STUDIES ON CANCRINITES I—POLYMORPHISM IN SODIUM CARBONATE RICH CANCRINITE—NATRODAVYNE

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ABSTRACT

A cancrinite of composition $3NaAlSiO_4 . Na_2CO_3$ has been synthesized and its stability field in the presence of excess water determined. This cancrinite, which the authors term natrodavyne, appears to transform to a nosean type structure above 600° C. Crystallographic evidence indicates that this may be a reconstructive transformation. Evidence is also available that this transformation is present in certain cancrinites, but not in others. The chemistry, crystallography and limited field evidence of this transformation are discussed.

INTRODUCTION

The term cancrinite applies to a family of minerals of approximate composition $3NaAlSiO_4.R(CO_3,SO_4,Cl,OH) \pm H_2O$ where R = Na, Ca, K. The relationships between cancrinites and other feldspathoids are imperfectly understood. In addition the chemistry, and, as a result, the nomenclature of this family are not well established. Although Winchell & Winchell (1951) note that the composition of cancrinite is variable they suggest six compositions as end-members of the cancrinites. These compositions and corresponding names, with slight modifications, were used in the present study and are given in Table 1.

TABLE 1. COMPOSITIONS AND NAMES OF END MEMBERS OF CANCRINITE FAMILY

	Composition —after Winchell & Winchell (1951)	Compositions used in present study
Cancrinite proper	$3NaAlSiO_4 . Ca[CO_3,(OH)_2]$	$3NaAlSiO_4 . CaCO_3,(OH)_2$
Microsommite	$3NaAlSiO_4 . Ca(Cl,OH)_2$	—
Wischnewite	$3NaAlSiO_4 . (HNaSO_4,NaOH)$	—
Davyne	$3NaAlSiO_4 . (HKCO_3,KOH)$	$3NaAlSiO_4,K_2CO_3$ $3NaAlSiO_4,KHCO_3$
Natrodavyne	$3NaAlSiO_4 . (HNaCO_3,NaOH)$	$3NaAlSiO_4,Na_2CO_3$ $3NaAlSiO_4,NaHCO_3$
Sulphatic cancrinite	$3NaAlSiO_4,Ca[SO_4,(OH)_2]$	—

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The stability fields and cell parameters of each end-member have been determined in the temperature range 200° C. to 800° C. and at water pressures of 10,000 p.s.i. to 30,000 p.s.i. The present paper gives the results obtained on the sodium carbonate rich end-member, termed natrodavyne. This mineral undergoes a polymorphic transformation not exhibited by the other end-members investigated.

In 1910 Zambonini coined the term natrodavyne for a mineral from Vesuvius similar to davyne, but differing from davyne in containing no potassium and a high CO_2 content. Many other examples of cancrinites rich in sodium carbonate have been recorded and given a variety of names (*cf.* Rauff, 1878; Cesaro, 1917; Eitel, 1923; Zambonini & Ferrari, 1930).

Previous synthetic studies of sodium carbonate cancrinites have been at a fairly low temperature and the compositions used have not been strictly controlled. In 1949 Wyart & Michel-Levy reported synthesizing a cancrinite from mixtures of H_2O, Na_2O, Al_2O_3, SiO_2 and Na_2CO_3. This cancrinite, together with minor analcite, formed at temperatures of 368° C. to 420° C. and had parameters of $a = 12.65 \pm 0.02$Å and $c = 5.15 \pm .02$Å. If excess Na_2CO_3 was used, both cancrinite and sodalite were synthesized as well developed crystals, the former having $\omega = 1.492$ and $\epsilon = 1.489$, and a chemical composition corresponding to the formula $Na_{0.87}Al_{0.89}Si_{1.12}O_4$ $(0.81H_2O.0.162Na_2CO_3)$. If this cancrinite was then treated with a solution rich in Na_2CO_3, sodium rich nepheline was formed. Unfortunately in Wyart & Michel-Levy's work neither the pressure nor the temperature could be accurately controlled. The autoclaves which they used could withstand a maximum pressure of 700 kg/cm^2 at 500° C. The cancrinite mineral synthesized was probably natrodavyne.

