative.

Keywords. Tremolite; pargasite; clinopyroxene; forsterite.

1. Introduction

Hornblende, which commonly occurs in metamorphic and igneous rocks, has a wide range of P-T stability. It is a solid solution of tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$), pargasite ($\text{NaCa}_2\text{Mg}_4\text{AlSi}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$), tschermakite ($\text{Ca}_2\text{Mg}_3\text{Al}_2\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$) and edenite ($\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{AlO}_{22}(\text{OH})_2$). Pargasite can be derived from tremolite by the following type of substitutions, $\text{MgSi} = \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$ and $\text{Si} = \text{NaAl}^{\text{IV}}$. It is generally known that hornblende changes from tremolitic to more pargasitic composition during progressive metamorphism.

Boyd (1959) determined the high temperature stability relations for pargasite under low pressure (~ 1.2 kb). Preliminary experiments by Gilbert (1969) indicated that pargasite is still stable at temperatures between 800 and 900°C under water vapour pressure of 20 kb, but it becomes unstable at pressures close to 30 kb. Holloway (1973) determined the stability of pargasite at total pressures of 1.2 to 8 kb in presence of CO_2 and H_2O .

The upper stability limit of tremolite under low pressure was determined by Boyd (1959). The latter and Wones and Dodge (1977) could not produce 100% yield from either gels or synthetic anhydrous mineral assemblages in the presence of excess water. Troll and Gilbert (1972) concluded that solubility of $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ in synthetic tremolite is not significant, based on comparison of unit cell parameters of synthetic hydroxyl-bearing tremolite with those of several carefully-analysed natural tremolites. Oba (1980) reported phase relationships of intermediate amphiboles on the join tremolite and pargasite at 1 and 5 kb. There is a continuous series of solid solution

in the compositional range, $\text{Tr}_{90}\text{Pa}_{10}$ and Pa_{100} at 5 kb. In contrast, tremolite and pargasite might be separated by a solvus in the case of the 1 kb isobaric section. However, no experimental data are available for the solid solution series of tremolite-pargasite at 10 kb although phase relations in this join are important to define the condition of formation of igneous and metamorphic amphiboles.

2. Experimental method

Experiments were carried out with a piston-cylinder apparatus. The pressure-transmitting medium was molten pyrex glass. Temperatures were measured with chromel-alumel thermocouple. No correction was made for the effect of pressure on the e.m.f. of chromel-alumel thermo-couples. Temperature fluctuations were as much as $\pm 15^\circ\text{C}$ in longer runs and up to $\pm 10^\circ\text{C}$ for shorter runs. Reported pressures are believed to be correct to within ± 0.5 kb. All runs were made at $P_{\text{total}} = P_{\text{H}_2\text{O}}$. The samples were placed in platinum capsules.

All starting materials were prepared by heating oxide in air with intermediate crushing at 1000°C for 4 to 5 weeks. The anhydrous compositions of starting materials were plotted in the Ne-Fo-Qz-Di tetrahedron (figure 1). The anhydrous composition of pargasite lies in the tetrahedron, Ne-Fo-Pl(An + Ab)-Di and that of tremolite plots on the Di-En-Qz join. The anhydrous tremolite₆₆pargasite₃₃ composition lies on the Di-Pl-En plane, and the anhydrous, tremolite₅₀pargasite₅₀ composition plots on the Di-Pl-Fo plane.

Phase identification was made using an X-ray powder diffractometer and an optical microscope. Amphiboles, clinopyroxenes and glasses were analysed with an electron microprobe analyser (JEOL JXA-50A). These element analyses were obtained by using the matrix correction procedures of Bence and Albee (1968) at an accelerating potential of 15 kV. The beam diameter was about $3\ \mu\text{m}$.

Figure 1. Positions of five principal amphibole end members projected in the simple iron-free basalt system Di-Fo-Ne-Qz.

3. Experimental results and discussion

In the system tremolite-pargasite, amphibole, clinopyroxene, forsterite, orthopyroxene, plagioclase, quartz and spinel were encountered.

