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CRYSTALLIZATION IN THE SILICA-UNDERSATURATED PORTION OF THE SYSTEM DIOPSIDE-NEPHELINE-AKERMANNITE-SILICA AND ITS BEARING ON THE FORMATION OF MELILITES AND NEPHELINITES

by

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(with 2 Tables and 3 Text-figures)

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Abstract

A part of the system diopside-nepheline-akermanite-silica, where forsterite is a primary phase, was studied at 1 atm. and high pressure. It was confirmed that there is a thermal barrier cutting the forsterite primary volume and an invariant point at 1140°C where diopside, melilite, forsterite, and nepheline coexist with liquid. This point is a reaction point and forsterite disappears to react with the liquid at 1 atm. The compositions in the silica-poor side of the thermal barrier have crystallization trend (1) forsterite + liquid → (2) forsterite + diopside + liquid → (3) forsterite + melilite + diopside + liquid → (4) forsterite + diopside + melilite + nepheline + liquid → (5) diopside + melilite + nepheline + liquid: (3), (4) and (5) correspond to the differentiation trend olivine melilitite → olivine melilite nephelinite → melilite nephelinite. On the other hand, the compositions in the silica-rich side have a trend (1) forsterite + liquid → (2) forsterite + diopside + liquid → (3) forsterite + diopside + nepheline + liquid → (4) diopside + nepheline + liquid: (3) and (4) correspond to the differentiation trend of olivine nephelinite → nephelinite. These two different trends are caused by slight difference in the chemical composition of the starting liquids. The preliminary data at high pressure suggest that the crystallization at depth does not lead to melilite nephelinite but produces olivine nephelinite. Olivine melilitite and melilite nephelinite are possibly formed by the low-pressure fractional crystallization of the magma produced under high pressure condition.

Introduction

The systems diopside-nepheline-silica and diopside-nepheline-akermanite are the most important among the joins in the system of expanded basalt tetrahedron proposed by Schairer and Yoder (1964) with respect to the differentiation and the genesis of alkalic rocks. The former system, studied by Schairer and Yoder (1960), shows the relationship between alkali olivine basalt magma and tholeiite magma. The latter has two piercing points. Onuma and

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Yagi (1967) studied the latter system and showed the differentiation trend from the olivine melilitite to the melilitite nephelinite through the olivine-melilitite nephelinite at 1 atm.

The mineral assemblage at a piercing point (C in Fig. 1) in the system diopside-nepheline-silica corresponds to the olivine nephelinite and that at a piercing point (G in Fig. 1) in the system diopside-nepheline-akermanite

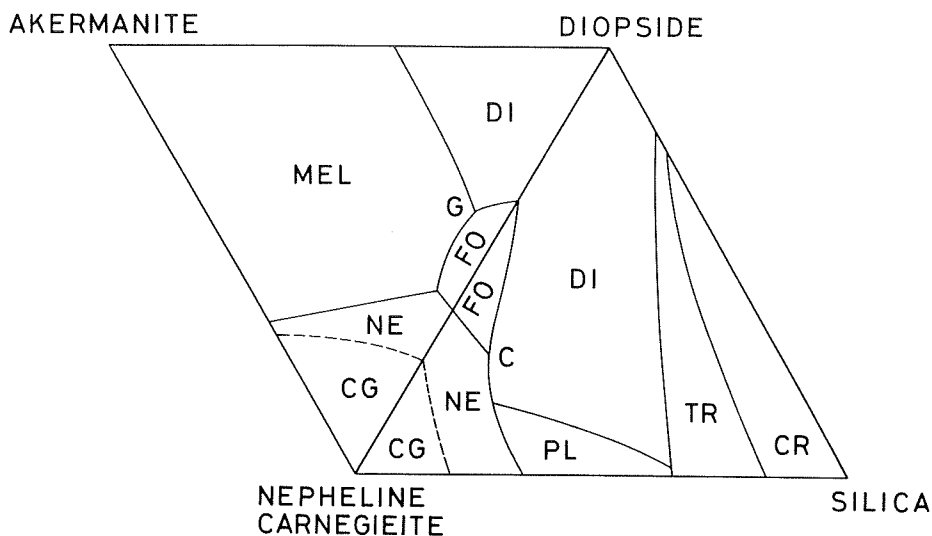


Fig. 1 Relationship between the joins diopside-akermanite-nepheline and diopside-nepheline-silica.

