THE AMERICAN MINERALOGIST, VOL. 52, JANUARY-FEBRUARY, 1967

THE SYSTEM DIOPSIDE-AKERMANITE-NEPHELINE

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ABSTRACT

The pseudobinary system $NaAlSiO_4$ (nepheline, carnegieite)—$Ca_2MgSi_2O_7$ (akermanite) has a pseudoeutectic point at 1210°±5°C and $Ne_{67}Ak_{33}$. Below the subsolidus temperatures forsterite appears and coexists with nepheline and melilite.

The pseudoternary system $CaMgSi_2O_6$(diopside)—$Ca_2MgSi_2O_7$(akermanite)—$NaAlSiO_4$ (nepheline, carnegieite), a join in the system $NaAlSiO_4$-CaO-MgO-SiO_2, has two piercing points: (1) One, at 1212°±5°C and $Di_{55}Ak_6Ne_{39}$, shows liquid coexisting with forsterite, melilite, and diopside, the phase assemblage corresponding to olivine melilitite; (2) the other, at 1169°±5°C and $Di_{38}Ak_3Ne_{59}$, shows forsterite, nepheline, and melilite coexisting with liquid, and this phase combination is found in nepheline melilitite. These two points are univariant and the crystallization moves towards the invariant point within the system $NaAlSiO_4$-CaO-MgO-SiO_2. At this point, about 1135°C, forsterite, diopside, melilite, and nepheline coexist with liquid, and this phase assemblage is the same as in olivine-melilite nephelinite.

Diopside, akermanite, nepheline, and carnegieite in the system diopside-akermanite-nepheline are solid solutions of varying compositions. The nepheline-carnegieite inversion, takes place over a range extending from 1250°C to 1208°C. The birefringence of melilite solid solution decreases with increasing content of $NaAlSiO_4$. It is likely that sodium melilite ($NaCaAlSi_2O_7$) is incorporated into akermanite as a solid solution.

INTRODUCTION

The compound $NaAlSiO_4$ is the mineral nepheline. Akermanite ($Ca_2MgSi_2O_7$) gehlenite, ($Ca_2Al_2SiO_7$), and soda melilite ($NaCaAlSi_2O_7$) are the principal solid solution molecules in the natural mineral melilite (Ferguson and Buddington, 1920, Osborn and Schairer, 1941). Yoder (1964) has shown that in terms of these three molecules natural melilites contain mainly akermanite and soda melilite solid solution and only minor gehlenite. Both nepheline and melilite are important constituents of mafic alkalic rocks, especially melilite basalt, melilitite, and nephelinite.

Melilite-bearing silicate systems have been studied by many workers. In 1945 Bowen showed the importance of the appearance of melilite in the system Na_2O-CaO-Al_2O_3-SiO_2. Melilite appears in some important nepheline-bearing systems, such as nepheline-forsterite-diopside (Schairer and Yoder, 1956), nepheline-diopside (Schairer, Yagi and Yoder, 1962) and acmite-diopside-nepheline (Yagi, 1963). In view of the appearance of melilite in these systems it seems desirable to study the nepheline-melilite and diopside-akermanite-nepheline systems. Of these, the system

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nepheline-gehlenite has been already studied by Smalley (1949). In the present paper the nepheline-akermanite and diopside-akermanite-nepheline equilibrium relations are given.

PREVIOUS WORK

Schairer, Yagi and Yoder (1962) determined the phase relations in the system diopside-nepheline, and found the system to be pseudobinary, forsterite and melilite appearing in the subsolidus regions. This system has a pseudoeutectic point at 1193°C and the composition of $Ne_{62}Di_{38}$ Melilite coexists with nepheline solid solution, forsterite, diopside and liquid. This system should be regarded as a join within a five component system.

Ferguson and Merwin (1919) studied the system diopside-akermanite and showed it to be binary, with a eutectic point at 1365°C and the composition of $Di_{38}AK_{42}$.

EXPERIMENTAL METHOD

Homogeneous glasses in the system diopside-akermanite-nepheline were prepared by melting pure chemicals in a platinum crucible at 1200°C to 1500°C. Pure quartz, (purified by the method described by Schairer and Bowen, 1956), Al_2O_3, $CaCO_3$, and MgO certified reagents from Toyo-Rosh Co., Japan and pure sodium disilicate powder were used.

Sodium disilicate was prepared by the same method as described by Schairer and Bowen (1956), except that Na_2CO_3 was used as a source of Na_2O in the present study instead of $NaHCO_3$.

The homogeneity of the glass was tested under the microscope by its uniformity of refractive index (Schairer, 1959). The crushed glasses were held at temperatures between 800°C and 1000°C until the crystallization of glass was complete. The refractive indices of the glasses are shown in Figure 1.

A $Pt_{80}Rh_{20}$ wire wound electric furnace was used as a quenching furnace, regulated with an accuracy of $\pm 1°C$. The Pt-$Pt_{87}Rh_{13}$ thermocouple used to measure the temperature was calibrated frequently at standard melting points.

A small platinum envelope containing about 10 mg. of 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. Equilibrium was checked by several criteria established at the Geophysical Laboratory (Schairer, 1959),

Crystalline phases were identified by petrographic microscope and X-ray diffractometer.