Tremolitic amphibole forms colourless, needle-shaped euhedral crystals up to 20 μm in length. In contrast, pargasitic amphibole occurs as colourless, tabular crystals (up to 40 μm long, 20 μm across). N_x and N_y of synthetic tremolite are 1.605 and 1.628, and those of synthetic pargasite are 1.617 and 1.636, respectively. Both refractive indices increase linearly with increase of pargasite in tremolite.

Clinopyroxene generally forms euhedral to subhedral crystals, and occurs as round inclusions within amphibole. Orthopyroxene forms elongated euhedral crystals with low birefringence. Plagioclase forms colourless, fine-grained crystals, and is identified by reflections ($\bar{2}04, 20\bar{2}$). Forsterite occurs as euhedral crystals, and is easily distinguishable from orthopyroxene by its birefringence. The analysed data indicate that olivines encountered in this study are pure forsterite. Spinel forms small octahedral crystals. Unit cell dimension ($a = 8.098 \text{ \AA}$) indicates that it has a composition approximating MgAl_2O_4 ($8.103 \text{ \AA}$). Quartz forms rounded or subhedral crystals.

The experimental results are given in table 1. Figure 2 shows the phase diagram

Table 1. Experimental results for the join tremolite-pargasite at 10 kb.

Composition (mol%)		Temp (°C)	Time (hrs)	Results
Tr	Pa			
100	0	800	96	Amph, Cpx, Qz, V
		850	142	Cpx, Opx, Qz, V
		900	100	Cpx, Opx, Gl, V
		1000	10	Cpx, Opx, Gl, V
		1100	5	Cpx, Opx, Gl, V
90	10	800	96	Amph, Cpx, Opx, Qz, V
		900	62	Cpx, Opx, Gl, V
		1100	72	Cpx, Opx, Gl, V
80	20	800	291	Amph, V
		850	107	Amph, Cpx, Opx, V
		900	48	tr. Amph, Cpx, Opx, Gl, V
		975	48	Cpx, Opx, Gl, V
		1000	10	Cpx, Opx, Fo, Gl, V
		1100	6	Cpx, Opx, Fo, Gl, V
70	30	825	168	Amph, V
		850	148	Amph, tr. Cpx, tr. Opx, tr. Pl, V
		950	40	Amph, Cpx, Opx, Gl, V
		975	48	Cpx, Opx, Fo, Gl, V
		1100	24	Cpx, Opx, Fo, Gl, V
60	40	800	290	Amph, V
		850	344	Amph, Cpx, tr. Opx, Pl, V
		900	240	Amph, Cpx, Opx, Gl, V
		950	48	Amph, Cpx, Opx, Gl, V
		1000	96	tr. Amph, Cpx, tr. Opx, Fo, Gl, V
		1050	15	Cpx, Fo, Gl, V
		1100	5	Cpx, Fo, Gl, V

(Continued)

Table 1. (Continued)

Composition (mol%)		Temp (°C)	Time (hrs)	Results
Tr	Pa			
50	50	875	110	Amph, Cpx, Opx, Gl, V
		1000	36	Amph, Cpx, Fo, Gl, V
		1050	15	Cpx, Fo, Gl, V
40	60	800	188	Amph, V
		850	188	Amph, Cpx, Opx, Pl, V
		900	95	Amph, Cpx, Fo, Gl, V
		950	72	Amph, Cpx, Fo, Gl, V
		1000	39	Amph, Cpx, Fo, Gl, V
		1050	6	Amph, Cpx, Fo, Gl, V
		1100	5	Cpx, Fo, Gl, V
30	70	900	240	Amph, tr. Cpx, V
		925	75	Amph, Cpx, Fo, Gl, V
		1100	5	Cpx, Fo, Gl, V
20	80	950	72	Amph, V
		1000	24	Amph, V
		1100	48	Cpx, Fo, Sp, Gl, V
		1150	4	Cpx, Fo, Gl, V
10	90	950	73	Amph, Gl, V
		1000	24	Amph, Gl, V
		1050	48	Amph, V
		1100	6	tr. Amph, Cpx, Fo, Sp, Gl, V
0	100	850	220	Amph, V
		950	96	Amph, V
		1000	73	Amph, V
		1050	48	Amph, V
		1100	5	Cpx, Fo, Sp, Gl, V
		1150	24	tr. Cpx, tr. Fo, Gl, V
Reversal runs				
70	30	825	240	Amph + Cpx + Pl + Opx → Amph
		850	240	Amph → Amph + Cpx + Pl + Opx
		950	124	Cpx + Opx + Fo + L → Amph + Cpx + Opx + L
		975	96	Amph + Cpx + Opx + L → Cpx + Opx + Fo + L
40	60	1050	54	Cpx + Fo + L → Amph + Cpx + Fo + L
30	70	900	120	Amph + Cpx + Fo + L → Amph + tr. Cpx
		925	112	Amph → Amph + Cpx + Fo + L
0	100	1050	240	Cpx + Fo + Sp + L → Amph

