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THE JOIN $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$ IN AIR AND ITS BEARING ON FASSAITIC PYROXENE

by

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(with 1 table and 9 text-figures)

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Abstract

Phase equilibrium diagram of the join $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$ was determined by the ordinary quenching method in air at 1 atm. One five-phase assemblage and three four-phase assemblages (univariant and divariant at constant pressure and constant pO_2) were confirmed. The univariant assemblage is clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ + spinel$_{ss}$ + liquid. Because of the complex solid solution of clinopyroxene, melilite, and spinel the crystallization ceases before invariant point is reached and the final phase assemblage in the $CaMgSi_2O_6$-rich region is clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$, and that in the $CaMgSi_2O_6$-poor region clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ + spinel$_{ss}$. The clinopyroxene$_{ss}$ field increases with increasing $CaFe^{3+}AlSiO_6$ content. The clinopyroxene$_{ss}$ in the join is discussed, with special reference to its bearing on the natural fassaitic pyroxene from alkalic volcanic rocks.

Introduction

In the previous paper (Onuma and Yagi, 1971) we pointed out that main constituent molecules of the pyroxene in undersaturated alkalic rocks (nepheline-and/or melilite-bearing rocks) are $CaMgSi_2O_6$ (Di), $CaTiAl_2O_6$ (Tp), $CaAl_2SiO_6$ (calcium-Tschermak's molecule, CaTs), and $CaFe^{3+}AlSiO_6$ (ferri-aluminium-Tschermak's molecule, FATs). In his study of fassaitic augite in alkali basalt Huckenholz (1973) showed that Fe^{3+} or Fe^{3+} +Al in excess of Na is incorporated in the diopside structure as $CaFe^{3+}_2SiO_6$ (ferri-Tschermak's molecule, FTs) and FATs.

From the viewpoint above mentioned, the system Di-CaTs-FATs-Tp, which is now under the investigation by the authors, is important to understand the

role of the pyroxene in the differentiation of alkalic rocks. In the present paper, the data of the join in the system Di-CaTs-FATs are presented and the clinopyroxene in the join is discussed with special reference to its bearing on the natural fassaitic pyroxene from alkalic volcanic rocks.

Experimental Results

In the present investigation ordinary quenching method was employed in air at 1 atm. The starting material was prepared by complete crystallization of homogeneous glass at 900°C. The furnace used in quenching experiments was regulated to a precision of ±1°C. Pt-$Pt_{87}Rh_{13}$ thermocouples used to measure the temperature were calibrated at the standard melting points of Au, 1062°C and diopside, 1931.5°C (the Geophysical Laboratory temperature scale). The results of quenching experiments are given in Table 1.

Table 1. Results of the queching experiments of the join $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$

Composition (wt.%)			Temp.	Time	Results
Di	CaTs	FATs	(°C)	(hrs.)	
80	10	10	1335	2	gl
			1330	2	cpx, gl
			1220	72	cpx, gl
			1200	72	loose powder, cpx only
70	20	10	1305	1	gl
			1300	2	cpx, gl
			1220	72	cpx, an, gl
			1200	72	loose powder, cpx, an, mel?
60	30	10	1265	16	gl
			1260	4	cpx, gl
			1250	18	cpx, trace an, gl
			1220	72	barely fritted cake, cpx, an, mel?
			1200	72	loose powder, cpx, an, mel
57	33	10	1265	2	gl
			1260	2	an, gl
			1250	16	an, gl
			1245	46	cpx, an, gl
			1240	42	cpx, an, gl
			1230	46	cpx, an, mel, gl
			1200	72	loose powder, cpx, an, mel
53	37	10	1250	16	an, gl
			1245	46	an, cpx, sp, gl
			1240	42	an, cpx, sp, gl
			1230	46	an, cpx, sp, mel, gl
			1200	72	loose powder, an, cpx, sp, mel