CRYSTALLINE PHASES

Carnegieite and nepheline. The carnegieite shows typical fish-egg form, exhibiting characteristic polysynthetic twinning in nearly all cases. Its extinction angle measured against the trace of the twinning plane is 37°, Bowen (1912) obtained 36°. The nepheline occurs in typical prismatic form and has a somewhat higher refractive index than pure nepheline.

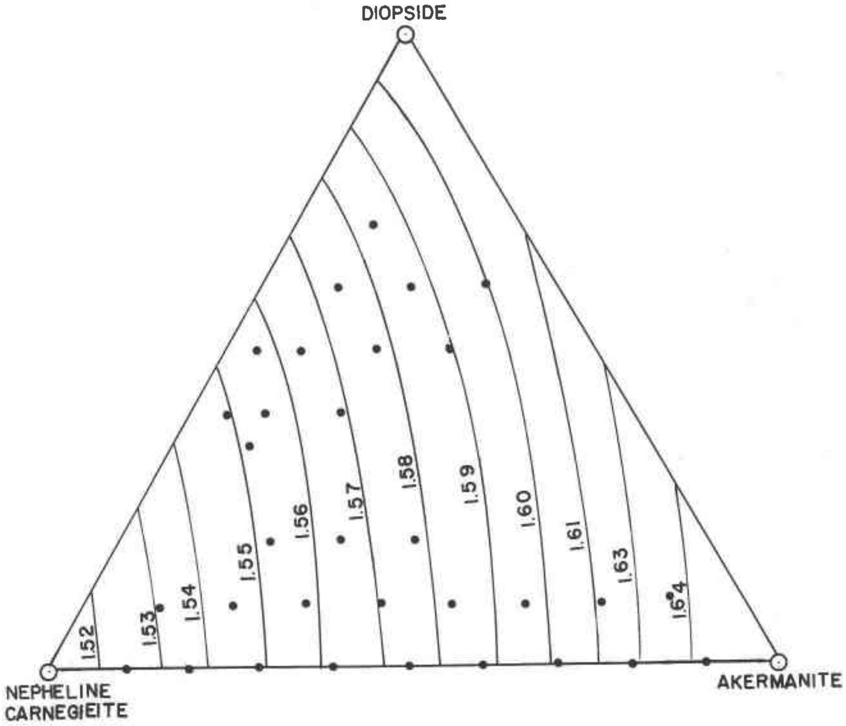

FIG. 1. Isofract lines of the glasses of the system $CaMgSi_2O_6$-$Ca_2MgSi_2O_7$-$NaAlSiO_4$.

The carnegieite-nepheline inversion is at 1248°C in pure $NaAlSiO_4$, but the nepheline-carnegieite inversion takes place over a rather wide range (Smalley, 1947; Bowen, 1912; Tilley, 1933; Greig and Barth, 1938). In the system akermanite-nepheline the inversion also takes place over a wide range, the upper limit of which lies at a temperature of about 1250°C in the mixtures of 95 percent $NaAlSiO_4$ and falls gradually with decreasing content of $NaAlSiO_4$. Its lower limit lies at about 1208°C and the composition of $Ne_{80}AK_{20}$ (Fig. 2), and is raised in mixtures poorer in $NaAlSiO_4$. These facts indicate nepheline and carnegieite are solid solutions. Greig and Barth (1938) showed that nepheline contains the albite molecule in solid solution. Albite molecule can be expected from the reaction between nepheline and akermanite as shown in the following section.

Melilite. The melilite obtained in the present investigation has usually a tetragonal habit; but sometimes it forms fine granular round crystals, clustered together. This melilite is not pure akermanite in composition, and birefringence becomes lower with increase in $NaAlSiO_4$ content as shown in Figure 3. Nurse and Midgley (1953) showed that the amount of nepheline decreases with increase in soda-melilite molecule. The birefringence also decreases until it is zero. The melilite obtained in the present investigation shows a similar character with increase in $NaAlSiO_4$. Soda melilite molecule, $NaCaAlSi_2O_7$, can be expected from the reaction between nepheline and akermanite in the system akermanite-nepheline

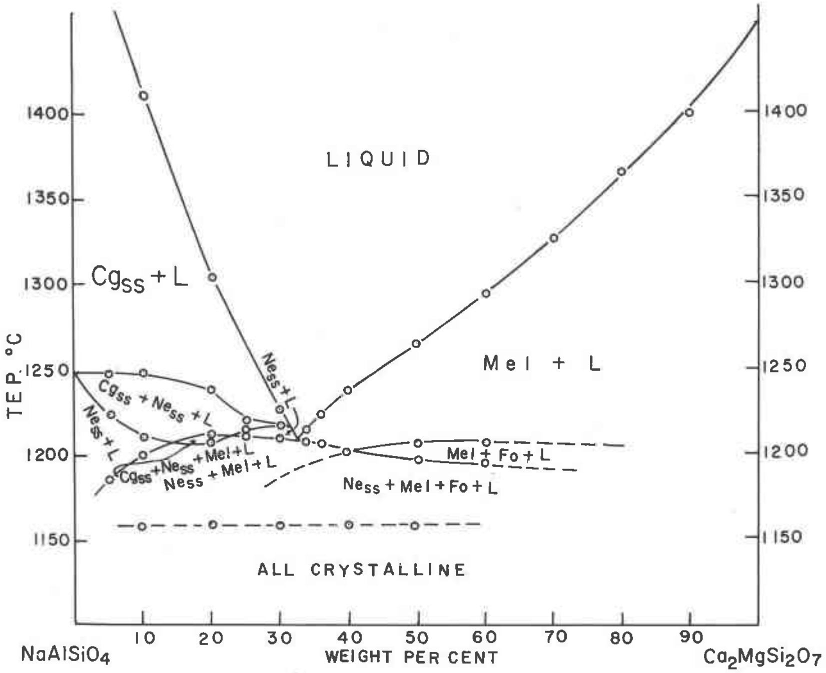

FIG. 2. Phase equilibrium diagram of the system $NaAlSiO_4$-$Ca_2MgSi_2O_7$.