Barrer & White (1952) succeeded in synthesizing a cancrinite of composition $3(Na_2O.Al_2O_3.2SiO_2)Na_2CO_3$, by using a gel of composition $Na_2O.Al_2O_3.2SiO_2$ treated with excess aqueous sodium carbonate, at atmospheric pressure in the temperature interval 300° C. to 420° C. The cancrinite synthesized had $\omega = 1.500$, $\epsilon = 1.497$ and unit cell dimensions of $a = 12.63$Å and $c = 5.18$Å.

Sand, Roy & Osborn (1957) also reported a cancrinite of the sodium carbonate type, synthesized in the temperature range 250° C. to 460° C. and at a water pressure of 15,000 p.s.i.

Experimental and Analytical Procedure

Dry material of the natrodavyne composition was prepared by mixing α-cristobalite, γ-alumina and Na_2SiO_3 in the correct stoichiometric proportions for the formation of nepheline, and then adding the required weight of anhydrous Na_2CO_3. 'Analar' grade reagents were used throughout.

Natrodavyne was synthesized by placing the starting material and distilled water, in the approximate weight ratio of 3:1, in gold cylinders. The cylinders were sealed, weighed and placed in cold seal test-tube type reaction vessels described by Tuttle (1949). The pressure and temperature were raised to the required value and the mixture allowed to react for five to seven days. At the end of this time the vessels were quenched in cold water and the cylinders removed and weighed. If the weight of the cylinders remained the same as the initial weight, the experiment was considered to have taken place in a closed system. If the weight had changed, the experiment was considered to have taken place in an open system and therefore to have leached material or gained water. All experiments taking place in the open system were discarded.

The synthetic products were ground to –200 mesh, and were identified by means of a Norelco diffractometer using Cu$K\alpha$ radiation and a Ni filter. The *d* spacings of the phases were determined from diffractograms using quartz as an internal standard. Approximate values of the cell parameters were determined from the diffraction pattern by comparing the observed $\sin^2\theta$ values for each peak with the calculated approximate $\sin^2\theta$ values, thus indexing each peak. The lattice parameters, *a* and *c*,

TABLE 2. EXPERIMENTAL DATA FOR NATRODAVYNE

No. of Run	Water Pressure (psi)	Temp. (° C.)	Time (hrs.)	Phase(s)
F20	20,000	750	95	High Natrodavyne
F21	20,000	700	95	High Natrodavyne
F28	25,000	750	95	High Natrodavyne
F37	10,000	500	190	Low Natrodavyne
F40	20,000	550	122	Low Natrodavyne
F43	15,000	500	140	Low Natrodavyne
F51	10,000	550	188	Low Natrodavyne
F52	10,000	600	188	Low Natrodavyne + High Natrodavyne
F57	30,000	600	95	Low Natrodavyne
F66	10,000	650	195	High Natrodavyne v. Minor low Natrodavyne
F68	15,000	550	145	Low Natrodavyne
F69	15,000	650	145	High Natrodavyne
F73	25,000	500	61	Low Natrodavyne
F80	25,000	550	61	Low Natrodavyne
F81	25,000	600	61	Low Natrodavyne
F94	15,000	600	141	Low Natrodavyne
F99	30,000	650	75	Low Natrodavyne
F103	20,000	650	168	High Natrodavyne
F104	20,000	600	168	Low Natrodavyne
F111	15,000	$\begin{cases}700\\400\end{cases}$	$\begin{cases}82\\84\end{cases}$	Low Natrodavyne

were then calculated from the observed $\sin^2\theta$ values for the indexed diffraction peaks.

EXPERIMENTAL RESULTS

The results are tabulated in Table 2 and plotted on Fig. 1. Figure 2 shows the diffraction patterns of the two phases above and below the transition temperature. The cell parameters for the low temperature hexagonal form, termed low natrodavyne are $a = 12.69 \pm .02$Å and $c = 5.18 \pm .02$Å. The cell parameter for the high temperature cubic form, similar in structure to nosean and here termed high natrodavyne, is $a = 9.02 \pm .02$Å.

