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## SOME ASPECTS OF THE SYSTEM $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$

JULIAN R. GOLDSMITH, *University of Chicago, Chicago, Illinois.*

### ABSTRACT

The thermal-equilibrium relationships in the system  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$  have been investigated. Complex relations exist at temperatures above the carnegieite-nepheline inversion range, the system at these temperatures being quaternary in nature. At lower temperatures, in the stability field of nepheline, simplification to a binary system is observed over a considerable portion of the system due to the ability of nepheline to take up somewhat over 60 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  in solid solution. The complexity at higher temperatures is due to the inability of carnegieite to include more than a small amount of  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  in its structure, and to the intrusion of fields of  $\beta\text{-Al}_2\text{O}_3$ , corundum, and  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ .

Soda volatilization is significant in the system, and apparently the rate is increased as lime is added. As soda is lost,  $\beta\text{-Al}_2\text{O}_3$  or corundum tends to crystallize. The possibility of this effect being related to the corundum present in some alkaline rocks, particularly those associated with limestone, and to soda enrichment (albitization, etc.) of the country rock is discussed.

### I. INTRODUCTION

Investigations in the quaternary system  $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$  have been confined for the most part to compositions fairly rich in silica. If this four component system be represented as a tetrahedron, it is seen that the synthetic counterparts of silicate minerals naturally occur toward the silica corner of the tetrahedron, and the equilibrium relations between these minerals are of primary interest to the petrologist. In a previous work by the author (1947) on the system anorthite-gehlenite-nepheline, it was noted that the high refractive indices of some of the nepheline crystals encountered presented a compositional problem not satisfied by assuming solid solution with any "end-member molecules" present in the system. Non-ternary behavior of crystallization paths also contributed to the conclusion that the hitherto recognized solid solutions of albite and anorthite (not considering  $\text{KAlSiO}_4$ ) in nepheline could not account for the nepheline formed in this system. Higher indices than those previously observed in synthetic nepheline had also been noted by Smalley (1947), in his study of the system nepheline-gehlenite.

Consideration of courses of crystallization within the three dimensional tetrahedron  $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$  led the writer (1947) to the con-

clusion that at least part of the material entering into solid solution with nepheline in the system anorthite-gehlenite-nepheline was alumina-rich in composition; i.e., the nephelines were undersilicated. A. N. Winchell (1933) had suggested the possibility that the lime observed in natural nephelines might be present as  $\text{CaAlAlO}_4$ . This calcium aluminate would satisfy the requirements discussed above, and was considered at that time, in addition to a sodium aluminate,  $\text{Na}_2\text{Al}_2\text{O}_4$ .  $\text{CaAlAlO}_4$  is known as an independent crystalline compound, and is commonly written as  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . If one assumes solid solution between it and nepheline,



it is apparent that the common Na-Ca and Al-Si replacement would be operative. The present investigation was begun primarily to determine the validity of this relationship.

The thermal-equilibrium relationships at atmospheric pressure along the join  $\text{NaAlSiO}_4$ - $\text{CaO} \cdot \text{Al}_2\text{O}_3$  within the parent four oxide system are here discussed. The relation of this join to the general quaternary system is shown in Fig. 1. One of the end members,  $\text{NaAlSiO}_4$  is the principal "molecule" of natural nepheline, whereas the compound  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  is not known to occur independently in nature.  $\text{NaAlSiO}_4$  is a polymorphic compound; carnegieite, the high temperature modification is also known only as a synthetic product. The compound  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , although an end member in the system, does not crystallize in those portions of the system here investigated (from zero to 80%  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ). A calcium aluminate phase is encountered, but in all cases it is the 1:2 compound ( $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ ) rather than the 1:1 compound. This phenomenon will later be discussed in the light of relations within the general four oxide system.

The crystalline phases encountered in this system are nepheline (solid solutions), carnegieite (solid solutions),  $\beta$ - $\text{Al}_2\text{O}_3$ , corundum, and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ . The compound  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  would undoubtedly form in mixtures very rich in this ingredient. Nine mixtures were prepared and subjected to thermal study. In addition, a few thermal and  $x$ -ray determinations were made on the three phases of pure  $\text{NaAlSiO}_4$ ,<sup>1</sup> and pure  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  was prepared for optical and  $x$ -ray examination. Thermal study was by the quenching method in all cases that involved a liquid phase. In runs below solidus temperatures the small charges, in platinum-foil envelopes, were rapidly cooled in air. The resulting products were examined microscopically, and in many cases, also by means of  $x$ -ray diffraction (powder pictures). Approximately 170 runs were made, the sig-

<sup>1</sup> Kindly supplied as glass, carnegieite, and nepheline by Dr. N. L. Bowen, of the Geophysical Laboratory, Carnegie Institution of Washington.

nificant data of which are summarized in Table 1. The equilibrium diagram, Fig. 2, was prepared from these data. Figure 3 is a composition-refractive index diagram of the homogeneous glasses prepared along the join studied.

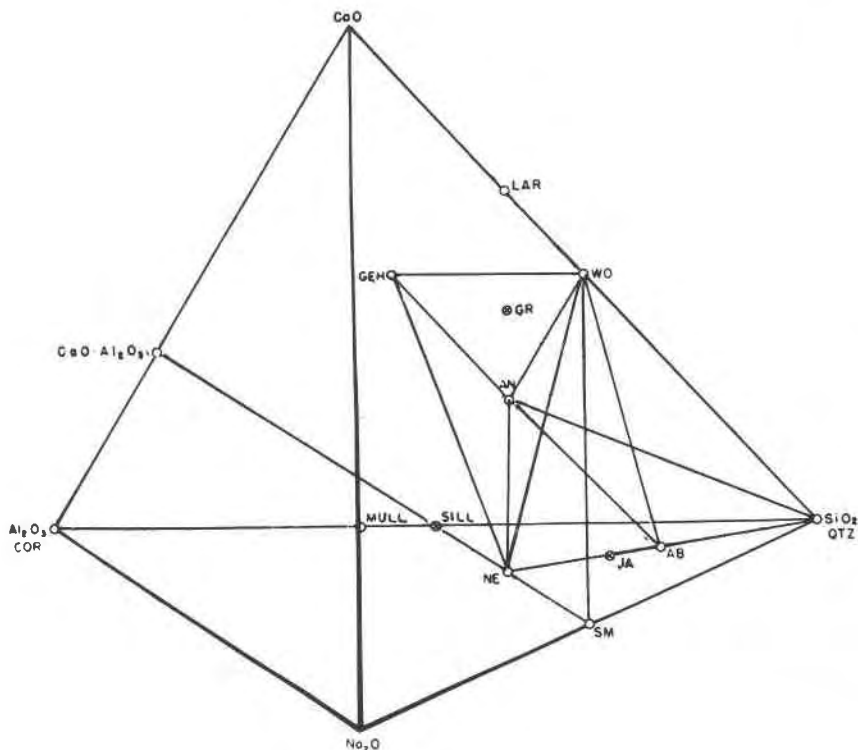


FIG. 1. The soda-lime-alumina-silica tetrahedron. The join here studied is represented by the line between NE and  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ . Other internal systems that have been investigated are shown by lines joining the composition points. The compounds that have been prepared synthetically are shown as  $\circ$ ; those that occur in nature but that have not been synthesized are shown thus:  $\otimes$ .