Table 1. continued

Composition (wt.%) Di	CaTs	FATs	Temp. (°C)	Time (hrs.)	Results
50	40	10	1310	1	gl
			1305	16	sp, gl
			1300	2	sp, gl
			1295	2	sp, an, gl
			1250	18	sp, an, gl
			1245	24	sp, an, trace cpx, gl
			1240	18	sp, an, cpx, gl
			1235	48	sp, an, cpx, mel, gl
			1220	72	fritted cake, sp, an, cpx, mel
			1200	72	loose powder, sp, an, cpx, mel
40	50	10	1335	2	sp, gl
			1330	2	sp, an, gl
			1275	22	sp, an, gl
			1270	18	sp, an, mel, gl
			1240	18	sp, an, mel, gl
			1235	48	sp, an, mel, cpx, gl
			1220	72	fritted cake, sp, an, mel, cpx
			1200	72	loose powder, sp, an, mel, cpx
70	15	15	1290	2	cpx, gl
			1200	336	barely fritted cake, cpx only
55	30	15	1270	2	gl
			1265	16	an, gl
			1260	12	an, cpx, gl
70	10	20	1305	1	gl
			1300	2	cpx, gl
			1200	72	lose powder, cpx only
60	20	20	1275	2	gl
			1270	18	cpx, gl
			1240	46	cpx, trace an, trace mel, gl
50	30	20	1300	15	gl
			1295	2	trace sp, gl
			1285	2	sp, gl
			1280	17	sp, trace an, gl
			1270	15	sp, an, gl
			1265	16	cpx, an, sp, gl
40	40	20	1375	16	gl
			1370	2	sp, gl
			1335	16	sp, gl
			1330	2	sp, an, gl
			1260	24	sp, an, gl
			1255	24	sp, an, cpx, gl
			1245	48	sp, an, cpx, gl
			1240	18	sp, an, cpx, mel, gl
35	45	20	1325	18	sp, gl
			1320	18	sp, an, gl
			1240	168	sp, an, gl
			1235	168	sp, an, cpx, mel, gl

Table 1. continued

Composition (wt.%) Di	CaTs	FATs	Temp. (°C)	Time (hrs.)	Results
52	25	23	1270	2	gl
			1265	16	cpx, gl
			1240	96	cpx, trace an, gl
			1230	96	cpx, an, mel, gl
50	25	25	1285	2	gl
			1280	16	trace sp, gl
			1260	18	sp, gl
			1255	46	sp, cpx, gl
			1200	36	loose powder, cpx, mel, an
60	10	30	1270	2	gl
			1265	16	cpx, gl
			1200	72	barely fritted cake, cpx only
55	15	30	1265	2	gl
			1260	2	cpx, gl
50	20	30	1270	2	gl
			1265	16	cpx, gl
			1200	72	loose powder, cpx only
48	22	30	1280	6	gl
			1275	5	sp, gl
			1265	72	sp, gl
			1260	16	cpx, gl
40	30	30	1375	16	gl
			1370	2	trace sp, gl
			1295	2	sp, an, gl
			1265	18	sp, an, gl
			1260	18	sp, an, cpx, gl
			1200	336	barely fritted cake, sp, an, cpx, mel
50	10	40	1275	15	gl
			1270	15	cpx, gl
			1200	72	barely fritted cake, cpx only
47	13	40	1280	6	gl
			1275	5	mt, gl
			1270	16	mt, gl
			1265	72	cpx, gl
40	20	40	1330	2	gl
			1325	1	mt, gl
			1285	16	mt, gl
			1280	44	mt, cpx, gl
			1275	15	mt, cpx, gl
			1270	15	px, gl
40	10	50	1345	1	gl
			1340	2	trace mt, gl
			1285	16	mt, gl
			1280	44	cpx, gl

gl, glass; cpx, clinopyroxene; an, anorthite; mel, melilite; sp, spinel; mt, magnetite.

Phase equilibrium diagrams: The phase equilibrium diagram at the liquidus temperature is given in Fig. 1. Clinopyroxene$_{ss}$ (ss: solid solution), anorthite, spinel$_{ss}$, and magnetite$_{ss}$ are encountered as the primary phases. In the liquidus diagram there are two points showing four-phase assemblage. One, at 1250° ±5°C, shows the liquid coexisting with clinopyroxene$_{ss}$, anorthite, and spinel$_{ss}$ and the other, at 1270° ±5°C, shows the liquid coexisting with clinopyroxene$_{ss}$, magnetite$_{ss}$, and spinel$_{ss}$. These points, however, are neither eutectic nor piercing points because of the nature of the six-component system at the liquidus temperature.

Sections with 10, 20, and 30 wt.% FATs are shown in Figs. 2, 3, and 4. Clinopyroxene$_{ss}$, melilite$_{ss}$, anorthite, and spinel$_{ss}$ are encountered as crystalline phases through out the three sections. The maximum phase assemblage is clinopyroxene$_{ss}$ + melilite$_{ss}$ + anorthite + spinel$_{ss}$ + liquid at the solidus temperatures showing univariant phase assemblage in the five-component system. Since at higher temperature the reaction $Fe_2O_3 = 2FeO + 1/2O_2$ takes place in air, the join is a part of the six-component system Fe-O-CaO-MgO-Al_2O_3-SiO_2. At lower temperature, however, this reaction does not occur and the join can be treated as a five-component system MgO-CaO-Fe_2O_3-Al_2O_3-SiO_2. In these sections, the phase assemblages clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ in the Di-rich region and clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ + spinel$_{ss}$ in the Di-poor region are found as the final phase assemblages at the subsolidus temperatures. These assemblages are expected from the following reactions with the formation of the complicate solid solutions of clinopyroxene and melilite.

