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THE TEN PER CENT CaTiAl$_2$O$_6$ PLANE IN THE SYSTEM DIOPSIDE-AKERMANITE-NEPHELINE-CaTiAl$_2$O$_6$

by

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(with 2 Tables and 5 Text-Figures)

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Abstract

Ten per cent CaTiAl$_2$O$_6$ is added to the system diopside-akermanite-nepheline. This plane is a part of six-component system and two reaction relations and a eutectic relation are confirmed. The first reaction occurs at 1160°±5°C with phase assemblage of forsterite+nepheline+melilite+spinel+perovskite+liquid. At this temperature spinel disappears to react with liquid and perovskite comes in. The second reaction, marked by disappearance of forsterite and appearance of diopside, is at 1130°±10°C with phase assemblage of forsterite+diopside+melilite+nepheline+perovskite+liquid. The eutectic is at 1100°±10°C and is also a goal of crystallization of the system diopside-akermanite-nepheline-CaTiAl$_2$O$_6$. The phase assemblage of this point is diopside+melilite+nepheline+perovskite+corundum+liquid.

Contents

Introduction

The most abundant minerals in undersaturated mafic alkalic rocks are olivine, clinopyroxene, nepheline, and melilite. These minerals all occur on the liquidus in the system diopside-akermanite-nepheline (SCHAIRER and YODER, 1964;

ONUMA and YAGI, 1967). While the clinopyroxene in this undersaturated mafic rocks contains considerable amount of Ti. The chemistry of this titaniferous pyroxene shows that substitution of Ti$\rightleftharpoons$Mg is accompanied by Al$\rightleftharpoons$Si (KUSHIRO, 1960; YAGI and ONUMA, 1967) and the system between diopside and the hypothetical titanpyroxene molecule CaTiAl$_2$O$_6$ (henceforth abbreviated Tp) was investigated by YAGI and ONUMA (1967) to understand the solubility of Tp in diopside.

In this study 10 weight per cent Tp molecule is added to the system diopside-akermanite-nepheline, so that we can find the equilibrium relations in the most crucial plane of the pseudo-quaternary system diopside-akermanite-nepheline-CaTiAl$_2$O$_6$. This join provides a clue to understand the relation between titaniferous pyroxene and other minerals and the behavior of Ti in undersaturated alkalic rocks. The equilibrium in this system as the whole and its petrologic application are discussed by the present authors elsewhere (YAGI and ONUMA, in Press).

Experimentals

Homogeneous glasses in the present system were prepared by melting pure chemicals in a platinum crucible. Pure quartz, Al$_2$O$_3$, CaCO$_3$, MgO, and TiO$_2$ certified reagents from Fisher Scientific Co. and pure sodium disilicate were used. Sodium disilicate was made by the same method as described by SCHAIRER and BOWEN (1956). The homogeneity of the glass was tested under the petrographic microscope by the uniformity of refractive indices. The refractive indices of the glasses are shown in Fig. 1.

The crushed glasses were held at temperatures between 900 and 1000°C until crystallization of glass was complete. The crystalline phase assemblages of these starting mixtures, determined by X-ray diffractometer, are given in Table 1.

A platinum-wound resistance furnace was used for quenching experiments, regulated to an accuracy of ± 1°C. The Pt-Pt$_{90}$Ph$_{10}$ thermocouple used to measure the temperature was calibrated at standard melting points of NaCl 800.4°C, Au 1062.6°C and pure diopside 1391.5°C.

A small platinum envelope containing completely crystalline mixture was placed in the hottest portion of the quenching furnace. After equilibrium was attained, the charge was quenched by dropping rapidly into water. Crystalline phases were identified both by microscope and X-ray diffractometer.

