THE JOIN $CaMgSi_2O_6$-$CaTiAl_2O_6$ AND ITS BEARING ON THE TITANAUGITES

by

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(with 7 Text-Figures)

(Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University No. 1064)

Abstract

The chemistry of the titanaugites from alkalic rocks shows that substitution of Ti-Mg is accompanied by that of Al-Si, and the titanium component is regarded to be present in a hypothetical titan pyroxene molecule, $CaTiAl_2O_6$ (henceforth abbreviated Tp). Therefore the join $CaMgSi_2O_6$-$CaTiAl_2O_6$ was studied in air. The phase equilibrium diagram indicates that the join is pseudobinary, with only limited binary solid solutions of pyroxene between diopside and $Di_{89}Tp_{11}$ (wt per cent). At atmospheric pressure pure $CaTiAl_2O_6$ decomposes into perovskite and corundum, and spinel appears in place of corundum when Mg is available. Crystalline phases found in the join are pyroxene solid solutions, forsterite, perovskite, spinel and melilite, all of which, probably except perovskite, are solid solutions. Melilite is confined to subsolidus temperatures, but other phases have their liquidus curves in this join. The maximum solubility of $CaTiAl_2O_6$ in diopside at atmospheric pressure is about 11 per cent, which corresponds to about 4 per cent TiO_2 (wt per cent), whereas experiments under high pressures (10–25 kb) indicate that the solubility of Tp in diopside decreases nearly to nil. This suggests that the titanaugites are usually formed at relatively low pressures.

Optical properties of the pyroxene solid solutions show the increase of refractive indices of about 0.006 for each per cent TiO_2. They are always colorless, in contrast to distinct pleochroism in natural titanaugites. Crystal chemistry and crystallization of natural titanaugites are discussed in the light of the present experiments.

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Introduction

The pyroxenes in alkalic basalts or related rocks are usually high in titanium content, sometimes as high as 5 per cent TiO_2. The chemistry of these titanaugites shows that substitution of Ti-Mg is accompanied by that of Al-Si and the titanium component may be regarded to be present in a hypothetical titan pyroxene molecule, $CaTiAl_2O_6$ (Tp). Although much progress has been made recently in the experimental studies on various rock-forming pyroxenes, relatively little is known yet on the titan-bearing pyroxenes from the view point of experimental petrology.

In order to elucidate the crystallization of titanaugites from the magma and their crystal chemistry, the join $CaMgSi_2O_6$-$CaTiAl_2O_6$ has been studied as a first step in air at atmospheric pressure and under high pressures. In the present paper the results of these experiments are given, with special reference to crystal chemistry and crystallization of natural titanaugites.

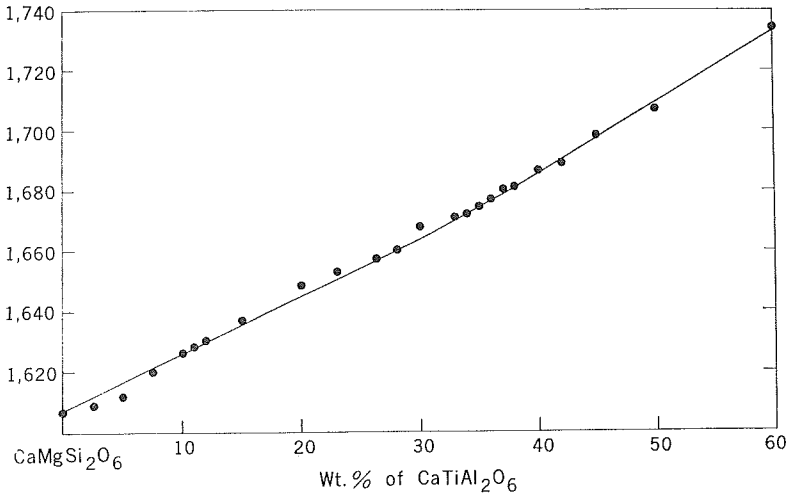

Fig. 1
Refractive indices of glasses of the join $CaMgSi_2O_6$–$CaTiAl_2O_6$ (weight per cent)

Experimental method

The glasses were prepared by melting the reagent chemicals of calcium carbonate, magnesia, titania and alumina, and pure quartz at temperatures from 1300° to 1500°C. Melting and crushing were repeated until homogeneous glasses were obtained. The glasses were made at first in 10 weight per cent intervals, and then with progress in the experiments, more glasses of intermediate compositions were prepared to locate the invariant points or field boundaries. The melting point of pure $CaTiAl_2O_6$, which decomposes into perovskite and corundum is very high and caused much difficulty in preparation of glasses and there is not much

Table 1. Initial Treatment for Crystallizing Glasses Used in Quenching Experiments

No.	Composition Wt%		Refractive Index of glass	Temperature °C	Time Days
	$CaMgSi_2O_6$	$CaTiAl_2O_6$			
$DT_{2.5}$	97.5	2.5	1.609	900	10
DT_5	95	5	1.612	900	32
$DT_{7.5}$	92.5	7.5	1.620	900	10
				1000	12
DT_{10}	90	10	1.626	900	5
				1000	10
DT_{11}	89	11	1.628	900	17
				1000	1
DT_{12}	88	12	1.630	900	30
DT_{15}	85	15	1.637	900	30
DT_{20}	80	20	1.648	900	33
				1000	1
DT_{23}	77	23	1.653	1000	20
DT_{25}	75	25	1.657	900	3
				1000	10
DT_{27}	73	27	1.660	1000	20
DT_{30}	70	30	1.668	1000	11
DT_{33}	67	33	1.671	1000	15
DT_{34}	66	34	1.672	1000	15
DT_{35}	65	35	1.674	900	25
DT_{36}	64	36	1.677	800	54
DT_{37}	63	37	1.680	900	32
DT_{38}	62	38	1.681	800	16
DT_{40}	60	40	1.686	800	10
				1000	10
DT_{42}	58	42	1.689	1000	20
DT_{45}	55	45	1.698	900	19
DT_{50}	50	50	1.707	800	14
				1000	1
$DT_{52.5}$	47.5	52.5	—	1000	0.1
DT_{60}	40	60	1.734	800	5
				1000	14

petrologic meaning to study the high titanium part of the join. Therefore the composition studied covers the range from diopside to 60 wt per cent $CaTiAl_2O_6$. In total 24 glasses were prepared for the experiments.