In the Di-rich region:

$$xCaMgSi_2O_6 + yCaAl_2SiO_6 + zCaFe^{3+}AlSiO_6 = (x\text{-}3n)CaMgSi_2O_6.(y\text{-}3n)CaAl_2SiO_6.zCaFe^{3+}AlSiO_6.2nMgSiO_3$$

clinopyroxene solid solution

$$+ nCa_2MgSi_2O_7.nCa_2Al_2SiO_7 + 2nCaAl_2Si_2O_8 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

melilite solid solution anorthite

In the Di-poor region:

$$xCaMgSi_2O_6 + yCaAl_2SiO_6 + zCaFe^{3+}AlsiO_6 = (x\text{-}4n)CaMgSi_2O_6.(y\text{-}9n)CaAl_2SiO_6.zCaFe^{3+}AlSiO_6.2nMgSiO_3$$

clinopyroxene solid solution

$$+ nCa_2MgSi_2O_7.5nCa_2Al_2SiO_7 + 5nCaAl_2Si_2O_8 + nMgAl_2O_4 \quad \ldots\ldots (2)$$

melilite solid solution anorthite spinel

This fact and the equations indicate that the crystallization ceases on the divariant surface or the univariant line before invariant point is reached, because clinopyroxene and melilite form complicate solid solutions.

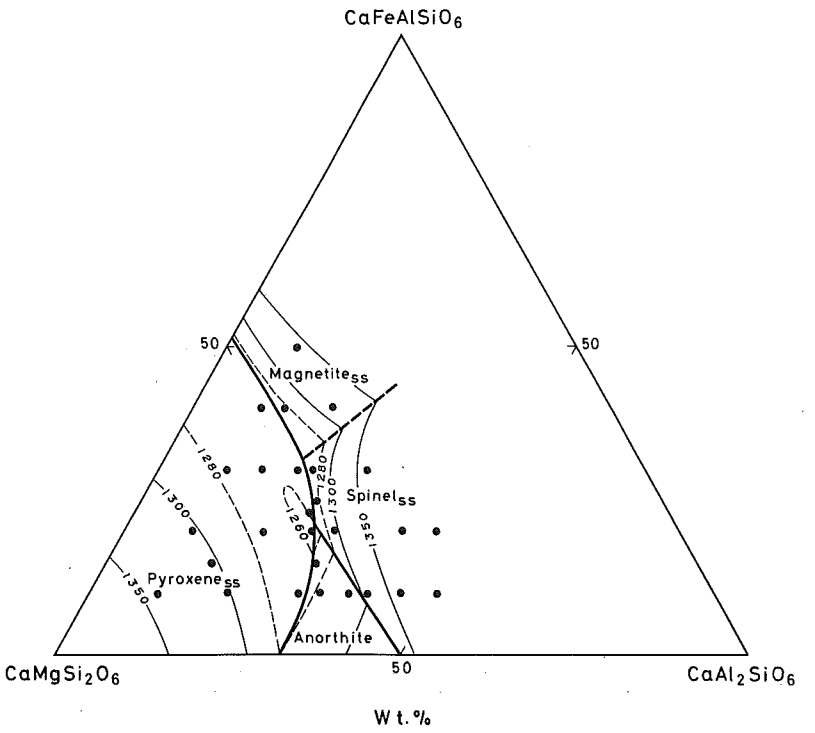

Fig. 1 Liquidus diagram of the join $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$.