Abbreviations used: amphibole = Amph, clinopyroxene = Cpx, orthopyroxene = Opx, plagioclase = Pl, quartz = Qz, spinel = Sp, forsterite = Fo, glass = Gl, liquid = L and vapor = V. tr. = trace amount.

at 10 kb. The join tremolite-pargasite forms a continuous solid solution of amphibole between the composition $\text{Tr}_{80}\text{Pa}_{20}$ and Pa_{100} at 800°C. As the temperature rises with the increasing content of tremolite in pargasite, the stability field of a single phase amphibole drastically decreases in the pargasite-rich portion, but gradually decreases in the tremolite-rich region. Pargasite is stable at 1100°C, on the other hand tremolite with minor cummingtonite molecule is stable only up to a temperature of about

Figure 2. T-X section in the join tremolite-pargasite at 10 k. Abbreviations are as in table 1.

830°C. At the high temperature portion of the phase diagram near the single phase-field, amphibole decomposes to amphibole₂+other phases. The melting of pargasite end member is incongruent. Boyd (1959) and Holloway (1973) also reported the incongruent melting of pargasite at pressures of 700–1200 bars and 1–8 kb, respectively. The variation in phase assemblages with increasing pargasite content is as follows: Amph+Cpx+Qz+V (tremolite-rich region), Amph+Cpx+Opx+V, Amph+Cpx+Opx+Pl+V, Amph+Cpx+Opx+L+V and Amph+Cpx+Fo+L+V (in the pargasite-rich region). The stability field of amphibole+other phases also becomes smaller with increasing tremolite content in pargasite. When the pargasite content in the join increases, the phase assemblages at 1100°C are progressively as follows: Cpx+Opx+L+V, Cpx+Opx+Fo+L+V, Cpx+Fo+L+V and Cpx+Fo+Sp+L+V. Oba (1980) reported that at 5 kb pargasite and tremolite break down at 1075°C and 850°C, respectively. In contrast to the stability field of this phase at 5 kb, that of amphibole at 10 kb increases in pargasite-rich region and decreases in tremolite-rich region with increasing temperature. Figure 2 shows that the stability fields of amphiboles are extended to a higher temperature with increasing pargasite content, and only pargasitic amphibole is stable at a high temperature. The present experimental results support that amphiboles, which have been observed in many rocks of possible upper-mantle origin, are pargasite or pargasitic hornblende.

Reversal experiments were carried out across selected phase boundaries. For example, when the assemblage Amph+Cpx+Opx+Pl obtained from the composition, Tr₇₀Pa₃₀ at 10 kbar, was held at 825°C for 240 hours, only amphibole was obtained at the expense of other phases. The composition of amphiboles listed in table 2, is the average of measurements made on several grains (10–15). The site occupancies of cations and the molecular proportions of the end members were calculated following the methods of Oba (1980). According to the classification of Deer *et al* (1963), all amphiboles are identified as calciferous ones, belonging to the

Figure 3. Relationship between Na in A site and Al^{IV}. Numbers indicate temperature (°C). Open circles show the amphiboles formed at variable temperatures from Tr₄₀Pa₆₀ bulk composition. Solid circle and square indicate the amphiboles synthesized at 850°C and 10 kb from Tr₆₀Pa₄₀ and Tr₈₀Pa₂₀ bulk compositions, respectively.