Quenching data and equilibrium diagram

The result of quenching experiments are given in Table 2 and the phase equilibrium diagram with isothermal line is presented in Fig. 3. Diopside, forsterite, spinel, melilite, nepheline, and carnegieite appear as primary phases in this plane. All these crystalline phases except spinel are solid solutions of variable, but un-
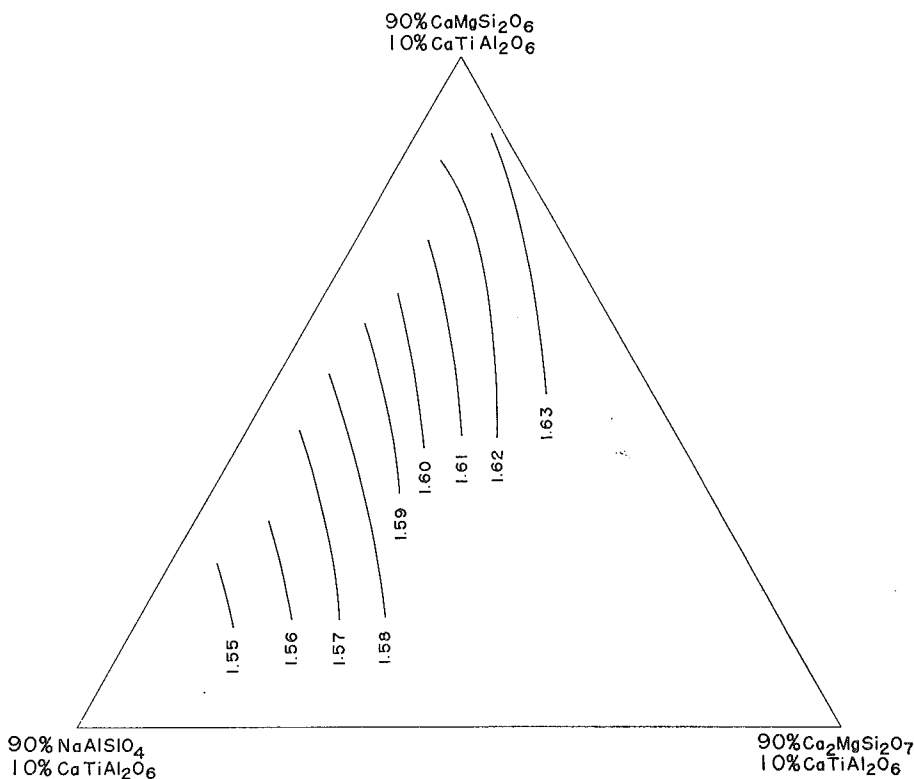
Fig. 1.
Isofract lines of the glasses of the plane CaMgSi$_2$O$_6$–Ca$_2$MgSi$_2$O$_7$–NaAlSiO$_4$–10%CaTiAl$_2$O$_6$.

Table 1.   Phase assemblage of starting materials (crystallized at 1000°C).

Composition (wt %)				Time for crystallization	Phase assemblage
Di	Ak	Ne	Tp		
68	20	2	10	18 days	mel+di+ne
6	27	57	10	18 days	mel+di+ne+pv+cor
50	10	30	10	14 days	mel+di+ne+pv+cor
40	4	46	10	48 days	mel+di?+ne+pv+cor
39	5	46	10	30 days	mel+di?+ne+pv+cor
67	21	2	10	7 days	mel+di+ne+pv??+cor?

di: diopside;   mel: melilite;   ne: nepheline;   pv: perovskite;   cor: corundum

known, composition and the details of these phases are discussed elsewhere (ONUMA and YAGI, 1967; YAGI and ONUMA, 1967).

There are three points V, S, and G' at which three crystalline phases coexist with liquid. The phase assemblages at these three points are as follows: forsterite+melilite+spinel+liquid at V (1175°C, $Di_{39.5}Ne_{45.5}Ak_5Tp_{10}$), melilite+nepheline+spinel+liquid at S (1194°C, $Di_{5.5}Ne_{57}Ak_{27.5}Tp_{10}$), and diopside+forsterite+melilite+liquid at G' (1292°C, $Di_{69}Ne_{1.5}Ak_{19.5}Tp_{10}$). The runs for almost all mixtures show that with falling temperature the fourth crystalline phase joins to the assemblage of the three crystalline phases and liquid. After that, however, liquid still remains and the four crystalline phases continue to crystallize together. For example, the quenching data on the mixtures of $Di_{40}Ne_{46}Ak_4Tp_{10}$ and $Di_{38}Ne_{45}Ak_7Tp_{10}$, both of which are close to V, show that nepheline joins to the assemblage of forsterite+melilite+spinel+liquid at 1174°C as the fourth phase. This assemblage continues to crystallize together until spinel begins to disappear and perovskite comes in at about 1160°C. This fact indicates that V, S, and G' are not piercing points in a quaternary system, but merely the points at which three primary phase volumes meet together.

