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PHASE RELATIONSHIP OF $Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2$ – $Ca_2Mg_3Fe^{3+}_2Si_6Al_2O_{22}(OH)_2$ JOIN AT HIGH TEMPERATURE AND HIGH PRESSURE – THE STABILITY OF TSCHERMAKITE –

by

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(with 3 tables and 4 text-figures)

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Abstract

The join tschermakite(Ts) – ferri-tschermakite(Fts) was studied at temperatures between 750 and 1000°C under water vapor pressures of 5 to 24 kb.

Tschermakite is stable up to 800°C between approximately 7 and 17 kb. Run products at pressures higher than 17 kb include amphibole associated with clinopyroxene + garnet + quartz + vapor. With increasing temperature at vapor pressures more than about 18 kb, amphibole breaks down to the assemblage, garnet + clinopyroxene + orthopyroxene + quartz + vapor. At lower pressures, the equilibrium mineral assemblage consists of anorthite + orthopyroxene + forsterite + vapor. At 950°C and 15 kb, no amphibole was found, and run products contain clinopyroxene + orthopyroxene + quartz + vapor. At 1000°C and 12 kb, a liquid phase is found.

No pure ferri-tschermakite could be synthezised at temperatures between 800 and 1000°C, and pressures of 7 to 20 kb. Amphibole, associated with clinopyroxene + orthopyroxene + magnetite + hematite + vapor, is stable up to 850°C at pressures between 8 and 19 kbar. The solubility limit of $Ca_2Mg_3Fe^{3+}_2Si_6Al_2O_{22}(OH)_2$ in tschermakite is 35 mole % at 850°C and 12 kb.

Introduction

Hornblende, which commonly occurs in metamorphic and igneous rocks, has wide range of P-T stability. It is a solid solution of tschermakite ($Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2$), tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and edenite ($NaCa_2Mg_5Si_7AlO_{22}(OH)_2$). Recently, many investigators have suggested the presence of amphibole in the upper mantle and the lower crust (Oxburgh 1964, Mysen 1973, Merrill and Wyllie 1975). On the basis of analyses of natural amphiboles Leake (1971) concluded that maximum Al^{VI} should be expected in amphiboles, crystallized under high pressures in a high aluminous environments with moderate or low alkali contents. Yamasaki *et at.* (1966) also reported the occurrence of amphibole with high tschermakite molecule in a hornblende-gabbroic inclusions within calc-alkalic rocks. Above discussion thus

supports the idea that amphibole with high tschermakite molecule may crystallize under high pressure.

Many investigators have attemped to synthesize pure tschermakite. Gilbert (1969) was able to crystallize this amphibole with trace of garnet at 800°C and 10 kb. Jasmund and Schäfer (1972) reported that pure tschermakite is unstable and the solubility limit of tschermakite in tremolite is 55 mole %. at temperatures between 450 and 900°C under water vapor pressures of 1 to 3 kb.

The study of the stability field of tschermakite may therefore be important to define the conditions of formation of metamorphic and igneous amphiboles rich in tschermakite molecule.

Experimental method

The high pressure experiments were carried out with a piston-cylinder apparatus. The pressure transmitting medium was molten pyrex glass and the design of pressure cells was similar to that figured by Hariya and Kennedy (1968).

Temperatures were meassured with chromel-alumel thermo-couple. No correction was made for the effect of pressure on the e. m. f. of chromel-alumel thermocouples. Temperature fluctuations were as much as ±15°C in longer runs and up to ±10°C for shorter runs. Reported pressures are believed to be correct to within ±0.5 kb. The samples with iron were placed in gold capsules, while platinum capsules were used for iron-free samples.

All starting materials were prepared by heating oxide mixtures in air with intermediate crusing at 1000°C for 3 to 4 weeks. The formed phase assemblages from tschermakitic and ferri-tschermakitic compositions are anorthite + forsterite + enstatite and anorthite + clinopyroxene + orthopyroxene + hematite, respectively.

Phase identification was made with X-ray powder diffraction patterns and optical microscope. All calculations of the unit-cell dimensions were accomplished with the aid of a program written by Sakurai (1967).

