THE HYDROXYL FELSPATHOIDS

PHASE RELATIONS OF THE HYDROXYL FELSPATHOIDS IN THE SYSTEM $NaAlSiO_4$-$NaOH$-H_2O

By

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SCOPE AND CONTENTS: A study was made of the phase relationships in the system $NaAlSiO_4$-$NaOH$-H_2O, at 15,000 p.s.i. and at 450°C, 520°C, 600°C and 700°C. The following phases were found and characterised: hydroxyl varieties of nosean, sodalite and cancrinite, with formulae approximating to $3NaAlSiO_4.NaOH.xH_2O$, $1 \leq x \leq 1.5$, sodic nepheline and phase X, apparently a previously unreported phase, with composition approaching $Na_4Al_2Si_2O_9$. Approximate phase diagrams were deduced for the four temperatures.

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CHAPTER I

INTRODUCTION, AND SYNOPSIS OF THE THESIS

This is the record of an experimental study, concerning those hydroxyl analogues of the felspathoidal minerals, which form in the system $NaAlSiO_4$-$NaOH$-H_2O. The intention was to delineate the properties and stability relationships of these substances, at 15,000 p.s.i. total pressure, and at temperatures from 450°C to 600°C.

The chemical compositions of this system range far from those likely to be found in nature, and the connection with natural rocks and minerals is, at first sight, tenuous. Investigation of this system is, however, a logical early step in the experimental study of the felspathoids, the natural forms of which require at least eleven chemical components for description of their compositions.

The system Na_2O-Al_2O_3-SiO_2-H_2O is an obvious starting point for the felspathoids, because it would appear to be the only system of four components in which representatives of all distinct groups of this type of mineral are found. In fact, the compositions of these hydroxyl felspathoids lie on, or near to, the plane $NaAlSiO_4$-$NaOH$-H_2O. Knowledge of the phase relationships on this plane should be an excellent foundation for extension into more complex systems.

About two hundred charges, with chemical compositions lying at various points on or near the composition plane $NaAlSiO_4$-$NaOH$-H_2O, were held at fixed temperature and pressure for two to three weeks. The crystalline contents of the charges were then examined optically, by x-ray diffraction and by chemical analysis, and the relationships of the crystalline types were studied. The range of the investigation was somewhat extended, to include the temperature of 700°C, and some excess Na_2O in the range of compositions.

Five crystalline phases were encountered and characterised. Nepheline, hydroxyl-nosean, hydroxyl-cancrinite and hydroxyl-sodalite were present, as had been expected. A further substance, with composition approximating to $Na_4Al_2Si_2O_9$, appeared in many charges. This last phase was not identified with any previously reported compound, and was, with a certain lack of originality, termed "phase X". A fluid phase was commonly present.

Chemical analyses of the nosean, cancrinite and sodalite formed, gave very similar compositions for the three, these compositions being quite close to those expected by comparison with the natural forms of these phases.

The results indicate that hydroxyl-sodalite is not stable in the system, above about 520°C, although it persists to higher temperatures when enclosed in hydroxyl-nosean. Hydroxyl-cancrinite was found at 450°C and 520°C, and hydroxyl-nosean grew at and above 520°C. Nepheline and phase X were stable over the whole range of temperature. Some interesting strain and x-ray diffraction phenomena were seen in nepheline, related to the amount of excess NaOH in the charges; these phenomena are suggestive of structural inversion on cooling.

CHAPTER II

RELEVANT PREVIOUS INFORMATION, AND DESIGN OF THIS INVESTIGATION

This chapter contains a review of relevant earlier work, dealing first with the felspathoids, and then with work in the system $Na_2O-Al_2O_3-SiO_2-H_2O$. The chapter concludes with an account of the reasons underlying the choice of the ranges of the intensive parameters, which were used in this study.

A. THE FELSPATHOIDS

The felspathoids tend to assume an analogous role, in silica-undersaturated rocks, to that occupied by the felspars, in silica-saturated and oversaturated rocks. Felspathoids are found in undersaturated rocks associated with carbonatites, in undersaturated volcanic rocks such as nepheline basalts or nosean phonolites, and in undersaturated plutonic and metamorphic complexes, such as those of southern Ontario and the Kola peninsula. In fact, the occurrence of a felspathoid is the prime indicator of silica undersaturation in felsic rocks; felspathoids are unstable in the presence of free silica.

The felspathoid families are:

1. Nepheline-kalsilite.
2. Sodalite-hackmanite.
3. Nosean-hauyne-lazurite.
4. The cancrinites.
5. Leucite.

The structures of all these minerals involve three-dimensional aluminosilicate frameworks, and all have Si:Al:O in the ratio 1:1:4, except leucite ($KAlSi_2O_6$), which is not a subject of this investigation.

NEPHELINE FAMILY

GENERAL. Nepheline is the best-known and commonest felspathoid, occurring usually as a primary igneous phase in both felsic and basic rocks. It is probably also of metasomatic origin, in some occurrences (Tilley, 1957, and D.H.Z.[1]).

COMPOSITION. Nepheline in nature is a solid solution of sodic nepheline ($NaAlSiO_4$) and kalsilite ($KAlSiO_4$), and tends to the composition $Na_3KAl_4Si_4O_{16}$, in plutonic rocks. Volcanic nepheline is generally poorer in K_2O, but not necessarily richer in Na_2O; there is a solid solution series between $Na_3KAl_4Si_4O_{16}$ and $Na_3Al_3Si_5O_{16}$, i.e. the "omission solid solution" of Tuttle and Smith (1958), and Donnay, Schairer and Donnay (1959).

STRUCTURE. Nepheline is of hexagonal symmetry, with space group $P6_3$. The structure is a distorted version of the tridymite framework (Hahn and Buerger, 1955), with a≐10Å, c≐8.4Å. Two other distinct polymorphs of sodic nepheline are known; high nepheline and carnegieite. High nepheline is hexagonal, according to Donnay et al (1959), with a≐10.0Å, c≐8.3Å; Tuttle and Smith (1958) report it to be orthorhombic, with a=10.2Å, b=17.6Å, c=8.5Å. Carnegieite is cubic, and is reportedly not stable at a partial pressure of water of 1000 bars. Borchert and Keidel (1949 a,b)

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[1] D.H.Z.: Deer, Howie and Zussman. The Rock-forming Minerals, vol. 4, Longmans, London, 1963.

synthesised sodium-rich cubic carnegeites, which correspond in composition with an orthorhombic phase synthesised by the writer (phase X).

STABILITY OF NEPHELINE. Sodic nepheline, $NaAlSiO_4$, has often been synthesised as a stable phase in dry, atmospheric pressure experiments, and in hydrothermal, elevated pressure and temperature experiments. Good crystals can be grown from silicate liquids, or in sub-solidus systems containing some NaOH. Saha (1961) reported good crystals (≐ 2 mm. length) below the solidus in the system $NaAlSiO_4$-H_2O, and the writer has obtained similar results, using oxide mixtures as starting reagents. As will be mentioned below, well-crystallised nepheline was not synthesised in the present study, in the absence of excess NaOH, the starting reagents being gels.

The sodic end of the system $NaAlSiO_4$-$KAlSiO_4$ is shown as figure A, taken from Tuttle and Smith (1958).

NOSEAN AND SODALITE

GENERAL. Nosean and sodalite are normally grouped together as one "family", for evident reasons. Less evident, but more compelling arguments indicate that attention should be directed to their differences, as well as to their similarities.

STRUCTURE. Sodalite and nosean are both cubic, with three-dimensional aluminosilicate framework structures, and cell parameters of $a \doteq 8.9\,\text{Å}$ and $a \doteq 9.1\,\text{Å}$ respectively. The structures are very similar (Barth, 1932 a,b). In natural sodalite, large cavities in the structure are

FIGURE A

The Sodic End of the System $NaAlSiO_4$-$KAlSiO_4$

The diagram is for dry (P_{total}=1 atmosphere) conditions, and is taken from Tuttle and Smith (1958). The compositions are in weight per cent. Cg = carnegeite; Ne = nepheline; Ne_H = high nepheline.

FIGURE B

The System Na_2O-Al_2O_3-SiO_2-H_2O

This figure is given by Koster van Groos (1966), to illustrate the probable relationships, at 1 kilobar, in the four ternary systems bounding the system Na_2O-Al_2O_3-SiO_2-H_2O. The vapour-saturated liquidus is shown by lines with cross-hatching in the ternary systems, and by the stippled surface, in the quaternary system.

Key:

Symbol	Number of composition point	Formula	Name
Ab	1	$NaAlSi_3O_8$	Albite
Carn	2	$NaAlSiO_4$	Carnegeite
Ne	2	$NaAlSiO_4$	Nepheline
Co	-	Al_2O_3	Corundum
Cr	-	SiO_2	Cristobalite
Q	-	SiO_2	Quartz
Tr	-	SiO_2	Tridymite
Mu	3	$Al_6Si_2O_{13}$	Mullite
-	4	$NaAlO_2$	Sodium aluminate
N_2S	5	Na_4SiO_4	Sodium orthosilicate
NS	6	Na_2SiO_3	Sodium metasilicate
NS_2	7	$Na_2Si_2O_5$	Sodium disilicate

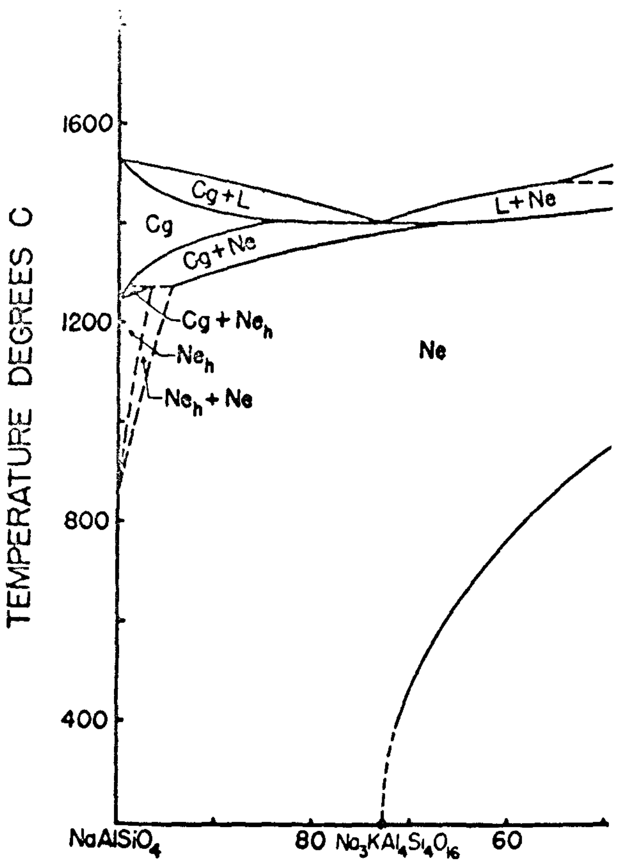

FIGURE A

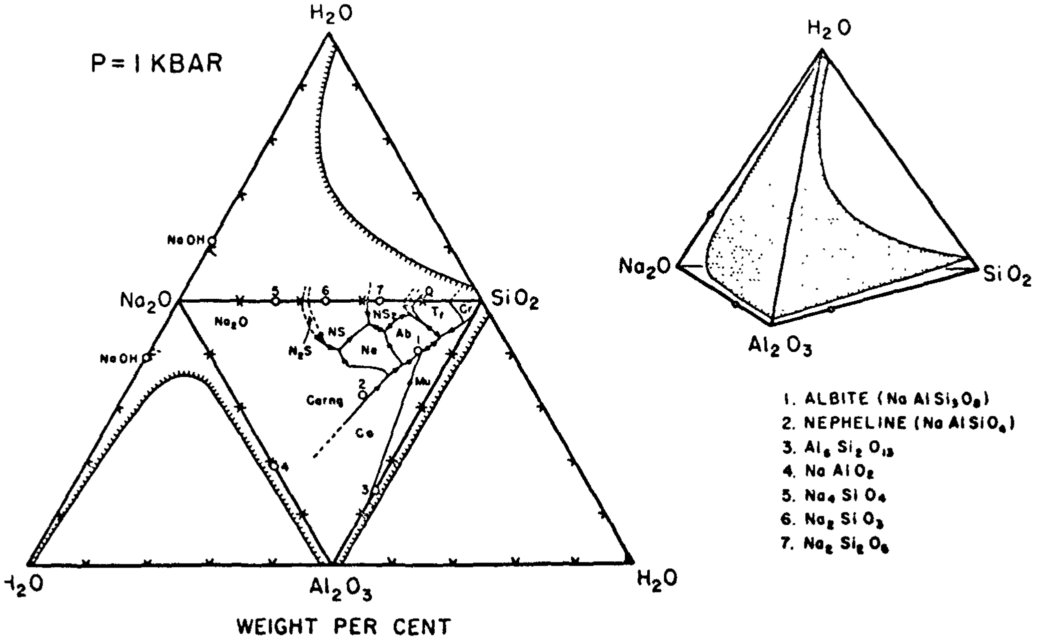

FIGURE B

occupied by Cl^-, tetrahedrally coordinated by Na^+. In natural nosean, one half of the cavities contain $SO_4^{=}$, distributed at random (Saalfeld, 1959, in D.H.Z.). Both have the space group $P\bar{4}3m$[1](D.H.Z.), and the x-ray diffraction patterns of the two phases are very similar indeed.