The abbreviations signify; AN, anorthite; GEH, gehlenite; NE, nepheline; WO, wollastonite; AB, albite; JA, jadeite; SM, sodium metasilicate; SILL, sillimanite; MULL, mullite; LAR, larnite; GR, grossularite; QZ, quartz; COR, corundum.

## II. THE CRYSTALLINE PHASES

### $\text{NaAlSiO}_4$

The properties of carnegieite, the high temperature modification of  $\text{NaAlSiO}_4$ , and of nepheline, the low temperature form, have been described by Bowen (1912), and by Bowen and Greig (1925). Carnegieite

TABLE 1. THERMAL DATA FOR THE SYSTEM  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$ 

Wt. per cent		Time	Temperature (° C.)	Final Condition*
$\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$				
95	5	3½ hrs.	1344	CG, thin films of glass
		3¼ hrs.	1340	CG, NE
		90 hrs.	1060	NE, CG
		15 days	795	CG, NE
90	10	30 min.	1488	All glass
		30 min.	1484	Glass, CG
		4 hrs.	1345	CG, glass, rare $\beta\text{-Al}_2\text{O}_3$
		4 hrs.	1350	CG, glass
		20 hrs.	1336	CG, glass, $\beta\text{-Al}_2\text{O}_3$
		5½ hrs.	1330	CG, NE, $\beta\text{-Al}_2\text{O}_3$
		22 hrs.	1306	NE, CG, very rare $\beta\text{-Al}_2\text{O}_3$
		20 hrs.	1300	NE, CG
		10 days	795	NE, CG
80	20	30 min.	1440	All glass
		30 min.	1437	Glass, rare CG
		3¼ hrs.	1368	CG, glass
		3¼ hrs.	1362	CG, glass, rare $\beta\text{-Al}_2\text{O}_3$
		3¼ hrs.	1336	CG, $\beta\text{-Al}_2\text{O}_3$ , sparse glass
		3¼ hrs.	1331	CG, $\beta\text{-Al}_2\text{O}_3$ , NE (some glass?)
		3½ hrs.	1323	CG, NE, rare $\beta\text{-Al}_2\text{O}_3$
		3½ hrs.	1317	CG, NE
		10 days	795	NE, CG
70	30	30 min.	1398	All glass
		30 min.	1394	Glass, sparse CG
		30 min.	1384	Glass, CG
		30 min.	1380	Glass, CG, rare $\beta\text{-Al}_2\text{O}_3$
		3½ hrs.	1390	Glass, fairly abundant $\beta\text{-Al}_2\text{O}_3$ †
		3½ hrs.	1340	CG, $\beta\text{-Al}_2\text{O}_3$ , glass
		3½ hrs.	1335	NE, CG, $\beta\text{-Al}_2\text{O}_3$
		3½ hrs.	1325	NE, CG, $\beta\text{-Al}_2\text{O}_3$
		3½ hrs.	1319	NE, CG
		10 days	795	NE, CG

\* CG = Carnegite SS

NE = Nepheline SS

1:2 cpd. =  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ 

cor. = corundum

† Here is seen effect of  $\text{Na}_2\text{O}$  volatilization. A longer run shows  $\beta\text{-Al}_2\text{O}_3$  in place of CG. (Compare with run at 1394° for 30 minutes.)

TABLE 1—(continued)

Wt. per cent		Time	Temperature (° C.)	Final Condition*
$\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$				
65	35	30 min.	1410	All glass
		30 min.	1406	Glass, rare $\beta\text{-Al}_2\text{O}_3$
		30 min.	1374	Glass, $\beta\text{-Al}_2\text{O}_3$
		30 min.	1370	Glass, $\beta\text{-Al}_2\text{O}_3$ , rare CG
60	40	30 min.	1423	All glass
		30 min.	1419	Glass, rare $\beta\text{-Al}_2\text{O}_3$
		30 min.	1356	Glass, $\beta\text{-Al}_2\text{O}_3$
		30 min.	1352	Glass, $\beta\text{-Al}_2\text{O}_3$ , rare CG
		30 min.	1348	Glass, $\beta\text{-Al}_2\text{O}_3$ , sparse CG, rare 1:2 cpd
		45 min.	1340	NE, CG, sparse glass, $\beta\text{-Al}_2\text{O}_3$
		3 hrs.	1336	NE, CG, $\beta\text{-Al}_2\text{O}_3$
		4 hrs.	1315	NE, CG, rare $\beta\text{-Al}_2\text{O}_3$
		3 hrs.	1305	NE, CG
		10 days	795	NE, rather sparse CG
50	50	30 min.	1457	All glass
		30 min.	1453	Glass, rare 1:2 cpd.
		30 min.	1437	Glass, 1:2 cpd.
		30 min.	1433	Glass, 1:2 cpd, very rare cor.
		45 min.	1356	1:2 cpd, glass, rather rare cor.
		45 min.	1352	1:2 cpd, glass, rare CG, rather rare cor.
		3½ hrs.	1348	1:2 cpd, glass, rare CG, rare cor.
		2½ hrs.	1344	1:2 cpd, NE, CG, glass
		3½ hrs.	1335	NE, CG, sparse 1:2 cpd, rare glass
		3½ hrs.	1331	NE, CG, very rare 1:2 cpd., very rare $\beta\text{-Al}_2\text{O}_3$
		24 hrs.	1322	NE, sparse CG, sparse 1:2 cpd., rare $\beta\text{-Al}_2\text{O}_3$
		3 hrs.	1310	NE, sparse CG, sparse 1:2 cpd. (?)
		5 days	795	Glass, CG, NE
25 days	795	NE, sparse CG		
40	60	30 min.	1507	All glass
		30 min.	1503	Glass, sparse 1:2 cpd.
		30 min.	1462	1:2 cpd., glass
		30 min.	1458	1:2 cpd., glass, rare cor.
		45 min.	1370	1:2 cpd., glass, cor.
		45 min.	1366	1:2 cpd., glass, cor., rare CG
		1½ hrs.	1352	1:2 cpd., glass, sparse CG, cor. (?)
		1½ hrs.	1347	1:2 cpd., glass, CG, NE
		3½ hrs.	1334	NE, 1:2 cpd., CG, rare glass
3½ hrs.	1330	NE, 1:2 cpd., CG (rare cor. ?)		

TABLE 1—(continued)

Wt. per cent		Time	Temperature (° C.)	Final Condition*
NaAlSiO <sub>4</sub> -CaO·Al <sub>2</sub> O <sub>3</sub>				
40	60	24 hrs.	1322	NE, rather sparse 1:2 cpd., sparse CG (rare $\beta$ -Al <sub>2</sub> O <sub>3</sub> ?)
		3½ hrs.	1310	NE, sparse CG, small high index inclusions (1:2 cpd. ?)
		5 days	795	Glass, sparse CG
		25 days	795	NE, CG, sparse glass
		46 days	795-900	NE, moderate CG
20	80	1½ hrs.	1444	1:2 cpd., glass
		1½ hrs.	1440	1:2 cpd., glass, cor.
		2½ hrs.	1387	1:2 cpd., cor., rare CG, rare glass

melts at 1526° C., is isometric up to its melting point, but inverts to a triclinic form below 690° C. A second inversion, accompanied by a marked change in birefringence, occurs at 226.5° C. The indices of refraction of the low-temperature form are  $\alpha = 1.514$ ,  $\beta = 1.514$ ,  $\gamma = 1.509$ . Carnegieite typically occurs in globular masses showing no external crystal form, but with intricate twinning that forms as a result of inversion.