FO, forsterite; DI, diopside; MEL, melilitite; NE, nepheline; PL, plagioclase; TR, tridymite; CR, cristobalite.

corresponds to the olivine melilitite. In order to elucidate the relationship between olivine melilitite magma and olivine nephelinite magma and their differentiation trend it is necessary to understand the mutual relation between these two piercing points. In this respect an experimental study of the system diopside-nepheline-akermanite-silica was performed and the discussion on a possible differentiation trend of alkali rocks undersaturated in silica, such as melilitite, nephelinite, and basanite, is given in this paper.

Experiments at 1 atm. and Crystallization Courses

In the present investigation ordinary quenching methods were employed. The starting material was prepared by complete crystallization of homogeneous

glass at temperatures between 800°C and 1000°C. The furnaces used in quenching experiment were regulated to a precision of $\pm 1^\circ\text{C}$. Pt-Pt₈₇Rh₁₃ thermocouples used to measure the temperature were calibrated at the standard melting points of NaCl 800.4°C, Au 1062.6°C, and diopside 1391.5°C.

Forsterite (Fo), diopside (Di), melilite (Mel), and nepheline (Ne) are the crystalline phases encountered in the present study. The X-ray diffraction patterns and the unit cell dimensions of these crystalline phases show that these phases are not pure compounds but solid solutions except forsterite.

Table 1. Unit-cell dimensions

a. Diopside solid solutions					
Comp. of Mixture	a(Å)	b(Å)	c(Å)	$\beta(^{\circ})$	V(Å ³)
Di(54)Ak(2)Ne(42)Qz(2)	9.731(7)	8.927(2)	5.250(3)	105.84(9)	438.7(4)
Di(53)Ak(4)Ne(41)Qz(4)	9.722(6)	8.924(2)	5.248(3)	105.83(8)	438.0(3)
Di(44)Ak(2)Ne(50)Qz(4)	9.721(5)	8.927(1)	5.246(2)	105.78(6)	438.1(2)
Di(34)Ak(2)Ne(58)Qz(6)	9.731(10)	8.926(2)	5.246(4)	105.78(12)	438.5(5)
Di(33)Ak(4)Ne(57)Qz(6)	9.710(14)	8.926(3)	5.249(7)	105.64(20)	438.1(7)
Diopside	9.745	8.925	5.250	105.87	439.2
CaAl ₂ SiO ₆	9.615	8.661	5.272	106.12	421.8

b. Nepheline solid solutions			
Comp. of Mixture	a(Å)	c(Å)	V(Å ³)
Di(54)Ak(2)Ne(42)Qz(2)	9.990(4)	8.359(4)	722.4(7)
Di(53)Ak(4)Ne(41)Qz(4)	9.983(3)	8.356(3)	721.2(5)
Di(44)Ak(2)Ne(50)Qz(4)	9.992(3)	8.359(3)	722.8(5)
Di(34)Ak(2)Ne(58)Qz(6)	9.992(5)	8.356(5)	722.5(8)
Di(33)Ak(4)Ne(57)Qz(6)	9.989(10)	8.354(9)	721.8(16)

The unit-cell dimensions of the diopsides(ss) (ss: solid solution) are given in Table 1a. All of the diopsides(ss) have smaller cell volumes than synthetic pure diopside, indicating the substitution of CaAl₂SiO₆ for diopside as suggested by Onuma and Yagi (1967). The nephelines(ss) have larger cell volumes than pure nepheline as shown in Table 1b. This is probably due to the coupled substitution of CaAl for NaSi as suggested by Donney et al. (1959). The shift of the peak (211) was observed in the melilites(ss), indicating that this mineral is also solid solution.