Amphiboles were analyzed with electron microprobe analyzer (JEOL JXA-50A).

Phase relation

Tschermakite

Tschermakite was studied at temperatures between 750 and 1000°C and at pressures between 5 and 24 kb P_{H_2O} ($P_{H_2O}=P_{total}$). Experimental results are summarized in Table 1 and Fig. 1, which shows that tschermakite is stable

at 800°C between 7 and 17 kb. However, tschermakite breaks down to amphibole + garnet + clinopyroxene + quartz + vapor at higher pressures. At 900°C and 20 kb amphibole completely breaks down, and run products contain garnet + clinopyroxene + orthopyroxene + quartz + vapor. The following reaction is suggested to account for the appearance of anorthite, orthopyroxene, forsterite and vapor at low pressure (Fig. 1):

Table 1 Experimental results on the join $Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2$-$Ca_2Mg_3Fe_2^{3+}Si_6Al_2O_{22}(OH)_2$

Composition (mole %) Ts	Fts	Temp. (°C)	Press. (kb)	Time (hrs)	Results
100	0	750	18	249	Amph,Cpx,Gar,V
		800	5	144	An,Fo,Opx,V
		800	7	190	An,Fo,Opx,trace Amph,V
		800	10	240	Amph,V
		800	20	117	Amph,Gar,Cpx,trace Opx,V
		800	24	274	Amph,Gar,Cpx,V
		810	15	188	Amph,V
		850	10	240	Amph,V
		850	12	211	Amph,V
		850	15	112	Amph,Gar,Cpx,trace Qz,V
		850	17	48	Amph,Cpx, trace Opx, Gar, V
		850	20	139	Amph,Gar,Cpx,trace Qz,V
		850	24	71	Amph,Gar,Cpx,trace Opx,V
		900	7	79	An,Fo,Opx,V
		900	9	44	Amph,An,Fo,trace Opx,V
		900	12	140	Amph,An,Opx,Cpx,Fo,V
		900	13.5	50	Amph,Cpx,Opx,V
		900	15	52	Cpx,Opx,Qz,V
		900	18.5	68	Gar,Cpx,Opx,trace Amph,V
		900	20	36	Gar,Cpx,Opx,(Qz),V
		900	23	55	Gar,Cpx,Opx,V
		950	10	58	An,Cpx,Opx,V
		950	12	45	Cpx,Opx,trace Qz,Sp,trace Gl,V
		950	15	120	Cpx,Opx,trace Qz,V
		950	19	48	Gar,Cpx,Opx,Qz,V
		1000	7	33	An,Fo,Opx,V
		1000	9	11	Cpx,Sp,Gl,V
		1000	12	37	Cpx,Sp,Gl,V
		1000	15	22	Cpx,Opx,Sp,Gl,V
		1000	18	48	Cpx,Opx,Sp,trace Qz,Gl,V
		1000	20	46	Gar,Cpx,Opx,(Qz),V

$$\underset{\text{Tschermakite}}{Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2} = \underset{\text{Anorthite}}{2CaAl_2Si_2O_8} + \underset{\text{Orthopyroxene}}{MgSiO_3} + \underset{\text{Forsterite}}{Mg_2SiO_4} + H_2O$$

At 950°C and 15 kb amphibole was not found, and run products consist of clinopyroxene + orthopyroxene + quartz + vapor. At 1000°C and 12 kb, glass

Table 1 (continued)