COMPOSITIONS. Nosean and sodalite share the same general composition $6NaAlSiO_4.Y$, where Y is 2NaCl (sodalite) or Na_2SO_4 (nosean). Nosean exhibits solid solution with the hypothetical calcium-bearing analogue $Ca_4Al_6Si_6O_{24}\cdot SO_4$ (Van Peteghem and Burley, 1963), the natural mineral hauyne being of intermediate composition. There appears also to be a solid solution series between nosean/hauyne and lazurite, $Na_8Al_6Si_6O_{24}S_2$ (Rogers, 1938, in D.H.Z.).

Sodalite, on the other hand, is quite constant in composition, approximating closely to $6NaAlSiO_4\cdot 2NaCl$ (Van Peteghem and Burley, 1961, 1963; James, 1965, and D.H.Z.). OH^- and $S^{=}$ are commonly present in small amount; one or both of these are probably responsible for the tenebrescence of the hackmanite variety of sodalite.

Barth (1932a) considered nosean and sodalite to be end-members of a complete solid-solution series. This is refuted by Van Peteghem and Burley (1961, 1963), who determined the maximum solubility at 600°C to be approximately 30 percent. sodalite in nosean. Anderson (1963) found that hydroxyl forms of sodalite and nosean grew together and co-existed over a range of temperature. Clearly, there is some essential difference between the two substances, other than difference of composition and cell size.

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[1] Lons and Schulz (1967) have recently shown chloride sodalite to belong to the space group $P\bar{4}3n$. Saalfeld (1959) determined the space group of sulphate nosean to be $P\bar{4}3m$.

HYDROXYL VARIETIES OF NOSEAN AND SODALITE. Hydroxyl varieties of nosean and sodalite have been synthesised by Barrer and White (1952), by Van Peteghem (1961) and by Anderson (1963), among others. The only clear distinction between the two substances is the difference of cell size. Anderson (1963) found that hydroxyl nosean is stabilised relative to hydroxyl sodalite by increase of either temperature or the NaOH content of the system.

Barrer and Falconer (1956) analysed a hydroxyl sodalite, synthesised at 100°C and 1 atmosphere, obtaining the composition (weight per cent): Na_2O-22.0; Al_2O_3-31.2; SiO_2-37.7; H_2O-9.2. This gives the formula, $2NaAlSiO_4 \cdot 0.32NaOH \cdot 1.51H_2O$, with 0.5 excess SiO_2.

NATURAL ASSOCIATIONS. Nosean and sodalite in nature are associated with different rock types. Nosean is found almost exclusively in phonolites and related volcanic rocks, the only reported exception being a series of nosean-bearing syenites in northern China (Nystrom, 1927, in D.H.Z.). Sodalite is most commonly found in nepheline syenites and related plutonic rocks, as a primary igneous phase, or as a vein alteration product, but is also found in undersaturated extrusive rocks from Portugese East Africa, the Laacher See, and elsewhere.

CANCRINITE

GENERAL. "Cancrinite" is a general term covering a family of felspathoids, apparently capable of extensive or complete solid solution.

COMPOSITION. The general formula for natural varieties, is, as for sodalite and nosean, $6NaAlSiO_4.Y$, where Y is $(Na,Ca,K)_{1-2}.(CO_3,SO_4,Cl)_{1-2}.1-5H_2O$. The principal variation is between the $CaCO_3$-rich types (cancrinite proper) and the bisulphate-rich varieties, termed vishnevite. A rational nomenclature is given by Edgar and Burley (1963).

STRUCTURE. The structure of cancrinite was determined by Nithollon (1956) and Jarchow (1966), both of whom confirmed the framework structure inferred by Pauling (1930) from comparison of the cell dimensions of a=12.6Å, c=5.2Å, with various stackings of six-membered rings of silicon, aluminum and oxygen. The space group is $P6_32$. Kozu and Takane (1932) had proposed a different structure, based on columns of six-membered rings of silicon-aluminum-oxygen tetrahedra, these columns being joined together by the metal ions.

NATURAL ASSOCIATIONS. Cancrinite is well-known for its association with carbonatite complexes, where it is commonly a primary constituent (D.H.Z., and Watkinson, 1964). Eckermann (1948) described such an occurrence, in which he considered cancrinite to be the last primary phase. Elsewhere, as in the nepheline syenite complexes of southern Ontario, cancrinite is a vein deposit in nepheline syenite and nepheline syenite pegmatite.

In the Gill Quarry nepheline pegmatite, near Bancroft, Ontario, cancrinite is seen in reaction zones between nepheline and calcite; elsewhere, in the same area, nepheline and calcite coexist without reaction. Eckermann (1948) considered this phenomenon in the Alno rocks to be due to local variation of CO_2 pressure, higher P_{CO_2} favouring the formation of cancrinite.

HYDROXYL CANCRINITE. Barrer and Falconer (1956) present an analysis of "basic" cancrinite, synthesised from a gel, at 390°C, and elevated, but unspecified, pressure. They found the composition to be (in weight per cent): Na_2O-23.5; Al_2O_3-29.3; SiO_2-41.1; H_2O-6.1. This gives the molecular formula, $NaAlSiO_4$. 0.32NaOH. $0.43H_2O$, with 0.4 SiO_2 in excess. Hydroxyl cancrinite was also synthesised by Barrer and White (1952), Edgar (1961), Van Peteghem (1961) and Anderson (1963), among others.

RELATIONSHIP OF CANCRINITE AND NOSEAN. Edgar and Burley (1961, 1963) showed that some cancrinites are converted to nosean structures with rising temperature, and suggested that the change may be a polymorphic transition.

B. THE SYSTEM $NaAlSiO_4$-NaOH-H_2O, AND ITS PARTS

NaOH-H_2O. The system NaOH-H_2O probably shows complete miscibility above the melting point of NaOH (318.4°C). Barnes and Ernst (1963) pointed out that NaOH, in aqueous solution, is only slightly dissociated, above the critical point, with consequent increase of the thermodynamic ideality of mixing of the components. The pH at high pressure and temperature is thus very much lower than at room temperature. They conclude that dilute aqueous NaOH solutions approach ideality at high pressure and temperature.

$NaAlSiO_4$-H_2O. Yoder (1958) determined the water-saturated melting point of sodic nepheline in this system; at P_T (total pressure) of 1 kilobar, nepheline melts at about 1150°C. Evidently, at temperatures of 450°C to 700°C, the solubility of nepheline in water will be small. Burnham, reported in Koster van Groos (1966) p. 17, found that nepheline melts at 1 kilobar dissolve "more H_2O" than do albite melts at the same pressure; Burnham and Jahns (1962) determined the solubility of water in albite melt at 1 kilobar and 900°C to be 4.2 weight per cent, and the aqueous fluid to contain about 1 weight per cent of albite. The highest reported water content in natural nepheline is 1.57 weight per cent (D.H.Z.).

Saha (1961) determined the curve of the reaction

$$\text{nepheline hydrate I} \rightleftharpoons \text{nepheline} + H_2O;$$

the reaction proceeds to the right with increasing pressure and temperature, and crosses the 1 kilobar isobar at about 440°C.

$NaAlSiO_4$-$NaOH$. No determinations of phase relations have previously been made precisely on this join. Borchert and Keidel, in the work mentioned below, stress the importance of water in their reactions.

$NaAlSiO_4$-$NaOH$-H_2O. Borchert and Keidel (1949a) reacted kaolinite ($Al_2O_3.2SiO_2.2H_2O$) with NaOH at 1 atmosphere and temperatures of 100°C to 600°C. They worked with mixtures dried at 100°C, and deduced the composition of the resulting phases from: a) the composition of the starting charges, and b) the presence of only one phase, as seen in x-ray powder photographs. They found, at 100°C, a solid solution series of sodalites, varying from $NaAlSiO_4 \cdot nH_2O$ to $3NaAlSiO_4 \cdot 2NaOH \cdot Na_2O \cdot nH_2O$ in composition; these constitute "β-hydroxysodalite". Above 300°C, slight changes of the x-ray diffraction patterns lead them to use the term "α-hydroxysodalite". Upon heating the composition $NaAlSiO_4$ quickly to 500°C, a cubic phase pseudonepheline was formed; this gave way, at 600°C, to nepheline. Heating the compositions 3-4 Mol NaOH : 1 Mol kaolin to 600°C gave a "Na_2O-rich carnegieite". The various cell dimensions given were: hydroxysodalite, a=8.72 to a=8.62Å; pseudonepheline, a=8.915Å; Na_2O-rich carnegieite,a=7.273Å. The cell size of hydroxysodalite decreased with increasing temperature. The apparent lack of control of CO_2 uptake (by the NaOH), and absence of any optical control of the phase identification and phase purity, render this work of Borchert and Keidel difficult to evaluate, in view of the serious contamination and identification problems experienced by the present writer.

Barrer and White (1952) worked extensively with the system $NaAlSiO_4$-$NaOH$-H_2O, in the temperature range 150°C to 450°C, and in systems of higher and lower silica content. Their bulk composition data was vague, and pressures were not given (estimated by this writer to be about ½ kilobar). They synthesised, starting with gels, some zeolitic phases, and nepheline, "basic" sodalite, "basic" cancrinite and "basic" nosean. Their determinations of the pH of the residual aqueous fluids suggest that the sequence:

NaOH+nepheline→cancrinite→sodalite or nosean

is realised by progressively increasing the content of NaOH in the system.

Sand, Roy and Osborn (1957) assembled the existing data on the system $Na_2O-Al_2O_3-SiO_2-H_2O$, but had only the data of Barrer and White (ibid) of direct relevance to the system $NaAlSiO_4-NaOH-H_2O$.

Koster van Groos (1966) presents a diagram of the system $Na_2O-Al_2O_3-SiO_2-H_2O$ at 1 kilobar pressure, this being constructed chiefly from the work of Morey and Hesselgesser (1952) on $Na_2O-SiO_2-H_2O$, Schairer and Bowen (1956) and Aramaki and Roy (1962) on $Na_2O-Al_2O_3-SiO_2$. This diagram is shown as figure B.

The writer (Anderson, 1963), working in this system over a restricted temperature and composition range (440°C to 540°C), concluded that the phases increased in NaOH content in the order cancrinite $<$ sodalite $<$ nosean, and that the field of sodalite was restricted to temperatures below 520°C. Nosean and cancrinite persisted above this temperature, possibly with a polymorphic relationship. Figure C is the section $NaAlSiO_4.H_2O-NaOH$, taken from that reference.

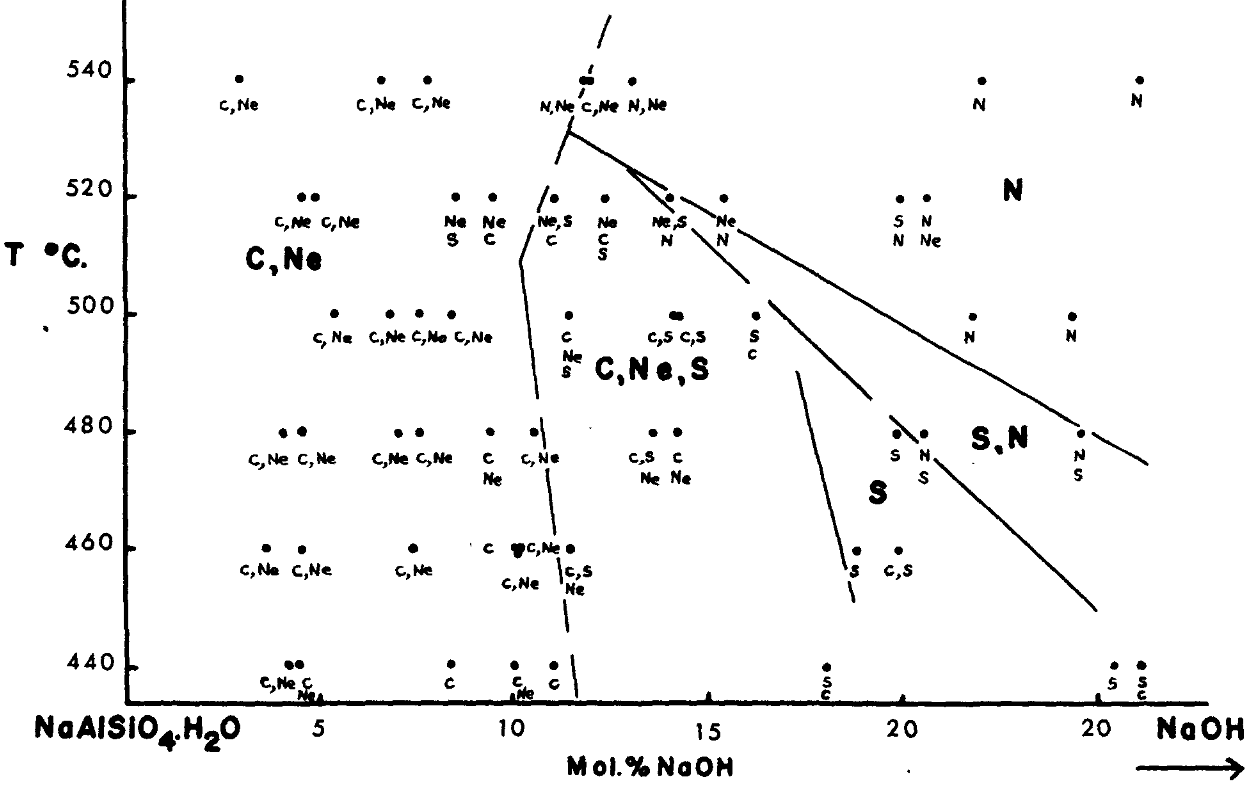
C. THE DESIGN OF THIS INVESTIGATION

GENERAL. With the exception of nepheline (and leucite), the essential conditions for felspathoid formation are known only in outline. The importance of felspathoids in undersaturated rocks renders the group worthy of further study.