The results of quenching experiments are given in Table 2 and a part of the inferred phase equilibrium diagram of the system diopside-akermanite-

Table 2. Results of quenching experiments at 1 atm. (1)

Temp.	°C	Time	Results
Di(54)Ak(2)Ne(42)Qz(2)			
1230	3	hr	glass
1225	3	hr	trace Fo + glass
1205	3	hr	Fo + glass
1200	13	hr	Fo + trace Di + glass
1195	18	hr	Fo + Di + glass
1190	21	hr	Fo + Di + Mel + glass
1145	72	hr	Fo + Di + Mel + glass
1140	96	hr	trace Fo + Di + Mel + Ne + glass
1135	144	hr	Di + Mel + Ne + glass
1000	14	days	fritted cake, Di + Ne + Mel
980	96	hr	loose powder
Di(53)Ak(4)Ne(42)Qz(2)			
1220	1	hr	glass
1215	3	hr	Fo + glass
1210	3	hr	Fo + glass
1205	8	hr	Fo + trace Di + glass
1190	21	hr	Fo + Di + Mel + glass
1145	72	hr	Fo + Di + Mel + glass
1140	96	hr	trace Fo + Di + Mel + Ne + glass
1135	144	hr	Di + Mel + Ne + glass
1100	168	hr	fritted cake, Di + Mel + Ne
1000	14	days	fritted cake, Di + Mel + Ne

Table 2. (2)

Temp.	°C	Time	Results
Di(44)Ak(2)Ne(50)Qz(4)			
1210	3	hr	glass
1205	3	hr	trace Fo + glass
1185	5	hr	Fo + glass
1180	22	hr	Fo + trace Di + glass
1175	24	hr	Fo + Di + glass
1170	48	hr	Fo + Di + trace Mel + glass
1145	72	hr	Fo + Di + Mel + glass
1140	96	hr	trace Fo + Di + Mel + Ne + glass
1135	144	hr	Di + Mel + Ne + glass
1100	168	hr	fritted cake, Di + Mel + Ne
1000	14	days	loose powder Di + Mel + Ne
Di(34)Ak(2)Ne(58)Qz(6)			
1190	3	hr	glass
1185	5	hr	trace Fo + glass
1155	5	hr	Fo + trace Di + glass
1142	13	hr	Fo + trace Di + glass
1140	13	hr	Fo + Di + Ne + glass
1140	96	hr	Ne + Di + glass
1135	14	hr	rare Fo + Ne + Di + glass
1135	144	hr	Ne + Di + glass
1000	14	days	Ne + Di, fritted cake

Table 2. (3)

Temp.	°C	Time	Results
Di(33)Ak(4)Ne(57)Qz(6)			
1180	3	hr	glass
1175	5	hr	trace Fo + glass
1155	5	hr	Fo + glass
1150	6	hr	Fo + Di + glass
1145	13	hr	Fo + Di + glass
1142	13	hr	Fo + Di + Mel + glass
1140	13	hr	rare Fo + Di + Mel + Ne + glass
1135	144	hr	Ne + Di + Mel + glass
1100	168	hr	Hard cake, Ne + Di + Mel
1000	14	days	loose powder, Ne + Di + Mel

Table 2. (4)

Temp.	°C	Time	Results
Di(44)Ak(2)Ne(50)Qz(4)			
1180	3	hr	glass
1175	5	hr	trace Fo + glass
1155	5	hr	Fo + glass
1150	6	hr	Di + Fo + glass
1145	13	hr	Di + Fo + glass
1142	13	hr	Di + Mel + Fo + glass
1140	13	hr	Di + Mel + Ne + Fo + glass
1135	144	hr	Di + Mel + Ne + glass
Di, diopside; Ak, akermanite; Ne, nepheline; Qz, quartz; Fo, forsterite; Mel, melilite.			

nepheline-silica is presented in Fig. 2. A modified schematic diagram is given in Fig. 3 to explain the crystallization courses. The liquidus phase volume of forsterite is a part of the liquidus volume of forsterite in the more expanded system forsterite-melilite-nepheline-silica, and is surrounded by the three divariant phase boundary planes, Fo + Mel(ss) + liquid, Fo + Ne(ss) + liquid, and Fo + Di(ss) + liquid. An invariant point Fo + Mel(ss) + Di(ss) + Ne(ss) + liquid is inferred. Four univariant curves emanate from this invariant point.