Composition (mol %) Ts	Fts	Temp. (°C)	Press. (kb)	Time (hrs)	Results
90	10	850	12	320	Amph,V
		850	15	44	Amph,Gar,Cpx,trace Qz,V
70	30	850	7	50	An,Cpx,Opx,Fo,V
		850	9	79	Amph,Sp,Cpx,Opx,An,V
		850	12	273	Amph,V
		850	15	170	Amph,Cpx,Gar,trace Qz,V
		850	18	48	Amph,Cpx,trace Opx,Gar,V
		850	20	53	Gar,Cpx,Opx,V
60	40	850	12	273	Amph,Sp,Cpx,Opx,V
		850	15	48	Amph,Sp,Cpx,Opx,V
50	50	850	12	360	Amph,Sp,Cpx,Opx,V
		850	7	126	An,Cpx,Opx,Fo,V
0	100	800	10	62	Amph,Cpx,trace Opx,Hm,Mt,V
		800	16	258	Amph,Cpx,Opx,Hm,trace Mt,V
		850	7	141	An,Cpx,Opx,Hm,Mt,V
		850	9	65	Amph,An,Cpx,Opx,Mt,Hm,V
		850	12	268	Amph,Cpx,trace Opx,Hm,V
		850	17	48	Amph,Cpx,Opx,Hm,Mt,V
		850	20	84	Gar,Cpx,Opx,Mt,Hm,V
		900	10	52	An,Cpx,Opx,Mt,Hm,V
		900	12	23	Amph,Cpx,Opx,Mt,Hm,V
		900	15	66	Amph,Cpx,trace Opx,Mt,Hm,V
		900	18	44	Gar,Cpx,Opx,Mt,Hm,V
		900	20	23	Gar,Cpx,Opx,Mt,Hm,V
		950	10	22	Cpx,Opx,An,Mt,Hm,V
		950	12	56	Cpx,Opx,Ol,Mt,Hm,V
		950	16	25	Cpx,Opx,Ol,Mt,Hm,V
		950	19	58	Gar,Cpx,Opx,Mt,Hm,V
		1000	10	30	Cpx,Opx,Ol,Mt,Gl,V
		reversal runs			
100	0	800	7	190	An,Opx,Fo,trace Amph,V
		850	17	240	Amph,Gar,Cpx,Qz,V

Abbreviations: Amph=Amphibole, An=Anorthite, Cpx=Clinopyroxene Fo=Forsterite, Gar=Garnet, Opx=Orthopyroxene, Sp=Spinel, Fe-oxides (Hm=Hematite,Mt=Magnetite) Gl=Glass, V=Vapor, Ol=Olivine, Ts=Tschermakite, Ts_{ss}=Tschermakite solid solution, Qz=Quartz.

is present.

Attempt was made to reverse two runs, the results of which are given in Table 1. In these reversal runs of a single phase tschermakite heated at 800°C and 7 kb for 190 hrs, and at 850°C and 17 kb for 240 hrs, the assemblages were anorthite + orthopyroxene + forsterite + trace amount of amphibole + vapor and amphibole + garnet + clinopyroxene + quartz + vapor, respectively.

Chemical compositions of two amphiboles crystallized at 15 and 20 kb at 850°C are $Ca_{1.9}Mg_{3.8}Al_{1.5}Si_{6.1}Al_{1.9}O_{22}(OH)_2$ and $Ca_{1.6}Mg_{3.9}Al_{1.7}Si_{5.9}Al_{2.1}O_{22}(OH)_2$. These two amphiboles are in equilibrium with garnet. The change in the chemical composition of these two amphiboles is related to the following type of substitution: $Ca = Mg$, $2Al^{VI} = 3Mg$ and $Al^{IV}Al^{VI} = SiMg$. Excess cation in the octahedral site may occur due to the substitution of