FIGURE C

The Join $NaAlSiO_4.H_2O$-NaOH

The results of earlier work by the writer (Anderson, 1963). The compositions of the charges were points in the plane $NaAlSiO_4$-NaOH-H_2O, and were projected on to this section along lines of constant NaOH content, i.e. lines parallel to the $NaAlSiO_4$-H_2O join. In general, therefore, the ratio $NaAlSiO_4$:H_2O differs somewhat from 1.


T °C.
540
520
500
480
460
440
C,Ne
C,Ne,S
N
S,N
S
c,Ne
c,Ne c,Ne
N,Ne c,Ne N,Ne
N
N
c,Ne c,Ne
Ne S
Ne C
Ne,S C
Ne C S
Ne,S N
Ne N
S N
N Ne
c, Ne c,Ne c,Ne c,Ne
c Ne S
c,S c,S
S c
N
N
c,Ne c,Ne
c,Ne c,Ne
c Ne
c,Ne
c,S Ne
c Ne
S
N S
N S
c,Ne c,Ne
c,Ne
c c,Ne
c,Ne
c,S Ne
S
c,S
c,Ne c Ne
c
c Ne
c
S c
S
S c
NaAlSiO4.H2O
5
10
15
20
20
NaOH
Mol.% NaOH

The study of minerals can usefully (but arbitrarily) be divided to two approaches: firstly, investigation of the physical and chemical properties of the several distinct mineral types; secondly, study of the physico-chemical interrelationships of these types, including their conditions of stability and of formation. The latter approach is of greater potential value to petrological theory, and was emphasised from the start, in the present work.

THE "NATURAL" FELSPATHOID SYSTEM. Natural felspathoids lie in the system Na_2O-Al_2O_3-SiO_2-H_2O-Cl^--SO_4^--HSO_4^--$SO_3^=$-HSO_3^--$CO_3^=$-HCO_3^--CaO-K_2O-S; all of these are major constituents of one or more felspathoid type. Such a system obviously is not, taken all at once, amenable to experimental study.

THE MINIMAL FELSPATHOID SYSTEM. The simplest system in which representatives of all the felspathoid types occur, is the system Na_2O-Al_2O_3-SiO_2-H_2O, in the neighbourhood of the plane $NaAlSiO_4$-NaOH-H_2O. While none of the felspathoids in this system are identical in composition with the natural forms, information concerning their phase relationships should offer a versatile foundation for extension, by addition of other components of interest.

SPECIFIC PROBLEMS FOR STUDY. For purposes of comparison within the join $NaAlSiO_4$-NaOH-H_2O, and with related systems, basic physical and chemical parameters of the phases must be determined, in addition to the general phase relations. Furthermore, it was desirable to resolve, if possible, some specific questions:

1. Are there any crystalline phases in the system, other than those mentioned above?
2. What is the relationship of nosean and sodalite; do the hydroxyl forms become isomorphous under any conditions, or are they always distinct?
3. Are hydroxyl-nosean and hydroxyl-cancrinite polymorphic forms?

CHOICE OF VALUES FOR EXPERIMENTAL PARAMETERS, AND EXPERIMENTAL METHOD

PRESSURE. 1 kilobar was the total pressure chosen, since it is easily and reliably accessible to the available experimental equipment, and is the same as, or relatively near to, the pressures used by other experimenters in related studies, permitting better comparison with those studies than would another pressure.

TEMPERATURE. The lower temperature limit was set at 450°C, in view of Saha's (1961) finding that nepheline hydrate is stable below 440°C. 520°C was chosen for the second isothermal section, on the basis of earlier results of the writer (Anderson, 1963), which suggested that this is the temperature range above which hydroxyl sodalite is not a stable phase. 600°C was the rather arbitrary choice for the third section, as was 700°C for the fourth; the need for results at the last temperature, to clarify the results at 600°C was realised half-way through this project.

CHOICE OF METHOD, REAGENTS AND COMPOSITIONS. In the absence of supplies of the hydroxyl felspathoids, it was necessary to determine stability by the method of synthesis. Because of the difficulty of handling NaOH solutions without contamination by H_2O and CO_2, gels were used as starting materials; high-sodium gels are relatively easy to make and to handle. Thus, pure water would be mixed, in the correct proportion, with one of several gels of the composition $xNaAlSiO_4.yNaOH$, in order to make up a given charge. The work of Barrer and White (1952) had shown that, at given pressure and temperature, the NaOH concentration of the residual fluid (measured as pH), tended to vary with the phases present. It was thus necessary, in the present investigation, to have the water concentration as one of the measured parameters.

CHAPTER III

EXPERIMENTAL METHOD

This chapter is a brief statement of the experimental methods employed. The actual procedures are described in detail in Appendix I, section 1.

Phase stability was determined by synthesis of phases in about 200 isolated systems of known composition, and subsequent identification of the phases formed, by optical and x-ray examination. A sample of each of the crystalline phases formed was analysed chemically, and other characteristics of these phases, such as refractive index and cell dimensions, were determined.

HYDROTHERMAL SYNTHESIS. The starting materials were eight gels, the compositions of which lay on the plane $NaAlSiO_4$-Na_2O-H_2O. Each charge was made up by sealing about 55 mg. of one of these gels, with 0 mg. to 35 mg. of water, in a small gold capsule. The charges were placed in heated pressure vessels, and held, for periods of two to three weeks, at a pressure of 15,000 p.s.i. (±5 per cent), and at 450°C, 520°C, 600°C, or 700°C, ±10°C, with a precision of ±2°C (see p.58). At the end of this period, the pressure vessel ("bomb") was cooled as quickly as possible to room temperature, at which reaction rates are presumed to be very slow. About three hundred and forty charges were attempted, but about one hundred and forty were rejected. Most of the losses were due to changes in the weights of the capsules during reaction; considerable losses also arose through power failures.

EXAMINATION OF REACTION PRODUCTS. In most cases, the capsule was opened, part or all of the contents were removed, washed in water, dried in acetone, and examined. About one-third of the charges were subjected to partial analysis of the fluid phase. These capsules were carefully perforated, and the weight loss on dehydration was determined. They were then opened under water, and the contents were washed throughly. The total sodium in the filtered washings was determined. These water and sodium determinations were taken to represent the composition of the fluid phases of the charges, to a first approximation.

OPTICAL AND X-RAY PROCEDURES. The reaction products were immersed in oils of suitable refractive index, and were examined under a petrographic microscope. Refractive index measurements were made by comparison with standard immersion oils, calibrated at intervals of .002 units. X-ray identification was effected, for the most part, with a Norelco diffractometer, the diffraction patterns so obtained being compared with those of pure samples of the phases. In some cases, a powder camera of radius 5.7 cm. was used, to detect phases present in small amount, or to obtain powder data from a single crystal, picked from a charge, and ground. Cell parameters were determined from powder data, except in the case of phase X, for which rotation and Weissenberg photographs were taken, by the writer, by Dr. C. Calvo, and by Dr. H.D. Grundy.

ANALYTICAL PROCEDURES. The reagent gels were analysed by Mr. J. Muysson, using slightly modified "Rapid Methods" (Shapiro and Brannock, 1956). The crystalline phases were also analysed by Mr. Muysson, with some assistance by the writer, using essentially the same methods as were used for the reactant gels. The small size (10 mg. to 40 mg.) of the crystalline samples necessitated some changes to the standardisation and water determination procedures. Attempts to analyse the crystalline phases on the electron microprobe were unsuccessful, probably due to the intracrystalline water present.

CALCULATION OF CHARGE COMPOSITIONS. The compositions of the charges were calculated on an I.B.M. 7040 computer, from the known weights of water and gel in each charge. The program computed: a. total charge composition; b. the composition of the fluid phase, for those charges with fluid phase analyses; c. the composition of the solids in the charge, by subtraction of the fluid phase content from the total charge composition.

THE USE OF PALLADIUM BLACK IN CHARGES. About 0.5 mg. of palladium black was introduced into a number of the charges, to assist in distinguishing between the isotropic crystalline phases,on the one hand,and glass,on the other. The growing crystals excluded the palladium,which was concentrated in the glass, particularly around the crystal margins. The practice was discontinued, after its use had shown that the glasses were consistently of lower refractive index than the crystalline phases, and could be distinguished on this basis.

The errors in the chemical analyses are discussed in Appendix I, section 1, F.

CHAPTER IV

THE PROPERTIES OF THE PHASES

INTRODUCTION. Five crystalline phases were encountered in the study; nepheline, hydroxyl varieties of nosean, sodalite and cancrinite, and a phase X. A fluid phase was also present. The principal physical and chemical parameters of the crystalline phases are gathered in table 1, with photographs of the phases in figure D. X-ray diffraction data for selected specimens are presented in table App.-3. The compositions of analysed specimens are given in table App.-3, and are plotted in figure E. Comments on the specific types follow.

NEPHELINE. Nepheline is the most common crystalline substance in the join, and shows some curious phenomena. Usually free of inclusions, nepheline forms either anhedrally or as stubby prisms, in charges with compositions near the $NaAlSiO_4$-H_2O join. The forms shown on these crystals are $(10\bar{1}0)$ and (0001). No straining is seen, and the extinction is sharp. Centered interference figures are hard to obtain in these low-NaOH charges, but one seen (charge no. 515) was perfectly uniaxial. An analysis of nepheline from a charge of low NaOH content gave the composition $Na_{0.95}Al_{0.89}SiO_{3.91}(H_2O)_{0.09}$.

Nepheline formed at high NaOH concentration is markedly different. The crystals are often elongate (length/diameter varies from 1 to 5),

FIGURE D

Photographs of the Phases

a. Nepheline, nosean and fluid. Mostly nepheline, with a large nosean crystal above, and to the right of, centre. The immersion medium has a refractive index of 1.492, and the focal plane is high, so that the Becke line is inside the nepheline (R.I.≐1.534), and outside the nosean (R.I.≐1.485). The fluid is represented by the dark concentration of palladium black. X 170. Charge 583.

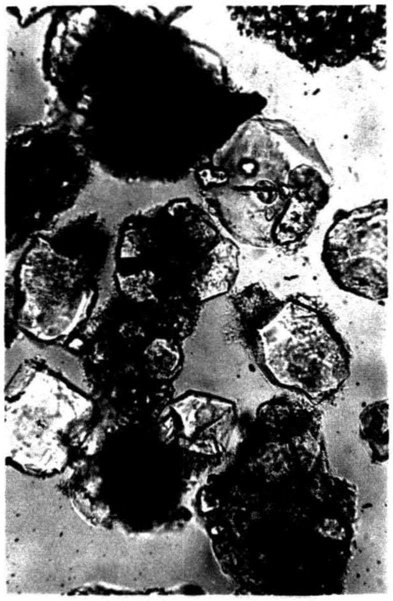
b. Nepheline (high relief) and nosean. The nepheline is unusual in containing quite a lot of inclusions, of both fluid and isotropic crystals. X 250. Charge 513.

c. Nepheline (to the left) and cancrinite. X 250. Charge 501.