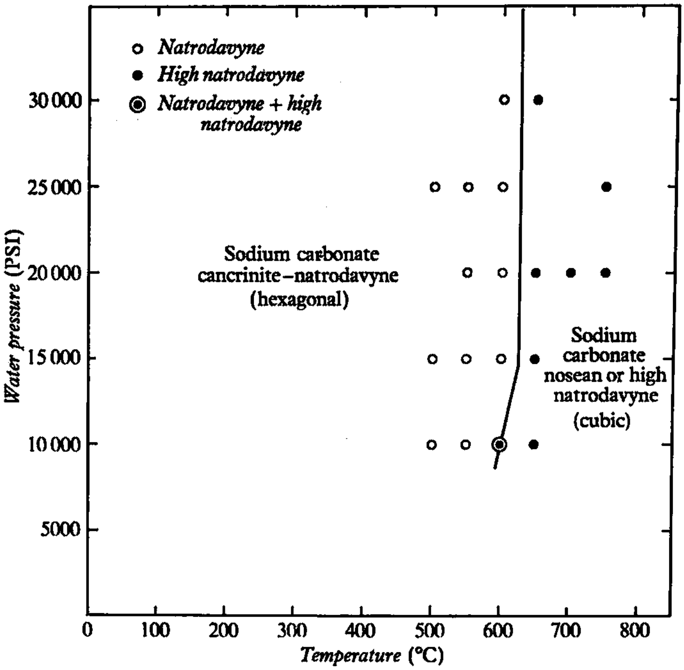

FIG. 1. Plot of experimental results from Table 2.

A similar transition was also observed in natrodavynes of composition $3NaAlSiO_4.NaHCO_3$. The cell parameters and transition temperature were almost identical with those of the sodium carbonate composition. The reason for this similarity is discussed in a later section.