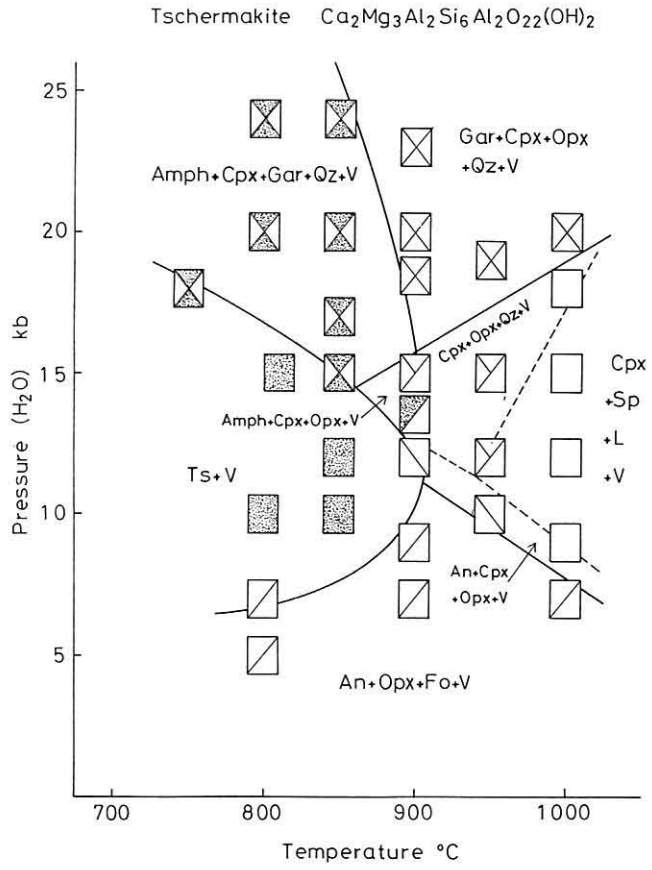

Fig. 1 Phase diagram of the composition of tschermakite at different temperatures and pressures. Abbreviations are same as in Table 1.

$2Al^{VI}$ for 3Mg in the A site. At 850°C and 15 kb, the following reaction may take place:

$$9Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2 = 9nCa_{1.9}Mg_{3.8}Al_{1.5}Si_{6.1}Al_{1.9}O_{22}(OH)_2 \quad \text{(Amphibole)}$$
$$+ (15\text{-}11.4n)CaMgSi_2O_6 \quad \text{(Clinopyroxene)} + (13\text{-}5.8n)Al_2O_3 + (1\text{-}1.9n)Ca_{0.6}Mg_{2.4}Al_2Si_3O_{12} \quad \text{(Garnet)}$$
$$+ (9\text{-}3.6n)SiO_2 \quad \text{(Quartz)} + 9(1\text{-}n)H_2O \quad \text{(Vapor)} \qquad (1)$$

Spinel, garnet, forsterite, orthopyroxene, clinopyroxene, anorthite, quartz and amphibole were encountered in the present investigation. Spinel forms small octahedral crystals. Unit-cell dimension indicates that it has a composition approximating $MgAl_2O_4$. Garnet shows anhedral and granular forms, and is usually larger than coexisting minerals. Unit-cell dimensions of garnet in the field of clinopyroxene, garnet, orthopyroxene and quartz suggest that its composition is $CaMg_2Al_2Si_3O_{12}$. Anorthite occurs as very small granular crystals, and was identified by reflections ($\bar{2}04$, $\bar{2}02$). Excess quartz should be present according to reaction (1), but it could be found only in trace amounts in anhedral forms. Amphibole occurs as long needle-sharped euhedral grains. The synthetic crystal of this amphibole is colorless. The unit-cell dimensions and refractive indices are given in Tables 2 and 3.

Ferri-tschermakite

The phase equilibrium diagram is given in Fig. 2, which shows that amphibole, clinopyroxene, orthopyroxene, olivine, garnet, anorthite, magnetite

Table 2 Unit-cell dimensions of amphiboles

Composition (mole %) Ts	Fts	Temp. (°C)	Press. (kb)	a Å	bÅ	cÅ	β°	VÅ³
100	0	810	15	9.749(4)	17.95(1)	5.294(1)	104.93(2)	895.4(5)
		850	10	9.843(3)	17.90(1)	5.284(3)	105.51(2)	897.3(3)
		850	12	9.839(2)	17.89(1)	5.283(3)	105.43(3)	896.5(2)
		850	15	9.822(4)	17.87(1)	5.290(3)	105.21(4)	896.2(6)
		850	20	9.742(4)	17.95(1)	5.326(3)	104.96(4)	899.9(6)
90	10	850	12	9.874(3)	17.91(1)	5.291(1)	105.61(2)	901.0(3)
90	30	850	12	9.887(3)	17.94(1)	5.294(4)	105.23(4)	905.5(3)
60	40	850	12	9.761(6)	17.99(1)	5.319(5)	105.16(4)	901.6(5)
50	50	850	12	9.763(4)	18.01(1)	5.312(5)	105.02(4)	902.4(3)
0	100	850	12	9.770(4)	18.02(1)	5.309(3)	105.14(3)	902.6(7)

