

PERTHITE-LIKE EXSOLUTION IN THE NEPHELINE-KALSILITE SYSTEM

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Introduction

The analogy between the alkali feldspars and the feldspathoids of composition $(\text{Na,K})\text{AlSiO}_4$ would suggest that, within a certain range of the alkali ratio, an exsolution into a sodium-rich and a potassium-rich component takes place in the NaAlSiO_4 - KAlSiO_4 system. In fact, the existence of a relatively large gap in solid solubility between nepheline and kalsilite has been demonstrated by Tuttle and Smith (1958) using synthetic materials. The phase relationships presented by these authors are very complicated, especially in the potassium-rich part of the phase diagram. Due to loss of alkalis at high temperatures, some of the charges used may have been off the strict NaAlSiO_4 - KAlSiO_4 system. Therefore, as was mentioned by these authors, the phase diagram presented may be considered only tentative. The existence of the large solvus limiting the two-phase field is, however, definite.

In contrast to the alkali feldspars, the exsolution of an extremely potassian homogeneous nepheline into a less potassian nepheline and a kalsilite phase is exceedingly rapid. Tuttle and Smith (*op. cit.*) report that, in the more potassium-rich part of the system, the synthetic material is not quenchable as a homogeneous solid solution. The exsolution takes place momentarily.

Kalsilite is very rare in natural rocks. It can crystallize only in rocks that are poor in silica and rich in potassium. Such rocks must be exceptional. Up to the present, kalsilite is known from four localities three of which (Bunyaruguru field and Katunga in SW. Uganda;

Mt. Nyiragongo in Congo) are in Central Africa and one in Italy (San Venanzo). Only on the volcano Mt. Nyiragongo it occurs together with nepheline partly as separate kalsilite grains in the groundmass of the lavas and mainly as perthite-like exsolutions in the euhedral phenocrysts. So far, these phenocrysts in the Nyiragongo lavas represent the only source of natural material available for studying the exsolution in the nepheline-kalsilite system.

Heating experiments made with the complex nepheline-kalsilite phenocrysts that are contained in the Nyiragongo lavas have shown that the process of exsolution is slightly less rapid than that found in synthetic materials. The phases stable only at high temperatures may well be quenched down to room temperature for X-ray identification. The different steps in the process of the exsolution can thus be studied. Because the nepheline-kalsilite exsolution forms an analogue to the exsolution in alkali feldspar, it may be briefly summarized in the following. This report that is based on data for the complex Nyiragongo phenocrysts is only provisional in character. The work dealing with these phenocrysts is being continued by the author.

Mode of occurrence

The mode of occurrence of the complex nepheline-kalsilite phenocrysts in the Nyiragongo lavas has been described and interpreted by the author on a previous occasion (Sahama, 1960). The complex phenocrysts are mainly found in the melilitite (bergalite) lavas of the mountain and, in the inner pit of the crater, in the dark kalsilite aggregate lavas (Sahama, 1962b). Exsolution structures are not found in every single nepheline phenocryst of a specimen. Some phenocrysts consist only of nepheline, often more or less zoned, while other phenocrysts in the same thin section show both nepheline and kalsilite phases beautifully exsolved. The bulk chemical composition of the Nyiragongo melilitites is such that, had the magma crystallized slowly in plutonic conditions, no kalsilite had been formed but the potassium compound KAlSiO_4 had entered the nepheline structure. The $(\text{Na,K})\text{AlSiO}_4$ phenocrysts found in the lavas evidently represent different stages in the early intravolcanic begin of crystallization of the magma that, by the turbulent currents of the boiling lava lake, have been collected together and, through the rapid cooling after