$$\underset{\text{akermanite}}{8Ca_2MgSi_2O_7} + \underset{\text{nepheline}}{5NaAlSiO_4} + \underset{\text{forsterite}}{2Mg_2SiO_4} = \underset{\text{soda-melilite}}{4NaCaAlSi_2O_7} + \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{merwinite}}{4Ca_3MgSi_2O_8}$$

Merwinite appears in the mixtures of 80 and 90 weight percent $Ca_2MgSi_2O_7$ at solidus temperatures, though it was not found in other mixtures. It is therefore expected that merwinite appears at subsolidus temperature. Yoder and Tilley (1962) showed that soda-melilite molecule can be formed from the reaction between diopside and nepheline as follows:

$$\underset{\text{diopside}}{4CaMgSi_2O_6} + \underset{\text{nepheline}}{5NaAlSiO_4} = \underset{\text{forsterite}}{2Mg_2SiO_4} + \underset{\text{soda-melilite}}{4NaCaAlSi_2O_7} + \underset{\text{albite}}{NaAlSi_3O_8}$$

It is more likely that CaMg⇌NaAl substitution occurs and the soda-melilite molecule, $NaCaAlSi_2O_7$, is incorporated in solid solution with the akermanite.

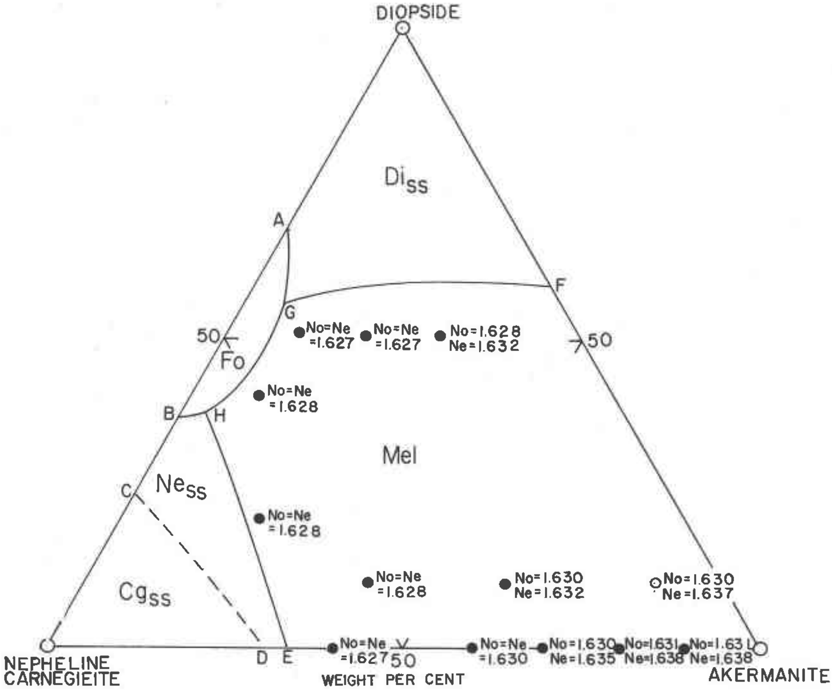

FIG. 3. Refractive indices of melilite solid solution of the system $CaMgSi_2O_6$-$Ca_2MgSi_2O_7$-$NaAlSiO_4$.

Diopside. The diopside obtained in the present investigation usually has a typical stout prismatic crystal habit and is sometimes twinned on (100). However, it forms rounded grains when coexisting with melilite, forsterite and melilite, and forsterite at lower temperatures. The refractive indices differ from pure synthetic diopside. Refractive index of the diopside from the mixture $Di_{70}Ak_{10}Ne_{20}$ crystallized at 1280°C is $\alpha = 1.665$ and $\gamma = 1.691$, indicating diopside solid solution rather than pure diopside. It is more likely that $CaAl_2SiO_6$ molecule is incorporated into diopside. $CaAl_2SiO_6$ molecule may be produced from the following reaction:

$$\underset{\text{diopside}}{5CaMgSi_2O_6} + \underset{\text{nepheline}}{6NaAlSiO_4} = \underset{\text{forsterite}}{2Mg_2SiO_4} + \underbrace{Ca_2MgSi_2O_7 + 2NaCaAlSi_2O_7}_{\text{melilite}} + CaAl_2SiO_6 + \underset{\text{albite}}{2NaAlSi_3O_8} + \underset{\text{sodium-metasilicate}}{Na_2SiO_2}$$

where albite molecule and Na_2SiO_3 are in solid solution with nepheline (Greig & Barth, 1938, Tilley, 1933).