The carnegieite obtained in the present study is considerably altered by solid solution. Refractive indices as high as 1.535 were observed, and in mixes containing approximately 20 per cent or more CaO·Al<sub>2</sub>O<sub>3</sub>, the high temperature isometric form becomes stabilized so that the low temperature inversions to the triclinic form do not take place during cooling. The carnegieite in these mixes appears under the microscope as a completely isotropic material, and if not characteristically globular, can be distinguished from glass that may be present only by difference in refractive index or by x-ray diffraction pattern. Smalley (1947) notes that carnegieite in the system NaAlSiO<sub>4</sub>-Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> shows increasing refractive index and decreasing birefringence with added Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>. He also states that glass (liquid) persists down to the lowest temperatures of observation throughout the system. It is probable that stabilized isometric carnegieite also was formed in the system studied by Smalley, and mistaken for glass.

Pure synthetic nepheline inverts to carnegieite at a temperature of  $1254 \pm 5^\circ$  C. (Greig and Barth, p. 108). Nepheline may take up to 35 per cent anorthite in solid solution, with a resulting rise in the inversion temperature of 100° C. (Bowen, 1912, p. 571). Albite also forms a solid solution with nepheline, raising the inversion temperature 30° at its

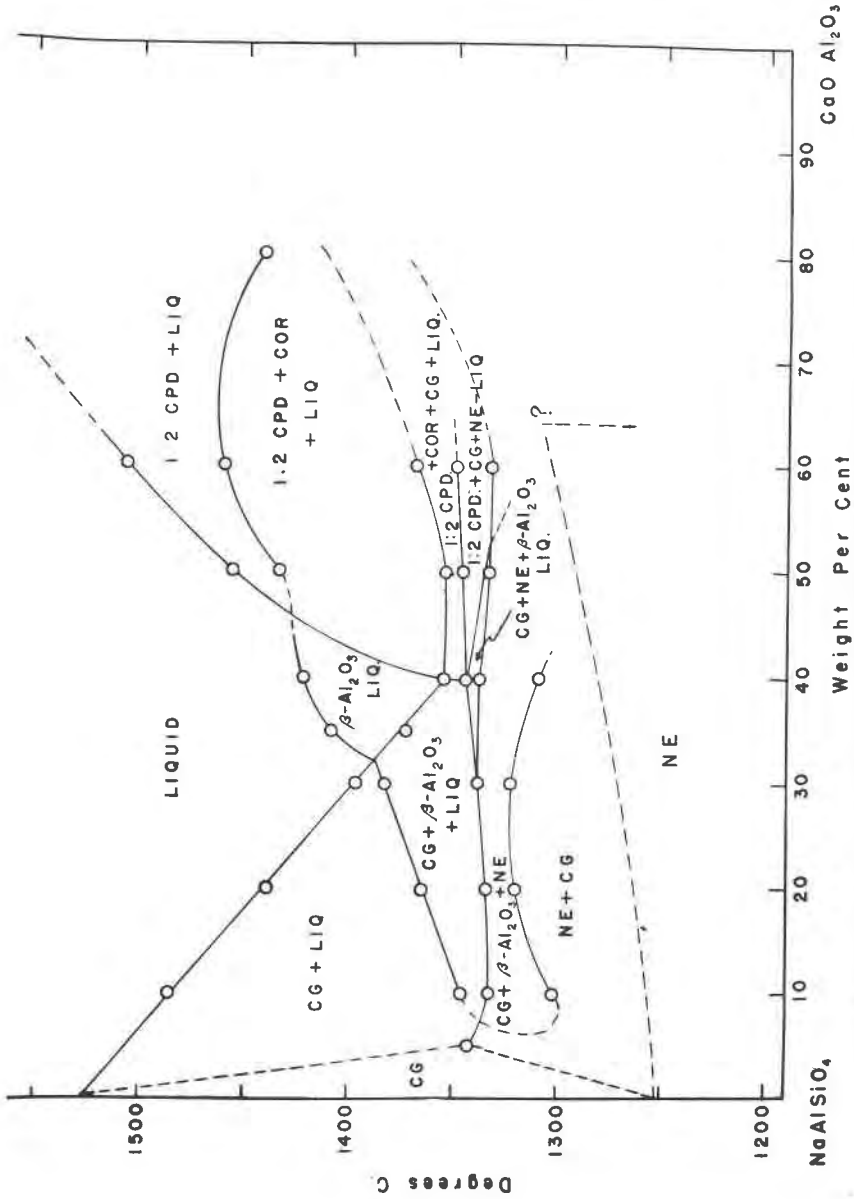


Fig. 2. Equilibrium diagram for the system  $\text{NaAlSi}_3\text{O}_8\text{-CaO}\cdot\text{Al}_2\text{O}_3$ . NE and CG are solid solutions.

maximum concentration (Greig and Barth, p. 109). Smalley, in the system  $\text{NaAlSiO}_4\text{-Ca}_2\text{Al}_2\text{SiO}_7$ , found an inversion range extending from about  $50^\circ$  above, to  $100^\circ$  below the normal inversion point. The likelihood of the metastable existence of carnegieite below its stable inversion range will be later considered in more detail; it is possible that this could account for the apparently large interval observed by Smalley. The upper limit of the carnegieite-nepheline inversion observed in the present study varies between approximately  $1330^\circ\text{-}1350^\circ\text{ C.}$ , a maximum increase of  $100^\circ\text{ C.}$  over that in pure  $\text{NaAlSiO}_4$ .

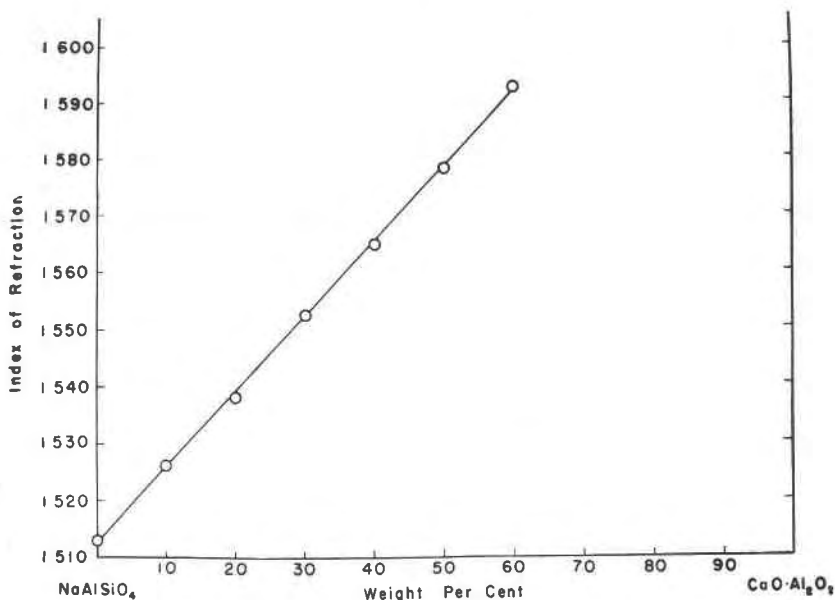


FIG. 3. Refractive indices of the glasses in the system  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$ .