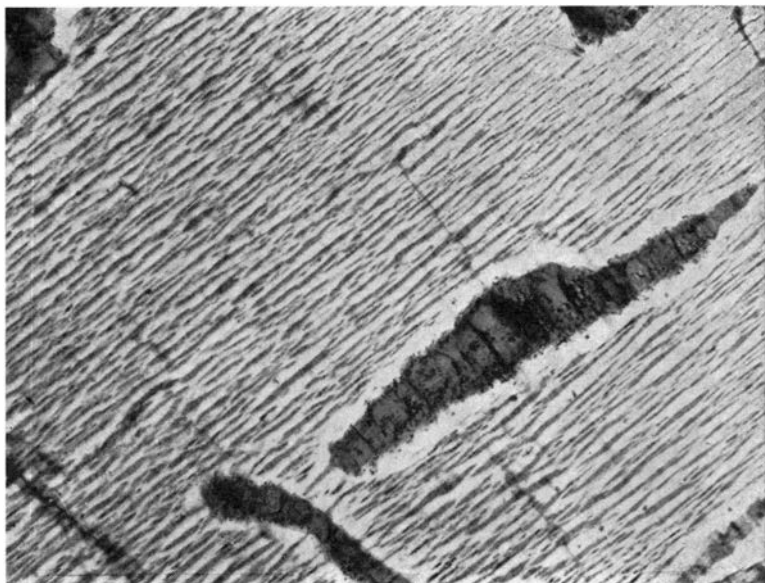


Figure 1. Perthite-like exsolution in a complex nepheline-kalsilite phenocryst, Nyragongo. Thin nepheline lamellae (dark) in a kalsilite base (white). Nicols crossed. $140\times$.

extrusion, have been preserved in aggregates of phenocrysts. The phenocrysts that originate from the very first crystallization are most rich in potassium and those phenocrysts that have been crystallized slightly later on decreasing temperature are less rich in potassium. The most potassium-rich phenocrysts are easily exsolved while the phenocrysts less rich in potassium may remain unexsolved.

Figures 1–3 illustrate examples of the complex phenocrysts. Figure 1 shows a beginning stage of exsolution with thin nepheline lamellae (dark) in a kalsilite base (white). In the phenocryst of Figure 2 the nepheline lamellae are relatively coarse. The kalsilite kernel of the crystal is surrounded by a continuous nepheline margin. In Figure 3 the nepheline lamellae have disappeared and the crystal consists of a homogeneous kalsilite kernel surrounded by a nepheline margin.

The succession of the different stages in the exsolution process is schematically summarized in Figure 4, *A–D*. The very potassium-rich homogeneous phenocryst (*A*), most probably in a nepheline structure,

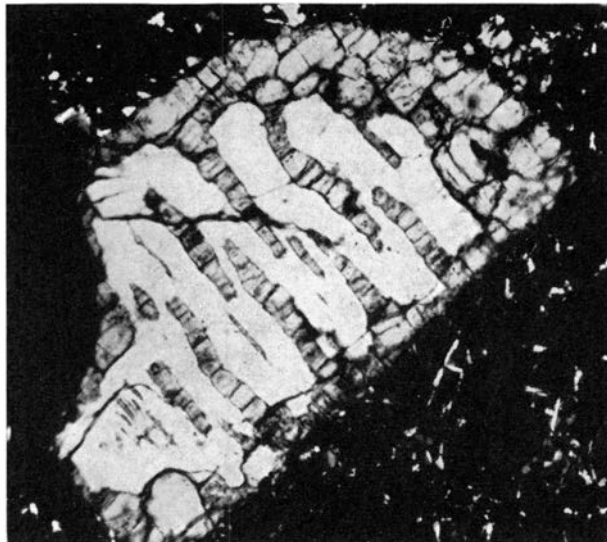


Figure 2. Exsolution in a complex nepheline-kalsilite phenocryst, Nyiragongo. Thick nepheline lamellae (dark) in a kalsilite base (white) surrounded by a homogeneous nepheline margin. Nicols crossed. $70\times$.