The crushed glasses, heated at subsolidus temperatures of 800°–1000°C for periods from several days to more than 50 days were found to consist of minute granular crystals of pyroxene, perovskite, spinel, and melilite or their aggregates. The initial treatment for crystallizing the glasses is given in Table 1, and refractive indices of the glasses are shown in Fig. 1.

The furnace was regulated with an accuracy of ± 1°C. The temperature was measured by $Pt\text{-}Pt_{87}Rh_{13}$ thermocouple, which was frequently calibrated at standard melting points of NaCl 800.4°, Au 1062.6° and diopside 1391.5°C.

Experimental results

The results of the determination of liquidus and solidus temperatures by the quenching experiments are given in Table 2, and the equilibrium diagram of the

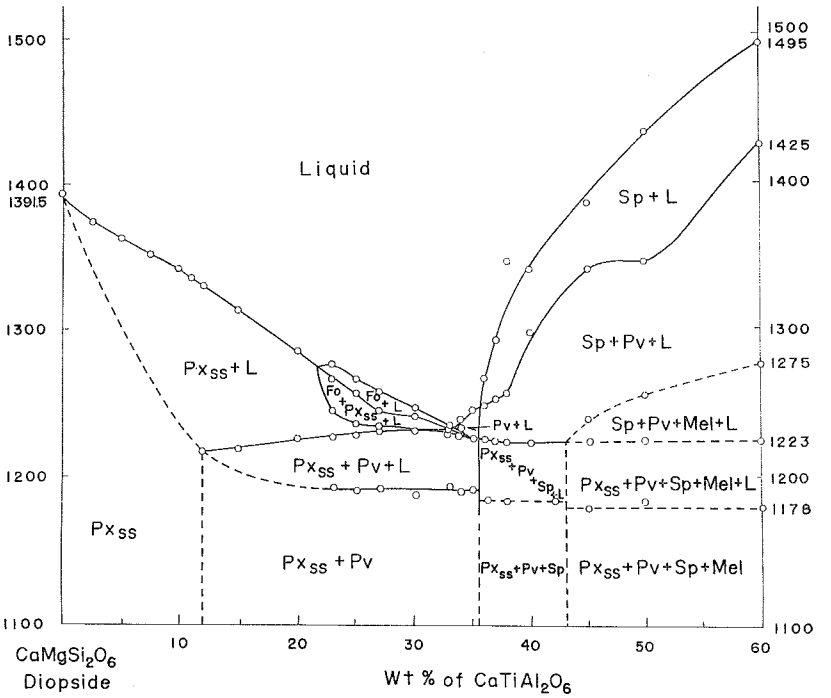

Fig. 2
Equilibrium diagram of the join $CaMgSi_2O_6$–$CaTiAl_2O_6$. Fo, forsterite; Mel, melilite; Pv, perovskite; Px_{ss}, pyroxene solid solution; Sp, spinel; L, liquid.

Table 2. Results of Quenching Experiments

No.	Composition wt%		Temperature, °C	Time hrs	Results
	$CaMgSi_2O_6$	$CaTiAl_2O_6$			
$DT_{2.5}$	97.5	2.5	1375	1	All glass
			1370	10	Moderate amount px in glass
DT_5	95	5	1365	4	All glass
			1360	2	Small amount px in glass
$DT_{7.5}$	92.5	7.5	1355	1	All glass
			1350	1	Rare px in glass
DT_{10}	90	10	1345	1	All glass
			1340	1	Moderate amount px in glass
DT_{11}	89	11	1340	1	All glass
			1335	1	Very rare px in glass
			1330	1	Lots px in glass
DT_{12}	88	12	1335	40	All glass
			1330	2	Very rare px in glass
			1220	168	Lots px in glass
			1215	72	Lots px and rare pv with small amount glass
			1210	16	Well-fritted cake
DT_{15}	85	15	1315	1	All glass
			1310	1	Small amount px in glass
			1220	24	Lots px in glass
			1215	24	Lots px and small amount pv with small amount glass
DT_{20}	80	20	1285	1	All glass
			1280	24	Small amount px in glass
			1230	10	Lots px in glass
			1225	1	Lots px and rare pv with small amount glass
DT_{23}	77	23	1280	1	All glass
			1275	3	Very rare fo in glass
			1270	1	Rare fo in glass
			1265	1	Rare fo and rare px in glass
			1245	2	Very rare fo and moderate amount px in glass
			1240	2	Lots px in glass
			1230	18	Lots px in glass
			1225	18	Lots px and small amount pv in glass
			1190	72	Barely fritted cake
			1185	72	Loose powder
DT_{25}	75	25	1270	11	All glass
			1265	1	Very rare fo in glass
			1260	1	Rare fo in glass
			1258	1	Small amount fo in glass
			1255	1	Small amount fo and rare px in glass
			1235	2	Lots px and rare fo in glass
			1230	1	Lots px in glass