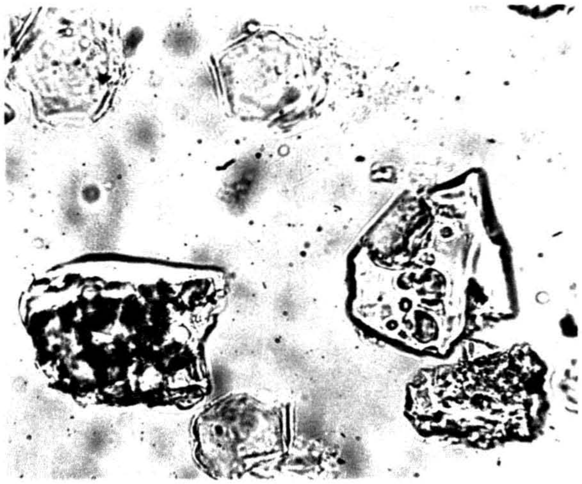
d. A core, from the centre of an aggregate of nosean, presumed to be sodalite. The grain generally resembles a glassy precipitate from the vapour phase, described by Koster van Groos (1966), but its enclosure by crystalline nosean shows that it is not a quench phenomenon. X 150. Charge 515.

e. Nosean, enclosing trains of gas bubbles. X 500. Charge 514.

f. Sodalite (subhedral, with higher relief) and cancrinite. X 100. Charge 625.



a



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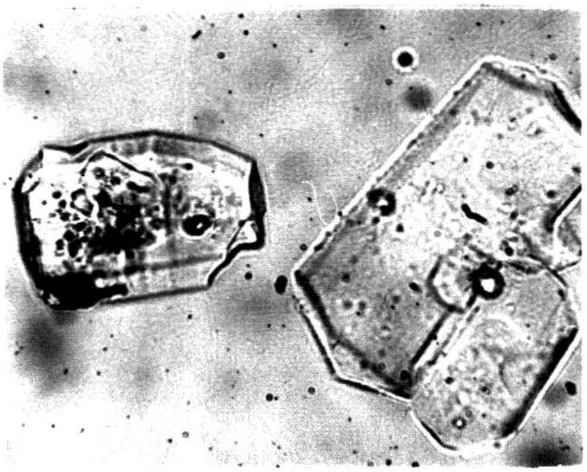

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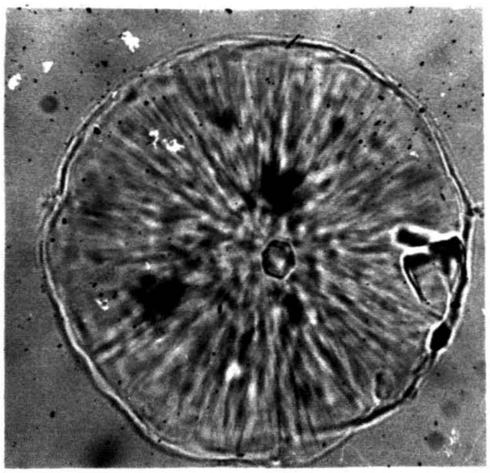
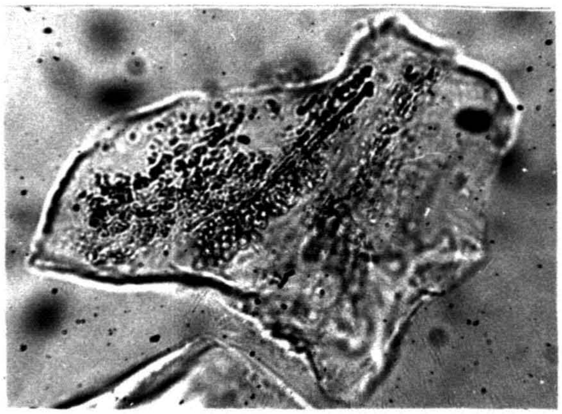
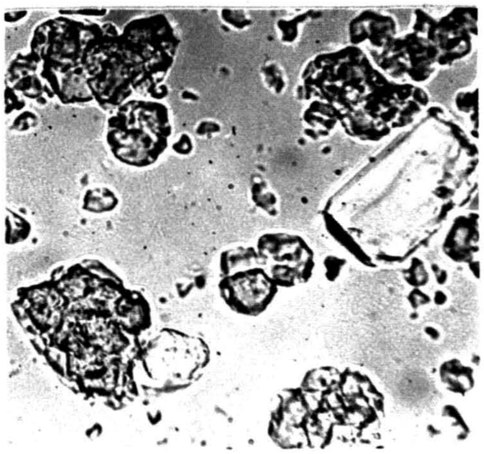


d



e



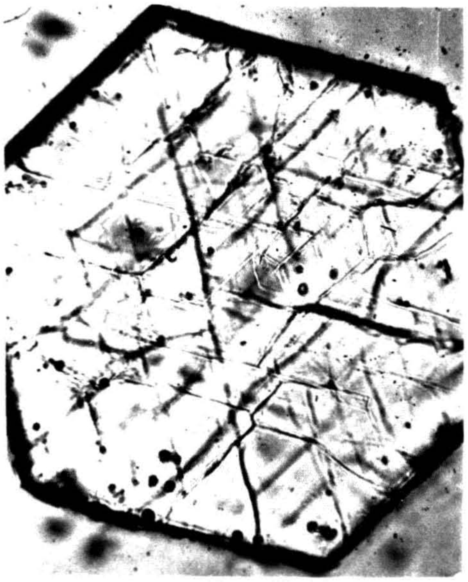
f

FIGURE D (continued)

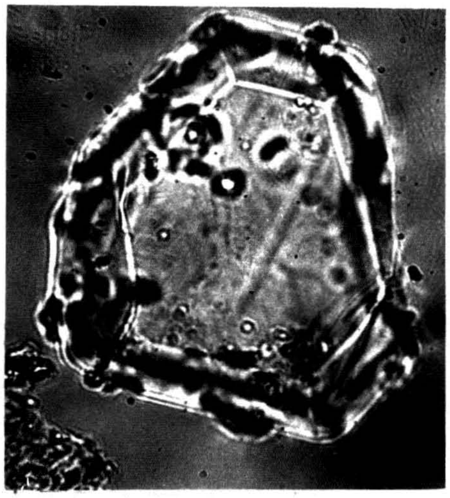
g. Nepheline (0001) face, showing prismatic cleavage. This is not the sodium-rich form of nepheline. A uniaxial figure was obtained from another crystal in this charge, no. 515. X 300.

h. Nepheline of the high-sodium type, from charge 509. This crystal gave a biaxial interference figure, with 2V estimated to be 40°. X 300.

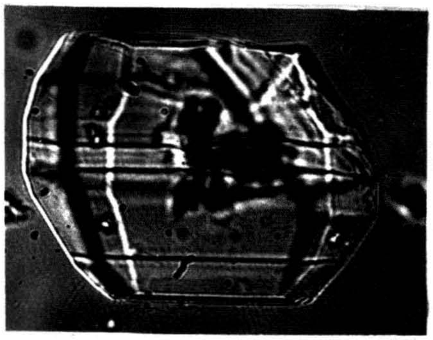
i,j, More nepheline from charge 509, showing twinning (i,j), and
k,l. cracking and strain extinction (k,l). Photographs j and l were taken with crossed polarisers. X 280.



g

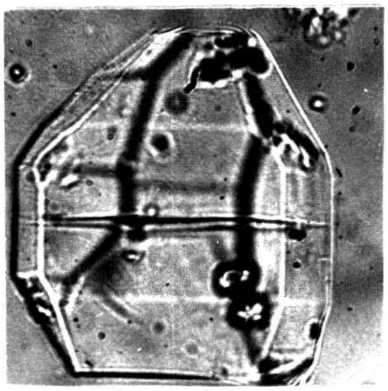


h

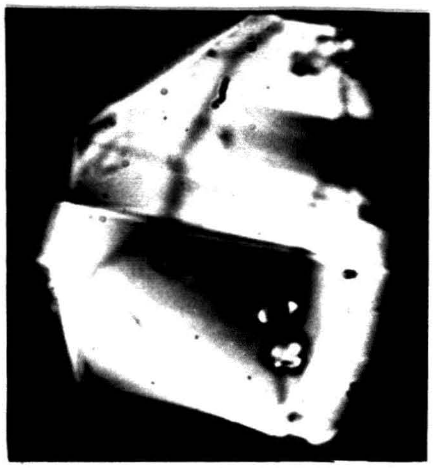


i

j



k



l

FIGURE D (continued)

m,n. Charge 582. This charge showed a much higher concentration of sodalite, as estimated from x-ray data, than did the other charges at 700°C. These photographs show three concentric zones in the palladium-covered mass:

1. an inner zone, presumed to be sodalite, with a small mass of palladium black at the centre;
2. a middle zone of nosean;
3. an outer zone of fluid.

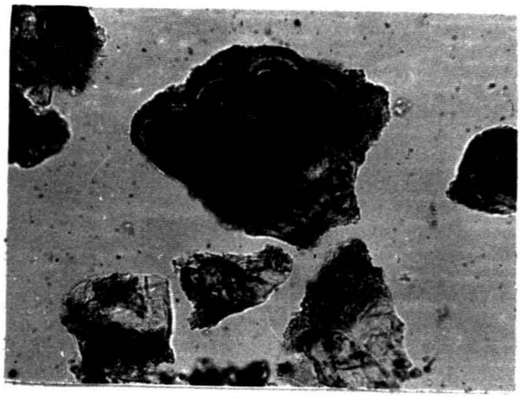
The zone boundaries are marked by Becke lines, with the outer boundary, between nosean and glass, being more clearly visible than the inner boundary, between sodalite and nosean. X 100.

o. Charge 416, on the $NaAlSiO_4$-H_2O join. The x-ray diffraction data indicates the presence of nepheline and cancrinite. The only crystal discernible is a small, anhedral nepheline, just to the left of centre. Reaction is considered to be incomplete. No palladium black was present. X 250.

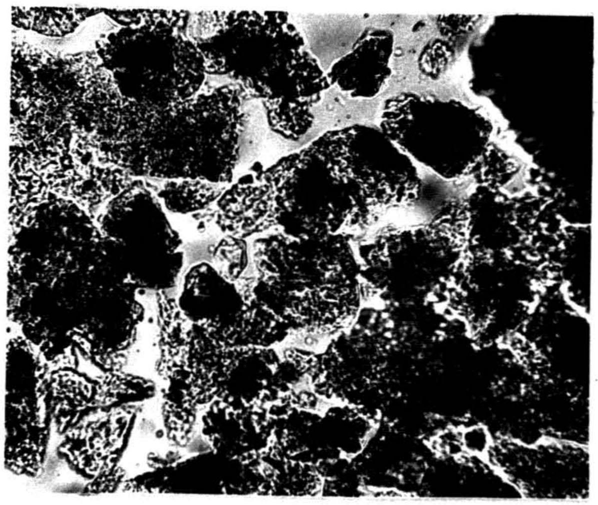
p. Nosean, with some small nepheline crystals. In some cases, nosean grew as large and flawless crystals, such as this one. X 100. Charge 514.

q. Phase X, typical. The black masses represent a fluid phase, although no palladium was present. X 100. Charge 629.

m

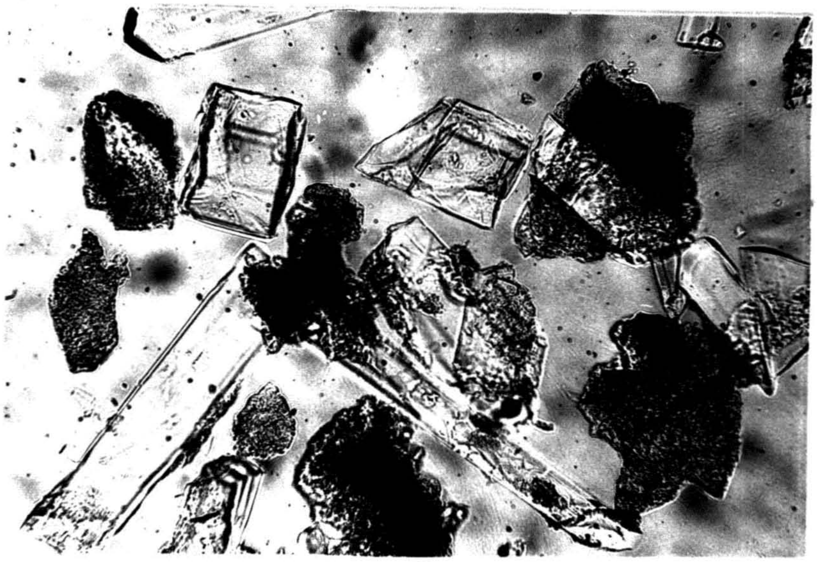


n



o

p



q

FIGURE E

Compositions of The Analysed Phases

Key:

+ ... Compositions of phases analysed in this investigation, recalculated from the data in table App.-2.

• ... The bulk compositions of the charges from which the various analysed samples came.