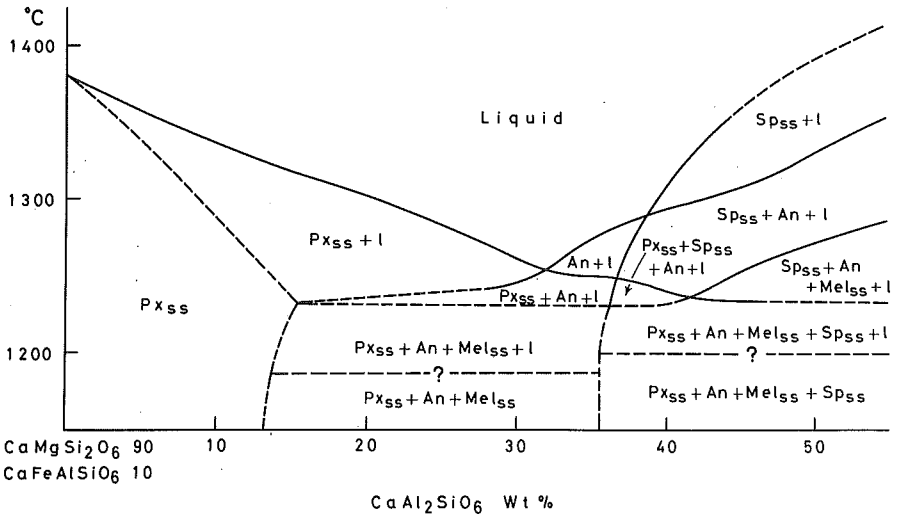

Fig. 2 Phase equilibrium diagram of 10% $CaFe^{3+}AlSiO_6$ section.

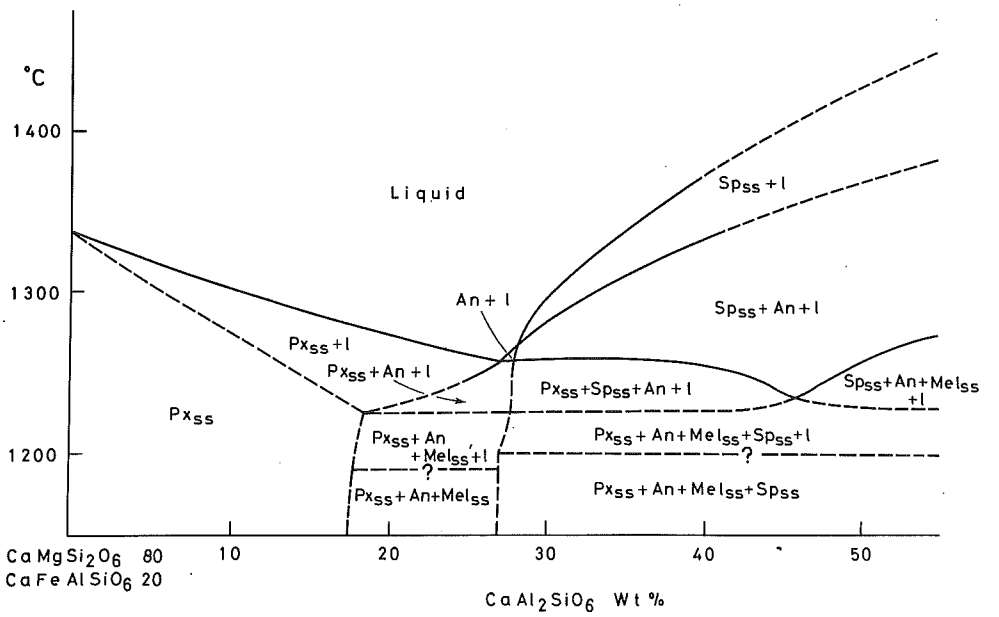

Fig. 3 Phase equilibrium diagram of 20% $CaFe^{3+}AlSiO_6$ section.

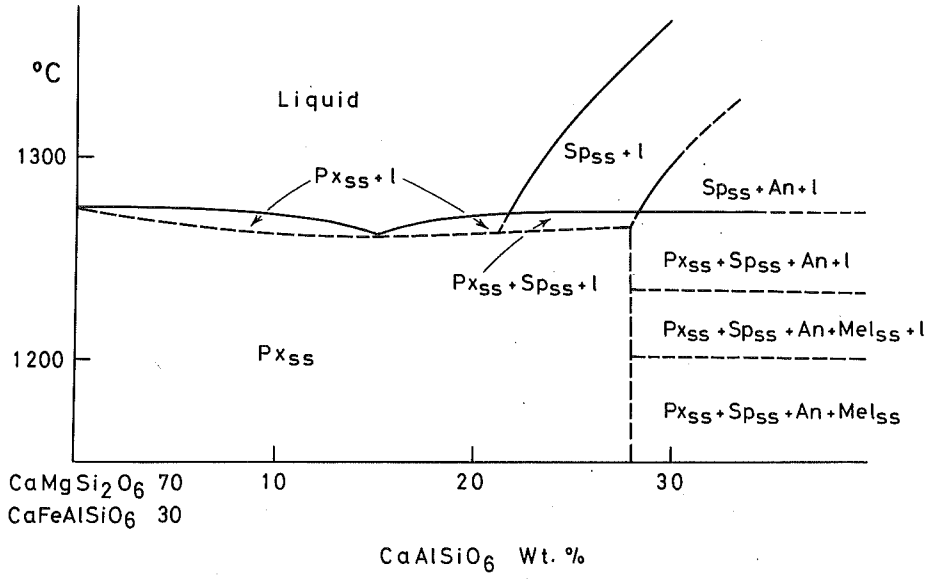

Fig. 4 Phase equilibrium diagram of 30% $CaFe^{3+}AlSiO_6$ section.