			1225	1	Lots px and rare pv in glass
			1190	72	Barely fritted cake
			1185	72	Loose powder
DT_{27}	73	27	1260	3	All glass
			1255	1	Rare fo in glass
			1245	2	Small amount fo in glass
			1240	2	Moderate amount px and rare fo in glass
			1235	3	Moderate amount px and rare fo in glass
			1230	18	Lots px and rare pv in glass
			1225	18	Lots px and small amount pv with small amount glass
			1190	72	Barely fritted cake
			1185	72	Loose powder
DT_{30}	70	30	1250	3	All glass
			1245	11	Very rare fo in glass
			1240	1	Rare fo and very rare px in glass
			1230	3	Lots px, very rare pv and very rare fo in glass
			1225	3	Lots px and small amount pv in glass
			1185	72	Well-fritted cake
			1180	144	Loose powder
DT_{33}	67	33	1235	2	All glass
			1233	1	Very rare fo in glass
			1230	1	Rare fo, small amount px and very rare pv in glass
			1225	1	Lots px and rare pv in glass
			1190	72	Barely fritted cake
			1185	72	Loose powder
DT_{34}	66	34	1240	2	All glass
			1235	2	Rare pv in glass
			1230	2	Small amount pv and small amount fo in glass
			1225	20	Lots px and small amount pv in glass
			1185	72	Barely fritted cake
			1180	72	Loose powder
DT_{35}	65	35	1250	10	All glass
			1245	48	Rare pv in glass
			1230	1	Moderate amount pv in glass
			1225	3	Lots pv, rare px and very rare fo in glass
			1220	12	Moderate amount pv and lots px in glass
			1190	70	Barely fritted cake
			1185	72	Loose powder
DT_{36}	64	36	1270	2	All glass
			1265	12	Rare sp in glass
			1250	2	Small amount sp in glass
			1245	2	Small amount sp and rare pv in glass
			1225	3	Moderate amount sp and moderate amount pv in glass
			1223	3	Small amount sp, moderate amount pv and rare px in glass

			1185	72	Barely fritted cake
			1180	72	Loose powder
DT_{37}	63	37	1295	20	All glass
			1290	20	Rare sp in glass
			1255	4	Small amount sp in glass
			1250	3	Small amount sp and rare pv in glass
			1225	3	Small amount sp and moderate amount pv in glass
			1223	3	Small amount pv, small amount sp and moderate amount px in glass
			1220	168	Lots px, small amount pv and rare sp in glass
			1190	70	Barely fritted cake
			1185	72	Loose powder
DT_{38}	62	38	1350	12	All glass
			1345	2	Rare sp in glass
			1260	18	Moderate amount sp in glass
			1255	4	Moderate amount sp and rare pv in glass
			1225	12	Moderate amount sp and moderate amount pv in glass
			1220	12	Lots px, small amount pv and small amount sp in glass
			1185	72	Barely fritted cake
			1180	72	Loose powder
DT_{40}	60	40	1345	10	All glass
			1340	1	Rare sp in glass
			1300	1	Small amount sp in glass
			1295	1	Moderate amount sp and small amount pv in glass
			1225	12	Moderate amount pv and small amount sp in glass
			1220	5	Moderate amount pv, moderate amount px and small amount sp in glass
			1185	72	Barely fritted cake
			1180	72	Loose powder
DT_{42}	58	42	1185	72	Well-fritted cake: Lots px, moderate amount pv and small amount sp with small amount glass
			1180	72	Loose powder
DT_{45}	55	45	1390	2	All Glass
			1385	2	Rare sp in glass
			1345	2	Small amount sp in glass
			1340	2	Moderate amount sp and very rare pv in glass
			1240	3	Lots pv and moderate amount sp in glass
			1230	15	Moderate amount pv, moderate amount sp and small amount mel in glass
			1220	6	Moderate amount pv, moderate amount sp, moderate amount px and moderate amount mel in glass
			1190	72	Well-fritted cake: lots px, lots pv, small amount sp and small amount mel with small amount glass

			1180	72	Barely fritted cake
			1175	72	Loose powder
DT_{50}	50	50	1440	1	All glass
			1435	3	Very rare sp in glass
			1350	12	Small amount sp in glass
			1345	2	Small amount sp and very rare pv in glass
			1260	24	Moderate amount pv and small amount sp in glass
			1255	10	Lots pv, small amount sp and small amount mel in glass
			1225	3	Lots pv, small amount sp and rare mel in glass
			1220	6	Lots pv, small amount sp, small amount px and rare mel in glass
			1190	72	Barely fritted cake
			1185	72	Loose powder
DT_{60}	40	60	1500	2	All glass
			1495	2	Very rare sp in glass
			1430	11	Moderate amount sp in glass
			1425	1	Moderate amount sp and rare pv in glass
			1350	6	Lots pv and moderate amount sp in glass
			1270	48	Lots pv, small amount sp and rare mel in glass
			1230	12	lots pv, small amount sp and small amount mel in glass
			1221	5	Lots pv, small amount sp, small amount mel and small amount px in glass
			1180	72	Barely fritted cake
			1175	72	Loose powder

fo, forsterite ; mel, melilite ; pv, perovskite ; px, pyroxene solid solution ; sp, spinel.

join $CaMgSi_2O_6$-$CaTiAl_2O_6$ is shown in Fig. 2. It is noticed that the join is very similar to the join $CaMgSi_2O_6$-$CaAl_2SiO_6$ at atmospheric pressure (de Neufville and Schairer, 1962) and there is a series of binary solid solutions between diopside and $Di_{89}Tp_{11}$, and the join can be treated as binary only in this portion. The composition of Tp_{11} represents the maximum solubility of Tp in diopside. The pyroxene solid solutions crystallizing out from the melts more Tp-rich than Tp_{11} are always associated with perovskite, and the composition of pyroxenes remains the same as Tp_{11} as will be described later. At atmospheric pressure pure $CaTiAl_2O_6$ decomposes into perovskite and corundum, and spinel appears in place of corundum when Mg is available. In addition to these phases, forsterite and melilite also crystallize out below the liquidus or solidus curves, and the join ceases to be binary.