The indices of pure synthetic nepheline (Hexagonal  $\text{NaAlSiO}_4$ ), determined by Bowen (1912, p. 566), are  $\epsilon = 1.533$  and  $\omega = 1.537$ . He found that the indices of the limiting solid solution with anorthite are  $\epsilon = 1.539$ ,  $\omega = 1.537$ . Solid solution of albite in nepheline lowers the indices (Foster, p. 157). Unusually high indices were noted by Smalley in nephelines crystallizing from the system  $\text{NaAlSiO}_4\text{-Ca}_2\text{Al}_2\text{SiO}_7$ , and by the writer (1947) in the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-Ca}_2\text{Al}_2\text{SiO}_7\text{-NaAlSiO}_4$ . Smalley found values as high as 1.552 in crystals from melts of 35 per cent gehlenite. The present study, which is primarily an outgrowth of these results, has produced nepheline solid solutions with indices above 1.590. The optic



sign changes from negative to positive, passing through a range of optically isotropic crystals. It is very likely that the material in solid solution producing these extremely high values of refractive index is the same as that responsible for the high values observed in the two works last mentioned.

Nepheline crystallizes from melts in well formed prismatic crystals with basal pinacoid. In the present study, however, nepheline solid solutions do not occur at liquidus temperatures, but as the secondary or tertiary phase. When crystallized under these conditions, or below the solidus curve, euhedral crystals would not be expected to form. Thus the nepheline solid solutions here produced appear as xenomorphic crystals, often containing the other phases that may be present as inclusions.

#### $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$

The 1:2 compound of lime and alumina has been for the most part improperly identified as  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$  in this country since its description in 1909 (Shepherd, Rankin, and Wright, 1909). A note by the present author (Goldsmith, 1948) discusses this improper formulation and summarizes the data on hand for  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ . The 1:2 compound is monoclinic (Lagerqvist, Wallmark, and Westgren, 1937), although optically uniaxial or very nearly so. Wright noted the uniaxial character and determined the indices as  $\epsilon=1.651$  and  $\omega=1.617$  in the original (1909 description).  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  melts incongruently at a temperature of about  $1765^\circ\text{C}$ . (Tavasci, 1937).

In the present study  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  forms as well defined lath-shaped crystals, terminated with asymmetrical dome-like faces. Occasionally small crystals are blocky. The maximum extinction angle is highly inclined to the elongation, although the interference figures obtained are either uniaxial or biaxial with a very small value of  $2V$ . The refractive indices appear to be the same as those described by Wright indicating little if any solid solution. The 1:2 compound was identified with certainty on the basis of its  $x$ -ray diffraction pattern as well as by optical means.

The end-member compound of the system  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ , does not form in any of the mixtures studied, i.e., up to 80 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  by weight. It was, however, prepared in pure form by sintering of carefully mixed  $\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$ , and the optical properties and  $x$ -ray pattern were checked against published data. Wright (1909) lists  $\alpha=1.641$ ,  $\beta=1.654$ , and  $\gamma=1.661$  but could not determine whether the compound was monoclinic or triclinic. The melting point is given as  $1600\pm 5^\circ\text{C}$ . by Brownmiller and Bogue (1932, p. 505).

### $\beta$ - $Al_2O_3$

$\beta$ - $Al_2O_3$  is here encountered as both a primary and secondary phase, occurring as thin hexagonal plates exhibiting high birefringence and parallel extinction when viewed on edge.  $\beta$ - $Al_2O_3$  is optically negative, as indicated by the positive elongation of the platy crystals. The relation between  $\beta$ - $Al_2O_3$  and corundum and the effects of soda volatilization on the abundance of  $\beta$ - $Al_2O_3$  will be more fully discussed in a later section.

### Corundum ( $Al_2O_3$ )

Synthetic corundum forms as rather small blocky crystals, for the most part somewhat elongated in the direction of the  $c$  axis. Some of the crystals, particularly when quite small, have rounded corners. The tendency toward elongation generally gives a negative sign of elongation, as corundum is optically negative. The refractive indices could not be determined on the crystals here encountered embedded in glass, but Wright (1909, p. 321) gives values of  $\omega = 1.768$  and  $\epsilon = 1.760$  on synthetic crystals. Corundum is most easily identified in this system by its low birefringence, parallel extinction, and sign of elongation, although when occurring along with large amounts of  $CaO \cdot 2Al_2O_3$  its presence may be difficult to detect.

## III. COMPLEXITY OF THE SYSTEM

If the system  $NaAlSiO_4$ - $CaO \cdot Al_2O_3$  were binary, no more than three phases could coexist under equilibrium conditions, and as many as three phases only under invariant conditions at a point on the equilibrium diagram. The condensed phase rule,  $P + F = C + 1$ , as applied to systems in which the vapor phase is negligible, expresses this relationship. Inspection of the equilibrium diagram, Fig. 2, shows that three phases coexist in several fields, and in two fields there are four phases present. At one point five phases coexist, the maximum number that can be present at an invariant point in a four component system. The composition of three of the crystalline phases,  $CaO \cdot 2Al_2O_3$ ,  $\beta$ - $Al_2O_3$ , and corundum cannot be expressed in terms of the end members; in a truly binary system all phases can be so expressed. The number of phases that coexist, as well as the fact that the composition of the phase assemblages can be expressed only in terms of the four constituent oxides, make it apparent that the system is quaternary.

Complexity may be introduced in a system by virtue of the formation of mix crystals whose composition cannot be expressed in terms of the composition of the end members of the system. Behavior of this sort has been previously discussed by the author (1947). In the system under consideration, however, complex solid solutions are not primarily re-

possible for its non-binary nature, rather the intrusion of the phases  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ ,  $\beta\text{-Al}_2\text{O}_3$  and corundum introduce the complexity. This is a consequence of the stability fields of these substances, within the quaternary tetrahedron, intersecting the join  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$ . A four component system must be represented by a three dimensional figure; it should be emphasized that the equilibrium diagram (Fig. 2) cannot be interpreted as a binary diagram would be. Particularly above solidus temperatures, the compositions and the proportions of phases cannot be precisely determined from the diagram, and the curves do not represent lines of univariant equilibrium.

Relations in the system become less complex as a result of the inversion of carnegieite to nepheline, and will shortly be considered in more detail. Indeed, binary relations are developed at lower temperatures (below the carnegieite to nepheline inversion range) over a considerable portion of the system as a result of the rather large amounts of calcium aluminate taken in solid solution by nepheline.