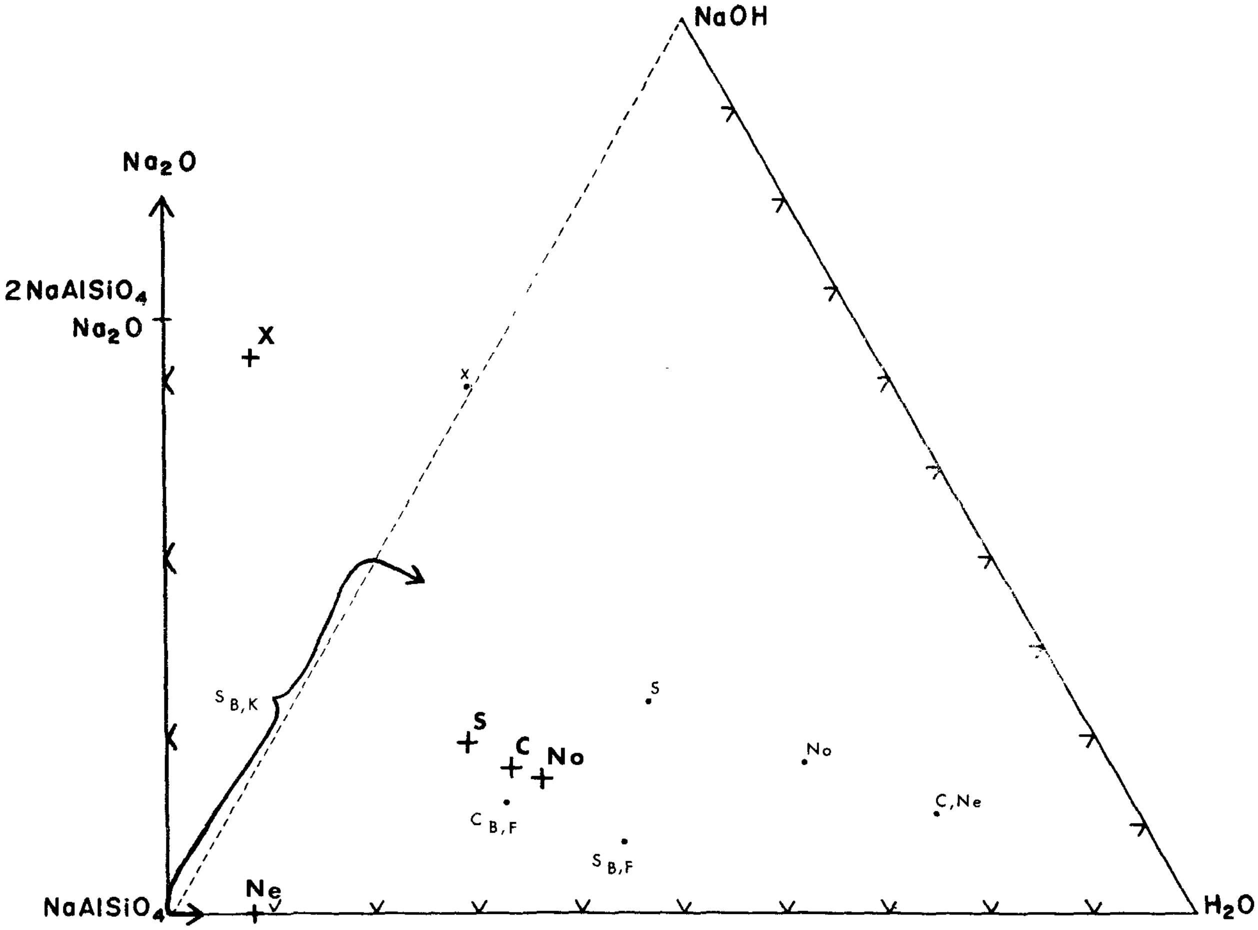
Phase	Symbol	Charge nos.	Temp. °C
Nepheline	Ne	619, 622	520
Hydroxyl nosean	No	623, 624	520
Hydroxyl sodalite	S	632, 633, 634	450
Hydroxyl cancrinite	C	619, 622	520
Phase X	X	628	600

• $S_{B,F}$ ... "Basic" sodalite, Barrer and Falconer (1956)

• $C_{B,F}$ ... "Basic" cancrinite, Barrer and Falconer (Ibid.)

• $S_{B,K}$ ... The range of hydroxyl sodalite compositions reported by Borchert and Keidel (1949a).

For the analyses of the present study, and the sodalite of Barrer and Falconer, the molecular proportions of $NaAlSiO_4$, NaOH and H_2O were calculated by ascribing one molecule of $NaAlSiO_4$ to every Si atom of the analysis. For the cancrinite of Barrer and Falconer, which had a large excess of silica, the quantity $\frac{Si+Al}{2}$ was used as the number of $NaAlSiO_4$ molecules. In all of these cases, the true compositions are somewhat off this plane, in terms of the ratio Si:Al.


NaOH
Na₂O
2NaAlSiO₄
Na₂O
X
x
S B,K
S
C
No
S
No
C B,F
C,Ne
S B,F
NaAlSiO₄
Ne
H₂O

with an acute pyramid form, perhaps $(20\bar{2}1)$, in addition to the prism and base. In extreme cases, (e.g. charge no. 509), the symmetry is clearly trigonal, with at least two pyramid forms, base and prism. Some such crystals exhibit apparent hemimorphism, with pyramids on one end differing from those on the other.

The nephelines from NaOH-rich charges show varying degrees of cracking or strain extinction. In the most severe cases of strain, there is no clear extinction at all. Some grains from such charges have cracked to form a number of irregular zones, each of which shows good extinction and no apparent strain, but which extinguishes at an angle to the extinction of the other zones. The x-ray diffraction pattern of the "trigonal" nepheline of charge no. 509 showed apparent splitting of some of the major reflections (see table App.-3, in which the reflections are listed), and smearing out of reflections below 20° of 2θ, into a single diffuse maximum. Interference figures of the same crystals were biaxial, with 2V of 30 to 40 degrees, and with the acute bisectrix lying along the trigonal $\vec{c}$ axis. The differences between the two types of nepheline are emphasised in table 2.

TABLE 1

SUMMARY OF THE PROPERTIES OF THE CRYSTALLINE PHASES

Phase / Parameter	Nepheline	Hydroxyl nosean	Hydroxyl sodalite	Hydroxyl cancrinite	"X"
Crystal sys.	Hexagonal	Cubic	Cubic	Hexagonal	Orthorhombic
Probable space group	$P6_3$*	$P\bar{4}3m$*	$P\bar{4}3n$***	$P6_32$*	$P2_12_12_1$
Cell dimensions, Å	a = **9.98 c = 8.33	9.00 to 9.04	8.895 to 8.91	12.6_8, 5.1_4	a = 12.3_3 b = 14.0^3 c = 5.0
Molecular composition, determined by analysis.	Na - 0.954 Al - 0.892 Si - 1 O - 3.905 H_2O - 0.091	Na - 1 Al - 1.04 Si - 1 O - 4.06 NaOH- 0.273 H_2O - 0.50	Na - 1 Al - 1.02 Si - 1 O - 4.01 NaOH- 0.32 H_2O - 0.32	Na - 1 Al - 0.94 Si - 1 O - 3.91 NaOH- 0.29 H_2O - 0.43	Na - 1 Al - 0.92 Si - 1 O - 3.87 Na_2O- 0.49 H_2O - 0.14
Refr. index	1.530 - 1.536	1.482 - 1.488	1.482 - 1.486	1.486 - 1.492	1.530 - 1.536
Birefringence	.004	Isotropic	Isotropic	.004	.006
Opt. sign	neg.			neg.	pos.;2V≐40°
Habit	(10$\bar{1}$0),(0001) stubby prism	Usually anhedral, sometimes globular, or six-sided outline	Usually six-sided outline, sometimes globular.	(10$\bar{1}$0),(0001) elongated usually.	euhedral, elongated.
Max. size	2 mm.	3 mm.	0.5 mm.	2 mm.	4 mm.

* The information is from Deer, Howie & Zussman (1963). ** Donnay, Schairer & Donnay (1959), low temperature sodic nepheline.

*** Lons and Schulz (1967), chloride sodalite.

TABLE 2

Comparison between nepheline from charges very rich in NaOH, and those of lower NaOH content.

Nepheline from NaOH-rich charges	Nepheline from lower-NaOH charges
Biaxial, $2V \doteq 30°$, negative.	Uniaxial, negative.
Acute strain extinction and/or cracking to zones of differing orientations.	No strain extinction, occasional cracking to zone with parallel extinction.
Multiple twinning on prismatic and basal planes.	Little twinning, most of which is on basal plane.
Reflections below 20° of 2θ are spread out to a single diffuse zone. Several major reflections appear to be split.	Diffraction pattern similar to normal nepheline, except that even a small NaOH content causes the (100,001) and (110) reflections to disappear.

The peculiarities of nepheline formed at high NaOH concentrations require further study. It evidently grows as hexagonal or trigonal crystals, as the prism angles are exactly 60° (see photographs, figure D). The diffuseness of the reflections below 20° of 2θ (110, 001, 101, 110), the splitting of other reflections and the straining and cracking, are very suggestive of inversion during the quench. Possible products of such an inversion include: Na_2O-rich cubic carnegieite, or cubic pseudonepheline (Borchert and Keidel), 1949); low carnegieite, or orthorhombic high nepheline (Smith and Tuttle, 1957). The change of the diffraction pattern of nepheline from charge no. 509 does not suggest an increase of symmetry, and cubic carnegieite and pseudonepheline do not, therefore, appear to be likely inversion products. High nepheline is normally more stable at higher temperatures than is ordinary nepheline, and the symmetry of low carnegeite is unknown.

The x-ray diffraction patterns of nepheline synthesised on, or near, the $NaAlSiO_4$-H_2O join, differed somewhat from those of nepheline crystallised in charges with about 5 mole per cent or more of NaOH. The NaOH-free nepheline gave a normal pattern, including reflections at 10.4° of 2θ (100) , and 17.7° (110), similar to that reported by Saha (1961). The presence of five mole per cent of NaOH in the charges resulted in the disappearance of the (100) and (110) reflections, all of which lie below 18° of 2θ. Barrer and White (1952), also working in the system $NaAlSiO_4$-NaOH-H_2O, report no nepheline reflections below 21° of 2θ. Their nepheline showed other similarities to that of the present study, in that most of their specimens "... formed as elongated hexagonal prisms with pyramidal ends, terminated by basal pinacoids ...", and "The larger crystals were 1 - 2 mm in length, and under crossed nicols showed a cross-hatched structure, presumably due to complex twinning.". Since such descriptions of nepheline have not been seen elsewhere, it appears that nepheline formed in the presence of NaOH has distinctive properties, not otherwise found in this substance.

HYDROXYL NOSEAN. Chemical analysis gave the composition $NaAl_{1.04}SiO_{4.06}(NaOH)_{.273}(H_2O)_{0.5}$, for a specimen of this phase. Nosean was found at 520°C, 600°C and 700°C, but not at 450°C, and was usually more or less anhedral. When present, it generally constituted the largest grains in the charge. In many charges, nosean was visibly zoned, with an inner zone of slightly, but distinctly, lower refractive index than that of the outer zone of nosean. Many of the noseans which were not seen to be zoned,may have been zoned in fact, since the phenomenon involved two isotropic phases of very similar refractive indices. In other cases, aggregates of nosean enclosed small spherical cores, which had a nepheline crystallite, or a linear or three-pronged crack, at the centre; figure D, d, is a photograph of such a core. For reasons enumerated in the next chapter, these isotropic inner zones and cores in nosean are presumed to be sodalite. Nosean also frequently enclosed considerable quantities of nepheline or phase X.

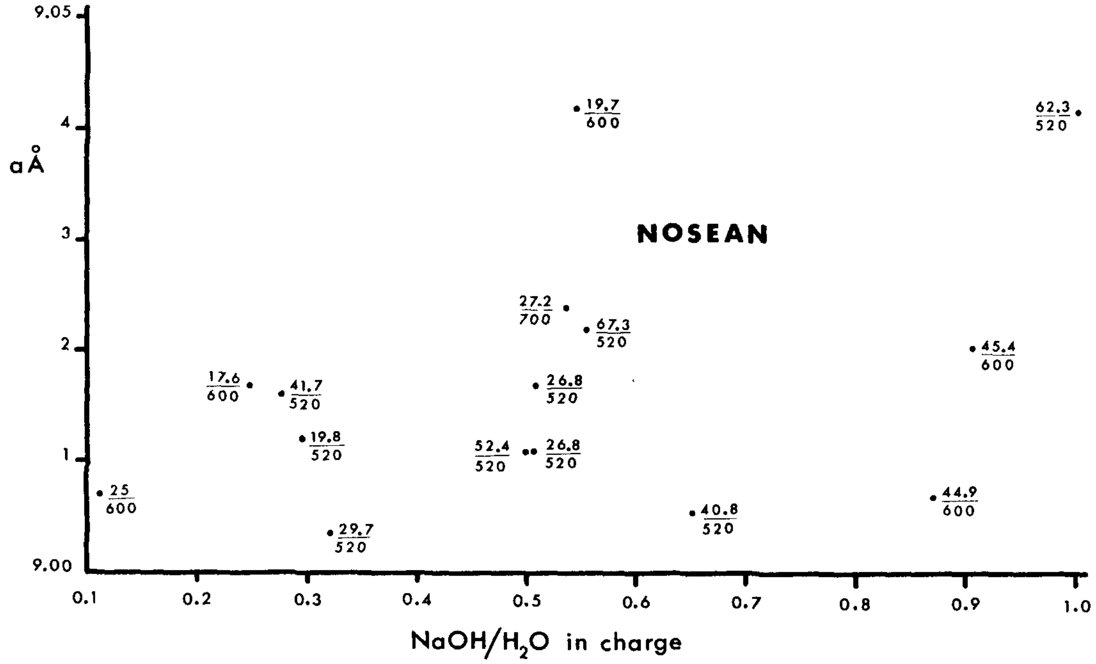
Figure F shows the variation of nosean and sodalite cell parameters, plotted against the molar ratio $NaOH/H_2O$ of the appropriate charges. The cell parameter changes were not correlated with variation of charge composition or temperature.

HYDROXYL SODALITE. The sodalite of this system is almost indistinguishable from the nosean; the small differences of d-spacings, seen in the otherwise virtually identical diffraction patterns, is the only clear criterion for distinguishing one from the other. Evidence from charges at 450°C, from which nosean was absent, suggest that sodalite tends to be more euhedral than does nosean, but optical methods were inadequate for positive identification of individual grains, in mixtures of the two. The outline of sodalite is usually six-sided, being similar to a (110) section of a dodecahedron. Sodalite was found over the whole range of temperatures investigated, but the evidence indicates that it is unstable, at and above 520°C (see next chapter). Chemical analysis of a single specimen gave the composition $NaAl_{1.02}SiO_{4.01}(NaOH)_{0.32}(H_2O)_{0.32}$.