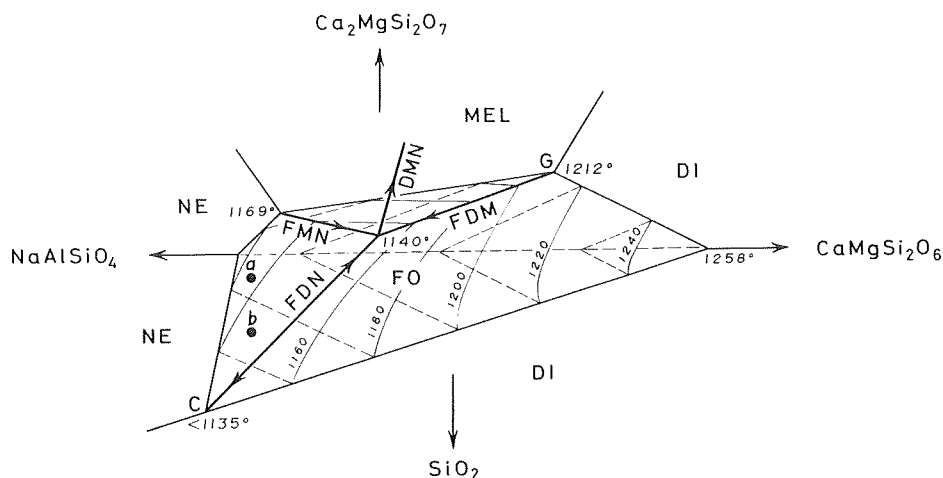


Fig. 2 Inferred phase diagram of the silica-undersaturated portion of the system diopside-akermanite-nepheline-silica. a and b are starting compositions belonging to different trend (trends a and b in Fig. 3)

F, FO; forsterite; D, DI; diopside; M, MEL; melilite; NE; nepheline.

They are Fo + Di(ss) + Ne(ss) + liquid, Fo + Di(ss) + Mel(ss) + liquid, Fo + Mel(ss) + Ne(ss) + liquid, and Di(ss) + Mel(ss) + Ne(ss) + liquid. Among the phase assemblages mentioned above the following assemblages were confirmed in the present experiments. An invariant point Fo + Di(ss) + Mel(ss) + Ne(ss) + liquid, three univariant curves, Fo + Di(ss) + Mel(ss) + liquid, Fo + Di(ss) + Ne(ss) + liquid, and Di(ss) + Mel(ss) + Ne(ss) + liquid, and one divariant plane Fo + Di(ss) + liquid. Beside these assemblages a divariant phase boundary plane Di(ss) + Ne(ss) + liquid was also confirmed.

The data in Table 2 show that the invariant point is a reaction point where forsterite disappears to react with the liquid at $1140 \pm 3^\circ\text{C}$. Two crystallization courses were observed. The first course (a in Fig. 3) is as follows. Forsterite crystallizes first and the liquid changes in composition towards the boundary plane Fo + Di(ss) + liquid. After the boundary plane is reached, forsterite and diopside(ss) continue to crystallize together and the liquid moves along boundary plane towards the univariant curve Fo + Di(ss) + Mel(ss) + liquid. Forsterite, diopside(ss), melilite(ss) crystallize together and the liquid changes in composition along the univariant line. At 1140°C the liquid reaches an invariant point where forsterite begins to react with the liquid to form nepheline(ss). The phase assemblage at this invariant point is Fo + Di(ss) + Mel(ss) + Ne(ss) + liquid. After forsterite disappears, diopside(ss), melilite(ss), and nepheline(ss) crystallize together and the liquid moves along the univariant curve Di(ss) + Mel(ss) + Ne(ss) + liquid towards another invariant point. The