Figure 4. Relationship between Al^{VI} and Al^{IV}. Numbers and symbols are as in figure 3.

category of the common hornblende or pargasitic hornblende (figures 3 and 4). The major variation in the chemical compositions of the amphiboles can be explained by edenite and tschermakite substitutions, in the tremolite formula. In other words, compositional variation of amphiboles proceeds along pargasitic substitution from tremolite ignoring subordinate chemical variation. The sum of the molecular proportions of tremolite and pargasite is more than about 83%. The amphiboles formed at variable temperatures are plotted on the join tremolite-pargasite, as shown in figures 3 and 4. With increasing temperature, the composition of amphibole shifts toward pargasite. The minor variation in the chemical compositions of the amphiboles may be related to the presence of glaucophane and cummingtonite (table 2) as solid solutions in addition to tremolite and pargasite. The solubility of glaucophane in amphibole decreases with increasing temperature. At 20 kb and 850°C amphibole composition plots on the tschermakite-rich side of the join tremolite-pargasite, whereas at 1050°C it lies on the line. Preliminary experiments suggest that at high

Table 2. Chemical compositions of amphiboles.

Starting composition Temp°C	Tr ₄₀ Pa ₆₀ 1000	Tr ₄₀ Pa ₆₀ 950	Tr ₄₀ Pa ₆₀ 900	Tr ₄₀ Pa ₆₀ 850	Tr ₆₀ Pa ₄₀ 850	Tr ₈₀ Pa ₂₀ 850
SiO ₂	44.68	45.10	46.95	48.01	48.20	54.63
Al ₂ O ₃	17.11	16.12	15.21	13.61	13.27	5.95
MgO	20.08	20.55	20.93	21.20	21.25	23.11
CaO	12.44	11.90	11.78	11.87	11.97	12.52
Na ₂ O	3.05	3.20	3.18	3.22	3.02	1.15
Total	97.36	97.87	98.05	97.91	97.71	97.36
Structural formulae						
Si	6.197	6.280	6.439	6.591	6.627	7.445
Al ^{IV}	1.803	1.720	1.561	1.409	1.373	0.555
T	8.000	8.000	8.000	8.000	8.000	8.000
Al ^{VI}	0.994	0.925	0.898	0.793	0.777	0.401
Mg	4.006	4.075	4.102	4.207	4.223	4.599
Ml23	5.000	5.000	5.000	5.000	5.000	5.000
Mg	0.146	0.191	0.177	0.132	0.132	0.096
Ca	1.849	1.775	1.731	1.746	1.763	1.828
Na	0.005	0.034	0.092	0.122	0.105	0.076
M4	2.000	2.000	2.000	2.000	2.000	2.000
Na(A)	0.815	0.830	0.754	0.735	0.700	0.228
Molecular proportions						
Richterite	—	—	—	—	1	—
Glaucophanite	—	2	5	6	3	4
Edenite	—	—	—	6	—	—
Tschermakite	9	3	3	—	—	5
Pargasite	82	83	74	67	68	23
Tremolite	2	3	9	19	20	64
Gedrite	—	—	—	—	—	—
Cummingtonite	7	9	9	2	6	5

pressure and low temperature, tschermakite substitution is active in addition to incorporation of pargasite. In the iron- and titanium-free system, amphiboles from Cawthorn (1976) are plotted on the tschermakite-rich side of the join tremolite-pargasite.