The quenching data on the mixtures in the vicinity of V show that spinel disappears and perovskite appears at 1160°±5°C. Perovskite continues to crystallize
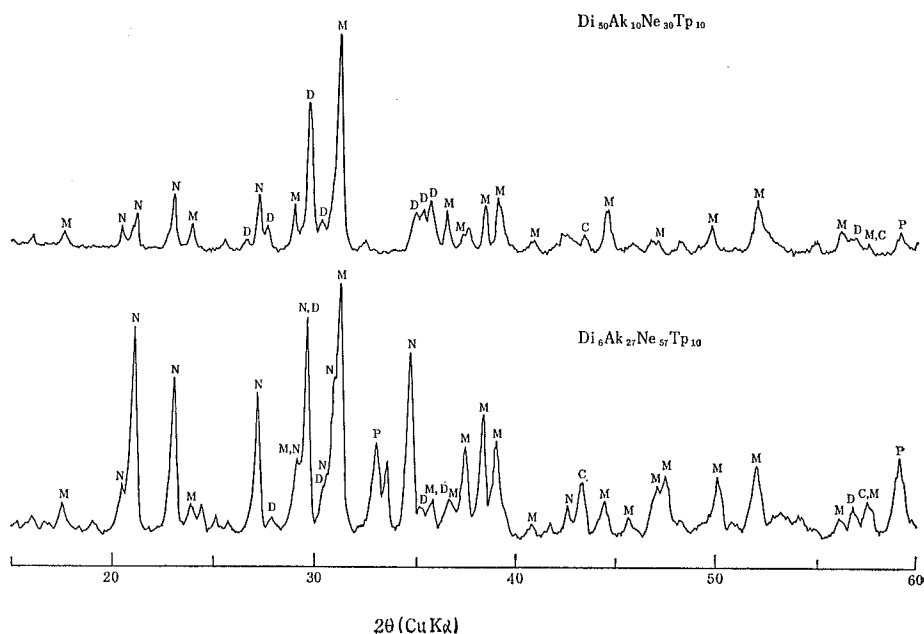

Fig. 2.

X-ray diffraction patterns of the starting material crystallized at 1000°C.

D: diopside, M: melilite, P: perovskite, N: nepheline, C: corundum.

together with forsterite, nepheline, and melilite. Forsterite disappears and in its stead diopside comes in at around 1130°C. Finally the starting materials after quenching runs at about 1100°C remain loose powder, indicating that liquid has already been consumed. The final phase assemblage is diopside+melilite+nepheline+perovskite+corundum as shown in Figs. 2 and 5.