Attention is called to the narrow field of forsterite on the liquidus surface in the range of Tp_{23} to Tp_{34}. There is a pseudoeutectic where forsterite and perovskite are in equilibrium with a liquid of Tp_{34} in composition at 1233°C. Below the liquidus, however, the forsterite once crystallized out decreases in amount due

to the reaction with liquid to form pyroxene solid solutions, probably Tp_{11} in composition, until forsterite completely disappears. Such reaction relation between forsterite and diopsidic pyroxene was first found by BOWEN (1922) in the join nepheline-diopside and was later reaffirmed by SCHAIRER, YAGI and YODER (1962). In this case forsterite remains stable under the subsolidus regions, but it ceases to be stable below the liquidus in the present join, and it does not coexist with perovskite in the subsolidus region. In the portion more Tp-rich than Tp_{43}, melilite appears in the subsolidus region, along with spinel and perovskite.

Spinel has a wide field in the liquidus surface in the range more Tp-rich than Tp_{36}. From the melt Tp_{38} spinel crystallized out at temperature much higher than that expected from the result obtained from nearby points. Same result was obtained in the carefully repeated experiments, although no satisfactory explanation is given for this discrepancy. This point is shown in Fig. 2, but the liquidus curve of spinel was drawn omitting this point.

Solidus curves were determined by the temperatures at which the starting materials of crystallized powder were barely fritted, and the accuracy was not so high as the determination of liquidus curves.

Crystalline phases encountered in the present join will be briefly described. Forsterite assumes usually colorless rounded form, without distinct crystal faces, and shows high interference color, by which it can be distinguished from pyroxene solid solutions. Forsterite is estimated to be solid solutions of Mg_2SiO_4 with small amounts of monticellite moleucule $CaMgSiO_4$. It is not clear whether Ti is is present in forsterite or not.

Perovskite occurs usually in minute octahedral or irregular crystals, slightly brownish in color. It can easily be identified by its high relief due to extremely high refractive index. Spinel forms small octahedral crystals, slightly pale greenish in color. Melilite forms small granular or tabular, colorless crystals with weak birefringence. Since it appears only in the subsolidus temperatures along with spinel, perovskite or pyroxenes, the crystal forms are not well-developed. The melilite is regarded to form solid solutions between akermanite ($Ca_2MgSi_2O_7$), gehlenite ($Ca_2Al_2SiO_7$) and some Ti-bearing molecules, although the estimate of composition was not possible in the present experiments. Pyroxene solid solutions will be described in the following section.

Physical properties of pyroxene solid solutions

Pyroxene solid solutions in the present join form usually stout prismatic crystals, rarely twinned on (100) in the temperature ranges near the liquidus, but form rounded grains when coexisting with melilite, perovskite, and spinel at lower temperature ranges near the liquidus, but form rounded grains when coexisting with melilite, perovskite, and spinel at lower temperatures. They are always colorless

and show oblique extinction. Refractive indices of the pyroxenes are given in Table 3 and are shown in Fig. 3. Data on the optical properties of other synthetic titan-bearing pyroxenes obtained by BARTH (1931) and SEGNIT (1953) are also summarized in the same table for comparison. It is noticed that the increase of refractive indices for each per cent TiO_2 is different in the three series of pyroxene solid solutions, probably owing to the effects of the coexisting ions.

It is noteworthy that all these synthetic titan-pyroxenes are colorless, in contrast to distinct pleochroism in natural titanaugites. This is probably due to the presence of Ti^{4+} instead of Ti^{3+} in the synthetic titan-pyroxenes formed in air and also to the absence of Fe^{2+} and Fe^{3+} ions.

A systematic shift of the peaks was found in the X-ray powder patterns of pyroxene solid solutions from pure diopside to Tp_{11}. Of these the most remarkable change is observed in the 2θ difference between $(22\bar{1})$ and (002) reflections. Each

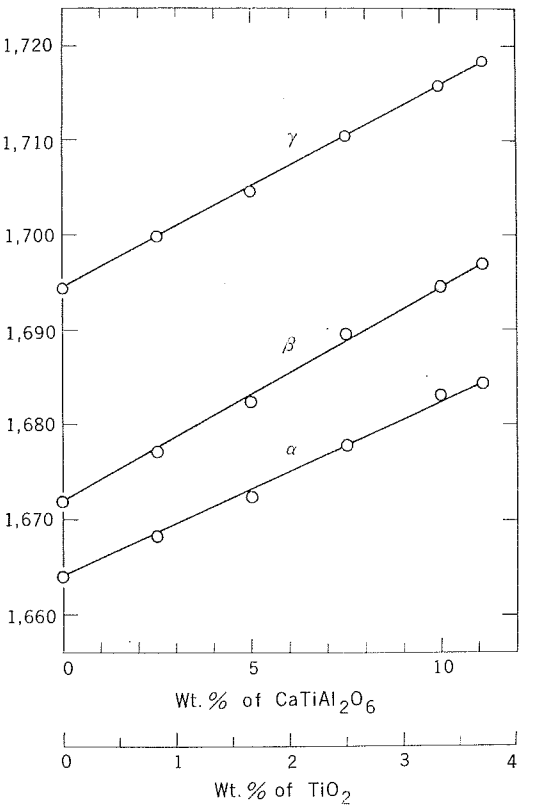

Fig. 3
Refractive indices of synthetic pyroxene solid solutions of the join $CaMgSi_2O_6$–$CaTiAl_2O_6$.