Forsterite. The forsterite field is shown by the area AGHB (Fig. 3), although its composition does not lie within this diagram. The forsterite obtained in the present investigation is usually long prismatic with straight extinction but also assumes rounded granular form. The refractive indices of the forsterite obtained from the mixture $Di_{55}Ak_5Ne_{40}$ at 1200°C are as follows: $\alpha = 1.637$ and $\gamma = 1.672$.

QUENCHING DATA AND THE EQUILIBRIUM DIAGRAMS

The result of quenching experiments are given in Tables 1 and 2, and the phase equilibrium diagrams are presented in Figures 2 and 4. The system akermanite-nepheline (Fig. 2) has a pseudoeutectic point at a temperature of 1210°C and a composition of $Ne_{67}Ak_{33}$ .The upper boundary of the carnegieite-nepheline inversion slopes downward from the point 1254°C, at which pure nepheline inverts into carnegieite, towards the pseudoeutectic point, while the lower boundary goes up from the point 1208°C at 80 percent $NaAlSiO_4$ towards the pseudoeutectic point.

Figure 4 shows the phase equilibrium diagram of the system diopside-akermanite-nepheline. The compositions studied are shown as black dots. The curves separating the five primary crystalline phases (diopside, forsterite, melilite, nepheline, and carnegieite) are projections of the phase boundary surfaces. The points G and H are piercing points. At point G (1212° ± 5°C), diopside, melilite, and forsterite coexist with liquid; at point H (1169° ± 5°C), melilite, olivine, nepheline and liquid coexist.

DISCUSSION

Since the system diopside-akermanite-nepheline consists of five oxides, Na_2O, CaO, MgO, Al_2O_3, and SiO_2, the present system can be represented as part of a quinary system Na_2O-CaO-MgO-Al_2O_3-SiO_2. It is difficult to show the five component systems schematically, however, the writers use the diagram of the system $NaAlSiO_4$-CaO-MgO-SiO_2 (Fig. 5), which was proposed by Bowen (1928) in his study of the melilite and nepheline-bearing rocks. The simple basalt tetrahedron of Yoder and Tilley (1962) is included in this system.

TABLE 1. RESULTS OF QUENCHING EXPERIMENTS FOR THE SYSTEM NEPHELINE-AKERMANITE

Refractive index of glass ±0.003	Composition (wt %)		Temp. °C	Time	Phases
	Ne	Ak			
1.520	95	5	1185	24 hr.	$\mathrm{Ne_{ss}}$+rare Mel+Gl
			1190	24 hr.	$\mathrm{Ne_{ss}}$+Gl
			1220	15 hr.	$\mathrm{Ne_{ss}}$+Gl
			1225	24 hr.	$\mathrm{Ne_{ss}}$+Cg+Gl
			1245	15 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Gl
			1250	15 hr.	$\mathrm{Cg_{ss}}$+Gl
1.525	90	10	1150	5 days	loose powder
			1160	5 days	fritted cake
			1180	24 hr.	$\mathrm{Ne_{ss}}$+Mel+Gl
			1200	20 hr.	$\mathrm{Ne_{ss}}$+rare Mel+Gl
			1205	24 hr.	$\mathrm{Ne_{ss}}$+Gl
			1210	20 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Gl
			1245	15 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Gl
			1250	15 hr.	$\mathrm{Cg_{ss}}$+Gl
			1410	½ hr.	rare $\mathrm{Cg_{ss}}$+Gl
			1415	½ hr.	Gl
1.539	80	20	1155	7 days	loose powder
			1160	7 days	$\mathrm{Ne_{ss}}$+Mel+rare Fo+Gl
			1180	7 days	$\mathrm{Ne_{ss}}$+Mel+Gl
			1205	20 hr.	$\mathrm{Ne_{ss}}$+Mel+Gl
			1210	20 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Mel+Gl
			1215	18 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Gl
			1230	20 hr.	$\mathrm{Ne_{ss}}$+$\mathrm{Cg_{ss}}$+Gl
			1235	48 hr.	$\mathrm{Cg_{ss}}$+Gl
			1305	1 hr.	trace $\mathrm{Cg_{ss}}$+Gl
			1310	1 hr.	Gl
1.545	75	25	1210	24 hr.	$\mathrm{Ne_{ss}}$+Mel+Gl
			1215	24 hr.	$\mathrm{Ne_{ss}}$+rare $\mathrm{Cg_{ss}}$+Mel+Gl
			1220	15 hr.	$\mathrm{Cg_{ss}}$+Gl
1.555	70	30	1150	5 days	loose powder $\mathrm{Ne_{ss}}$+Mel+Fo
			1160	5 days	slightly fritted cake
			1205	24 hr.	$\mathrm{Ne_{ss}}$+Mel+Gl
			1210	48 hr.	$\mathrm{Ne_{ss}}$+Gl
			1215	18 hr.	$\mathrm{Cg_{ss}}$+Gl
			1225	1 hr.	rare $\mathrm{Cg_{ss}}$+Gl
			1230	1 hr.	Gl

TABLE 1—(*Continued*)