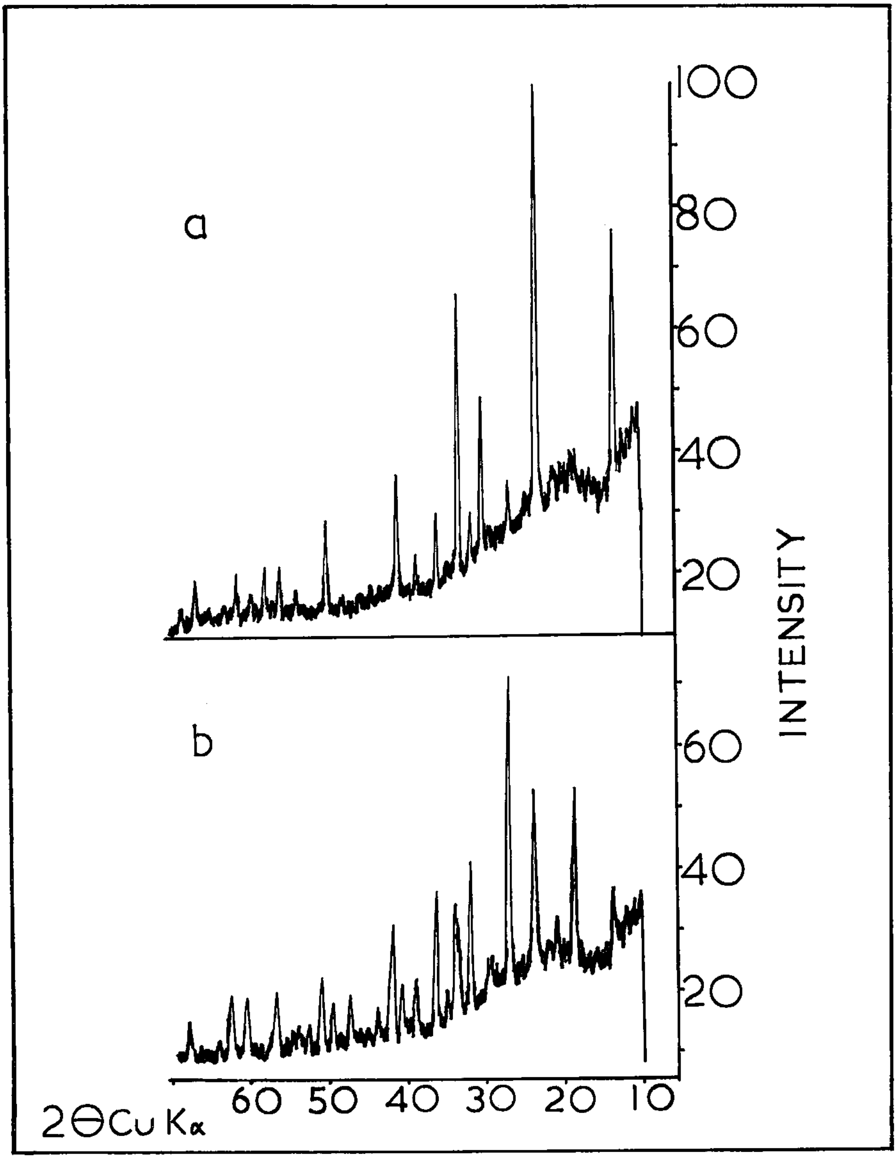

FIG. 2. X-ray diffraction patterns of natrodavynes (*a*) above transition temperature (high natrodavyne—cubic); (*b*) below transition temperature (low natrodavyne—hexagonal).

DISCUSSION OF RESULTS

(a) *Composition of the High Temperature Phase*

The high temperature modification of natrodavyne appears to resemble the nosean-hauyne group. There are two possible explanations to account for this modification. First, that the transition represents polymorphism from a hexagonal low natrodavyne to a cubic high natrodavyne. Second, that the transition boundary represents the temperature at which natrodavyne decomposes to a "basic nosean" similar to that described by Barrer & White (1952). This possibility can be represented by the equation:

$$\underset{\text{(natrodavyne)}}{3NaAlSiO_4.Na_2CO_3} + H_2O \xrightarrow{600^\circ\text{ C.}} \underset{\text{("basic nosean")}}{(1.5Na_2O.1.5Al_2O_3.3SiO_2.2NaOH)} + CO_2$$

This second possibility was investigated by synthesizing material of composition $NaAlSiO_4 + NaOH$. This produced a nosean type structure, but with different *d* spacings from the nosean type structure produced by the regular natrodavyne composition. A comparison of the *d* spacings of high natrodavyne and sodium hydroxide nosean is given in Table 3.

TABLE 3. A COMPARISON OF *d* SPACINGS OF HIGH NATRODAVYNE AND SODIUM HYDROXIDE–NOSEAN

High Natrodavyne F21 ($3NaAlSiO_4.Na_2CO_3$)		Sodium hydroxide Nosean ($NaAlSiO_4 + NaOH$)	
I (visual)	*d* (Å)	*I* (visual)	*d* (Å)
70	6.38	40	6.40
10	4.64	5	4.67
100	3.676	100	3.687
10	3.206	—	—
25	2.848	40	2.860
35	2.600	75	2.608
5	2.496	—	—
10	2.404	15	2.415
10	2.250	15	2.256
20	2.120	40	2.127
—	—	5	1.927
20	1.764	20	1.771
7	1.587	15	1.598
5	1.498	10	1.506
5	1.461	15	1.465

The composition $NaAlSiO_4 + NaOH$ synthesized at low temperatures gave a cancrinite type diffraction pattern, but with different *d* spacings from those of low natrodavyne (see Table 4). This indicates that polymorphism also exists in sodium hydroxide cancrinites. The transition boundary of this latter type of cancrinite has been established as 570° C. at the water pressures used in this study (P. Anderson—personal communication).

TABLE 4. A COMPARISON OF *d* SPACINGS OF LOW NATRODAVYNE AND SODIUM HYDROXIDE CANCRINITE

Natrodavyne $3NaAlSiO_4.Na_2CO_3$		Sodium Hydroxide Cancrinite $NaAlSiO_4 + NaOH$	
I (visual)	*d* (Å)	*I* (visual)	*d* (Å)
50	6.36	—	—
65	4.69	80	4.70
15	4.15	—	—
—	—	—	—
70	3.663	80(diff.)	3.672
—	—	—	—
100	3.234	100	3.252
—	—	—	—
—	—	—	—
—	—	15	2.816
50	2.747	35	2.758
10	2.628	30	2.634
—	—	30	2.589
15	2.515	15	2.566
5	2.426	15	2.431
20	2.264	—	—
7	2.172	5	2.184
5	2.113	—	—
—	—	15	2.096
15	2.021	—	—
5	1.977	—	—
5	1.883	5	1.886
7	1.804	—	—
10	1.758	7	1.763
5	1.705	—	—
10	1.590	5	1.593