Table 3. Optical Properties of Ti-bearing Pyroxene Solid Solutions

Composition, wt%		1)	α	β	γ	2Vz
$CaMgSi_2O_6$	$CaTiAl_2O_6$					
97.5	2.5		1.669	1.677	1.700±.003	—
95	5		1.673	1.683	1.705±.003	—
90	10		1.678	1.690	1.711±.003	—
89	11		1.684	1.697	1.718±.003	—
Increase of indices for each per cent TiO_2					0.006	
$CaMgSi_2O_6$	$CaMgTi_2O_6$ 2)					
100	0		1.664	1.672	1.695±.003	59°±4°
94	6		1.685	1.691	1.712±.003	60°±4°
90	10		1.700	1.708	1.730±.003	60°±4°
Increase of indices for each per cent TiO_2					0.005	
$CaMgSi_2O_6$	TiO_2 3)					
98	2		1.667	—	1.695	—
96	4		1.677	—	1.704	77°
Increase of indices for each per cent TiO_2					0.004	

1) Present study
2) Barth (1931)
3) Segnit (1953)

$\Delta 2\theta$ value is an average of the values obtained by five repeated procedures. The $\Delta 2\theta$ changes from 0.08° for pure diopside to 0.33° for Tp_{11} for CuKα radiation. The pyroxene solid solutions obtained from the melt more Tp-rich than Tp_{11} have also nearly the same value as that of Tp_{11} as shown in Fig. 4. Therefore it is expected that the stable pyroxene solid solutions from the more titan-rich melts have also composition similar to Tp_{11}, which represent the maximum solubility of Tp in diopside.

A systematic change of $\Delta 2\theta$ between $(31\bar{1})$ and $(22\bar{1})$ from 1.03° for pure diopside to 0.99° for Tp_{11} for CuKα radiation is shown in Fig. 5. These diagrams are useful for the accurate determination of the composition of the pyroxene solid solutions in the diopside-$CaTiAl_2O_6$ series.

Metastable pyroxene solid solutions form readily during the devitrification of glasses lying outside the limit of the stable solid solutions, but on prolonged heating they are gradually replaced by the stable ones. For example, glass of $DT_{52.5}$ (Di 47.5, Tp 52.5 wt per cent, or Di 50, Tp 50 mol per cent) devitrified at 1000° for 2 hrs was used as the starting materials for the following experiments in subsolidus regions.

Since the crystallinity was poor, the determination of the phases was made only by X-ray. In the runs Nos. 1 and 2, pyroxene solid solutions show X-ray powder patterns in which (002) and $(22\bar{1})$ reflections are widely separated, but these peaks

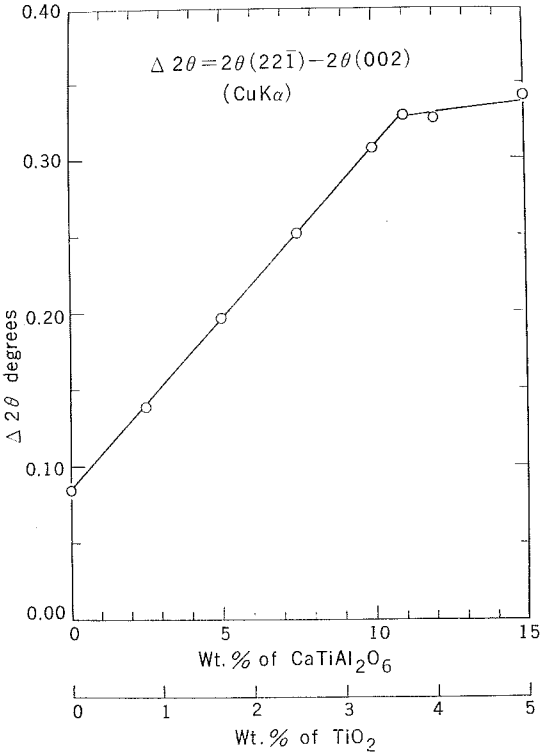

Fig. 4
Δ2θ CuK*α* radiation (22$\bar{1}$)-(002) for pyroxene solid solutions of the join $CaMgSi_2O_6$–$CaTiAl_2O_6$.

Run No.	Temperature °C	Time hrs	Results
1	840	24	Px only
2	840	96	Px only
3	1000	24	Px and Pv
4	1000	96	Px and Pv

lie much closer in the pyroxenes in the runs Nos. 3 and 4, and perovskite was also found in addition to pyroxene. Reflections due to spinel and melilite were not ascertained.

This suggests that pyroxene solid solutions, very rich in Tp, were formed metastably at lower temperatures, but they exsolve perovskite with prolonged heating at higher temperatures to transform into Tp-poor, stable pyroxene solid solutions. Such metastable formation of pyroxene solid solution in the join diopside-pyrope has been discussed by O'HARA and SCHAIRER (1963).

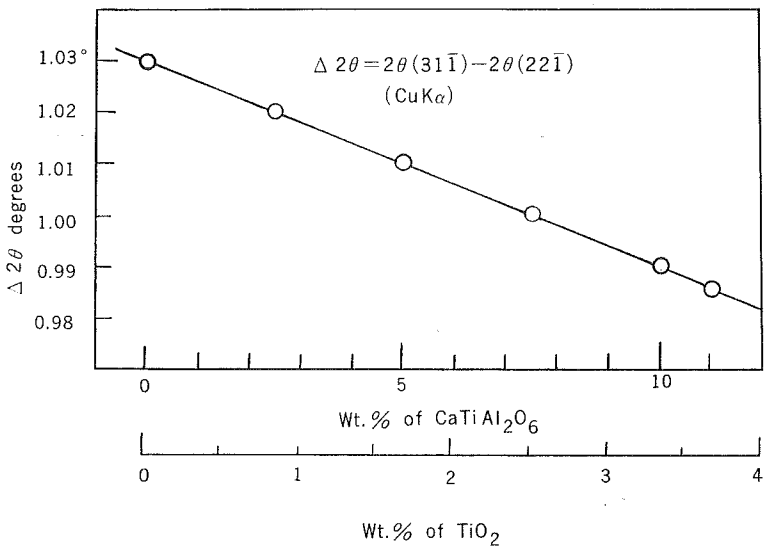

Fig. 5
Δ2θ CuK*α* radiation (31$\bar{1}$)-(22$\bar{1}$) for pyroxene solid solutions of the join $CaMgSi_2O_6$–$CaTiAl_2O_6$.