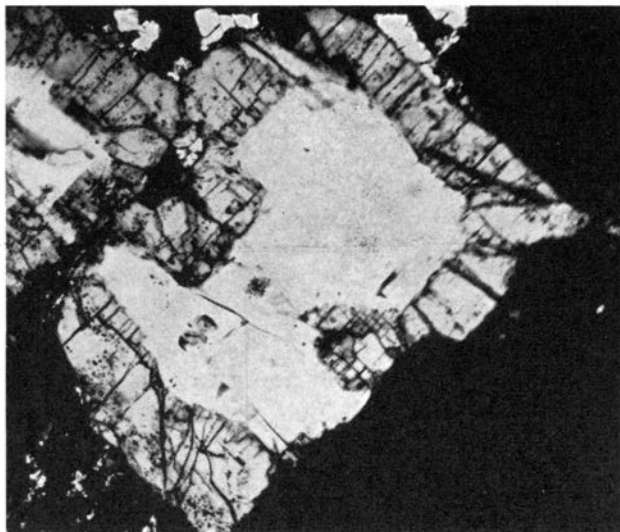


Figure 3. Completed exsolution in a complex nepheline-kalsilite phenocryst, Nyiragongo. Homogeneous kalsilite kernel (white) surrounded by a nepheline margin (dark). Nicols crossed. $60\times$.

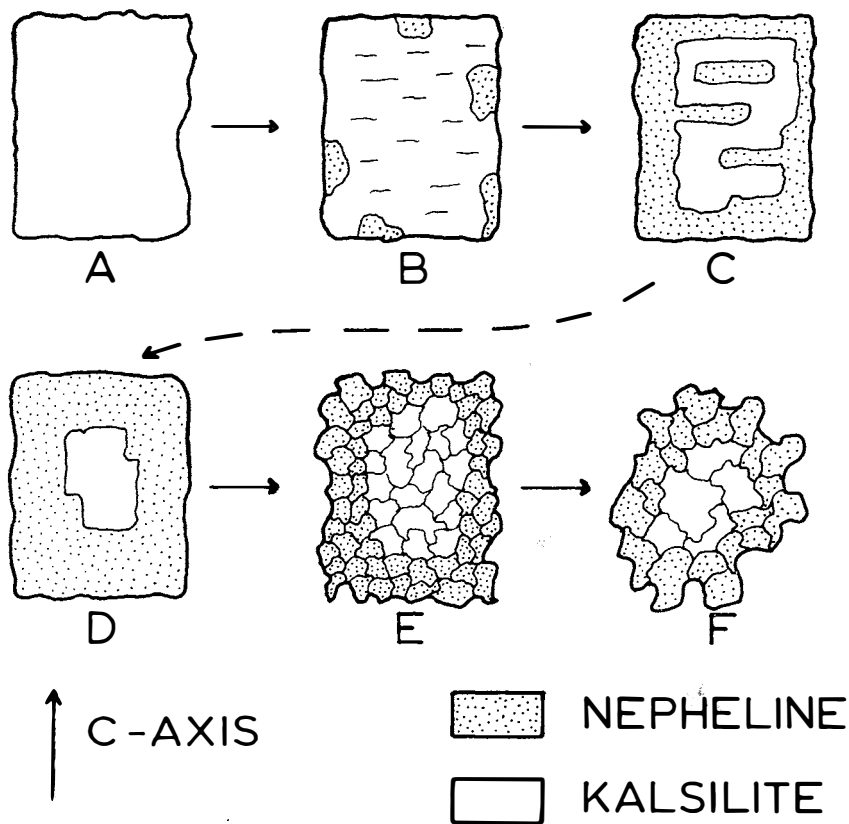


Figure 4. Schematical presentation of the progressing exsolution in the complex nepheline-kalsilite phenocrysts of Nyiragongo.

develops on cooling extremely fine-grained lamellae (*B*). The lamellae that are perpendicular to the *c*-axis of the crystal consist of a less potassian nepheline in a kalsilite base. On a few spots in the margin of the crystal, drop-like growths of nepheline occur. If the cooling is sufficiently slow or if a later heat flow from the lava lake permits a continued diffusion of the alkali atoms in the crystal, the nepheline lamellae in the kalsilite base will grow in thickness (*C*) and a continuous nepheline margin is developed. In the final stage of exsolution (*D*), there is a nepheline-free kalsilite kernel surrounded by a homogeneous nepheline margin. All intermediate steps between the stages *A-D* in Figure 4 are actually found in thin section.