Table 3 Refractive indices of amphiboles

Composition (mole %) Ts	Fts	Temp. (°C)	Press. (kb)	Refractive indices ±0.003 α	γ	Mineral assemblages
100	0	810	15	1.640	1.654	Ts,V
		850	10	1.639	1.654	Ts,V
		850	12	1.640	1.653	Ts,V
		850	15	1.642	1.652	Amph,Cpx,Gar,Qz,V
		850	20	1.643	1.655	Amph,Cpx,Gar,Qz,V
90	10	850	12	1.643	1.661	Ts_{ss},V
80	20	850	12	1.655	1.666	Ts_{ss},V
60	40	850	12	1.647	1.661	Amph,Sp,Cpx,Opx,V
50	50	850	12	1.642	1.660	Amph,Sp,Cpx,Opx,V
0	100	850	12	1.642	1.661	Amph,Cpx,Opx,Hm,Mt,V

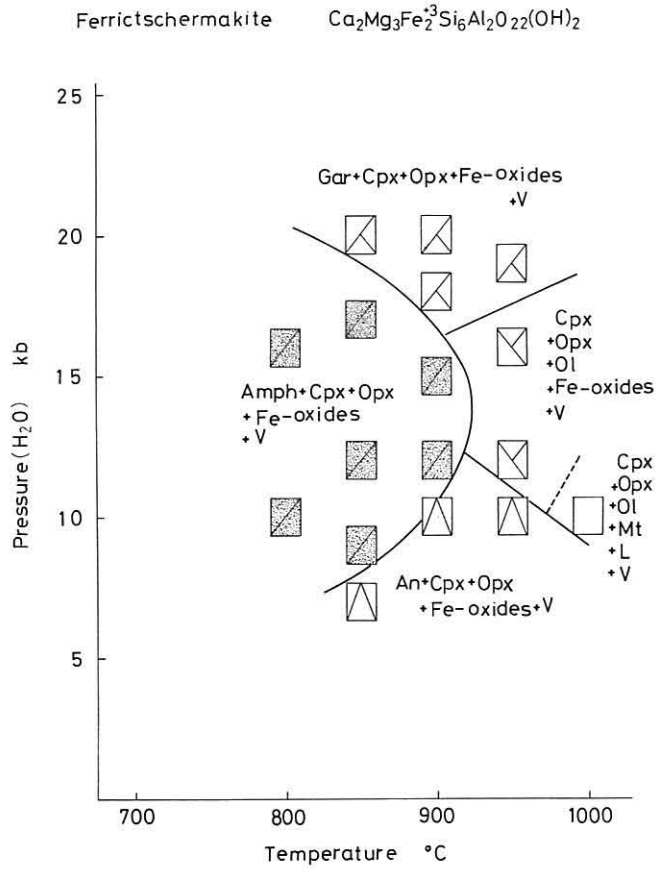

Fig. 2 Phase diagram of the composition of ferri-tschermakite at various temperatures and pressures. Abbreviations are same as in Table 1.

and hematite are the crystalline phases appearing from this composition. The investigation was made at temperatures between 800 and 1000°C under water vapor pressures between 7 and 20 kb. Ferri-tschermakite is not stable under these conditions. Amphibole, which coexists with clinopyroxene + orthopyroxene + Fe-oxides + vapor, is stable at 800°C under pressures between 8 and 20 kb and at 900°C under pressures between 12 and 15 kb. At 850°C and 20 kb amphibole breaks down, and the run products contain garnet + clinopyroxene + orthopyroxene + hematite + magnetite + vapor. The breakdown product at high temperature and intermediate pressure consists of clinopyroxene + orthopyroxene + olivine + Fe-oxides + vapor.

Investigation was carried out in absence of buffers, therefore oxygen fugacity in this study was not controlled. But the coexistence of hematite and magnetite suggest that oxygen fugacity approximately attained hematite-magnetite buffer condition.