Experiments under high pressures

Preliminary experiments under high pressures were made on the pyroxene solid solutions of $DT_{2.5}$ and DT_{11} and also metastable pyroxene of $DT_{52.5}$ by means of a girdle type high pressure apparatus, details of which is described elsewhere (HIJIKATA and YAGI, 1967). The results are given in Table 4. Attention

Table 4. Results of Experiments under High Pressures

No.	Composition, wt%		Temperature, °C	Pressure Kb	Time Min	Results
	$CaMgSi_2O_6$	$CaTiAl_2O_6$				
$DT_{2.5}$	97.5	2.5	1000	10	60	Px and Pv
			1000	20	60	Px and Pv
DT_{11}	89	11	1000	10	30	Px and Pv
			1000	20	60	Px and Pv
			1000	25	60	Px, Pv and very rare garnet
$DT_{52.5}$	47.5	52.5	1000	15	40	Px, Pv and (?)
			1000	20	40	Px and Pv
			1000	25	40	Garnet, Pv and (?)

Pv, perovskite; Px, pyroxene solid solution; (?), Mineral is present but not identified.

is called to the fact that perovskite is always exsolved from the homogeneous pyroxenes, even in the case of pyroxene with minimum content of Tp. The reaction may be represented by the following equation:

$$\underset{\text{pyroxene s.s.}}{m\ CaMgSi_2O_6.nCaTiAl_2O_6} \rightarrow \underset{\text{pyroxene s.s.}}{(m\text{-}n)CaMgSi_2O_6.n\underbrace{CaAl_2SiO_6+n}MgSiO_3} + \underset{\text{perovskite, where } m \gg n.}{nCaTiO_3}$$

The coupled substitution of Al-Al for Mg-Si in diopside, yielding the Ca-Tschermak's molecule has been demonstrated by CLARK, SCHAIRER and de NEUFVILLE (1962). They found that there is a complete series of solid solutions between diopside and Ca-Tschermak's molecule at 20kb. Since there is also a limited solid solution between diopside and enstatite (BOYD and SCHAIRER 1964), the assemblage of (m-n) $CaMgSi_2O_6.nCaAl_2SiO_6+nMgSiO_3$ may be represented by one phase of pyroxene. The pyroxene of Ca-Tschermak's molecule composition has a stability field at high pressure and temperature, as has been determined recently by HIJIKATA and YAGI (1967), and has much smaller molar volume than that of diopside. Perovskite has a density higher than that of pyroxene. Therefore the assemblage on the right side of the above equation is more stable under high pressures. Under still higher pressures there may be a possibility that part of this pyroxene will transform into garnet.

The reaction in the metastable pyroxene of $Tp_{52.5}$or equimolecular assemblage of Di and Tp may be represented by the following equation:

$$\underset{\text{pyroxene s.s.}}{3CaMgSi_2O_6.3CaTiAl_2O_6} \rightarrow \underset{\text{garnet}}{2(Ca,\ Mg)_3Al_2Si_3O_{12}} + \underset{\text{perovskite}}{3CaTiO_3} + \underset{\text{corundum}}{Al_2O_3}$$

Since the phases on the right side are all much denser than pyroxene, the reaction is expected to proceed from left to right under high pressures.

These experiments indicate that the solubility of Tp in the pyroxenes decreases under high pressures. This may be explained by the instability of $CaTiAl_2O_6$ molecule under high pressure, since four-coordinated Al ions will occupy the octahedral site with increasing pressures (THOMPSON, 1947). Therefore it may be regarded that titanaugites are formed under relatively low pressures. In nature, however, titanaguites are common in alkalic olivine basalts, which are regarded to have been formed at greater depth than tholeiites, of which augites are not so rich in titan (YODER and TILLEY, 1962, KUSHIRO and KUNO, 1963). This apparent discrepancy should be studied by means of more experimental and petrological data.

Crystal chemistry of titanaugites

The definition of titanaugite is rather arbitrary. For example, HUCKENHOLZ

(1965a) and TIBA (1966) called augites or salites with more than 3 per cent TiO_2 titanaugites or titansalites, and those with 2–3 per cent TiO_2 titaniferous augites or salites. In the present paper, all pyroxenes with more than 2 per cent TiO_2 are called titanaugites.

In the general pyroxene formula, $W_{1-p}(X, Y)_{1+p}Z_2O_6$, Ti is usually regarded to belong to Y group, together with Al, Fe^{3+} and Cr, whereas W=Ca, Na ; X=Mg, Fe^{2+}, Mn, Ni, Li, and Z=Si, Al (HESS, 1949). Similarly BRAGG and CLARINGBULL (1965) considered that Ti^{4+} can replace Al^{3+} in pyroxenes.

BARTH (1931), from the chemical composition of titanaugite from Marquesas, suggested the presence of $CaTiAl_2O_6$ molelule in the titanaugite, and pointed out the substitution of Ti for Mg, accompanied by that of Al for Si. He also made a synthetic study on solid solutions between $CaMgSi_2O_6$-$CaMgTi_2O_6$, and obtained homogeneous crystals of Di 94, $CaMgTi_2O_6$ 6 per cent, and Di 90, $CaMgTi_2O_6$ 10 per cent (see Table 3). From this experiment he concluded that Ti^{4+} can also replace Si^{4+}, without accompanying substitution. The maximum content of TiO_2 in these solid solutions is about 6 per cent TiO_2. Later SEGNIT (1953) made a synthetic study on solid solutions between diopside and Al_2O_3, Fe_2O_3 or TiO_2 and showed that the maximum solubility of TiO_2 in diopside is about 6 per cent. He also assumed that TiO_2 can substitute SiO_2 in diopside to a small extent (see Table 3).