Crystal *D* in Figure 4 represents the stage of completed exsolution in the Nyiragongo lavas. If the rock in which the crystal is embedded undergoes a slight metamorphic recrystallization, then the single crystal *D* will be transferred into the aggregates *E* and *F*, successively. These two last stages of development are merely hypothetical. Such a metamorphic recrystallization of the complex nepheline-kalsilite phenocrysts does not occur in the Nyiragongo rock suite. The results of progressing recrystallization *E* and *F* have been added to Figure 4 only to show that similar textures found in feldspars may perhaps be interpreted as recrystallized products of exsolution of the feldspar components.

The phases

A review of the existing phases known so far in the system $\text{NaAlSiO}_4\text{-KAlSiO}_4$ was given by Sahama (1961). This review was based largely on the studies published by Smith and Tuttle (1957) and by Donnay, Schairer and Donnay (1959). The hexagonal phases of composition $(\text{K,Na})\text{AlSiO}_4$ may be classified as given in Table 1. All the phases of the nepheline-kalsilite series mentioned in this table have been identified by X-ray methods in the Nyiragongo phenocrysts. On the other hand, kaliophilite has not been detected on Nyiragongo.

With the exception of the pure sodium nepheline ("subpotassic" nepheline of Donnay, Schairer and Donnay), the variation of the unit cell dimensions of the hexagonal $(\text{Na,K})\text{AlSiO}_4$ phases is given in Figure

Table 1. Classification of the hexagonal $(\text{K,Na})\text{AlSiO}_4$ -phases.

Nepheline-kalsilite series.

	a_0		a_0
<i>d</i> -kalsilite	5 Å	<i>o</i> -kalsilite	$\sqrt{3} \times 5$ Å
Nepheline	10	—	—
Trikalsilite	15	—	—
Tetrakalsilite	20	—	—

Kaliophilite.