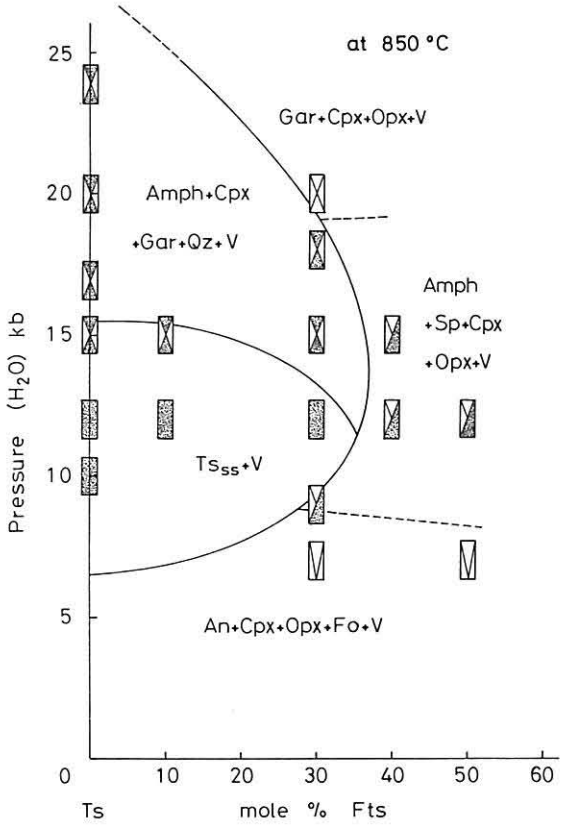

Fig. 3 Pressure-composition section at 850°C. Abbreviations are same as in Table 1.

Tschermakite – ferri-tschermakite solid solution

Experimental results on this join are given in Table 1. Fig. 3 is an isothermal section (850°C) of this join at various pressures. The solubility limit of ferri-tschermakite in tschermakite is 35 mol. % at 850°C and 12 kb. The phase assemblages at 850°C and 12 kb in this join changes as follows with increasing content of $Ca_2Mg_3Fe_2^{3+}Si_6Al_2O_{22}(OH)_2$: tschermakite$_{ss}$, amphibole + clinopyroxene + garnet + quartz + vapor and amphibole + spinel + clinopyroxene + orthopyroxene + vapor. At high pressures there is a single-phase field where tschermakite$_{ss}$ breaks down to amphibole + garnet + clinopyroxene + quartz + vapor. This system can be represented by the