10 and 20 wt.% FATs sections are similar to each other. In the both sections five-phase assemblage clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ + spinel$_{ss}$ + liquid is surrounded by three four-phase assemblages, clinopyroxene$_{ss}$ + melilite$_{ss}$ + anorthite + liquid, clinopyroxene$_{ss}$ + anorthite + spinel$_{ss}$ + liquid, and anorthite + melilite$_{ss}$ + spinel + liquid, which are divariant in five-component system. The relationship between the five-phase assemblage and the four-phase assemblages is shown in Fig. 5. Of the four four-phase assemblages, the assemblage clinopyroxene + melilite + spinel + liquid, which is confirmed in the system CaO-MgO-Al_2O_3-SiO_2 as a univariant line (O'Hara and Biggar, 1969), was not found in the present investigation.

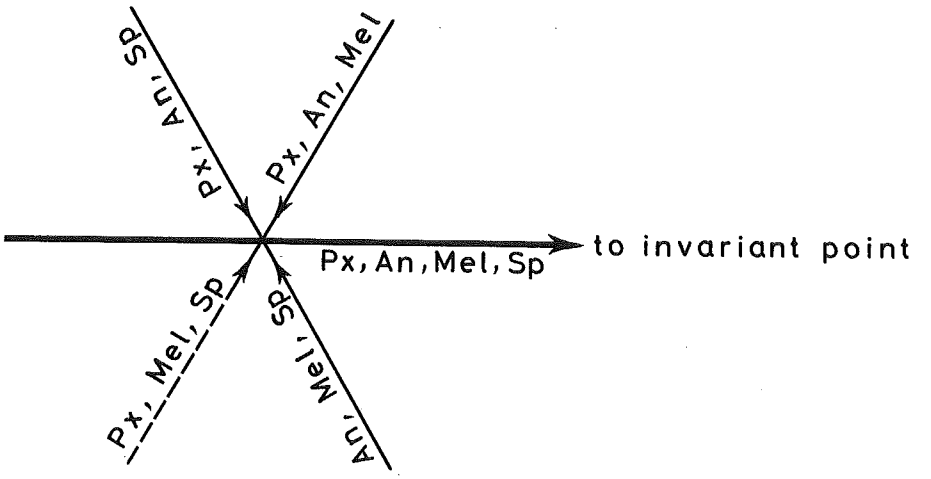

Fig. 5 Relationship between four four-phase assemblages and a five-phase assemblage. Liquid phase is eliminated.

The four-phase assemblage clinopyroxene$_{ss}$ + anorthite + melilite$_{ss}$ + liquid is no longer stable in 30% FATs section. Three three-phase assemblages clinopyroxene$_{ss}$ + anorthite + liquid, anorthite + spinel$_{ss}$ + liquid, and clinopyroxene$_{ss}$ + spinel$_{ss}$ + liquid were confirmed in the present system. The assemblage clinopyroxene$_{ss}$ + anorthite + liquid is not stable and the assemblage clinopyroxene$_{ss}$ + spinel$_{ss}$ + liquid is present in 30% FATs section.

Limit of clinopyroxene solid solution at subsolidus temperature: Hijikata and Onuma (1969) found that diopside and FATs forms complete solid solution below 1265°C. Schairer and Yoder (1970) showed that the maximum solubility of CaTs in diopside is about 12 wt.% at 1250°C. Through the