FIGURE F

Cell Parameters of Hydroxyl Nosean and Hydroxyl Sodalite

The method of measurement is described in Appendix I, section 1. The length of the cell edge of each sample is plotted against the molecular ratio $NaOH/H_2O$ of the charge from which it came. Against each point are two numbers, separated by a horizontal line; the upper number is the molecular percentage of $NaAlSiO_4$ in the charge, and the lower number is the temperature (in °C) at which the sample was synthesised. No correlation, between cell parameters and these other variables, was recognised.


NOSEAN
aÅ
9.05
4
3
2
1
9.00
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
NaOH/H₂O in charge
19.7/600
62.3/520
27.2/700
67.3/520
45.4/600
17.6/600
41.7/520
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19.8/520
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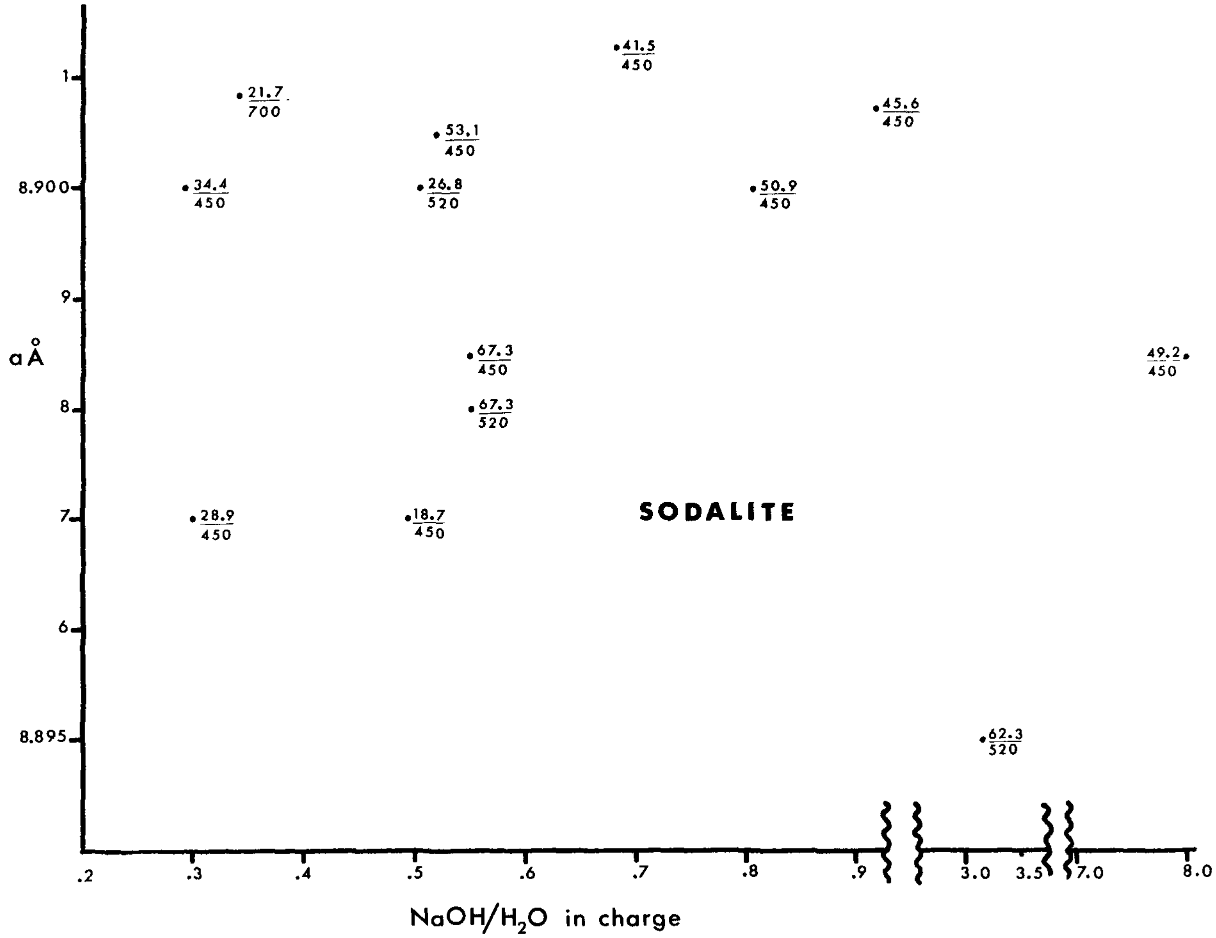
44.9/600
40.8/520
29.7/520


SODALITE
aÅ
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8.900
9
8
7
6
8.895
.2
.3
.4
.5
.6
.7
.8
.9
3.0
3.5
7.0
8.0
NaOH/H₂O in charge
41.5/450
21.7/700
53.1/450
45.6/450
34.4/450
26.8/520
50.9/450
67.3/450
49.2/450
67.3/520
28.9/450
18.7/450
62.3/520

Sodalite, like nosean, commonly contained large quantities of inclusions of fluid, X or nepheline.

Hydroxyl sodalite has received more attention from other workers than have hydroxyl nosean and hydroxyl cancrinite, particularly by Barrer and White (1952), Barrer and Falconer (1956) and Borchert and Keidel (1949a). The compositions quoted by these authors are plotted in figure E. The estimation of composition by Borchert and Keidel is poorly founded, the assumption being that reaction was complete, the bulk compositions of charges therefore representing the compositions of the sodalites formed. There were, apparently, no attempts made to confirm by optical means that reaction was complete, and no precautions appear to have been taken to protect the highly alkaline charges from CO_2 absorption. The absence of foreign lines on x-ray powder photographs was the criterion of complete reaction. By comparison: in the present study, although charges near the $NaAlSiO_4$-H_2O join were reacted for two to three weeks at 450°C and 520°C, at P_{H_2O} of nearly 15,000 p.s.i. (those of Borchert and Keidel were dry, and reacted for about 30 hours), reaction still appeared to be largely incomplete, with much remnant material of micron size. The only evidence of this fine material on the x-ray diffraction patterns was a general reduction of the intensities of the reflections from the crystalline phases. Incomplete reaction in these charges was further indicated by the results of the fluid phase analyses (see next chapter).

The sodalite composition reported by Barrer and Falconer is based on chemical analysis, and is considerably more hydrous, and less sodic, than that obtained by the writer. The difference of composition probably arises from the difference of pressure and temperature of formation; Barrer and Falconer synthesised sodalite at 100°C and 1 atmosphere, while that of the present study was formed at 450°C and 15,000 p.s.i. The reagents were similar, in the two cases.

THE NOMENCLATURE OF HYDROXYL SODALITE AND HYDROXYL NOSEAN. "Sodalite" and "Nosean" are terms which, in general usage, connote two natural mineral types differing in chemical composition, refractive index, density, etc. In the last forty years, a difference of cell size has also been associated with the two species. In the present study, the only incontrovertible distinction between hydroxyl nosean and hydroxyl sodalite is one of cell size, and other authors have not specified any further criterion which they used for distinguishing between these two synthetic phases. No similar phase, with cell size intermediate between those of hydroxyl nosean and hydroxyl sodalite, has been reported. Thus, the borrowing of the terms "sodalite" and "nosean" for these synthetic analogues is justified by the following:

a. The hydroxyl and natural forms have closely analogous chemical compositions, and generally similar physical properties.

b. The x-ray diffraction patterns of the natural and synthetic forms are very similar.

c. The hydroxyl analogues are not mutually soluble, in the range of conditions in which they have been studied, as has been shown for synthetic sulphate and chloride forms.

With the exception of the last, these are also the facts on which the naming of hydroxyl cancrinite is based.

HYDROXYL CANCRINITE. This phase grew at 450°C and 520°C, and was more specifically associated with charges of high water content, than were any of the other phases. Analysis of a specimen gave the composition $NaAl_{0.94}SiO_{3.91}(NaOH)_{0.29}(H_2O)_{0.43}$, which is very close to that of nosean, and not very different from that of sodalite. The analysis total was 95.5 per cent (see table App.-2), and since the water determination was the least reliable part of the analysis, the actual composition was probably more hydrous.

Cancrinite was subhedral to euhedral, showing $(10\bar{1}0)$ and (0001) forms only. The ratio length:diameter was about 2:1 in the less hydrous charges, and up to 5:1, in charges with about 60 per cent, or more, of water. Hydroxyl cancrinite was usually free of inclusions, but was often coated with rounded nepheline grains of ten to thirty microns diameter.

PHASE X. Chemical analysis of a sample gave the composition $NaAl_{0.92}SiO_{3.87}(Na_2O)_{0.49}(H_2O)_{0.14}$. This phase grew in charges on, and between, the $NaAlSiO_4$-Na_2O and $NaAlSiO_4$-NaOH joins, normally in the form of long, prismatic crystals, with length;thickness ratio of 5:1 to 10:1. X is stable over the whole temperature range of the study.

Density determinations gave a value of 2.5_2, and preliminary single-crystal x-ray studies indicate the orthorhombic cell parameters to be a=12.3Å, b=14.0Å, c=5.0Å, the cell volume being approximately 860Å^3, and the space group $P2_12_12_1$. The chemical analysis results, neglecting the small amount of water present, approximate to the formula $Na_4Al_2Si_2O_9$; using this formula, the unit cell contains 3 3/4 ($\doteq$ 4) formula units.

The acute bisectrix of X lies along $\vec{c}$, the axis of elongation, so that acute bisectrix figures are hard to obtain. Only three such figures were seen, and indicated a 2V of about 40°, and positive optical sign. The birefringence is low, about 0.004, and no dispersion is immediately discernible. Twinning appears to be entirely absent.

An extensive search of the literature has been made, to identify this phase with a known compound; no such correspondence has been found. Borchert and Keidel (1949a,b) reported an alpha-carnegeite-like phase of the same composition ($Na_4Al_2Si_2O_9$), but, apart from the shortcomings of these writers' compositional information, there is little chance of confusion of the cubic and orthorhombic lattices. Why they did not synthesise X, is not understood, since this phase grew comparatively quickly in the present study. X may be stable only at pressures greater than 1 atmosphere.

FLUID PHASE. The fluid phase observed was of watery consistency, in charges of lower sodium hydroxide content. At high NaOH concentrations, the fluid phase was a greyish translucent glass, largely soluble in water; the increase in viscosity is presumably due to the increased quantities of aluminum and silicon in solution. The refractive indices of the quenched glasses were about 1.47, but were generally difficult to measure, owing to attack of the exposed edges, probably by CO_2 and H_2O. Specific evidence of fluids of intermediate viscosities was not seen; such fluids would be difficult to detect, since the presence of NaOH necessitates washing of the charge contents, before microscopic examination.

CHAPTER V

THE GENERAL PHASE RELATIONSHIPS

EXPERIMENTAL RESULTS IN THE ISOTHERMAL SECTIONS. Figures G, H, I and J show the experimental results in isothermal sections of the plane $NaAlSiO_4$-$NaOH$-H_2O, at 15,000 p.s.i. total pressure. The plane is extended to include the point $2NaAlSiO_4.Na_2O$, because of the occurrence of phase X in this added segment. The detailed data for the individual charges is given in table App.-4. In these diagrams, the points representing the compositions of charges with similar phase assemblages are joined or enclosed by lines, for clarity of display. The presence of a fluid phase is shown in the diagrams only where it constituted most, or all, of the charge; it is very doubtful that any of the charges were entirely without fluid phases, at the end of the reaction period.[1]

GENERAL RELATIONSHIPS IN THE ISOTHERMAL SECTIONS. While the relationships in the isothermal sections are difficult to interpret in detail, the following general tendencies are well-defined:

a. Hydroxyl cancrinite was not formed above 520°C.

---

[1] The preparation of the charges for optical examination tended to obliterate traces of a fluid phase, but positive evidence of the presence of this phase was found in all charges subjected to fluid phase analysis.

FIGURE G

Experimental Results at 450°C, 15,000 p.s.i. total pressure

Symbols:

• ..... The plotted composition of a single charge

⊙ ..... The composition of the analysed crystalline phases, taken from figure E.

Ne ..... Nepheline

No ..... Hydroxyl nosean

C ..... Hydroxyl cancrinite

S ..... Hydroxyl sodalite

X ..... Phase X

F ..... Fluid phase. This is shown only when it constituted most, or all, of the equilibrium assemblage.

All points representing charges with the same crystalline assemblage, are joined, or enclosed, by straight lines.

Nepheline, X, hydroxyl sodalite and hydroxyl cancrinite form in this section. The area near the $NaAlSiO_4$-H_2O join probably represents incomplete reaction, as these charges contained a preponderance of very fine grained material, which did not appear to be crystalline. Also, the proportion of cancrinite in these low-NaOH charges as estimated from the x-ray results, increases towards the $NaAlSiO_4$ vertex, contrary to the behaviour to be expected, considering the compositions of these phases.