Refractive index of glass ±0.003	Composition (wt %)		Temp °C	Time	Phases
	Ne	Ak			
1.556	66	34	1205	18 hr.	Mel+Ne$_{ss}$+Gl
			1210	24 hr.	Mel+Gl
			1215	2 hr.	Gl
1.560	64	36	1205	18 hr.	Mel+trace Ne$_{ss}$+Gl
			1210	24 hr.	Mel+Gl
			1220	22 hr.	Mel+Gl
			1225	2 hr.	Gl
1.563	60	40	1155	5 days	loose powder
			1170	5 days	slightly fritted cake
			1200	24 hr.	Mel+trace Ne$_{ss}$+Gl
			1205	24 hr.	Mel+Gl
			1235	24 hr.	Mel+Gl
			1240	1 hr.	Gl
1.575	50	50	1150	5 days	Ne$_{ss}$+Mel+Fo
			1200	24 hr.	Mel+rare Ne$_{ss}$+rare Fo+Gl
			1205	24 hr.	Mel+rare Fo+Gl
			1210	24 hr.	Mel+Gl
			1265	2 hr.	rare Mel+Gl
			1270	2 hr.	Gl
1.591	40	60	1195	24 hr.	Mel+rare Ne$_{ss}$+rare Fo+Gl
			1200	24 hr.	Mel+rare Fo+Gl
			1205	24 hr.	Mel+rare Fo+Gl
			1210	24 hr.	Mel+Gl
			1295	1 hr.	trace Mel+Gl
			1300	16 hr.	Gl
1.602	30	70	1150	7 days	Mel+Fo+Ne$_{ss}$
			1195	24 hr.	Mel+Fo+Gl
			1320	1 hr.	trace Mel+Gl
			1325	1 hr.	Gl
1.619	20	80	1150	7 days	Mel+Fo+Ne$_{ss}$
			1200	7 days	Mel+trace Fo+Gl
			1360	1 hr.	rare Mel+Gl
			1365	1 hr.	Gl
1.629	10	90	1395	½ hr.	Mel+Gl
			1400	½ hr.	Gl

TABLE 2. RESULTS OF QUENCHING EXPERIMENTS FOR THE SYSTEM DIOPSIDE-AKERMANITE-NEPHELINE

Refractive index of glass ±0.003	Composition (wt %)			Temp. °C	Time	Phases
	Di	Ak	Ne			
1.534	10	10	80	1180	15 hr.	Ne$_{ss}$+Mel+Gl
				1200	16 hr.	Ne$_{ss}$+rare Cg$_{ss}$+Gl
				1240	15 hr.	Ne$_{ss}$+Cg$_{ss}$+Gl
				1250	15 hr.	Cg$_{ss}$+Gl
				1315	1 hr.	rare Cg$_{ss}$+Gl
				1320	1 hr.	Gl
1.543	10	20	70	1210	15 hr.	Ne$_{ss}$+rare Mel+Gl
				1215	24 hr.	Ne$_{ss}$+Gl
				1225	1 hr.	Ne$_{ss}$+Gl
				1230	15 hr.	Gl
1.559	10	30	60	1190	48 hr.	Mel+Ne$_{ss}$+Gl
				1200	18 hr.	Mel+Gl
				1225	1 hr.	rare Mel+Gl
				1230	15 hr.	Gl
1.573	10	40	50	1190	48 hr.	Mel+Ne$_{ss}$+Gl
				1200	18 hr.	Mel+Gl
				1260	1 hr.	Mel+Gl
				1265	1 hr.	Gl
1.549	30	10	60	1050	14 days	loose powder
				1080	14 days	slightly fritted cake
				1130	7 days	Mel+Ne$_{ss}$+rare Fo+rare Di$_{ss}$+Gl
				1140	4 days	Mel+Ne$_{ss}$+rare Fo+Gl
				1155	24 hr.	Mel+Fo+rare Ne$_{ss}$+Gl
				1160	48 hr.	Mel+Ne$_{ss}$+Gl
				1185	1 hr.	Mel+rare Ne$_{ss}$+Gl
				1190	18 hr.	Gl
1.547	35	5	60	1120	14 days	slightly fritted cake
				1155	24 hr.	Mel+Ne$_{ss}$+rare Fo+Gl
				1160	13 hr.	Mel+Ne$_{ss}$+Gl
				1175	24 hr.	Mel+Ne$_{ss}$+Gl
				1180	20 hr.	Gl
1.552	35	10	55	1170	24 hr.	Mel+Fo+rare Ne$_{ss}$+Gl
				1175	24 hr.	Mel+trace Ne$_{ss}$+Gl
				1190	4 hr.	Mel+Gl
				1195	3 hr.	Gl

TABLE 2—(*Continued*)