#### IV. RELATIONS ABOVE THE SOLIDUS, AND THE EFFECT OF SODA VOLATILIZATION

The carnegieite liquidus curve falls as a straight line from the melting temperature of pure carnegieite ( $1526^\circ\text{C.}$ ) to a point at approximately 32 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  where it is intercepted by the intruded field of  $\beta\text{-Al}_2\text{O}_3$ . From approximately 32 per cent to 46 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ,  $\beta\text{-Al}_2\text{O}_3$  becomes the primary phase, the liquidus curve showing a general convex upward configuration. The  $\beta\text{-Al}_2\text{O}_3$  curve is in turn intercepted by that of  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , which becomes the primary phase from 46 per cent to at least 80 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ , beyond which composition no preparations were made. The liquidus temperature of the mixture of 80 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ , 20 per cent  $\text{NaAlSiO}_4$  was not determined, because of the refractory nature of this mixture. The primary phase, however, was the 1:2 compound. Although the compound  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  was not encountered, a stability field at liquidus temperatures exists, but is not shown on Fig. 2. Examination of the phase diagram for the system  $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$  (Sosman and Anderson, 1942) gives an indication of the approximate location of this boundary. The compound  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  is quite near the boundary curve between the fields of  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  and  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , improperly identified as  $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$  on the above diagram, and the supposition that the field of the 1:1 compound is cut off by the field of the 1:2 compound a very short distance within the quaternary system is very likely. Thus the field of  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  would extend on Fig. 2 but a few per cent into the diagram.

$\beta\text{-Al}_2\text{O}_3$  exists as the secondary phase except over the short range where

it becomes the primary phase. At approximately 50 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , or where the 1:2 compound becomes the primary phase,  $\beta\text{-Al}_2\text{O}_3$  disappears however, and corundum takes its place, continuing as the secondary phase to the limit of composition studied.  $\beta\text{-Al}_2\text{O}_3$ , never really quantitatively abundant, also appears to fade out between 5 and 10 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . A maximum and minimum limit to its field can be detected in the mixture of 10 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , but no  $\beta\text{-Al}_2\text{O}_3$  was found in the mixture of 5 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The lower limit of the field of  $\beta\text{-Al}_2\text{O}_3$  falls below the solidus, and is rather well defined between 10 and 40 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , but cannot be traced beyond the 40 per cent mixture. In the 50 per cent and greater mixtures, below solidus temperatures, very rare  $\beta\text{-Al}_2\text{O}_3$  or corundum may occur, but no definite lower limit to the field can be fixed.

The upper limit of the stability field of carnegieite continues on under the primary phase field of  $\beta\text{-Al}_2\text{O}_3$ , where carnegieite becomes the secondary phase. Beyond 40 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , carnegieite becomes the tertiary phase; the upper temperature limit of the field of carnegieite slowly rises, and carnegieite is still evident in the mixture of 80 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ —20 per cent  $\text{NaAlSiO}_4$ .

The upper boundary of the carnegieite-nepheline inversion range shows a rather small temperature variation throughout the greater portion of the system. From the inversion point of pure nepheline and carnegieite at  $1254^\circ \text{C}$ ., the boundary rises sharply to  $1342^\circ \text{C}$ . at the composition 95 per cent  $\text{NaAlSiO}_4$ —5 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The upper limit of inversion then decreases slightly to a value of approximately  $1332^\circ \text{C}$ . between 10 and 20 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , beyond which it rises slowly, attaining a value of  $1350^\circ \text{C}$ . at 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . Nepheline does not occur as a primary phase; it is formed at or near solidus temperatures. The lower boundary of the inversion range was not determined, because of the metastable persistence of carnegieite at low temperatures. There is some evidence however, that the carnegieite that forms in the mixture of 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  is practically all transformed to nepheline at a temperature in the neighborhood of  $1300^\circ \text{C}$ . A sub-solidus curve delimiting the lower portion of this field has thus been indicated with dashed lines on Fig. 2.

The temperature of complete crystallization, represented by the solidus curve, drops sharply from the melting point of pure carnegieite at  $1526^\circ \text{C}$ ., to  $1342^\circ \text{C}$ . at 5 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . It then continues, coincidentally with the nepheline carnegieite inversion curve, to 30 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  at which point the inversion curve rises above it. The solidus curve was not followed beyond 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , where the temperature of complete solidification is  $1332^\circ \text{C}$ . It is to be noted that over

most of the range studied the temperature of complete crystallization varies but a few degrees. Indications are, however, that beyond the 60 per cent value the curve rises fairly rapidly.

### *Soda Volatilization*

The loss of soda by volatilization in preparations here considered merits some discussion. In melting the glass batches used for the equilibrium studies an appreciable weight loss was observed. This loss did not diminish with decreasing  $\text{Na}_2\text{O}$  content, i.e., as  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  was increased in the system, as might be expected if the loss were due solely to straightforward vaporization of soda. No attempt was made to evaluate quantitatively soda loss as a function of composition, but it appears that addition of the  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  tends to drive  $\text{Na}_2\text{O}$  from the batch. This effect is worthy of separate study; it is apparent that either alumina or lime tends to increase the rate of soda loss. The fact that the silica content of the mixtures is diminished concurrently with these additions may be important. The tendency for alumina to drive off soda has not been noted in the many studies dealing with these oxides, but there is evidence that lime may act in this manner. Madorsky (1931), in studying the possibility of obtaining potash from leucite-bearing rocks, shows that additions of  $\text{CaCO}_3$  to wyomingite with subsequent heating above  $1100^\circ\text{C}$ . increases the loss of potash by vaporization. The same effect, involving large losses of  $\text{K}_2\text{O}$  from wyomingite, is reported by Hignett and Royster (1931), who used both  $\text{CaCO}_3$  and  $\text{CaO}$  in a small blast furnace. This effect was greatly amplified if in addition to the lime a halogen salt such as  $\text{CaCl}_2$  were added so that the more volatile  $\text{KCl}$  was driven off; the chloride volatilization, however, is not to be considered here. Although potash is more volatile than soda there is little doubt that the two alkalis would behave qualitatively in similar fashion. The present investigation also seems to indicate that  $\text{CaO}$  tends to drive alkalis from alkali-silicate mixtures. In a discussion of this question, N. L. Bowen\* has stated that some of his investigations, particularly involving mixtures of a sodium aluminate and a calcium silicate, have led him to suspect that this phenomenon takes place.

This action is observed to take place in the fused mass (liquid state) as well as during reaction of the original batch before melting is complete, and may be the result of bond weakening in the glass with increased basicity. Loss of soda can be corrected for in preparing the original batches, but no corrections can be made during the equilibrium run itself. Runs of as short a time as possible that would insure equilibrium were

\* Personal communication.

made, although this precaution was not found necessary at temperatures somewhat below the solidus.