The quenching data on the mixtures which have more than 60 per cent CaMgSi$_2$O$_6$ show different crystallization sequence. Since forsterite disappears at various temperatures, it can coexist with diopside for variable temperture ranges. For example, the quenching data for the mixture of Di$_{67}$Ak$_{21}$Ne$_2$Tp$_{10}$ shows that diopside appears at 1300°C, while forsterite is consumed at 1230°C. The final phase assemblage for this mixture is diopside+melilite+nepheline+perovskite, but corundum is not confirmed.
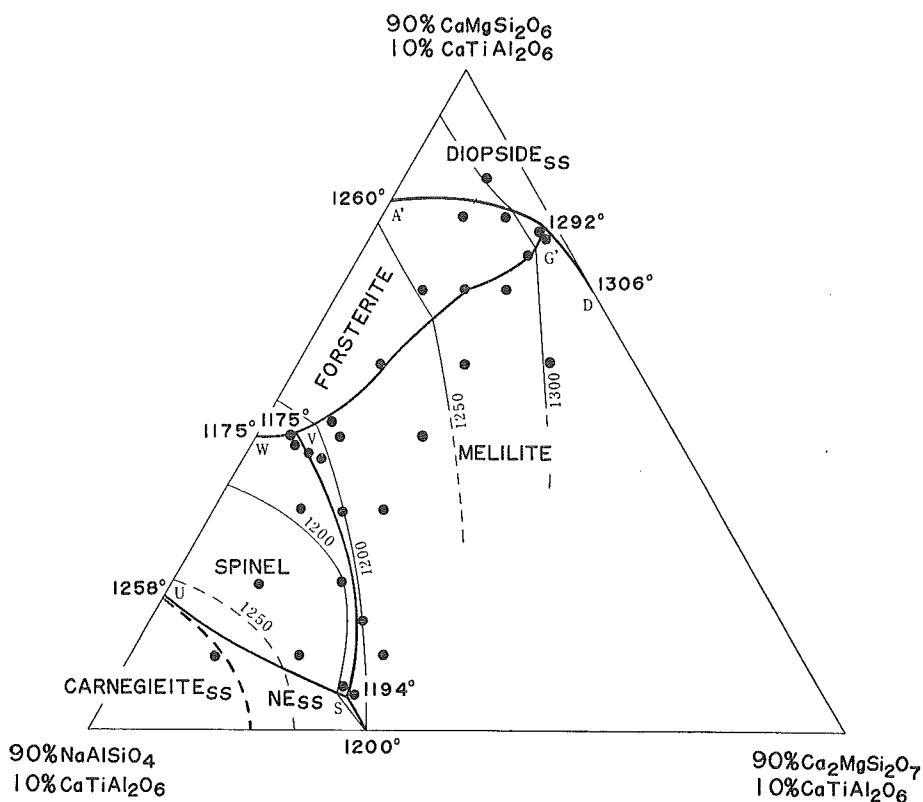
Fig. 3.
Phase equilibrium diagram for the plane CaMgSi$_2$O$_6$–Ca$_2$MgSi$_2$O$_7$–NaAlSiO$_4$–10%CaTiAl$_2$O$_6$.

DIOPSIDE
○ 1391.5°C

E {Ne 67
   {Ak 33

G {Di 55
  {Ak 6
  {Ne 39

H {Di 38
  {Ak 3
  {Ne 59

Di$_{ss}$

1258° A

1350

1300

G 1212°

50

Fo

F 1365°C

50

B

H 1169°C

1193°

1250

Mel

1200

1200

1250

1300

1350

1400

C

Ne$_{ss}$

1250

1300

1350

1400

1450

Cg$_{ss}$

1526° NEPHELINE CARNEGIEITE   D E   50   WEIGHT PER CENT   AKERMANITE 1454°C
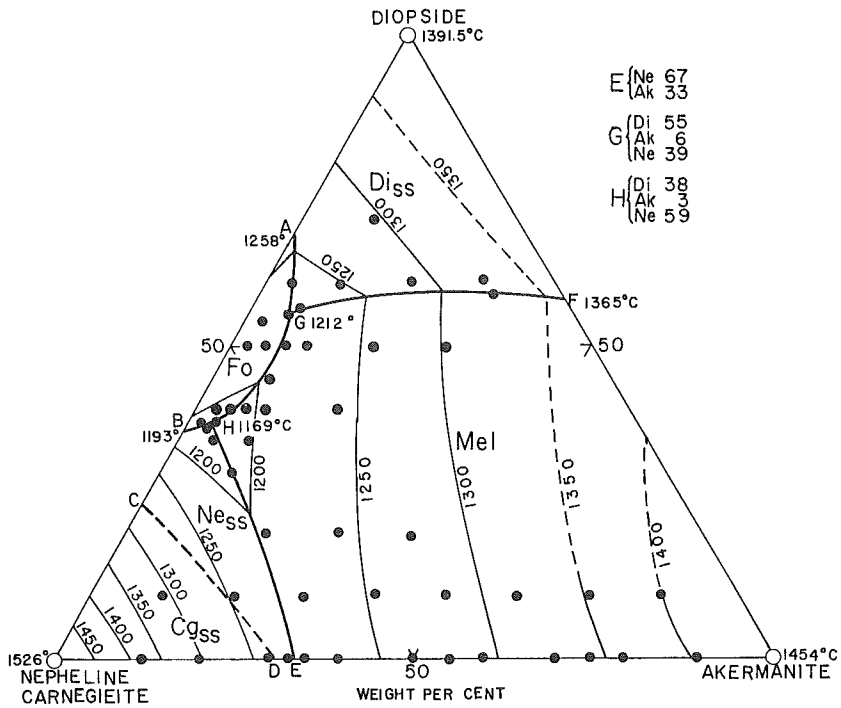
Fig. 4.