(b) *Chemistry of the Natrodavynes*

The compositions of the natrodavynes cannot be strictly determined as it is extremely difficult to analyse the small amounts of the synthesized phases. Three cancrinites have been synthesized using the initial compositions $3NaAlSiO_4.Na_2CO_3$, $3NaAlSiO_4.NaHCO_3$ and $NaAlSiO_4 + NaOH$. The first and second synthesized compositions gave very similar results both for *d* spacings and transformation curves. The third composition produced a cancrinite with markedly different *d* spacings and transformation temperatures. As all the experiments have been done in the presence of excess water, it is possible that the following reactions may take place, at some temperature below that of transformation:

(1) $3NaAlSiO_4.Na_2CO_3 + H_2O = 3NaAlSiO_4.NaHCO_3 + NaOH$

(2) $3NaAlSiO_4.Na_2CO_3 + H_2O = 3NaAlSiO_4.2NaOH + CO_2$

The second equation has already been discussed in the previous section and it seems unlikely that such a reaction takes place to any great extent. If this second mechanism was operative, the *d* spacings of the sodium hydroxide cancrinites would be expected to be the same as the carbonate varieties. The reason for the similarity between the sodium carbonate and bicarbonate cancrinites may be explained in terms of the first equation. In this case, an equilibrium constant can be set up which depends on the activities of NaOH and H_2O, i.e. on the ratio of the initial amounts of oxide to water in the starting material. This implies that the net composition of the sodium carbonate and bicarbonate cancrinites probably depends on the relative proportions of oxides to water in the starting material. Using an initial composition of $3NaAlSiO_4.NaHCO_3$, it is not possible to write an equation similar to (1) unless the cancrinite produced is deficient in sodium, *viz.*,

$$3NaAlSiO_4.NaHCO_3 + H_2O = 3NaAlSiO_4.\tfrac{1}{2}Na_2CO_3 + \tfrac{1}{2}H_2O + \tfrac{1}{2}CO_2.$$

The possibility of synthesizing cancrinites of this composition has not been investigated.

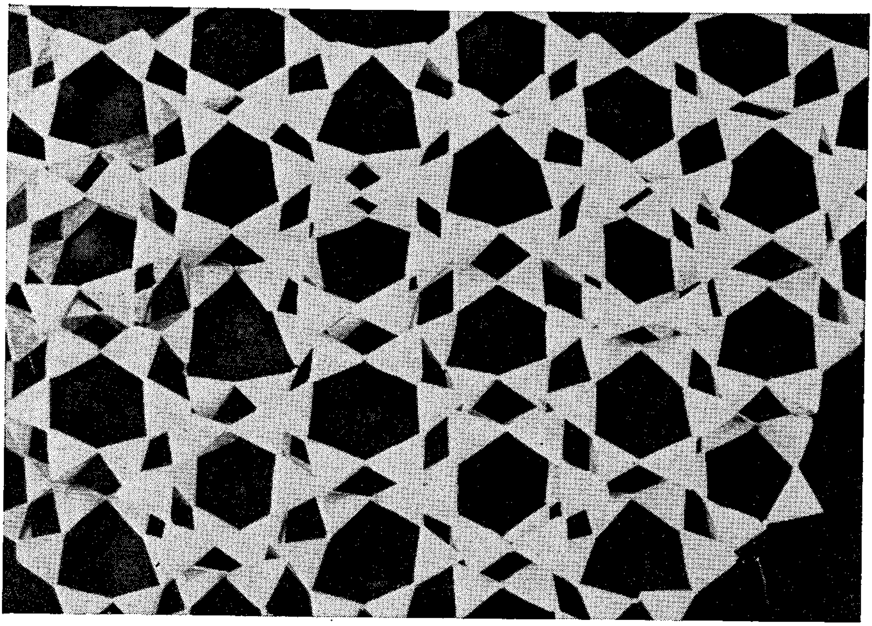

FIG. 3. The structure of nosean looking down the [111] axis (after Pauling, 1930).