The effect of soda loss during an equilibrium run is rather marked in certain parts of the system. In the region 30–40 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , where  $\beta\text{-Al}_2\text{O}_3$  and carnegieite are the primary and secondary phases, relations are strongly affected by the length of time the charge is held at near-liquidus temperatures. At the composition 70 per cent  $\text{NaAlSiO}_4$ —30 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , carnegieite is the primary phase, appearing at  $1396^\circ \text{C}$ . in runs of 30 minutes' duration. Under these conditions,  $\beta\text{-Al}_2\text{O}_3$  appears as the secondary phase, at  $1382^\circ \text{C}$ . If, however, the charge is held for three hours,  $\beta\text{-Al}_2\text{O}_3$  crystals, and *no* carnegieite, are found, even though the temperature be dropped  $10^\circ \text{C}$ ., to  $1386^\circ \text{C}$ . A run made at  $1420^\circ \text{C}$ . for  $3\frac{1}{2}$  hours showed only liquid to be present in the envelope containing the charge, except where present as thin films (in the edges of the platinum containing envelope); the thin portions of the quenched glass contained abundant  $\beta\text{-Al}_2\text{O}_3$ . Thus  $\beta\text{-Al}_2\text{O}_3$  persists even at temperatures considerably above the liquidus, if a rather large surface is present as in the films of glass, to make soda volatilization more effective. In the mixture of 35 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , abundant  $\beta\text{-Al}_2\text{O}_3$  is present in runs over three hours at  $1425^\circ \text{C}$ .; the  $\beta\text{-Al}_2\text{O}_3$  liquidus on a 30 minute basis is  $1408^\circ \text{C}$ . at this point. In the 40 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  mixture, the 30 minute phase assemblage at  $1348^\circ \text{C}$ . is glass,  $\beta\text{-Al}_2\text{O}_3$ , very sparse carnegieite, and very rare  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ . This same charge, when held three hours, is found to have crystallized rather large amounts of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  and in addition is rather frothy, indicating loss of a volatile ingredient.  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  appears at a temperature of  $1350^\circ \text{C}$ . in 30 minute runs at this composition, but if the temperature is raised to  $1360^\circ$  and held for two hours,  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  is present along with  $\beta\text{-Al}_2\text{O}_3$ .

These data make it evident that the quantity and even the presence of the non-sodic or soda-poor phases such as the 1:2 compound and  $\beta\text{-Al}_2\text{O}_3$  are influenced by volatilization of soda; loss of soda induces the crystallization of these phases. Conversely, replacement of carnegieite by  $\beta\text{-Al}_2\text{O}_3$  at temperatures below the carnegieite liquidus, as seen in the 30 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  mixture, indicates suppression of the sodic phase by volatilization. The liquidus curve for  $\beta\text{-Al}_2\text{O}_3$  as drawn on Fig. 2 is an arbitrary curve based on mixtures run for 30 minutes. Longer runs would fix the liquidus at a considerably higher level, and indeed, it is likely that as now located it is somewhat above what it would be if determinations were made in a closed system.

The problem of attaining equilibrium and maintaining composition is a difficult one when volatilization losses become significant. Removal of soda makes the already existing non-binary system even more complex.

In a quaternary (condensed) system five phases can coexist at equilibrium only at a point of fixed composition and temperature. In the narrow four-phase field of  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , carnegieite, nepheline, and glass (the wedge-shaped field just above the solidus beyond 40 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ ), several runs of approximately three hours show five phases—the above four plus very rare  $\beta\text{-Al}_2\text{O}_3$ . In the other small four-phase field of nepheline, carnegieite,  $\beta\text{-Al}_2\text{O}_3$ , and glass (adjacent and to the left of the above field on Fig. 2), a similar effect is noted. At the composition 50 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  and a temperature of  $1340^\circ\text{C}$ ., the four-phase assemblage is found in runs of 30 minutes. Runs of three hours or more show crystals of  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  as well—a fifth phase. The coexistence of five phases over a range of temperature is indicative of failure of equilibrium. Continuous loss of soda and the resulting continuous composition change with time makes impossible the establishment of equilibrium, and volatilization is undoubtedly the explanation for this effect. A true five-phase point does exist, at  $1344^\circ\text{C}$ . and at a composition of approximately  $39\frac{1}{2}$  per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ . A second five phase point is inferred at approximately 50–52 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ , and at a temperature of approximately  $1334^\circ\text{C}$ . It should be stated, however, that the true relations in this portion of the diagram are made somewhat uncertain by reason of the above discussed complications due to loss of soda.

The presence or absence of  $\beta\text{-Al}_2\text{O}_3$  as a function of soda volatilization is important in the above considerations. One cannot always decide whether its absence may not be due to insufficient time to establish equilibrium, or its presence due to an excessively long run resulting in significant soda loss. The earlier mentioned uncertainty as to the lower limits of the field of  $\beta\text{-Al}_2\text{O}_3$  may possibly be explained on this basis.

#### V. SUB-SOLIDUS RELATIONS

In the runs made at temperatures below the carnegieite-nepheline inversion, carnegieite was always found, in all of the compositions studied. The scarcity of carnegieite in certain runs was the basis for the roughly sketched curve on Fig. 2 delimiting its lower limit of existence, but accurate determinations were not made as the inversion to nepheline was never observed to be complete. As the temperature of devitrification of the glasses was lowered, more carnegieite was obvious, it being apparent that carnegieite was forming at temperatures well below its field of stability.

Extended runs at relatively low temperatures showed rather conclusively that even in the stability field of nepheline, carnegieite is the *first* phase to crystallize from the glass. For example, crushed glass of the composition 40 per cent  $\text{NaAlSiO}_4$ —60 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  held five days

at 795° C. showed small amounts of carnegieite "eating" into the glass. Re-examination after an additional 10 days showed some glass with carnegieite "replacing" it, but the bulk of the product was now nepheline solid solution. In the mixture of 50 per cent  $\text{NaAlSiO}_4$ —50 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , the crushed glass when held five days at 795° C. appeared under the microscope as illustrated in Fig. 4.

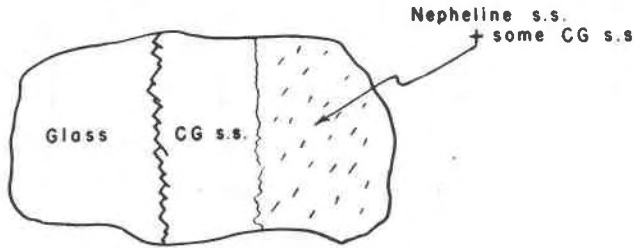


FIG. 4. Fragment, initially all glass. Note "shark-teeth" like aspect of carnegieite (crystal faces) at the glass-carnegieite contact.

Re-examination after an additional 10 days shows that the entire fragment has been devitrified, consisting of nepheline and a small amount (perhaps 10 per cent) of carnegieite. To determine the possible effect of lime and alumina on this metastable crystallization, glass of the composition of the pure end-member ( $\text{NaAlSiO}_4$ ) was devitrified. Holding pure  $\text{NaAlSiO}_4$  glass at 795° C. for five days produced virtually pure carnegieite; after 15 days no more than a trace of nepheline could be detected. The inversion temperature of the pure compound is 1254° C., yet it is here obvious that carnegieite forms initially far below its stable inversion point. The additions of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  in the system are not responsible for this effect, but rather tend to accelerate the inversion once the carnegieite has crystallized.

Bowen (1912, p. 560) noted that at a few degrees below the stable inversion glass crystallizes as both nepheline and carnegieite. He stated that "It seems possible that the unstable glass in assuming the stable form nephelinite passes through the 'less unstable' form carnegieite which may persist for a considerable time and is therefore found in the quenched products." Bowen, however, did not observe the formation of carnegieite at temperatures well below the inversion point. An analogous behavior is well known in the case of  $\text{SiO}_2$  where it is found that cristobalite, the high temperature form of silica (stable only above 1470° C.), is the first phase to crystallize from silica glass throughout the whole devitrification range and tends to persist metastably for long periods of time.