	a_0		a_0
Synthetic	5 Å	—	— Å
—	—	—	—
—	—	Natural	$\sqrt{3} \times 15$
—	—	—	—

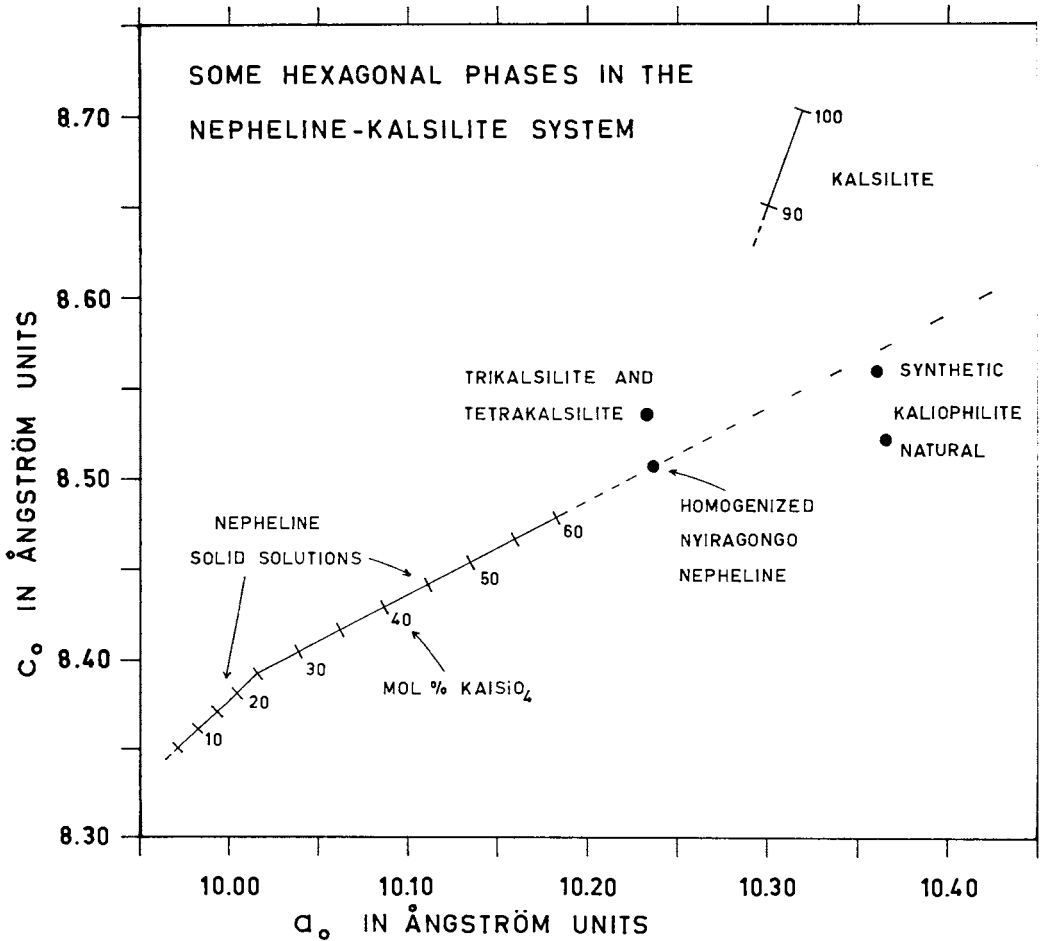


Figure 5. c_0 versus a_0 of some hexagonal phases in the $NaAlSi_3O_8$ - $KAlSiO_4$ system.

5. This figure represents a plot of the c -axes against the a -axes that have been converted to correspond to the a -axis of nepheline. The solid lines indicate the variation of the unit cell dimensions in synthetic solid solutions of nepheline and of kalsilite, respectively. The point representing the extremely potassian nepheline of Nyiragongo (Sahama, 1957) lies exactly on the continuation of the line for synthetic nepheline solid solutions. This extremely potassian nepheline was obtained through homogenizing an exsolved Nyiragongo phenocryst by heating

the crystal for a short while at ca. 1100 °C and quenching down to room temperature. The point indicating the Nyiragongo trikalsilite and tetrakalsilite is clearly off the line for nepheline.

In thin section, only the nepheline and kalsilite phases can be distinguished optically. The strict co-axial orientation of all the phases of the nepheline-kalsilite series listed in Table 1 is suggested by the homogeneous extinction of the entire complex phenocryst between crossed nicols and is confirmed by single crystal X-ray work.

Both in synthetic materials studied by Smith and Tuttle (1957) and in the natural Nyiragongo materials, only kalsilite and not kaliophilite has been found as an exsolution product from the nepheline structure. This fact, along with the known data for the unit cell dimensions of kaliophilite and kalsilite, seems to justify the statement according to which kalsilite is the form of KAlSiO_4 that shows a limited solid solubility with nepheline and not kaliophilite. The series of solid solutions should be called the nepheline-kalsilite series and not the nepheline-kaliophilite series. It is suggested that, in petrographic norm calculations and designations, kaliophilite should be replaced by kalsilite.

As is shown by analytical data of which Table 2 represents an unpublished example, the natural kaliophilite seems to be able to keep more NaAlSiO_4 in solid solution than does kalsilite at low temperatures. A kalsilite of that composition would become exsolved.

Table 2. Chemical composition of kaliophilite (phacellite),
Monte Somma, Italy.

Specimen E 120 No.2812. Analyst: Aarno Jurinen.

SiO_2	38.62 %
TiO_2	0.00
Al_2O_3	32.09
Fe_2O_3	0.80
FeO	0.29
MnO	0.00
MgO	0.00
CaO	0.00
Na_2O	3.77
K_2O	24.18
$\text{H}_2\text{O}+$	0.23
$\text{H}_2\text{O}-$	0.00
Total	99.98