Refractive index of glass ±0.003	Composition (wt %)			Temp. °C	Time	Phases
	Di	Ak	Ne			
1.560	37	3	60	1185	5 hr.	Mel+rare Fo+rare Ne$_{ss}$+Gl
				1190	16 hr.	Ne$_{ss}$+Gl
				1195	2 hr.	Gl
1.562	38	2	60	1160	2 hr.	Fo+rare Mel+Ne$_{ss}$+Gl
				1170	16 hr.	trace Fo+Gl
				1180	15 hr.	Gl
1.553	38	4	58	1160	1 hr.	Mel+Fo+rare Ne$_{ss}$+Gl
				1165	1 hr.	Mel+rare Fo+Gl
				1170	2 hr.	Gl
1.563	40	5	55	1080	14 days	slightly fritted cake
				1180	2 hr.	Fo+Mel+Gl
				1190	16 hr.	Fo+Gl
				1200	1 hr.	Gl
1.555	40	7	53	1140	15 hr.	Mel+Fo+rare Di$_{ss}$+rare Ne$_{ss}$+Gl
				1150	15 hr.	Mel+Fo+Gl
				1180	1 hr.	Mel+rare Fo+Gl
				1185	5 hr.	rare Mel+Gl
				1190	15 hr.	Gl
1.553	40	10	50	1130	7 days	Mel+rare Ne$_{ss}$+rare Fo+trace Di$_{ss}$+Gl
				1140	4 days	Mel+rare Fo+rare Ne$_{ss}$+Gl
				1150	72 hr.	Mel+Fo+Gl
				1170	24 hr.	Mel+rare Fo+Gl
				1180	24 hr.	Mel+Gl
				1200	24 hr.	Mel+Gl
				1205	18 hr.	Gl
1.573	40	20	40	1130	7 days	Mel+rare Fo+rare Di$_{ss}$+Gl
				1140	4 days	Mel+Fo+Gl
				1180	16 hr.	Mel+rare Fo+Gl
				1185	16 hr.	Mel+Gl
				1245	2 hr.	Mel+Gl
				1250	2 hr.	Gl
1.560	45	8	47	1140	4 days	Mel+Fo+Di$_{ss}$+trace Ne$_{ss}$+Gl
				1150	4 days	Mel+Fo+Di$_{ss}$+Gl
				1190	15 hr.	Mel+Fo+trace Di$_{ss}$+Gl
				1200	15 hr.	Mel+rare Fo+Gl
				1205	5 hr.	Gl

TABLE 2—(*Continued*)

Refractive index of glass ±0.003	Composition (wt %) Di	Ak	Ne	Temp. °C	Time	Phases
1.560	50	4	46	1200	1 hr.	Fo+Mel+Gl
				1205	1 hr.	Fo+Gl
				1210	1 hr.	trace Fo+Gl
1.563	50	10	40	1140	4 days	Mel+Fo+Di_{ss}+Gl
				1180	48 hr.	Mel+Fo+Gl
				1210	24 hr.	Mel+Fo+Gl
				1230	24 hr.	trace Mel+Gl
				1240	2 hr.	Gl
1.580	50	20	30	1250	24 hr.	Mel+Di_{ss}+Gl
				1260	24 hr.	Mel+Gl
				1265	24 hr.	trace Mel+Gl
				1270	24 hr.	Gl
1.598	50	30	20	1250	24 hr.	Mel+rare Di_{ss}+Gl
				1290	3 hr.	Mel+Gl
				1305	2 hr.	rare Mel+Gl
				1310	2 hr.	Gl
1.565	54	2	44	1080	7 days	slightly fritted cake
				1210	1 hr.	rare Fo+Gl
				1220	1 hr.	trace Fo+Gl
				1230	1 hr.	Gl
1.565	55	5	40	1200	1 hr.	Mel+Fo+rare Di_{ss}+Gl
				1215	1 hr.	trace Fo+Gl
				1220	1 hr.	Gl
1.567	56	6	38	1140	4 days	Di+Mel+trace Fo+trace Ne_{ss}+Gl
				1210	15 hr.	Fo+Di_{ss}+Mel+Gl
				1215	16 hr.	Fo+Di_{ss}+Gl
				1220	15 hr.	rare Di_{ss}+Gl
				1225	2 hr.	Gl
1.612	58	32	10	1310	3 hr.	Di_{ss}+Mel+Gl
				1315	1 hr.	Gl
1.570	60	4	36	1210	15 hr.	Mel+Fo+Di_{ss}+Gl
				1215	16 hr.	Di_{ss}+rare Fo+Gl
				1220	15 hr.	Di_{ss}+Gl
				1225	2 hr.	Gl

TABLE 2—(*Continued*)

Refractive index of glass ±0.003	Composition (wt %) Di	Ak	Ne	Temp. °C	Time	Phases
1.572	60	10	30	1050	14 days	loose powder
				1100	14 days	slightly fritted cake
				1240	18 hr.	Di_{ss}+rare Mel+Gl
				1245	24 hr.	Gl
1.589	60	20	20	1050	14 days	loose powder
				1100	14 days	slightly fritted cake
				1270	18 hr.	Di_{ss}+Mel+Gl
				1275	3 hr.	rare Di_{ss}+Gl
				1280	3 hr.	Gl
1.579	60	30	10	1335	2 hr.	Di_{ss}+Gl
				1340	3 hr.	Gl