Bowen's explanation for the carnegieite formed below its inversion



point is quite reasonable, particularly in view of the lack of knowledge in 1912 on the structure of glasses and crystals. A plausible explanation of this phenomenon from another point of view exists when one considers that the glass represents the most disordered state of the silicate material. The high temperature crystalline phase is most closely akin to the glassy state; in silica glass the random  $\text{SiO}_4$  network requires but slight re-arrangement or ordering to form cristobalite. The high temperature form might thus be expected to be the one most readily crystallized, even well below its stability range, especially in materials in which ionic movement and re-arrangement is inhibited because of high viscosity. Carnegieite has the same atomic arrangement as cristobalite; glasses from which carnegieite form as the primary phase, therefore, very likely have a random structure very similar to that of carnegieite. At higher temperatures, just below the carnegieite-nepheline inversion temperature, the decreased viscosity of the glass and resulting ease of ionic movement allows nepheline to form directly, but it is not improbable that the high temperature form crystallizes first and then rapidly inverts to the low temperature modification.

The fact that carnegieite tends to persist as well as to form metastably has already been noted. Carnegieite formed in mixes containing appreciable amounts of  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  inverts to nepheline more rapidly than does pure  $\text{NaAlSiO}_4$ , but even in the mixture of 50 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  carnegieite is intermixed with the nepheline solid solution after 25 days at  $795^\circ\text{C}$ . Beyond 50 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  the inversion is again slowed, as in the 60 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  mix a very significant amount of carnegieite was found in runs of 35 days at  $795^\circ\text{-}900^\circ\text{C}$ . Equilibrium is of course not established in these runs—to do so would require an unduly long period of time. The reconstructive transformation is very slow, especially at low temperatures and in the absence of a liquid phase.

#### *The Carnegieite and Nepheline Solid Solutions*

CARNEGIEITE.— $\text{CaO}\cdot\text{Al}_2\text{O}_3$  enters the structure of carnegieite to the extent of 5 per cent by weight. The carnegieite of this composition has a maximum refractive index of 1.521, and a birefringence somewhat less than that of the pure  $\text{NaAlSiO}_4$ . The inversion to a triclinic form takes place in carnegieite of this composition, and the resulting polysynthetic twinning is present. As the  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  content of the system is increased, however, a continued, although rather small, increase in refractive index is observable, and inversion to the triclinic form does not take place in the carnegieite that crystallizes from mixes with more than approximately 20 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ . The continued rise in index and the stabilization of the isometric lattice indicate that more solid solution in

carnegieite takes place than the 5 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  indicated by the thermal evidence. This additional solid solution cannot, however, be binary in nature. Either lime, alumina, or some combination of the two in proportions other than the 1:1 ratio enter the carnegieite structure. The exact nature of the non-binary solid solution cannot be determined from the data of the present system.

Stabilized isometric carnegieite has also been observed to form in portions of the system  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , by J. F. Schairer.\* Schairer and Bowen (1947, p. 197) have described solid solutions of carnegieite with  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ ; it is possible that this solid solution might also be forming in the present system.

The  $x$ -ray powder pictures of the carnegieite solid solutions are sufficiently different from the pattern of pure carnegieite ( $\text{NaAlSiO}_4$ ) that even the 5 per cent solid solution with  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  shows up markedly. The most obvious difference in the two patterns is the development of four lines of rather high  $d$  value in the solid solution. No attempt will be made here to present or interpret  $x$ -ray data—this will be done in a future note on carnegieite and nepheline.

NEPHELINE.—The exact limit of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  solid solution in nepheline was not determined, because of the previously mentioned difficulty of obtaining crystals free of carnegieite. Mixtures up to and including 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  were crystallized with but two phases, however, nepheline and carnegieite. It can thus be concluded that nepheline takes at least 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  in solid solution. It is probable that considerably less than 80 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  enters the nepheline structure, as evidenced from runs on the mixture of this composition. No definite statement can be made on this point, however, as the original preparation of 80 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  contained crystals of the 1:2 compound; a homogeneous glass could not be obtained with which to carry out crystallizations at the temperatures of the nepheline field.

The mixture of 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  when crystallized at  $800^\circ \text{C}$ . shows no trace of any calcium-aluminate phase, only nepheline solid solution and carnegieite being evident.  $X$ -ray as well as optical determinations were made. If, however, some calcium aluminate were present, it would not necessarily mean that the solid solution limit had been passed, as long as some carnegieite was intermixed. The reason for this is that the carnegieite takes but a small amount of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  in solid solution, whereas nepheline takes very much more. The carnegieite, which under equilibrium conditions would exist as nepheline, thus represents "potential" nepheline, capable of taking up additional  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

Solid solution of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  in nepheline produces a steady rise in

\* Unpublished data by J. F. Schairer and N. L. Bowen.

index of refraction. Values of as high as  $\epsilon = 1.600$  and  $\omega = 1.593$  are reached in the nepheline crystals from the 60 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  mix. The optic sign changes from negative in pure nepheline, to positive, passing through a zone of optically isotropic crystals at approximately 20 per cent  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ . Beyond this isotropic composition, the birefringence slowly increases up to the limiting composition studied. Figure 5 is a refractive index-composition diagram for the nepheline solid solution. As in the carnegieite, the solid solution can be readily detected by  $x$ -ray diffraction. The most obvious changes with solid solution observed in the

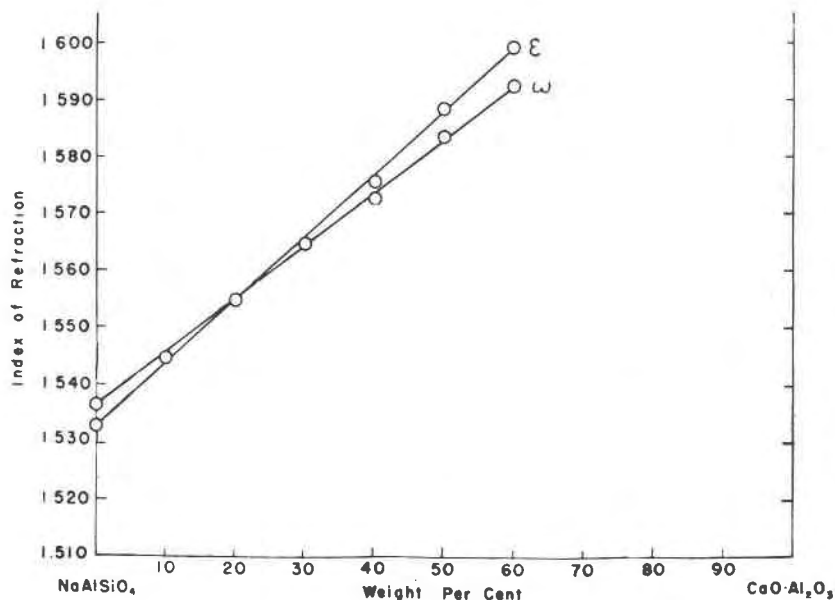


FIG. 5. Refractive indices of the nepheline solid solutions in the system  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$ .

powder pattern are the development of a 100 line not present in pure  $\text{NaAlSiO}_4$ , a great intensity increase in the 110 line, and the disappearance in the solid solution of the 200 reflection.