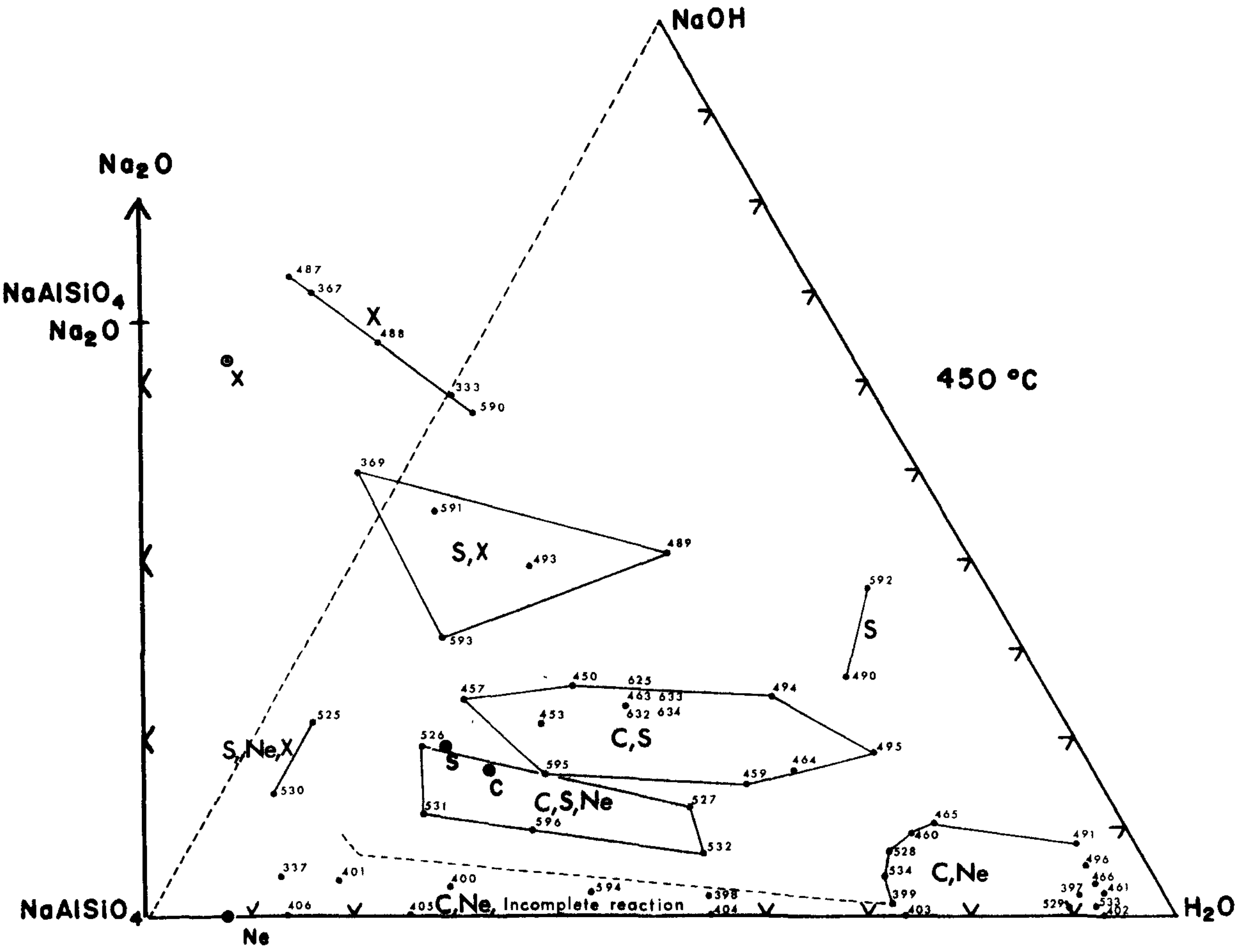

NaOH
Na$_2$O
2NaAlSiO$_4$·Na$_2$O
450 °C
X
487
367
488
333
590
369
591
S,X
493
489
593
592
S
490
457
450
625
463 633
632 634
494
453
C,S
495
525
S,Ne,X
530
526
S
C
595
459
464
C,S,Ne
527
531
596
532
465
460
491
528
534
C,Ne
496
466
399
397
461
529
533
402
403
337
401
400
594
398
406
405
C,Ne, Incomplete reaction
404
NaAlSiO$_4$
Ne
H$_2$O

FIGURE H

Experimental Results at 520°C, 15,000 p.s.i. total pressure

The symbols are the same as those of figure G.

All five crystalline phases are found at this temperature. As in the case of the 450°C section, charges near the $NaAlSiO_4$-H_2O join represent incomplete reaction.

Sodalite was found in many of the charges which contained nosean, but in erratically varying amount, and is denoted by the symbol (S). Charge no. 536 was unusual, in that it contained two visually distinguishable types of homogeneous isotropic crystals: a few, large and anhedral; many, small and six-sided in outline. The former were assumed to be nosean, and the latter, sodalite, because of the similarity of form of these smaller crystals, to known examples of sodalite at 450°C. The refractive indices of all of the isotropic crystals was 1.485±0.001, but the diffraction pattern indicated that nosean and sodalite were present in similar quantity.

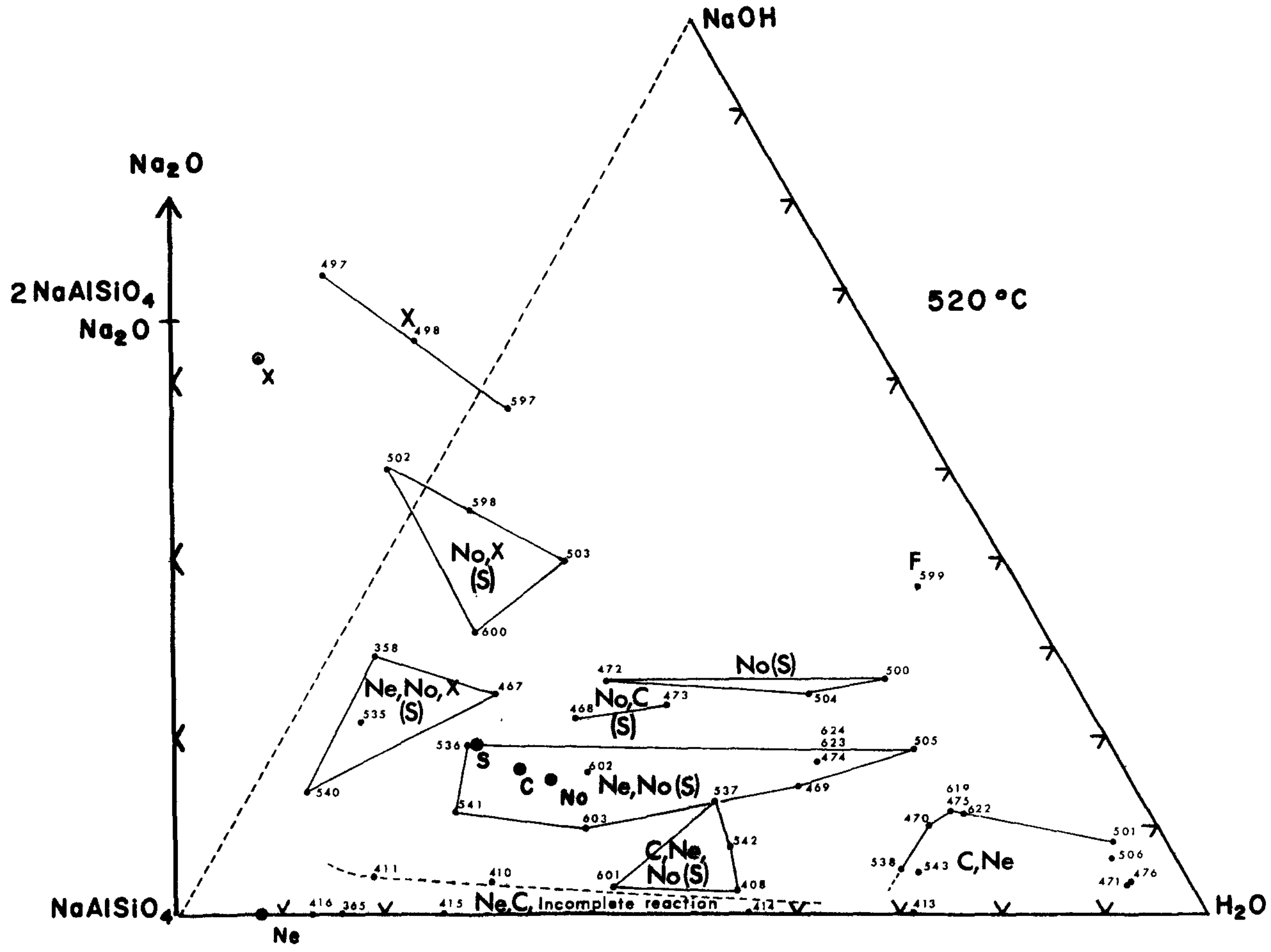

NaOH
Na_2O
$2NaAlSiO_4$
Na_2O
520 °C
X
497
498
597
X
502
598
503
No,X
(S)
600
F
599
358
467
Ne,No,X
(S)
535
540
472
500
No(S)
504
468
No,C
(S)
473
536
S
624
623
505
474
C
No
602
Ne,No(S)
537
469
541
603
619
475
622
470
501
542
C,Ne,
No(S)
538
543
C,Ne
506
476
471
411
410
601
408
416
365
415
Ne,C, Incomplete reaction
412
413
$NaAlSiO_4$
Ne
H_2O

FIGURE I

The Experimental Results at 600°C, 15,000 p.s.i. total pressure

The symbols are the same as those of figure G.

Cancrinite was not found at this temperature, but sodalite again was found in several occurrences of nosean. Charge no. 509 contained nepheline which is described in chapter IV.