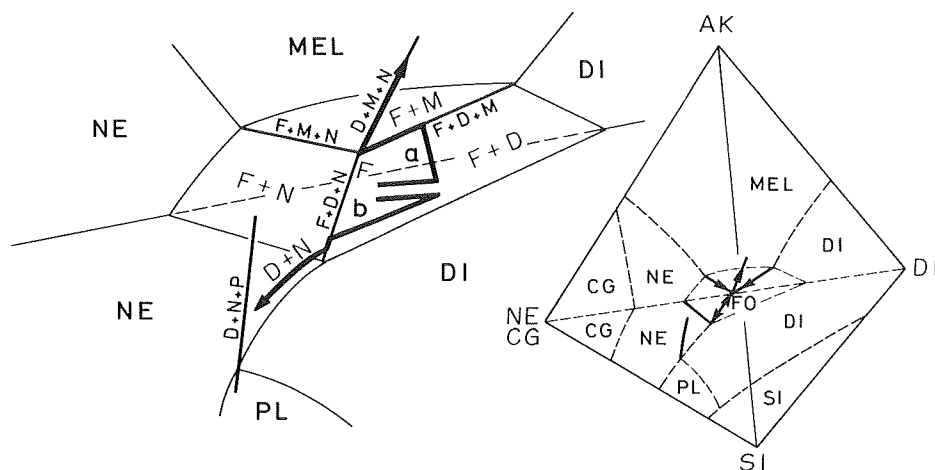


Fig. 3 Schematic diagram of the system diopside-nepheline-akermanite-silica indicating two crystallization courses, separated by a thermal barrier, which is not shown in the figure to avoid confusion.

D, DI; diopside; N, NE; nepheline; CG; carnegieite; PL, P; plagioclase; F, FO; forsterite; AK; akermanite.

temperatures at which the phase boundary plane $Fo + Di(ss) + liquid$ and the univariant curve are reached depend upon the bulk composition of the starting liquids. In the present experiments the boundary plane and the univariant curve are reached between $1153^{\circ}C$ and $1205^{\circ}C$ and between $1142^{\circ}C$ and $1192^{\circ}C$, respectively.

The second course (b in Fig. 2) is represented by the crystallization of the composition $[Di(34) Ak(2) Ne(58) Qz(6)]$. The liquid reaches the boundary plane ($Fo + Di(ss) + liquid$) at $1155^{\circ}C$. When the liquid reaches the univariant curve $Fo + Di(ss) + Ne(ss) + liquid$ at $1141^{\circ}C$ forsterite begins to be dissolved and nepheline(ss) to crystallize. Along this univariant curve forsterite continues to be dissolved and diopside(ss) and nepheline(ss) continue to crystallize out. Finally forsterite disappears at $1135^{\circ}C$ and the liquid leaves the univariant line. After leaving the univariant line, the liquid moves on the boundary plane $Ne(ss) + Di(ss) + liquid$. This shows that a part of the univariant curve $Fo + Di(ss) + Ne(ss) + liquid$ is a reaction curve and the liquid moves towards the piercing point C (Fig. 1) in the system diopside-nepheline-silica, not towards the invariant point I, because the assemblage $Fo + Di(ss) + Ne(ss) + liquid$ is kept until the lower temperature than that of the invariant point ($Fo + Di(ss) + Ne(ss) + Mel(ss) + liquid$).

The observations mentioned above suggest that there should be a thermal barrier passing through between the compositions $[Di(33) Ak(4) Ne(57)]$

Qz(6)] and [Di(34) Ak(2) Ne(58) Qz(6)]. All mixtures in the present experiment, except [Di(34) Ak(2) Ne(58) Qz(6)], crystallize to the assemblage Di(ss) + Mel(ss) + Ne(ss), indicating that the crystallization ceases on the univariant line Di(ss) + Mel(ss) + Ne(ss) + liquid because of the complicate solid solution of the crystalline phases. On the other hand, [Di(34) Ak(2) Ne(58) Qz(6)] crystallizes to the assemblage Ne(ss) + Di(ss). This suggests that the crystallization ceases on the boundary plane Di(ss) + Ne(ss) + liquid.

Experiments at high Pressure

All runs at high pressure were carried out with a piston-cylinder type high pressure apparatus under dry condition. The composition [Di(34) Ak(2) Ne(58) Qz(6)] crystallized to an assemblage Di(ss) + Ne(ss) + Mel(ss) at 1150°C and 20kb. This assemblage is the same as the final assemblage at 1 atm. On the other hand, the composition [Di(33) Ak(4) Ne(57) Qz(6)], crystallized to an assemblage Di(ss) + Ne(ss) + Mel(ss) at 1 atm., whereas the assemblage at high pressure consists of diopside(ss) and nepheline(ss), and melilite(ss) was not found. This observation indicates that the crystallization ceases on the isobaric divariant plane Di(ss) + Ne(ss) + liquid at higher pressure.