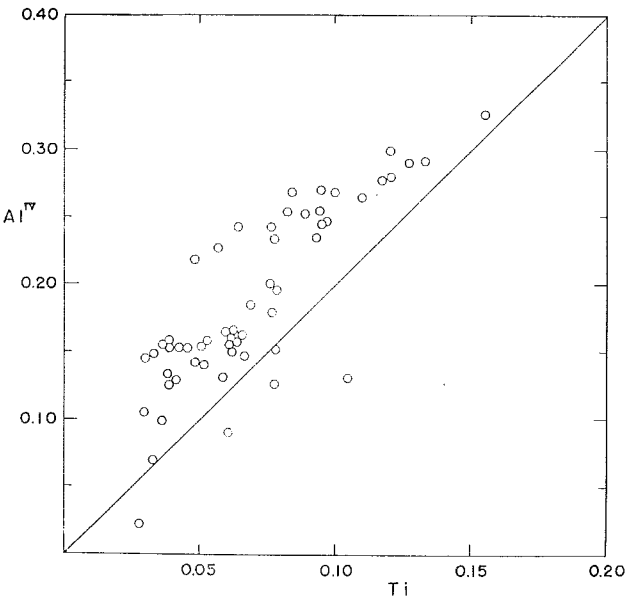

Fig. 6
Relation between the atomic proportions of Ti and Al^{IV} in the titanaugites from alkalic rocks. The straight line is $Al^{IV}=2Ti$.

Phase equilibrium studies on the systems TiO_2-SiO_2 (DeVRIES et al, 1954) and CaO-TiO_2-SiO_2 (DeVRIES et al, 1955), however, provide the evidence that substitution between Si and Ti is negligible and wide fields of liquid immiscibility lie in these systems, despite the chemical similarity between Si and Ti.

Recently KUSHIRO (1960), LeBAS (1962) and TIBA (1966) have discussed the crystal chemistry of clinopyroxenes from various igneous rocks and have pointed out the relation between the contents of Al, Ti and Si ions in the pyroxenes and their host rocks. Now the relation between Ti and Al ions in titanaugites will be considered. In most titanaugites Z position is not filled up with Si only, but the deficiency is filled by Al^{IV} (four-coordinated Al). The rest of Al ion is represented by Al^{VI} which enters Y group, or octahedral site. The relation between Ti and Al^{IV}, instead of total Al, is graphically shown in Fig. 6. Although the points show some scattering, they are more concentrated than in the diagram of Ti and total Al (AOKI, 1964, Fig. 5). It is worthy of note that most of the projected titanaugites fall near a straight line of $Al^{IV}=2Ti$. This relation seems to support that Ti and Al^{IV} ions are present in titanaugites as a hypothetical titan pyroxene molecule of $CaTiAl_2O_6$.

Crystallization of titanaugites

In the Morotu alkalic rocks, YAGI (1953) has shown that the evolution of pyroxenes is represented by the course from the early formed diopsidic augite poor in TiO_2 (estimated optically), through titanaugites with about 2.9 per cent TiO_2, sodic titanaugite with 2.7 per cent TiO_2, and aegirinaugites with 1–2 per cent TiO_2, to aegirines with only 0.6 per cent TiO_2. Therefore, TiO_2 contents increase in the earlier stage, but gradually decrease in the middle and later stages. A similar trend was also found by MURRAY (1954) in Garbh Eilean sill of Shiant Isles. The titanaugite from pegmatite patch has higher TiO_2 (2.2 per cent) than the pyroxenes in the early crystallized picrites or crinanites (TiO_2 1.3–1.8 per cent), whereas the last-formed ferroaugite has only 0.4 per cent TiO_2. The clinopyroxenes from teschenite of Black Jack sill have relatively small range in composition, in which TiO_2 contents show regular decrease from 3.2 to 2.1 per cent with fractional crystallization. No increase in TiO_2 is noticed in this case (WILKINSON, 1957).

Titanaugites from highly alkalic rocks of Nyiragongo volcano, have high contents of TiO_2, even more than 5 per cent, and show regular increase in Si and decrease in Ti (SAHAMA, 1958).

According to AOKI (1959, 1964) pyroxenes from alkalic rocks of Iki Island show a regular change in TiO_2 contents: diopsidic augites in the mafic and ultramafic inclusions in the alkalic rocks have 1–1.5 per cent TiO_2, and phenocrystic titanaugites and groundmass titanaugites in olivine basalts have 2.0–2.1 per cent TiO_2 and 2.5–2.7 per cent TiO_2, respectively, whereas the groundmass pyroxenes in trachytes have only 0.6–1.1 per cent TiO_2.

The pyroxenes from Atumi dolerites, though not so rich in TiO_2, show a similar trend of crystallization from diopsidic augite (Tp 2.4–2.5 per cent), through titaniferous augites (Tp 4.2–4.4 per cent) to aegirinaugites (Tp 1.9 per cent) (KUSHIRO, 1964).

In contrast to the above mentioned examples, HUCKENHOLZ (1965a, 1965b, 1966) has found only the increase of TiO_2 in the clinopyroxenes from alkalic rocks of Hocheifel volcanic district, Germany. The early stage pyroxenes are represented by greenish chromian salites in the core of phenocrystic augites, the middle stage pyroxenes by titansalites in the rim of zoned phenocrysts or as microphenocrysts, and the last stage pyroxenes by sodic titansalites in the groundmass. The contents of Tp molecule calculated from the analyses always show regular increase with fractionation, i.e., from 3 to 8 per cent in alkalic basalt-trachyte association, from 4 to 9 per cent in basanites, and from 5 to 10 per cent in ankaramites. In this district, however, decrease of TiO_2 in the later stage is not observed.