Helz (1973) completed experiments on the phase relations of three basalts at 5 kb water pressure, 680–1000°C, at the oxygen fugacities of fayalite-quartz-magnetite and hematite-magnetite buffers. She reported that Al^{IV} and Ti contents in amphibole increase steadily with increasing temperature. There is a positive linear correlation of approximately 3:1 between Al^{IV} and the number of cations in the A-site. In the case of Ti-tschermakite, substitution would require a 2:1 correspondence between Al^{IV} and Ti. The residual Al^{IV} requires additional substitutions involving Al^{IV} (e.g. edenite substitution). In this case substitution of Ti-tschermakite is preferred to that of pargasite.

Spear (1981) reported that calcic amphiboles synthesized from an olivine tholeiite under subsolidus hydrothermal conditions display systematic changes in composition with temperature (501–920°C), water vapour pressure (1 to 3 kb) and oxygen fugacity.

He described that pargasite and Ti-substitutions in amphiboles increase with increasing temperature. The amphiboles display an approximately linear trend with a slope of 2.0 in the diagram of Al^{IV} versus A site occupancy. This slope indicates that there are 2.0 Al^{IV} for A site cation, consistent with pargasite substitution. In this case, pargasite substitution is superior to Ti-tschemmakite substitution.

The stability fields of kaersutites were determined for the samples from various localities of the world by Oba *et al* (1982a, b). He reported that the compositions of amphiboles coexisting with other phases at pressures higher than 10 kb become Ti-pargasite, and that the Ti content in amphibole decreases with increasing pressure. Although the Ti-tschemmakite substitution is clearly important at low pressure, pargasite- and tschemmakite-substitutions are dominant at high pressure. Therefore, in attempting to explain Ti-tschemmakite and pargasite substitutions against temperature dependence, we must take pressure as well as Fe/Mg ratio and temperature into account.

Compositions of liquids formed by partial melting are determined by microprobe analysis of quenched liquid. The data given in table 3 show that those liquids are silica- and alumina-rich, being quartz-normative. The liquids that coexisted with amphiboles are plotted in the quartz-rich side of the Di-Fo-Qz-Ne tetrahedron

Table 3. Chemical compositions of andesite and liquids formed from $\text{Tr}_{40}\text{Pa}_{60}$ bulk composition at 10 kb.

Temp°C	Starting composition		Average* andesite	
	950	1000		
SiO_2	50.53	57.84	56.85	54.20
TiO_2				1.31
Al_2O_3	11.35	18.14	20.47	17.17
Fe_2O_3				3.48
FeO				5.49
MnO				0.15
MgO	21.94	8.13	8.25	4.36
CaO	13.87	11.40	11.21	7.72
Na_2O	2.30	2.51	3.40	3.67
K_2O				1.11
P_2O_5				0.28
Total	99.99	98.02	100.18	99.80
CIPW Norms				
Qz	—	23.3	18.9	5.9
Or				6.6
Ab	10.4	12.6	17.1	31.0
An	10.4	21.8	22.8	27.1
Di	47.2	33.8	31.6	7.9
Hy	15.5	8.6	9.7	12.3
Ol	16.5	—	—	
Mt				0.2
Il				5.0
Ap				6.6

*Carmichael *et al* (1974).

separated by Di-Pl-Fo plane, and those that coexisted with only anhydrous minerals are plotted in the nepheline-rich side of this tetrahedron. Except for the content of iron oxide and CaO, compositions of liquids, which are formed by partial melting of amphibole from $\text{Tr}_{40}\text{Pa}_{60}$ bulk composition (under water vapour pressure of 10 kb in the Amph + Cpx + Fo stability region), are fairly in agreement with those of some andesitic rocks (Carmichael *et al* 1974).

4. Conclusions

There is a continuous series of solid solution of amphibole in the compositional range between $\text{Tr}_{80}\text{Pa}_{20}$ and pargasite at 800°C and 10 kb. The composition of amphibole coexisting with other phases becomes rich in pargasite with increasing temperature. The stability fields of amphiboles are extended to higher temperatures as pargasite content increases and pargasite itself has the widest stability field.

The composition of liquid, which is formed by partial melting of amphibolite of composition, $\text{Tr}_{40}\text{Pa}_{60}$ under water vapour pressure of 10 kb, is quartz-normative.

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