Phase equilibrium diagram for the system $CaMgSi_2O_6$–$Ca_2MgSi_2O_7$–$NaAlSiO_4$
(ONUMA and YAGI, 1967).

fo
+
di
+
mel
+
pv
+
l

I (1160°C)   II (1130°C)   III (1100°C)

fo + mel + ne + sp + l   fo + mel + ne + pv + l   di + mel + ne + pv + l

fo + mel + ne + sp + pv + l   fo + di + mel + ne + pv + l   fo   di + mel + ne + pv + cor + l

+
di
+
mel
+
ne
+
l
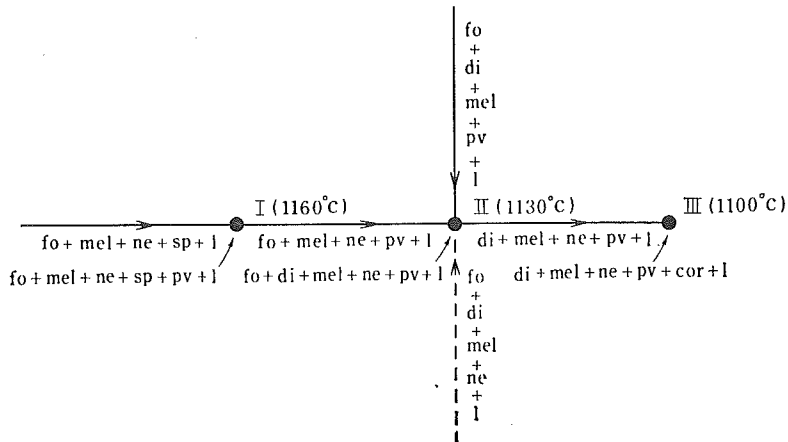
Fig. 5.

Flow sheet of the plane $CaMgSi_2O_6$–$Ca_2MgSi_2O_7$–$NaAlSiO_4$–10% $CaTiAl_2O_6$.

Table 2.   Quenching data for the plane diopside-akermanite-nepheline–10% CaTiAl$_2$O$_6$

Refractive index of glass ±0.003	Composition (wt %)			Temp.°C	Time	Phases
	Di	Ak	Ne			
1.568	5	29	56	1200	1 1/2 hr	trace mel+glass
				1195	2 hr	mel+glass
				1190	2 hr	mel+cg+glass
				1185	15 hr	mel+cg+sp+glass
				1180	4 hr	mel+cg+sp+ne+glass
				1175	72 hr	mel+sp+ne+glass
1.572	6	27	57	1200	2 hr	glass
				1195	2 hr	trace sp+glass
				1190	2 hr	sp+cg+mel+glass
1.554	10	10	70	1295	1 1/2 hr	glass
				1290	1 1/2 hr	cg+glass
				1225	6 hr	cg+glass
				1220	15 hr	cg+sp+glass
				1110	7 days	barely fritted cake
				1100	7 days	loose powder
1.564	10	20	60	1235	15 hr	glass
				1230	15 hr	sp+glass
				1225	17 hr	sp+glass
				1220	4 hr	sp+ne+glass
				1170	72 hr	sp+ne+glass
				1160	96 hr	sp+ne+mel+glass
				1100	7 hr	barely fritted cake
				1090	7 days	loose powder
1.580	10	30	50	1215	2 hr	glass
				1210	1 1/2 hr	mel+glass
				1190	4 hr	mel+glass
				1185	18 hr	mel+sp+glass
				1180	72 hr	mel+sp+ne+glass
				1110	7 days	barely fritted cake
				1100	7 days	loose powder
1.587	15	25	50	1205	2 hr	glass
				1200	1 1/2 hr	mel+glass
				1195	4 hr	mel+sp+glass
				1185	18 hr	mel+sp+glass
				1180	72 hr	mel+sp+ne+glass
				1170	96 hr	mel+sp+ne+trace fo+glass
1.560	20	10	60	1245	2 hr	glass
				1240	4 hr	trace sp+glass
				1220	4 hr	sp+glass
				1215	15 hr	sp+ne+glass
				1175	96 hr	sp+ne+glass
				1170	96 hr	sp+ne+mel+fo+glass