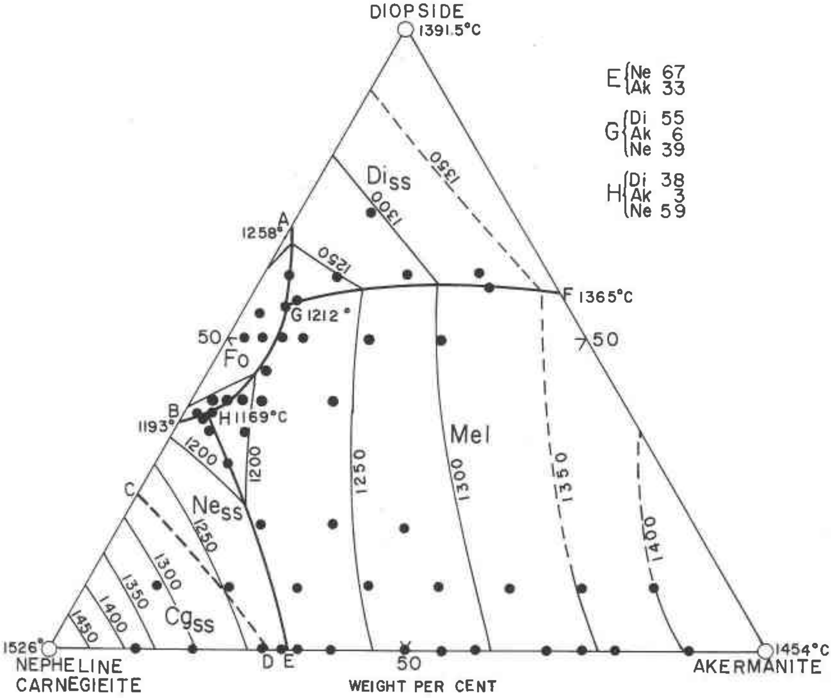

FIG. 4. Phase equilibrium diagram of the system $CaMgSi_2O_6$-$Ca_2MgSi_2O_7$-$NaAlSiO_4$.

The join $NaAlSiO_4$-$Ca_2MgSi_2O_7$. Along this join melilite, nepheline and carnegieite have their own primary phase volume. The primary phase volumes of nepheline and melilite cross each other at the point of $Ne_{67}Ak_{33}$ and the temperature of 1210°C on this join. The phase boundary surface between melilite and forsterite is at about 1210°C near the nepheline-akermanite join, and the temperature falls towards the nepheline apex.

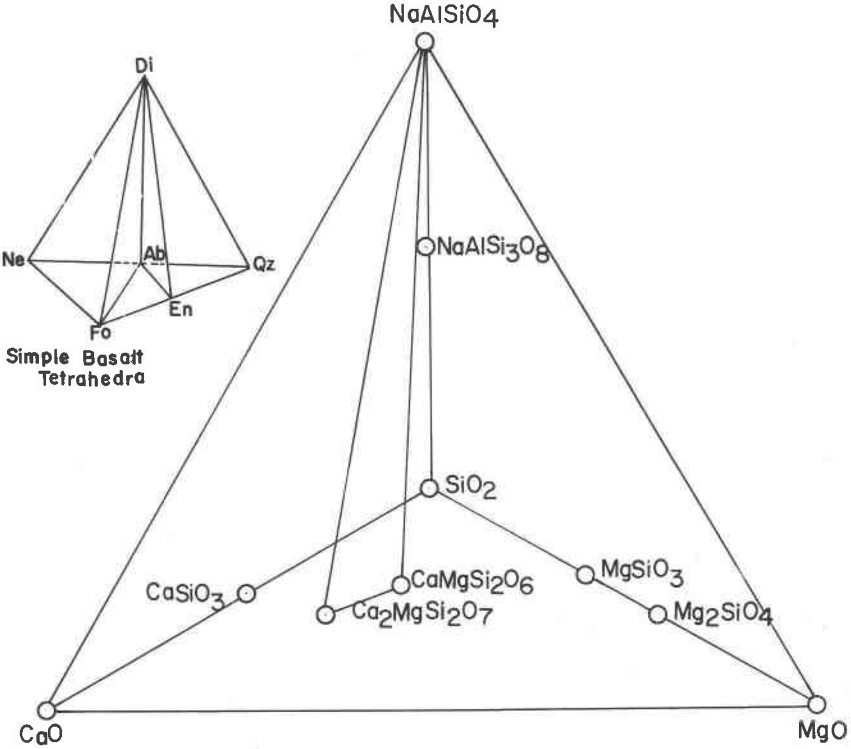

FIG. 5. The system $NaAlSiO_4$-CaO-MgO-SiO_2.

This plane intersects the phase boundary plane between nepheline and melilite. Along this intersection line, which is univariant, melilite, nepheline, and forsterite coexist with liquid.

Piercing points and crystallization. The system diopside-akermanite-nepheline does not have an invariant point; both G and H (Fig. 4 and 6) are piercing points. The point G lies on the phase boundary line separating the primary phase volume of melilite, forsterite and diopside in the system $NaAlSiO_4$-CaO-MgO-SiO_2 (Figures 4 and 5), and at this point melilite, forsterite, diopside and liquid coexist. The eutectic point, where akermanite, forsterite, diopside and liquid coexist in the system CaO-MgO-SiO_2 is at the temperature of 1357°C (Ricker & Osborn, 1954), while the temperature of piercing point G (1212°C) is lower than the former point. Therefore, along the phase boundary line between diopside, melilite and forsterite the temperature falls towards the nepheline apex in the system $NaAlSiO_4$-CaO-MgO-SiO_2 with crystallization of diopside, akermanite and forsterite.