Petrological Implication

The mineral assemblages in the crystallization course a in Fig. 3, Fo + Di(ss) + Mel(ss) (univariant curve), Fo + Di(ss) + Mel(ss) + Ne(ss) (invariant point), and Di(ss) + Mel(ss) + Ne(ss) (univariant curve) correspond to the olivine melilitite, olivine-melilitite nephelinite, and melilitite nephelinite, respectively. On the other hand the mineral assemblage in the crystallization course b, Fo + Di(ss) + Ne(ss) (univariant curve) and Di(ss) + Ne(ss) (divariant plane) corresponds to the olivine nephelinite and nephelinite, respectively. Therefore, the presence of the thermal barrier gives alkalic rock undersaturated in silica two differentiation trends.

When the composition of the initial liquid lies in the silica-poor side than the thermal barrier, the crystallization proceeds along the course a in Fig. 3. During this crystallization course olivine melilitite is formed and the residual liquid migrates towards the invariant point where the phase assemblage corresponds to the olivine-melilitite nephelinite.

On the other hand, when the composition of the primary liquid lies in the silica-rich side than the thermal barrier, the crystallization proceeds along the course b in Fig. 3 and the olivine nephelinite is produced. In this case, however, the residual liquid does not reach the point I but moves towards the piercing

point C (Fig. 2) in the system diopside-nepheline-silica, and if fractional crystallization continues, another invariant point is reached, where plagioclase joins the phase assemblage (nepheline basanite), or when the liquid leaves the univariant curve $Fo + Di(ss) + Ne(ss) + \text{liquid}$ by the disappearance of olivine, the liquid moves on the $Di(ss) + Ne(ss) + \text{liquid}$ plane (nephelinite) and the univariant curve $Di(ss) + Ne(ss) + Pl(ss) + \text{liquid}$ is attained (nepheline tephrite).

In their experimental study on the natural rocks Tilley et al. (1965) showed that olivine is the primary liquidus phase both in the olivine-melilite nephelinite and the olivine nephelinite and that the crystallization sequence of the minerals is olivine $\rightarrow$ clinopyroxene $\rightarrow$ nepheline in the former rock and is olivine $\rightarrow$ clinopyroxene $\rightarrow$ nepheline in the latter rock. These two sequences correspond to the two crystallization courses a and b obtained in the present study.

In the present study the compositions $[Di(33) Ak(4) Ne(57) Qz(6)]$ (silica-poor side) and $[Di(34) Ak(2) Ne(58) Qz(6)]$ (silica-rich side) have different crystallization trend each other, a and b in Fig. 2, respectively. This experimental result at 1 atm. clearly indicates that slight difference in the chemical composition of the starting liquid results in a different crystallization trend and consequently a different final product and that when the starting liquid lies in the silica-rich side of the thermal barrier the crystallization of this liquid at lower pressure does not produce the olivine-melilite nephelinite but produces the nepheline basanite and if the fractional crystallization is promoted the residual liquid could become tephritic composition. In other words, olivine-melilite nephelinite and the nepheline basanite is not derivative of each other at lower pressure, which was also found by Schairer et al. (1968) in the system nepheline-diopside-anorthite. The only slight difference in the chemical composition of the initial liquid leads to the different crystallization trend, olivine melilite $\rightarrow$ olivine-melilite nephelinite $\rightarrow$ melilite nephelinite and olivine nephelinite $\rightarrow$ nephelinite $\rightarrow$ nepheline basanite. Of course, it is possible to derive the olivine-melilite nephelinite from the olivine nephelinite when the univariant curve $Fo + Di(ss) + Ne(ss) + \text{liquid}$ is reached at the silica-poor side of the thermal barrier. O'Hara and Biggar (1969) suggested that the melilite nephelinite is formed by the low-pressure extreme fractional crystallization of alkali olivine basalt magma. The result obtained by the consideration mentioned above agrees with O'Hara and Biggar's suggestion.

The preliminary data at high pressure in the present study are not enough to establish the crystallization trend of the melilite nephelinitic magma. However, it is noticed that the end products at high pressure do not have melilite in the assemblage, suggesting that the crystallization at high pressure does not lead to (olivine) melilite nephelinite but produces olivine nephelinite

and nephelinite. Although Green (1969) discussed that the olivine-melilitite nephelinite is derived from the high-pressure fractional crystallization of the olivine nephelinite magma, the more data are necessary to elucidate the possibility of the formation of this rock series at high pressure.

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