Table 2.   Quenching date for the plane diopside-akermanite-nepheline-10% $CaTiAl_2O_6$

Refractive index of glass ±0.003	Composition (wt %)			Temp.°C	Time	Phases
	Di	Ak	Ne			
				1100	7 days	barely fritted cake
				1090	7 days	loose powder
1.576	20	20	50	1220	4 hr	glass
				1215	4 hr	sp+glass
				1185	72 hr	sp+glass
				1180	72 hr	sp+ne+glass
				1175	96 hr	sp+ne+mel+glass
				1165	96 hr	sp+ne+mel+fo+glass
1.572	30	10	50	1200	2 hr	glass
				1195	15 hr	sp+glass
				1185	20 hr	sp+glass
				1180	2 hr	sp+ne+glass
				1170	72 hr	sp+ne+glass
				1165	96 hr	sp+ne+fo+glass
				1160	48 hr	sp+ne+fo+mel+glass
				1100	7 days	barely fritted cake
				1090	7 days	loose powder
1.580	30	15	45	1205	15 hr	glass
				1200	15 hr	mel+glass
				1180	1 1/2 hr	mel+glass
				1175	72 hr	mel+sp+glass
				1170	2 hr	mel+sp+fo+glass
1.588	30	20	40	1220	15 hr	glass
				1215	4 hr	mel+glass
				1190	4 hr	mel+glass
				1185	72 hr	mel+fo+glass
				1180	72 hr	mel+fo+glass
				1175	72 hr	mel+fo+sp+glass
				1165	96 hr	mel+fo+sp+glass
				1160	96 hr	mel+fo+ne+glass
1.576	37	9	44	1200	1 1/2 hr	glass
				1195	15 hr	trace mel+glass
				1180	4 hr	mel+glass
				1175	2 hr	mel+fo+glass
				1170	72 hr	mel+fo+sp+glass
1.576	38	7	45	1190	3 hr	glass
				1185	2 hr	mel+sp+glass
				1180	2 hr	mel+sp+glass
				1175	2 hr	mel+sp+fo+glass
				1170	96 hr	mel+sp+fo+ne+glass
				1165	96 hr	mel+sp+fo+ne+glass
				1160	96 hr	mel+pv+fo+ne+glass

Table 2. Quenching data for the plane diopside-akermanite-nepheline–10% CaTiAl$_2$O$_6$

Refractive index of glass ±0.003	Composition (wt %)			Temp.°C	Time	Phases
	Di	Ak	Ne			
1.576	39	5	46	1190	2 hr	glass
				1185	2 hr	trace sp+glass
				1180	2 hr	sp+mel+glass
				1175	2 hr	sp+mel+fo+ne+glass
				1170	96 hr	sp+mel+fo+ne+glass
				1165	96 hr	sp+mel+fo+ne+glass
				1160	96 hr	pv+mel+fo+ne+glass
1.574	40	4	46	1180	2 hr	trace+sp+glass
				1175	4 hr	sp+mel+fo+trace ne+glass
				1170	15 hr	sp+mel+fo+ne+glass
				1165	96 hr	sp+mel+fo+ne+glass
				1160	96 hr	pv+mel+fo+ne+glass
1.584	40	10	40	1200	2 hr	glass
				1195	15 hr	mel+fo+glass
				1165	96 hr	mel+fo+glass
				1160	48 hr	mel+fo+ne+glass
				1100	7 days	barely fritted cake
				1090	7 days	loose powder
1.600	40	20	30	1245	18 hr	glass
				1240	2 hr	mel+glass
				1225	18 hr	mel+glass
				1220	18 hr	mel+fo+glass
				1090	7 days	barely fritted cake
1.580	42	8	40	1205	1 1/2 hr	glass
				1200	2 hr	mel+glass
				1195	18 hr	mel+glass
				1190	2 hr	mel+fo+glass
				1165	96 hr	mel+fo+glass
				1160	96 hr	mel+fo+ne+pv+glass
				1130	96 hr	mel+di+ne+pv+glass
1.596	50	10	30	1235	2 hr	glass
				1230	2 hr	fo+glass
				1225	18 hr	fo+glass
				1220	18 hr	fo+mel+glass
				1170	48 hr	fo+mel+glass
				1160	72 hr	fo+mel+di+glass
				1140	96 hr	fo+mel+di+trace pv+glass
				1130	96 hr	ne+mel+di+pv+glass
1.612	50	20	20	1265	18 hr	glass
				1260	2 hr	mel+glass
				1255	2 hr	mel+glass
				1250	2 hr	mel+trace fo+glass