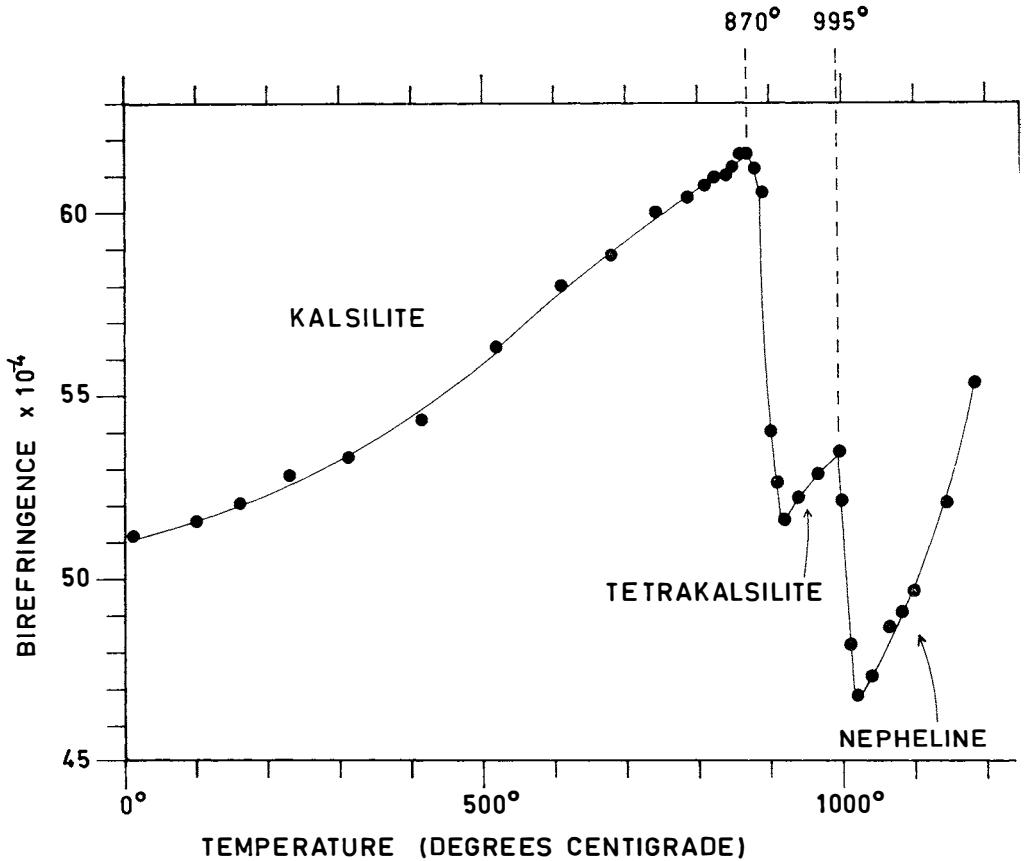


Figure 6. Optical birefringence versus temperature of a complex nepheline-kalsilite phenocryst of Nyiragongo.

Process of exsolution

The rapidity with which the phase transitions occur in the Nyiragongo phenocrysts makes it possible to watch the process of exsolving under the microscope. It was found that the phase transitions occurring in the crystal are accompanied by sudden changes in optical birefringence. By accurately measuring the value for birefringence, the succession of the phases and transformation temperatures could be determined.

Figure 6 illustrates the variation of the optical birefringence with temperature. The curve was obtained on heating. The curve obtained

on cooling back to room temperature has a similar shape and runs slightly below the heating curve. The sudden changes in birefringence occur at about the same temperatures than on heating. For clarity, the cooling curve was left out of the figure.

On heating up to a temperature of ca. 870 °C the birefringence of the kalsilite base of a complex phenocryst increases regularly. At that temperature the birefringence drops suddenly. The crystal becomes homogenized. The fine nepheline lamellae dissolve in the structure of the base and the homogenized crystal changes over into the structure of tetrakalsilite, the birefringence of which is lower than that of kalsilite. On further heating, the birefringence of tetrakalsilite increases until the temperature of ca. 995 °C is reached. At that temperature the tetrakalsilite structure transforms into the structure of a very potassium-rich nepheline of still lower birefringence. On continued heating, the birefringence of this nepheline increases rapidly.

Starting from the begin of crystallization in the melt, the series of phase transitions leading to an exsolution in the Nyiragongo phenocrysts proceeds in the following way. The highly potassian phenocrysts crystallized originally from the melt in a structure that probably was that of a zoned nepheline. At temperatures of—say—1050 °C the structure was that of nepheline. At about 1000 °C, this nepheline inverted into a homogeneous tetrakalsilite structure. This inversion is accompanied by a doubling of the *a*-axis and by slight expansion in direction of the *c*-axis. The inversion proceeded through the metastable trikalsilite structure.