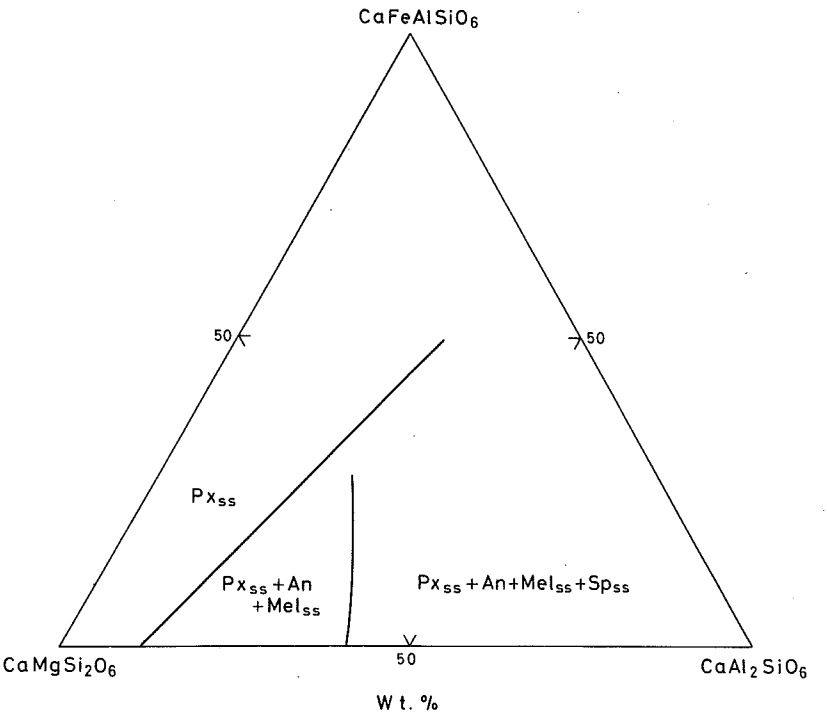

Fig. 6 Phase assemblages at subsolidus region.

sections 10, 20, and 30% FATs, the clinopyroxene solid solution area increases with the increase of FATs contents, that is, maximum solubility of CaTs in diopside is 15 wt.% at about 1230°C in 10% section, 18 wt.% at about 1225°C in 20% section, and 28 wt.% at 1270°C in 30% section with solid solution minimum at 1265°C and at $Di_{48}CaTs_{22}$ $FATs_{30}$. It is noticed in Fig. 6 that the limit of the clinopyroxene solid solution at 1250°C increases with increasing FATs.

Crystalline phases: $Clinopyroxene_{ss}$, anorthite, $melilite_{ss}$, $spinel_{ss}$, and $magnetite_{ss}$ are crystalline phases encountered in the present system. $Clinopyroxene_{ss}$ forms prismatic crystals near liquidus but forms rounded grains in subsolidus region. They are always bright yellow in color. X-ray diffraction patterns of the $clinopyroxene_{ss}$ crystallized at 1200°C for 72 hours in 10% FATs section are shown in Fig. 7. It is evident that the 002 peak shifts to lower angles and $\triangle 2\theta_{221\text{-}002}$ becomes larger with increasing CaTs, indicating that the clinopyroxene is not pure diopside but solid solution as shown in equations (1) and (2). The relationship between $\triangle 2\theta_{221\text{-}002}$ and phase assemblage is shown

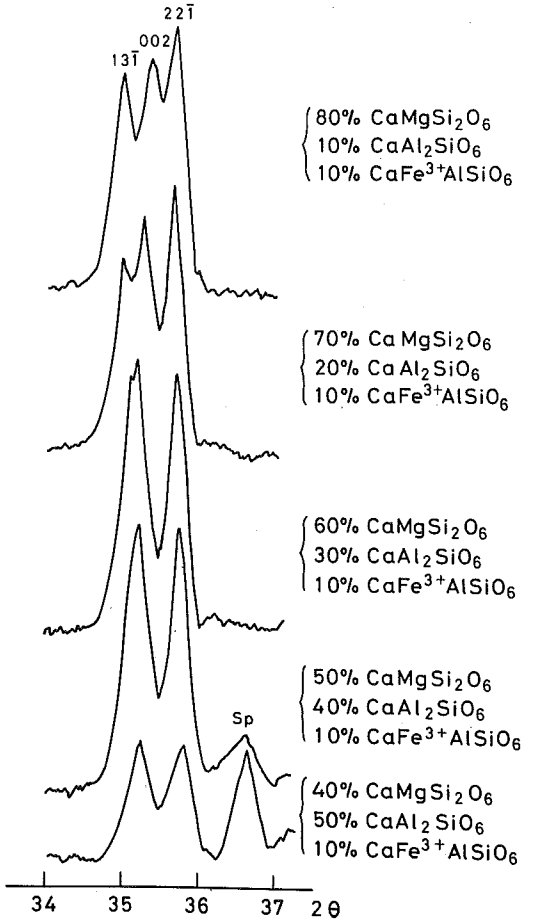

Fig. 7 X-ray diffraction patterns of the clinopyroxene solid solutions crystallized at 1200°C for 72 hours in 10% $CaFe^{3+}AlSiO_6$ section, showing the shift of the 002.