Clinopyroxenes from alkalic rocks of Takakusayama district includes augites ($TiO_2<2$ per cent), salites and titaniferous salites (TiO_2 1.7–2.8 per cent) and titansalites (TiO_2 3.3–4.4 per cent). On these pyroxenes, TIBA (1966) has shown that TiO_2 contents increase in titansalites with increasing $Fe/Ca+Fe+Mg$ ratio, whereas the augites from late differentiates of syenite or syenitic porphyry and soda-augites from hawaiite are relatively low in TiO_2.

From the above mentioned occurrences of pyroxenes two trends of crystallization of pyroxenes are discriminated as the behavior of Ti is concerned. In the first trend which is confined to the earlier stage, Ti is enriched in the pyroxenes with fractionation, whereas in the second trend Ti in pyroxenes decreases in the middle and later stages of differentiation.

The first trend can easily be explained by the equilibrium diagram obtained in the present study, in which the later-formed pyroxene solid solutions are always enriched in Tp molecule. The second trend is shown for several examples mentioned above in the Ti-Si diagram (Fig. 7). In these pyroxenes Ti decreases while Si increases as the fractionation proceeds. Increase of Si may be partly explained by the increase of Si which is available for pyroxenes in the magma (KUSHIRO, 1964).

Not only titan-bearing silicates but titan-iron-oxides, however, should be taken into consideration to clarify the behavior of Ti in silicates. VERHOOGEN (1962) has indicated that high temperature and high oxygen partial pressure favor the concentration of Ti in silicates, whereas Ti will enter preferentially oxide minerals at low oxygen partial pressures, when both silicates and oxides coexist. Thus TIBA (1966) has shown an increase of Ti with increase of $Fe^{3+}/Fe^{2+}+Fe^{3+}$ ratio, which may give a measure of oxygen partial pressure. YAGI (1966) has suggested, from the stability relations of acmitic pyroxenes, that oxygen partial pressure increases with the fractionation in some cases, for instance, in Morotu magma.

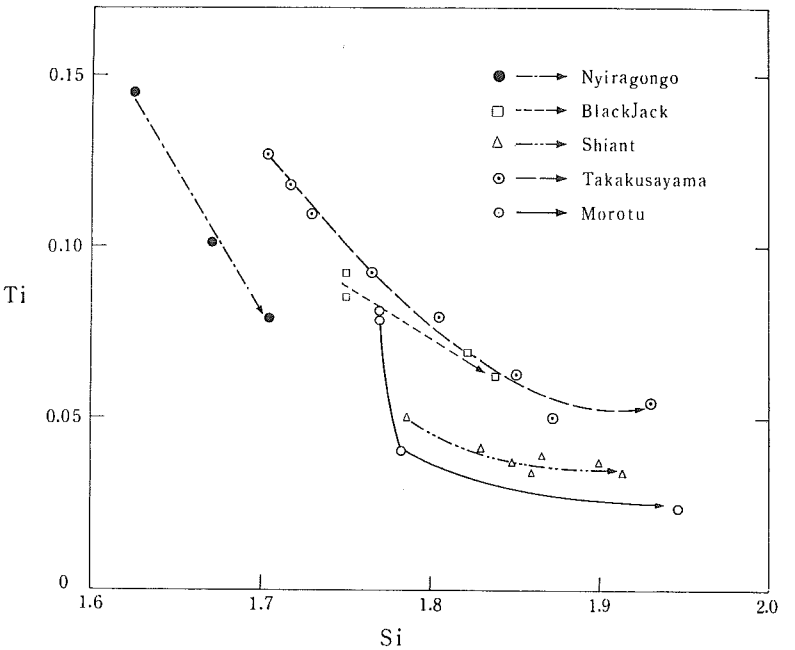

Fig. 7
Variations of atomic proportions of Si and Ti in titanaugites during the middle and later stages of fractional crystallization of the five different alkalic suites.

The Ti contents of pyroxenes in Morotu rocks, however, gradually decrease as described above. Experimental studies on the systems containing both Ti-bearing pyroxenes and Ti-Fe-oxides is necessary to attain some solution of this problem. In addition to oxides some mafic minerals, such as amphiboles or biotite, associated with pyroxenes and oxides may play an important role in deciding the partition of Ti among these minerals, especially when the water vapor pressure becomes sufficiently high to form these hydrous minerals. DEER et al. (1963) have ascribed the decrease of Ti in the later-formed pyroxenes to the composition and order of crystallization sequence, and not to the temperature of formation.

Conclusions

The join $CaMgSi_2O_6$-$CaTiAl_2O_6$ shows the existence of binary pyroxene solid solutions from pure diopside to $Di_{89}Tp_{11}$, and the join cannot be treated as binary beyond this limit, because perovskite, spinel, forsterite and melilite, in addition to pyroxene solid solutions, appear at the subliquidus and subsolidus temperatures. The solubility of TiO_2 determined in this experiment is lower than that

observed on natural titanaugites.

Under high pressures, ranging from 10 to 25 kb, these titan pyroxenes become unstable, exsolving Tp molecules as perovskite. This suggests that titanaugites are formed generally at relatively low pressures. The crystallization of titanaugites in alkalic rocks is discussed in the light of the experimental data. The increase of Ti in pyroxenes in the earlier stage is expected from the equilibrium diagram of this join, whereas the decrease in Ti in pyroxenes in the middle and later stages should be discussed from the view point of the relationship between Ti-bearing pyroxenes, biotite or amphiboles, and Ti-Fe-oxides.

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