Table 2.   Quenching data for the plane diopside-akermanite-nepheline-10% $CaTiAl_2O_6$

Refractive index of glass ±0.003	Composition (wt %)			Temp.°C	Time	Phases
	Di	Ak	Ne			
				1185	20 hr	mel+fo+glass
				1180	72 hr	mel+fo+di+glass
				1170	72 hr	mel+trace fo+di+glass
				1150	96 hr	mel+di+glass
				1140	96 hr	mel+di+pv+glass
1.628	50	30	10	1310	2 hr	glass
				1305	2 hr	mel+glass
				1285	2 hr	mel+glass
				1280	2 hr	mel+trace fo+glass
				1240	72 hr	mel+fo+glass
				1235	2 hr	mel+fo+di+glass
				1170	7 days	mel+di+pv+glass
				1100	7 days	barely fritted cake
				1090	7 days	loose powder
1.608	60	10	20	1260	18 hr	glass
				1255	18 hr	fo+glass
				1250	2 hr	fo+glass
				1245	18 hr	fo+trace mel+glass
				1200	15 hr	fo+mel+glass
				1195	18 hr	fo+mel+di+glass
				1170	72 hr	mel+di+glass
				1090	7 days	barely fritted cake
1.624	60	15	15	1270	1 1/2 hr	glass
				1265	9 1/2 hr	mel+trace fo+glass
				1110	9 days	barely fritted cake
				1090	7 days	loose powder
1.624	60	20	10	1290	18 hr	glass
				1285	2 hr	mel+glass
				1280	2 hr	mel+glass
				1275	2 hr	mel+fo+glass
				1260	18 hr	mel+fo+glass
				1255	18 hr	mel+fo+trace di+glass
				1175	72 hr	mel+di+glass
				1110	7 days	barely fritted cake
				1100	7 days	loose powder
1.630	65	30	5	1300	1 1/2 hr	glass
				1295	4 hr	mel+fo+glass
				1280	2 hr	mel+fo+glass
				1275	4 hr	mel+fo+di+glass
1.632	67	21	2	1315	1 1/2 hr	glass
				1310	15 hr	trace mel+glass
				1305	1 1/2 hr	mel+fo+glass

Table 2. Quenching date for the plane diopside-akermanite-nepheline-10% CaTiAl$_2$O$_6$

Refractive index of glass ±0.003	Composition (wt %)			Temp. C	Time	Phases
	Di	Ak	Ne			
				1295	3 hr	mel+fo+glass
				1290	15 hr	mel+fo+di+glass
				1230	96 hr	mel+trace fo+di+glass
				1200	96 hr	mel+di+ne
1·620	70	10	10	1290	18 hr	glass
				1285	2 hr	trace fo+glass
				1265	18 hr	fo+glass
				1260	18 hr	fo+di+glass
				1255	18 hr	fo+di+mel+glass
				1100	7 days	barely fritted cake
				1090	7 days	loose powder
1.622	70	10	5	1315	1 1/2 hr	trace di+glass
				1290	3 hr	di+glass
				1285	18 hr	di+fo+trace mel+glass
				1230	96 hr	di+trace fo+mel+glass
				1225	96 hr	di+mel+glass
				1110	7 days	fritted cake
				1100	7 days	loose powder
1.624	70	15	5	1300	2 hr	glass
				1295	4 hr	fo+glass
				1290	15 hr	fo+trace di+glass
				1285	3 hr	fo+di+mel+glass

mel : melilite; cg : carnegieite; sp : spinel; ne : nepheline; pv : perovskite; fo : forsterite; di : diopside