As earlier mentioned, the system becomes simplified below the carnegieite-nepheline inversion range because of the  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  taken up by the nepheline: binary relations exist at least up to the limit of solid solution. Thus although the general  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$  relations are quite complex, the *nepheline*- $\text{CaO}\cdot\text{Al}_2\text{O}_3$  relations are comparatively uncomplicated. The higher temperature complexities begin to simplify as soon as nepheline begins to form in the system; as it crystallizes it takes up lime

and alumina that in the presence of carnegieite would form independent phases. The binary solid solution of nepheline and  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  produces a single-phase field of nepheline solid solutions up to at least 60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

In mixtures of 50–60 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , and at temperatures below the solidus and above the field of nepheline solid solutions, the phases nepheline, carnegieite, and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  are found to coexist. If lime and alumina were taken in both carnegieite and nepheline in the 1:1 ratio, the 1:2 compound could not form; the calcium aluminate phase would of necessity be the 1:1 compound. The fact that the 1:2 compound is formed indicates that in this field either the carnegieite, the nepheline, or both form non-binary solid solutions. The tendency is seen throughout the system for alumina-rich phases to precipitate (corundum,  $\beta\text{-Al}_2\text{O}_3$ , and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  rather than  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), and if any of these phases persist, in the absence of liquid, with nepheline and carnegieite, it is obvious that lime in excess of the 1:1 lime-alumina ratio is in the structure of the nepheline and/or the carnegieite. It has been seen that the carnegieite solid solution is non-binary, so that it is probable that the tendency to form  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  is an indication that excess CaO is present in the carnegieite of this portion of the system. The possibility that the nepheline in this field also contains excess CaO cannot be precluded, however.

#### VI. THE $\beta\text{-Al}_2\text{O}_3$ -CORUNDUM RELATIONS

The field of  $\beta\text{-Al}_2\text{O}_3$  is known to extend well toward the silica rich corner of the  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  tetrahedron. The work of Gummer (1943, p. 506) has shown that a portion of the anorthite-wollastonite-nepheline plane is penetrated by the field of  $\beta\text{-Al}_2\text{O}_3$ ; the position of this plane can be seen in Fig. 1. The problem of the composition of  $\beta\text{-Al}_2\text{O}_3$  has been earlier discussed by the present writer (Goldsmith, 1947, p. 384), it being suggested that  $\beta\text{-Al}_2\text{O}_3$  might be a "stuffed lattice," in which Na atoms assume random interstitial positions in an  $\text{Al}_2\text{O}_3$  network. This explanation was used to account for the disagreements of different investigations on the soda content, as no fixed soda-alumina ratio is required in a structure of the proposed type. Schairer and Bowen (1947, p. 198) have indicated that  $\beta\text{-Al}_2\text{O}_3$  is metastable with respect to corundum; it is converted to corundum on long heating. The above view of the  $\beta\text{-Al}_2\text{O}_3$  structure was also considered consistent with this conversion to corundum, as the interstitial Na atoms, given sufficient time, might be squeezed out of the structure.

The present investigation tends to strengthen this picture of  $\beta\text{-Al}_2\text{O}_3$ . Between 40 and 50 per cent  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  the field of  $\beta\text{-Al}_2\text{O}_3$  changes over

to a field of corundum. It is thus likely that the change from a field of  $\beta\text{-Al}_2\text{O}_3$  to one of corundum takes place throughout the  $\text{Al}_2\text{O}_3$  rich corner of the tetrahedron, i.e., that the three dimensional corundum field is continuous with that of  $\beta\text{-Al}_2\text{O}_3$ . This is equivalent to saying that when sufficient soda (or in the general case, sufficient alkali) is present in the melt  $\beta\text{-Al}_2\text{O}_3$  crystallizes, and when less than the limiting value of alkali is present, corundum is formed. Inasmuch as some compositional change is involved, the  $\beta\text{-Al}_2\text{O}_3$ -corundum relation can hardly be called an inversion in the sense that temperature or pressure dependent inversions are defined. Although the results of Schairer and Bowen indicate that  $\beta\text{-Al}_2\text{O}_3$  is metastable, it might be a stable form under certain conditions, for example, where high alkali ion activity exists in the melt in equilibrium with the crystals.

## VII. PETROLOGIC CONSIDERATIONS

Several points of possible interest to the igneous petrologist are suggested by the present investigation, although it should be emphasized that the melts of the system here studied do not correspond in composition to any natural magmas.

Alkaline rocks of the phonolite-nepheline syenite type are frequently associated with limestone. If molten or magmatic material were injected into the limestone it might be expected that some contamination or reaction with the CaO of the limestone would result. Corundum is found in and associated with certain of the nepheline syenites. The tendency for formation of  $\beta\text{-Al}_2\text{O}_3$  (or corundum) as a result of soda volatilization when CaO is added to the system here studied, and the presence of corundum and associated lime rocks in nepheline syenite areas is suggestive of a related effect. The tendency of  $\beta\text{-Al}_2\text{O}_3$  to go over to corundum has already been mentioned—even though  $\beta\text{-Al}_2\text{O}_3$  may be first precipitated, corundum might be the end result. Soda “metasomatism” or enrichment of associated rocks in sodic minerals could also be a consequence of the freeing of soda by the above process. S. J. Shand has stated that he has often had reason to suspect that soda has been expelled at limestone contacts,\* and made this assumption in a paper dealing with the granite-syenite-limestone complex of Palabora. (Shand, 1931, pp. 99–101.) The phenomena above discussed, if operative, would be influenced by a “closed” vs. an “open” system, and the depth at which intrusion took place might be here important. In a fully closed system from which volatiles could not escape alumina formation would at least be inhibited, and no soda loss to the surroundings would take place. The usefulness of

\* Personal communication from S. J. Shand.

these observations as possible criteria for the determination of magmatic vs. replacement origin of these rocks cannot, however, be evaluated on the basis of the experimental system.

The large amounts of lime taken up by the nephelines that crystallize in the system  $\text{NaAlSiO}_4\text{-CaO}\cdot\text{Al}_2\text{O}_3$  might lead one to expect that such lime and alumina-rich nepheline might be found in rocks, especially those that crystallized from a magma that was associated with lime rich material. Most analyses of natural nephelines show an excess of  $\text{SiO}_2$ , whereas the nephelines of the present system are undersilicated. It must be remembered, however, that the present system is deficient in silica as compared to natural systems, and it is likely that in nature the silica content is always sufficient so that feldspar, rather than an aluminate, forms solid solutions with nepheline. Enrichment of a natural system in CaO by such a process as limestone contamination need not result in lime-enriched nepheline at any rate; feldspar or other lime containing minerals could well have a "buffer" effect, and take up considerable amounts of CaO before nepheline would do so. It should also be considered that the lowest temperature of the present investigation was approximately  $800^\circ\text{C}$ .; the stability of the nepheline-calcium aluminate solid solution at lower temperatures is not known. Nepheline bearing rocks for the most part have probably formed at temperatures below  $800^\circ\text{C}$ ., where the solid solution relations might be significantly different.

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