At a temperature of ca. 870 °C, the homogeneous tetrakalsilite structure splits up into a less potassian nepheline and a kalsilite structure. The equilibrium in the distribution of the sodium and the potassium atoms between the nepheline and kalsilite phases depends on temperature. On further cooling, the nepheline phase becomes less rich in potassium and the kalsilite phase less rich in sodium. It is a very remarkable fact that, in the Nyiragongo phenocrysts studied, the exsolution does not proceed from the highly potassian nepheline into a mixture of less potassian nepheline and kalsilite but proceeds through the tetrakalsilite phase.

The solvus

Figure 7 illustrates the solvus in the $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 system. The solid line indicates the solvus as given by Tuttle and Smith (1958) for synthetic materials. The top of the solvus lies at a temperature of 1070°C and the composition on the top is about 70% potassium component. Below that temperature the homogeneous crystal becomes unmixed. For the Nyiragongo phenocrysts that happen to have about the same composition there is a definite stability field between the homogeneous nepheline and the mixture of nepheline and kalsilite. The exsolution temperature is some 200° lower.

The lack of the tetrakalsilite field on the solvus in the phase diagram for synthetic materials might be a result of the extremely rapid exsolution which makes the quenching difficult. For the Nyiragongo phenocrysts the speed of the exsolution is considerably less rapid and allows a quenching of the tetrakalsilite phase.

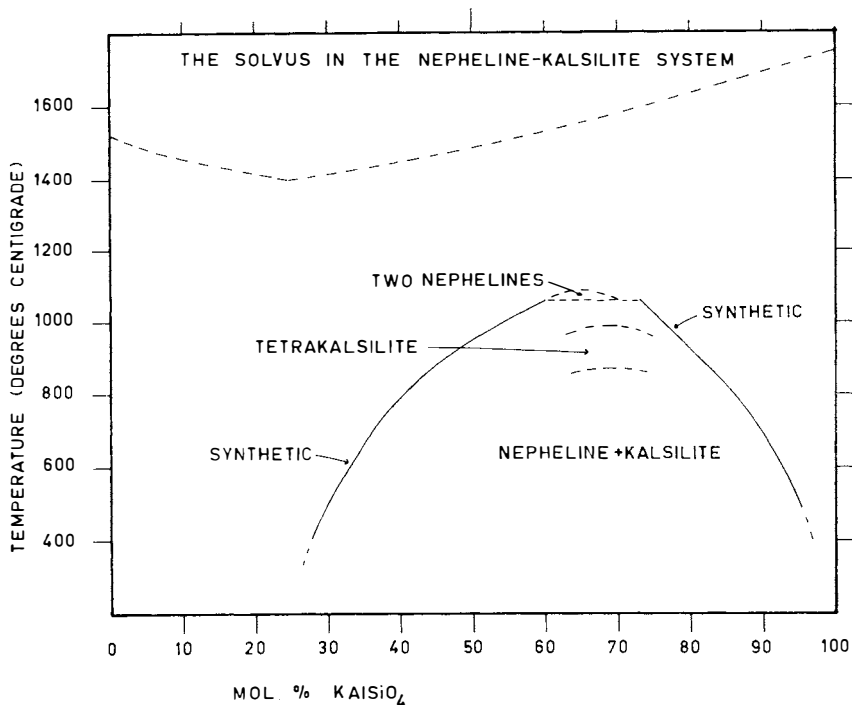


Figure 7. Location of the solvus in the $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 system.

On the other hand, the difference of ca. 200° in the exsolution temperature between the synthetic and the natural material must have some other reason. MacKenzie and Smith (1961) suggested that the different solvi found in alkali feldspars are explainable through a different degree of ordering. For nepheline, optical indications are known (Sahama, 1962a) suggesting an existence of an order-disorder transformation in the nepheline structure. If such an order-disorder transformation in nepheline can be proved crystal structurally, it might explain the discrepancy in the solvus between the synthetic and natural materials in the way suggested for the alkali feldspars.

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