in Fig. 8. $\triangle 2\theta_{221\text{-}002}$ increases with increasing CaTs in the phase assemblage clinopyroxene$_{ss}$ + melilite$_{ss}$ + anorthite and remains at constant value in the assemblage clinopyroxene$_{ss}$ + melilite$_{ss}$ + anorthite + spinel$_{ss}$. Since four-phase assemblage is divariant in five-component system, the composition of one of four crystalline phases is variable at constant temperature. Therefore, melilite$_{ss}$ or spinel$_{ss}$ has variable composition. Since melilite$_{ss}$ occurs at lower temperature region together with other minute crystals, sometimes it was difficult to identify this mineral under the microscope. The strongest peak of melilite obtained in the present study in X-ray diffraction has

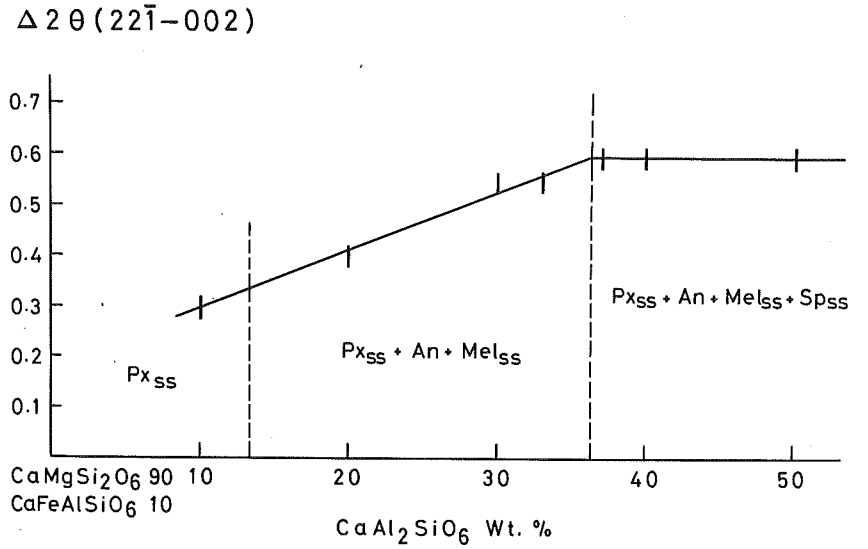

Fig. 8 Change of $\triangle 2\theta_{22\bar{1}\text{-}002}$ of the clinopyroxene solid solutions crystallized at 1200°C for 72 hours in 10% $CaFe^{3+}AlSiO_6$ section.

value between 31.1° and 31.3° in 2θ, suggesting that melilite$_{ss}$ consists of akermanite and gehlenite as indicated in the equations (1) and (2). Anorthite occurs as needles or platy crystals having low birefringence and 204 relfection is 27.92° in 2θ, indicating that anorthite is pure compound but not solid solution. Spinel$_{ss}$ forming small octahedral crystals is almost colorless in the FATs-poor region but is pale brown in color in the FATs-rich region. This color may be ascribed to substitution of Fe^{3+} in spinel$_{ss}$ and becomes deeper with increasing FATs. Magnetite$_{ss}$ was found only at the liquidus temperatures and subliquidus temperatures in the FATs-rich region as octahedral form with distinct crystal faces and probaly is solid solution with spinel molecule. Huchenholz *et al.* (1968) analysed the magnetite$_{ss}$ which appears at the liquidus temperatures in the analogous system diopside-FTs and found that this magnetite$_{ss}$ contains considerable amount of Mg. This may be also the case in the magnetite$_{ss}$ in the present investigation. It is estimated that Al is also incorporated in magnetite$_{ss}$.

The Join Bearing on Fassaitic Pyroxene

It is known that clinopyroxenes from alkalic rock are higher in Al and Ti contents than those from tholeiite basalt, and these ions are incroporated in diopside as CaTs and Tp (Kushiro, 1960 and Yagi and Onuma, 1967). The substitution of CaTs in diopside, according to Clark *et al.* (1962), is favored by high pressure, while Yagi and Onuma (1967) have shown that Ti-rich diopside decomposes into Ti-poor diopside and perovskite ($CaTiO_3$) at 10 kbar.

The clinopyroxene from undersaturated alkalic rocks, such as nephelinite and melilitite, is rich not only in CaTs but also in Tp, FTs, and FATs, and includes small amount of acmite moleule, usually less than 5%. The clinopyroxene in a kalsilite-bearing olivine melilitite of Nyragongo, East Africa (Sahama and Meyer, 1958) includes 21.4% total Tschermak's molecule (Ts = CaTs + FTs + FATs + Tp) and that in a melilite nepheline dolerite of Scawt Hill, Antrin (Tilley and Harwood, 1931) 30.7%, respectively. Therefore, these clinopyroxenes are fassaitic pyroxenes with the substitution of Al for Si. Huchenholz (1974), in a review on the chemical composition of the pyroxenes in alkalic basalts from various localities, pointed out that when $Na < Fe^{3+} + Al$ the pyroxenes are rich in total Ts and fassaitic rather than acmitic and quoted Hibsh's report (1943) showing that the fassaitic augite from a leucite tephrite of the Central Mountain of Bohemia contains 30% total Ts, of which FTs content is 58%.