Crystallization

Since the number of the component oxides of the system under investigation is six (Na$_2$O-CaO-MgO-Al$_2$O$_3$-TiO$_2$-SiO$_2$), the system may actually be a six-component system. However, the number of the crystalline phases, which are mostly solid solutions never exceeds five in number in one assemblage, and consequently the system is regarded to behave like a five-component system. The range of temperatures of each reaction lies within 10°C. Fig. 5 is not an ordinary flow sheet but shows only the phase assemblages and their mutual relation in the system. The lines, showing five-phase assemblages, are actually divariant phase assemblages and the points I, II, and III are actually not points with definite temperatures, but sections of lines with small temperature ranges, probably less than 10°C, representing univariant or six-phase assemblages in a six-component system. Of these I and II show the reaction relation, and III the eutectic relation.

As stated before, following reaction occurs at 1160°C forsterite+melilite+

nepheline+spinel+liquid=forsterite+melilite+nepheline+perovskite+liquid (I in Fig. 5). The left-side and right-side phase assemblages of this rection shows the divariant phase assemblages of a six-component system. The five-phase assemblage, forsterite+melilite+nepheline+spinel+liquid, passes through V at 1174°C (Fig. 3) and the composition of the liquid at this point is about $Di_{39.5}Ak_5Ne_{45.5}Tp_{10}$. When this five-phase assemblage reaches I spinel disappears, with simultaneous crystallization of perovskite and another five-phase assemblage, forsterite+ melilite+nepheline+perovskite+liquid, is generated from this point.

The second reaction, marked by the disappearance of forsterite, is reached at about 1130°C. With falling temperature the five-phase assemblage, forsterite+melilite+nepheline+perovskite+liquid, reaches the second reaction relation, where forsterite begins to react with liquid to produce diopside. After forsterite is completely consumed, crystallization of diopside, melilite, nepheline, and perovskite proceeds with decreasing temperature toward III.

Besides these two, another five-phase assemblage, diopside+forsterite+melilite +perovskite+liquid, is also confirmed. The phase assemblage diopside+forsterite +melilite+nepheline+liquid, though not yet confirmed, can be generated in the basal join diopside-akermanite-nepheline and will meet together with other five-phase assemblages.

III represents a eutectic relation and may presumably be a goal of crystallization in the system diopside-akermanite-nepheline-$CaTiAl_2O_6$. The five-phase assemblage diopside+melilite+nepheline+perovskite+liquid generated from II is joined by corundum at III, where the liquid is consumed at about 1100°C.

Comparison with the system diopside—akermanite—nepheline

The primary phase relation in the system diopside-akermanite-nepheline changes considerably by addition of 10 weight per cent $CaTiAl_2O_6$. The primary field of diopside becomes smaller while that of forsterite larger. The primary field of spinel appears between those of forsterite, melilite and nepheline, so that the four-phase assemblage of forsterite+nepheline+melilite+liquid disappears and two new four-phase assemblages, forsterite+melilite+spinel+liquid and melilite+spinel+nepheline+liquid appear instead. In the system diopside-akermanite-nepheline, four-phase assemblage is univariant and G and H in Fig. 4 are peircing points (Onuma and Yagi, 1967). In the plane diopside-akermanite-nepheline-10% Tp, however, four-phase assemblage is not univariant, because of the behavior as six-component system. The assemblages of spinel+melilite+nepheline+liquid (S in Fig. 3) and diopside+forsterite+melilite+liquid (G') become divariant assemblages by addition of perovskite and that of forsterite+melilite+spinel+liquid (V) by nepheline. Addition of the component Tp changes the quaternary invariant point in the system diopside-akermanite-nepheline to a

point on the divariant plane of six-component system, diopside+forsterite+melilite+nepheline+liquid.

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