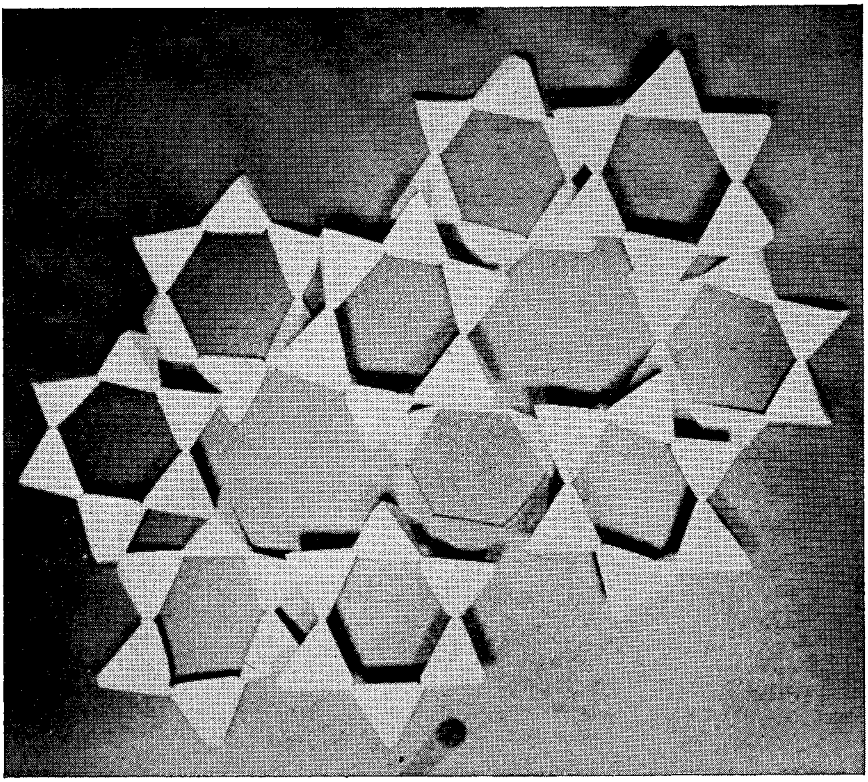

FIG. 4. The structure of cancrinite looking down the *c′* axis (after Pauling, 1930).

The mineral natrodavyne, as defined in this paper, is probably a phase at the temperature of the experiments in the system $NaAlSiO_4$–Na_2CO_3–H_2O; or, in the case of the sodium hydroxide cancrinite, the system $NaAlSiO_4$–$NaOH$–H_2O. The phase relations in these systems are at present being investigated. Results will be given in a later publication.

(c) *Crystallography*

The crystallographic evidence for the hexagonal to cubic transformation can only be discussed from a theoretical viewpoint as the structure of cancrinite has not been rigorously established. The structure of nosean has been determined by Pauling (1930) and Barth (1932) and later by Saalfeld (1959). The cancrinite structure has been deduced by Pauling (1930) and by Kozu & Takane (1933). Gossner & Mussgnug (1930) noted a similarity between the two minerals before the structure of either had been worked out. They showed that if the *c′* axis of the hexagonal

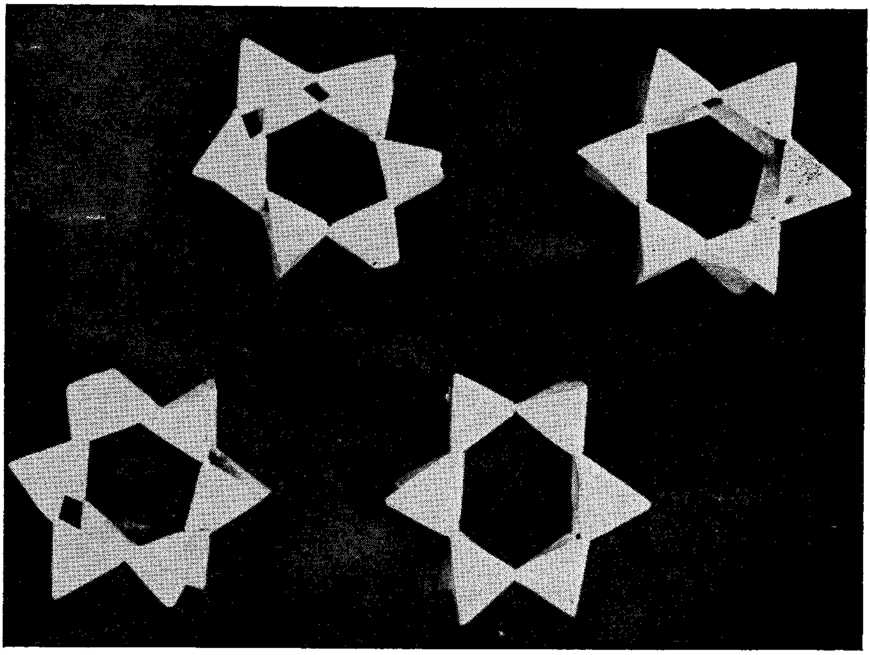

FIG. 5. The structure of cancrinite looking down the c' axis (after Kozu & Takane, 1933).