The present investigation seems to agree with these facts. The mixture $Di_{70}CaTs_{15}FATs_{15}$ crystallizes as single phase of clinopyroxene, indicating that this clinopyroxene contains 30% total Ts. The experimental results show that the solubility of total Ts in diopside considerably increases even at lower pressure, when oxygen partial pressure is high enough to form FATs. Diopside and FATs form a complete solid solution series in air at 1 atm. (Hijikata and Onuma, 1969), but all of these solid solutions richer in FATs than $Di_{90}FATs_{10}$ decompose into hedenbergitic pyroxene, melilite and hercynite above 1000°C at lower oxygen fugacity, say 10^{-11} (Onuma and Oba, unpublished data). Onuma and Hariya (unpublished data) showed that the clinopyroxene crystallized from the mixture $Di_{70}CaTs_{15}FATs_{15}$ decomposes into diopsidic pyroxene, garnet, and oxide at 10 kbar. These experimental results and chemical composition of natural fassaitic pyroxene suggest that the volcanic rocks including fassaitic pyroxene, such as melilitite, nephelinite, basanite, tephrite, and other alkalic rocks, were formed at rather low pressure, less than 10 kbar and at higher oxygen pressure.

Yagi (1966) suggested that when oxygen partial pressure in the magma is higher pyroxene becomes acmitic, while lower pyroxene includes more

hedenbergite molecule. However, if a magma is poor in Na and rich in Ca such as melilitite, pyroxene crystallizing from it incorporates Ts which is rich in Ca, and when nepheline and melilite crystallize together with pyroxene Na is incorporated in these minerals and pyroxene contains only small amount of Na.

Taking these discussions into account, pyroxenes from alkalic rocks rather low in Na and high in Ca can be described in terms of the four molecules Di, CaTs, FATs, and Tp, and the system Di-CaTs-FATs-Tp is relevant for understanding the crystallization of pyroxene in such alkalic rocks. It is noted in Fig. 9 that the estimated pyroxene solid solution volume at subsolidus in the system Di-CaTs-FATs-Tp expands towards the FATs corner and that the content of total Ts in diopside may exceed 30%, which is a maximum value in the natural fassaitic pyroxene in alkalic volcanic rocks.

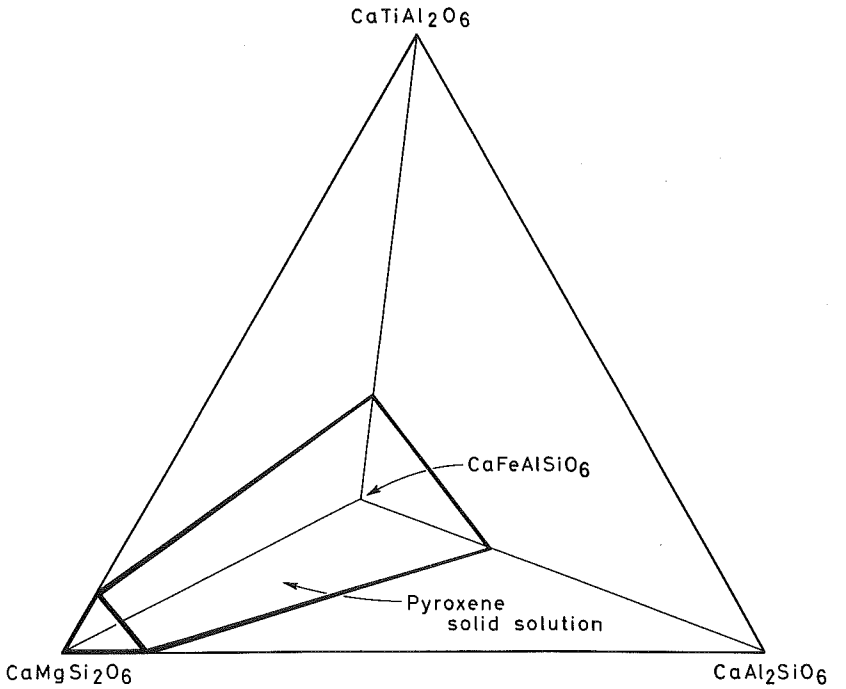

Fig. 9 Estimated clinopyroxene solid solution volume in the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$-$CaTiAl_2O_6$ at atmospheric pressure.

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