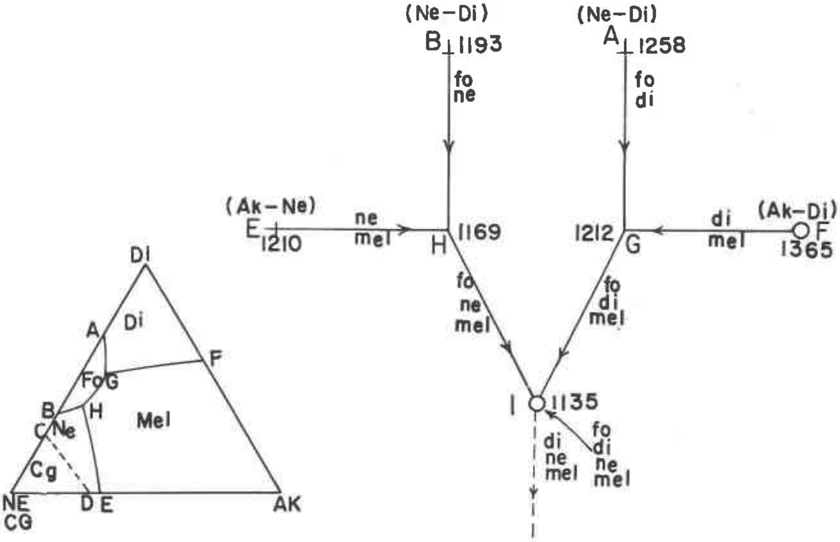

FIG. 6. Flow sheet of the system $CaMgSi_2O_6$-$Ca_2MgSi_2O_7$-$NaAlSiO_4$.

The point H (Fig. 3) lies on the boundary line of three primary phase volumes, nepheline, forsterite, and melilite. The maximum temperature at which nepheline, forsterite and liquid coexist in the system nepheline-diopside is 1193°C. This temperature is higher than that of H (1169°C). Therefore, the temperature falls toward the tie line of diopside and akermanite with crystallization of nepheline, forsterite and melilite. The boundary curve between diopside, forsterite and melilite and the one between nepheline, forsterite and melilite are quaternary univariant lines, and will join each other at some point within the system $NaAlSiO_4$-CaO-MgO-SiO_2 (Fig. 6), where nepheline, diopside, forsterite, melilite, and liquid coexist.

Diopside appears at 1135°C in the mixtures around H and coexists with nepheline, forsterite, and melilite. This is a quaternary invariant point, since five phases coexist at this temperature. Forsterite disappears below 1135°C even for starting composition within its own primary field. Schairer, Yagi and Yoder (1962) stated that olivine appears to react with liquid until consumed, producing diopside and melilite. From these data this invariant point is a reaction point, and the following reaction may occur at this point:

$$\underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{liquid}}{3CaSiO_3} = \underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{melilite}}{CaMgSi_2O_7}$$

When forsterite disappears by reaction with liquid, temperature falls towards another quaternary invariant point.

PETROLOGIC SIGNIFICANCE

Yoder and Tilley (1962) have proposed the simple basalt system, the apices of which are represented by four normative minerals calculated from natural basalts. Melilite-bearing rocks cannot be plotted in the simple basalt tetrahedron as they have large amounts of normative larnite. The tetrahedron $NaAlSiO_4$-CaO-MgO-SiO_2 includes both the simple basalt tetrahedron and melilite-bearing rocks.

The significance of melilite in the join nepheline-diopside has been discussed by Yoder and Tilley, who have suggested the following reaction:

$$\underset{\text{diopside}}{8CaMgSi_2O_6} + \underset{\text{nepheline}}{3NaAlSiO_4} = \underset{\text{akermanite}}{4Ca_2MgSi_2O_7} + \underset{\text{forsterite}}{2Mg_2SiO_4} + \underset{\text{albite}}{3NaAlSi_3O_8}$$

Diopside, nepheline, akermanite, and forsterite are essential constituents of melilite-bearing rocks. For the reason mentioned above, the join diopside-akermanite-nepheline is important for the consideration of the melilite-bearing rocks.

Both phenocrystic and groundmass minerals of olivine melilitite are melilite, olivine, clinopyroxene. This assemblage corresponds to the coexisting phases at the piercing point G in the system diopside-akermanite-nepheline. At G forsterite, melilite, diopside, and liquid are in equilibrium. With decreasing temperature, the liquid reaches I (Fig. 6) and nepheline appears. When equilibrium is maintained and reaches I the products are forsterite, nepheline, diopside and melilite. This corresponds to the mineral assemblage in olivine melilite nephelinite. Olivine melilite nephelinite is formed by the rapid cooling of the liquid crystallizing olivine, melilite, diopside, and nepheline. At point I olivine disappears owing to the reaction with liquid, and melilite, nepheline and diopside coexist with liquid. This mineral assemblage corresponds to melilite nephelinite, consisting of phenocrysts of nepheline and melilite and groundmass of nepheline, melilite and diopside.

From the above mentioned facts, we infer that the crystallization differentiation trend of melilite-bearing rocks takes the following course:

Olivine melilitite→olivine melilite nephelinite→melilite nephelinite.

The order of crystallization of minerals in the above differentiation scheme are as follows:

olivine→diopsidic augite→melilite→nepheline.

ACKNOWLEDGMENTS

The writers are greatly indebted to Dr. J. F. Schairer of the Geophysical Laboratory and Dr. E. G. Lidiak of the University of Pittsburgh for their critical reading of the paper in manuscript. Mr. S. Ota of Hokkaido University kindly helped the writers in the laboratory.

Most of the study was carried out at Hokkaido University, and some additional work was done at the University of Pittsburgh. The writers gratefully acknowledge the Fellowship given by the University of Pittsburgh and the Senior Foreign Scientist Fellowship of the National Science Foundation.

This study was supported partially by the National Science Foundation Grant GP 5494, which is gratefully acknowledged.

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Manuscript received, April 14, 1966; accepted for publication, June 29, 1966.