cancrinite was placed parallel to the [111] axis of the cubic nosean and the a' axis placed parallel to the $[0\bar{1}1]$ axis of the cube the resulting cells have the same dimensions. This relationship is found to hold for both the synthetic forms of natrodavyne, the hexagonal cell having the volume 722 ± 5 Å^3 and the cubic cell 724 ± 5 Å^3.

The structures of the two minerals have similarities. The structure of nosean looking down the [111] axis consists of six fold rings of Si–Al–O tetrahedra (Pauling, 1930). These rings are 12.78 Å apart on a hexagonal cell, with the layers stacked in an *a*, *b*, *c* arrangement (Fig. 3). The cancrinite structure looking down the c' axis (Fig. 4) is composed of exactly similar layers of six fold rings the same distance apart but stacked in an *a*, *b* arrangement (Pauling, 1930). Kozu & Takane (1933) suggest a similar structure but with an *a*, *a* arrangement (Fig. 5).

An examination of Figs. 3, 4, and 5 shows that if polymorphism exists the transformation must consist of a rearrangement of the layer stacking, requiring the breaking of Si—O bonds. Such a transformation, involving a reconstruction, would tend to be sluggish, would probably not be reversible unless catalyzed, and would likely have an easily quenchable high temperature form.

A consideration of the experimental data (Table 2) shows that the shortest time in which the transformation took place was 95 hours at a water pressure of 20,000 p.s.i. No runs of shorter duration were attempted and it is therefore difficult to determine the speed of this transformation. In only one case (F-111, Table 2) was it found possible to reverse this reaction, and even then only over a 300° C. interval. As the charge was not removed and examined before the temperature was lowered, it is possible that the high temperature form was not synthesized in the 82 hours at the higher temperature. It seems likely that this transformation is not readily reversible. In all experiments the high temperature phase was found to be easily quenchable.

(d) *Field Evidence*

The field evidence has not been closely studied. Noseans most commonly occur in lavas, typically in leucitophyres and phonolites; whereas cancrinites commonly occur in coarse grained slowly cooled rocks, typically in nepheline syenites. To the authors' knowledge, only once has nosean been reported in a coarse grained rock, this being a nosean bearing aegirine-augite syenite from northern China described by Nystrom (1927).

The Laacher See is an area in which the coexistence of a cancrinite and a nosean in the same rock has been reported. Schuster (1919) has described a possible carbonate nosean occurring in ejectamenta from this area. Brauns (1916) has analyzed a nosean type mineral from the same area and found a fairly high CO_2 content. There is, however, no suggestion of any polymorphic relationship between these minerals.

Clark (1948) has described the coexistence of cancrinite and nosean in boiler deposits and suggests that cancrinite is the high temperature phase. The compositions and cooling conditions of these deposits are unknown.

CONCLUSIONS

It is concluded that there is a polymorphic transition from a hexagonal cancrinite structure to a cubic nosean structure in the composition $3NaAlSiO_4 . Na_2CO_3$ at above 600° C. in the water pressure range 10,000 p.s.i. to 30,000 p.s.i. A similar transition takes place in the composition $NaAlSiO_4 + NaOH$ at a temperature of 570° C. Crystallographic evidence suggests that these are reconstructive types of transformation. Although previous experimental studies and field evidence support the probable existence of carbonate rich noseans, a polymorphic transition between cancrinite and nosean has not been previously recorded.

ACKNOWLEDGMENTS

One of the authors (A. D. E.) gratefully acknowledges the award of a National Research Council Studentship held during the period of this research. The other author (B. J. B.) gratefully acknowledges receipt of a grant (A612) from N.R.C. and also a grant from the Research Corporation of America. Dr. T. N. Irvine of McMaster University made many helpful suggestions and criticisms during the course of this study.

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Manuscript received February 13, 1962