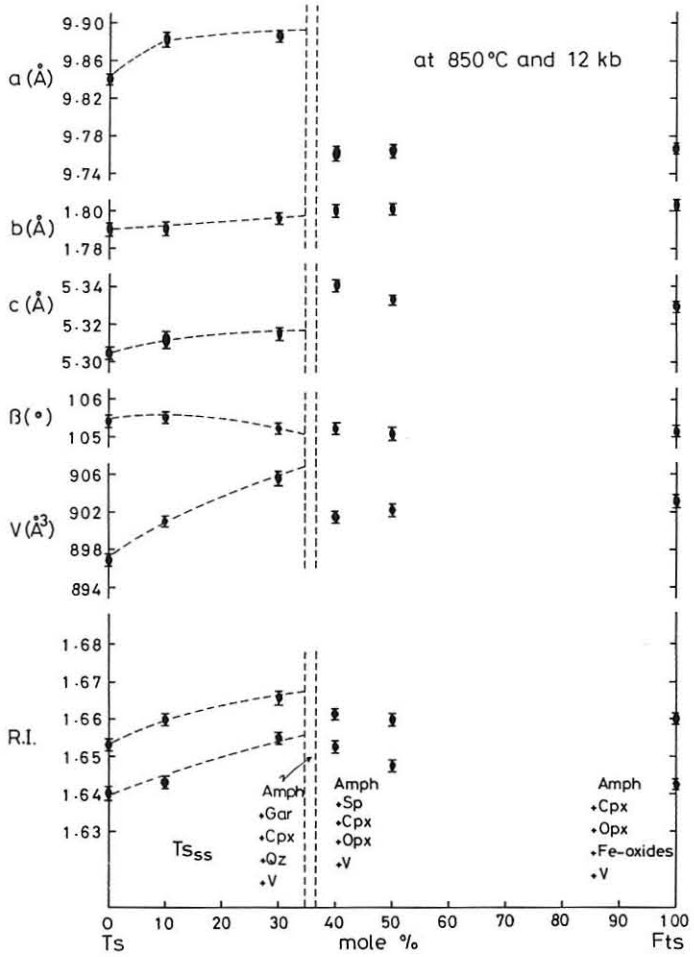

Fig. 4 Relationship between cell-dimensions or refractive indices of amphiboles with respect to chemical composition. Abbreviations are same as in Table 1.

following six components in the magnetite-hematite stability field: Fe-O-Ca-Mg-Al-Si.

Amphibole forms prismatic crystals with color varying from colorless to green with the increase of ferri-tschermakite molecule. Ferric-rich amphiboles are pleochroic.

The unit-cell dimensions and refractive indices of amphiboles in the present join are given in Table 2 and 3 and their variations against compositions were shown in Fig. 4. With increasing Fe^{3+} content, except for β all other cell parameters and refractive indices of amphibole in the tschermakite solid solution single-phase field increase, whereas the cell parameters of this phase roughly remain constant in the field of the assemblage amphibole + clinopyroxene + orthopyroxene + spinel or iron oxides (Fig. 4). These facts indicate that the solubility limit of ferri-tschermakite in tschermakite is 35 mol. % at 850°C and 12 kb.

Discussion

Many investigators consider that Al^{VI} in amphibole can be used as a pressure indicator. Amphiboles with the higher Al^{VI} values are often associated with kyanite, jadeite, Al-rich clinopyroxene and garnet. This mineral assemblage is often considered to represent high pressure condition.

Leake (1971) reported that amphibole in kyanite and garnet-bearing assemblages crystallized at higher pressures, should contain more Al^{VI} than amphibole on corundum-bearing assemblages at low pressures. These envidences indicate that calciferous amphiboles with high Al^{VI} value crystallizes at high pressure.

Chemical composition of amphiboles coexisting with garnet in the present investigation indicates that amphibole crystallized at higher pressure contains high Al^{VI}. But the Al^{VI} content in amphibole with garnet is lower than that of tschermakite. The present experimental results indicate that Al^{VI} in amphibole can not always be used as a pressures indicator.

Amphiboles such as pargasite (Boyd, 1959), richterite (Charles, 1975), edenite (Oba, unpublished), tremolite (Boyd, 1959), glaucophane (Ernst, 1961) are stable at 800°C and 1 kb, but tschermakite is unstable at this condition. The present study indicates that tschermakite is stable in the pressure range of 7 to 17 kb at 800°C, and amphibole with high Al^{VI} value crystallizes only under intermediate pressures.

Hariya *et al.* (1974) reported that richterite is stable at 900°C and 25 kb. Gilbert (1969) has also shown that pure pargasite is stable up to at least 900°C and 20 kb in the presence of clinopyroxene. As compared to other amphiboles,

sodium-bearing amphiboles are stable under higher pressures.

According to Leake (1965) natural amphiboles of composition similar to hypothetical tschermakite are not known and maximum Al^{VI} in natural amphiboles will occur only in those, crystallized in high aluminous environments with moderate or low alkali contents under high pressures.

The join tremolite-pargasite was studied at temperatures between 750 and 1100°C under 5 and 20 kb P_{H_2O} (Oba unpublished). The results indicate that clinopyroxene does not contain jadeite molecule in significant quantity and partition of sodium occurs only in amphiboles under these conditions, when they are pargasitic. The stability field of synthetic tschermakite in the low pressure region may coincide with the formation of some amphiboles belonging to the amphibolite facies. However, the stability of this phase up to 17 kb indicates that close study of the amphiboles present in the xenoliths of basalts brought from the deeper crust or upper mantle may reveal its presence.

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