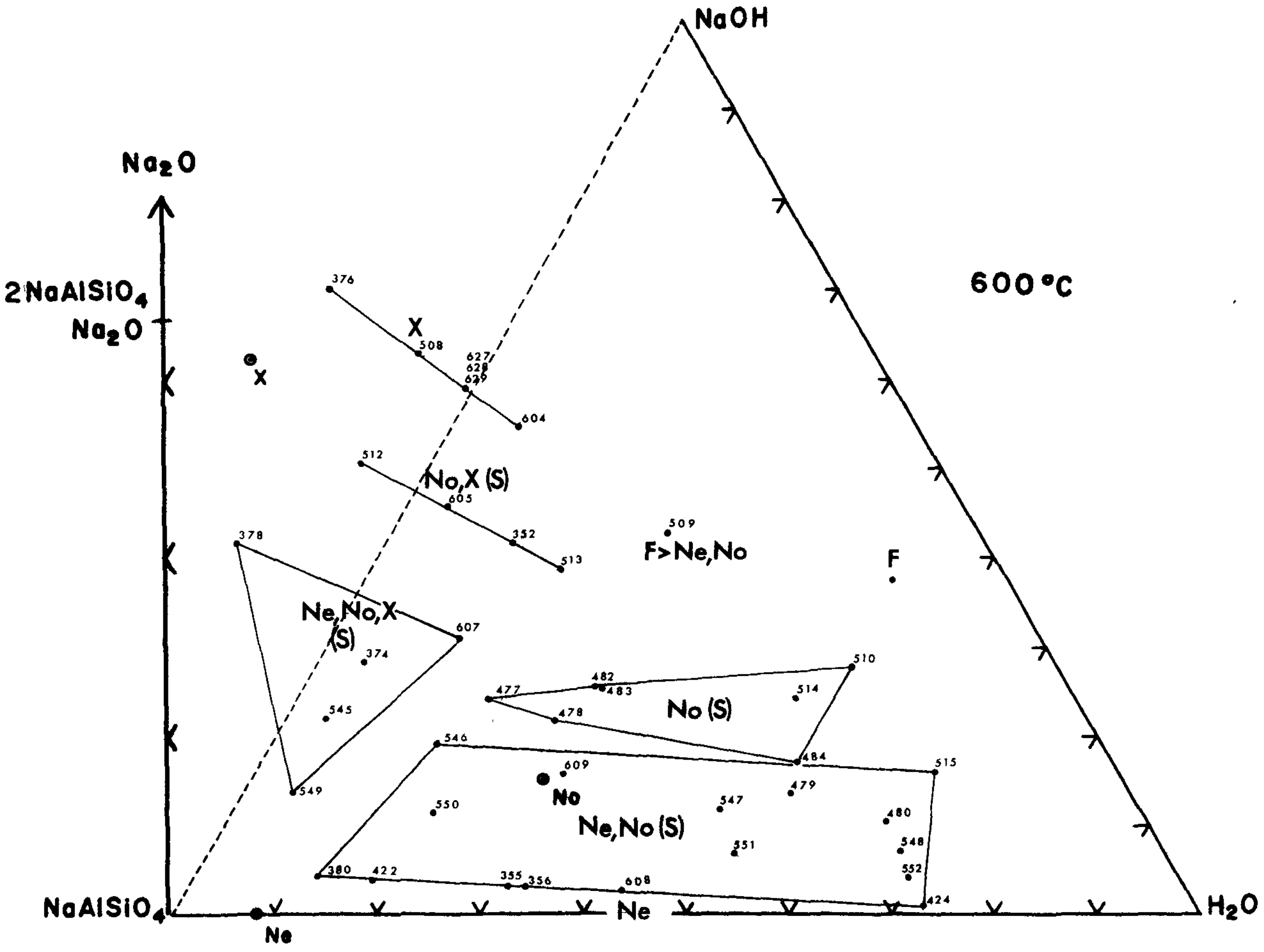
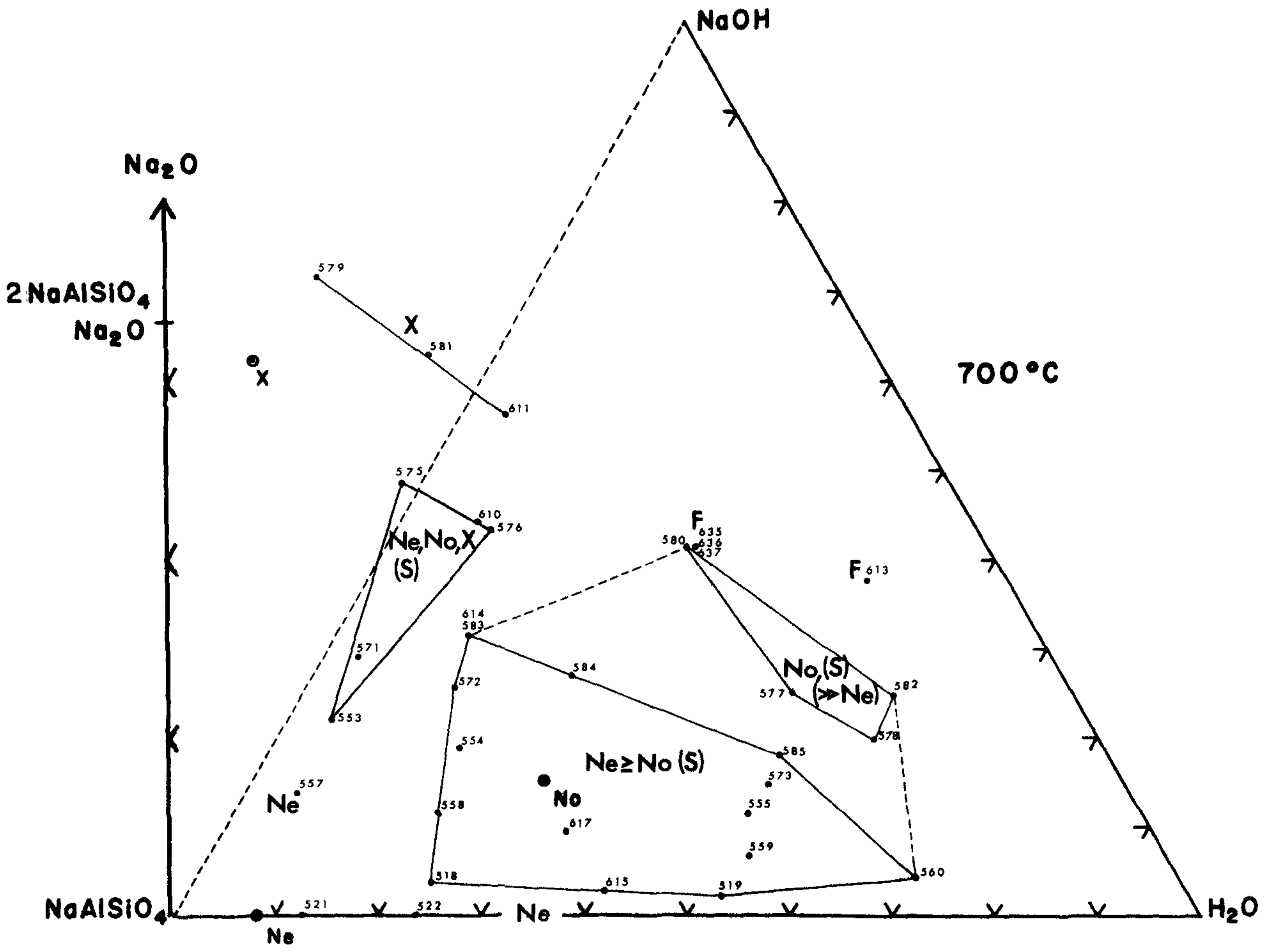

NaOH
Na$_2$O
2NaAlSiO$_4$
Na$_2$O
600 °C
X
376
508
627
628
629
604
512
No,X (S)
605
352
513
509
F>Ne,No
F
378
Ne,No,X
(S)
607
374
545
549
477
482
483
478
510
514
No (S)
546
484
515
609
No
550
479
547
Ne,No (S)
480
548
551
552
380
422
355
356
608
424
NaAlSiO$_4$
Ne
Ne
H$_2$O

FIGURE J

The Experimental Results at 700°C, 15,000 p.s.i. total pressure

The symbols are the same as those of figure G.

The data at this temperature generally resembles that at 600°C, except that nepheline was found in all charges but those containing fluid only, or X + fluid only. Charge no. 582 showed some of the most striking examples of zoning seen in nosean, and a photograph of a grain from this charge is shown in figure D. Owing to breakdown of the temperature control system, charges no. 635, 636 and 637 were reacted at 710°C, but are included to show the proximity of the liquidus to charge no. 580.


NaOH
Na_2O
$2NaAlSiO_4$
Na_2O
X
700 °C
579
X
581
611
575
610
576
Ne,No,X
(S)
F
580
635
636
637
F
613
614
583
584
571
572
553
No,(S)
(≫Ne)
577
582
578
554
Ne≥No (S)
585
573
557
Ne
No
558
555
617
559
518
615
519
560
$NaAlSiO_4$
521
522
Ne
H_2O
Ne

b. Hydroxyl nosean was found at 520°C and above, but not at 450°C, at which temperature it was presumed to be unstable.[1]

c. Hydroxyl sodalite is found as a major stable phase at 450°C, but at 520° and above, it is almost always a minor constituent of the charges, with the actual proportions varying erratically.

d. The chemical analyses of all three hydroxyl felspathoids are very similar, but the obvious association of the cancrinite with high water concentrations suggests that this phase is more hydrous than the others, at the conditions of reaction.

e. Nepheline occurs at all temperatures of the investigation, appearing in charges of progressively higher NaOH content, as the temperature increases.

f. There is only one fluid phase, in the range of conditions studied.

QUENCH PHASES. Little evidence of phases formed during the quenching process was seen. In some of the charges, a very thin layer of extremely fine-grained material covered the much larger grains of the stable phases, and some of the glasses contained wisps of anisotropic matter.

---

[1] This is in accord with earlier results (Anderson, 1963), also at 15,000 p.s.i., in which hydroxyl nosean was found at 480°C, but not at 460°C. Other studies (Edgar, 1961; van Peteghem, 1961), on sulphate and carbonate noseans, gave comparable results.

THE INCLUSION OF PHASES. The pronounced ability of nosean and sodalite to enclose early-formed phases is a source of potential disequilibrium. These two phases commonly enclosed large quantities of nepheline and X, possibly preventing later equilibration of the enclosed phases with the fluid phase.

KINETIC EFFECT EXPERIMENTS. Charges numbered 550, and 638 to 647 inclusive, were of closely similar composition, and were reacted for differing lengths of time, at 600°C. (550 is the only number shown for this composition, in figure I.) Estimating the presence and quantities of the phases from the diffraction patterns, the short reaction periods (1 to 100 hours) produced nepheline, nosean and sodalite in similar quantities; longer reaction times produced nepheline and nosean, with very little sodalite. The results were:

Reaction time :	1 hour	3 hours	18 hours	4 days	20 days
Crystalline phases present :	Ne,No,S	Ne,No,S	Ne,No>S	Ne,No>S	Ne,No>>S
Grain size of the phases :	≤ 10u	≤ 10u	≤ 50u	≤ 100u	≤ 1mm.

These results clearly establish that sodalite is slow to break down at this temperature, pressure and composition, and strongly suggest that it is not stable at these conditions. Twenty days is a typical reaction period for the whole set of experiments.

THE ANOMALOUS OCCURRENCE OF SODALITE. Several lines of evidence indicate that sodalite is entirely unstable in this system, at 520°C and above:

a. At and above 520°C, sodalite appears in variable quantity with many of the occurrences of nosean. Sodalite was not detected where the nosean was highly recrystallised, to grains of a millimetre or so in size. X-ray powder photographs of several of these large grains of nosean, separately ground and mounted, showed no sodalite reflections.

b. No field of sodalite by itself, or of sodalite + fluid, was found, except in the 450°C section.

c. At 520°C and above, there are fields of five phases, if sodalite is included, such as that of nepheline + nosean + X + fluid + sodalite, at 700°C. This violates the phase rule for quaternary equilibrium[1], in which the maximum number of phases in divariant fields is four. Of the five phases, sodalite is the only one with no definable field of stability, at these temperatures.

d. All charges passed through the temperature range of sodalite stability, during the initial heating to reaction temperature, and there was some sodalite structure present in the reactant gels.

---

[1] Neglecting the small quantities of air and CO_2 in the capsules, the charges contained Na, Al, Si and H, with enough oxygen to satisfy all these elements. It is exceedingly unlikely that there can be more than four components in the system.

e. The set of kinetic-effect experiments demonstrated that early-formed sodalite breaks down slowly, at 600°C.

f. The coring in nosean offers an explanation of the persistence of sodalite; if these cores are composed of sodalite, then this sodalite is isolated from reaction with the fluid phase.

It appears that, in many of the charges heated above 450°C, sodalite forms during the process of bringing the charges to the reaction temperature, probably often as spheroidal grains[1]. This sodalite then becomes encased in nosean, when that phase begins to grow. Further reaction between sodalite and fluid is impeded, with consequent preservation of sodalite. Charge no. 536, at 520°C, afforded some evidence that sodalite was present in contact with the fluid phase, but there is no field of sodalite itself, at that temperature. There may be a field of sodalite just below this temperature, so that the process of breakdown to form nosean is slow, despite contact between sodalite and fluid. This is consistent with the fact that the bulk composition of charge no. 536 is very close to that of sodalite.

THE WIDESPREAD OCCURRENCE OF NEPHELINE AT HIGHER TEMPERATURES. At 600°C and 700°C, nepheline is found at the NaOH-rich liquidus. This is difficult to explain on the basis of the ternary system, in view

---

[1] Barrer and Falconer (1956) formed spheroidal grains of hydroxyl sodalite from gels at 100°C, and 1 atmosphere.

of the analysed compositions of the crystalline phases, and the geometric limitations of the ternary phase diagram. Two aspects of this phenomenon are:

a. As the temperature increases from 450°C to 700°C, nepheline is found over an increasing area of the plane $NaAlSiO_4$-$NaOH$-H_2O, coexisting with nosean and fluid at the highly-sodic parts of the liquidus at 600°C and 700°C, but not at 450°C and 520°C (figures G,H.I and J). At 600°C, a field of nosean + fluid was found, but at 700°C, nepheline was found in all assemblages except that of X + fluid.

b. The nepheline from these higher temperature, sodium-rich charges was euhedral, in relatively large grain size. It was deficient in certain x-ray reflections (see chapter IV), and showed strain phenomena suggestive of inversion during the quench. Since the last two properties are not shared by nepheline reported from other systems (see, for example, Saha, 1961; Smith and Tuttle, 1957), it presumably reflects some deviation from the formula $NaAlSiO_4$, other than the well-known and common excess of SiO_2.

It appears, from the above, that the plane $NaAlSiO_4$-$NaOH$-H_2O is quaternary, at the higher temperatures. If the plane were ternary, the growth in the stability fields of nepheline should cause displacement of the fields of stability of the other phases; that this does not happen, is strong evidence for a quaternary condition of the system, at these temperatures.

It also appears from the foregoing that, with increasing temperature, nepheline is capable of accommodating increasing amounts of a component which has a high activity in the system $NaAlSiO_4$-$NaOH$-H_2O, but not in "natural" systems, and which causes the nepheline to become unstable on cooling. An obvious component for this role is NaOH, in view of the high sodium and water[1] content of the analysed specimen of nepheline, and the probability that natural environments do not contain such high NaOH concentrations.

THE FLUID PHASE ANALYSES. The details of the analytical method are given in Appendix 1, section C, and the results are shown in figure K. Sixty such analyses were made, but only 36 of these were accepted; subsequent optical examination showed, in many of the cases of rejection, that substantial amounts of glass remained with the solid phases. Several of the analyses merely confirmed the incomplete reaction near the $NaAlSiO_4$-H_2O join, at 450°C and 520°C.

The determined quantities of sodium and water are expressed as points on the $NaOH$-H_2O join, and the bulk compositions of the charges are shown. The "bulk compositions of the solid phases" were calculated, by subtracting the sodium and water of the fluid phases from the total compositions of the several charges, and plotted on the diagram. These analyses were originally made in an attempt to derive the compositions of the solid phases, before the latter were themselves analysed.

---

[1] The water content of nepheline from charges 619 and 622 was determined as 2.2 weight per cent, in contrast with 1.57 per cent, which is the highest value quoted for natural nepheline in D.H.Z. The determined water may represent (OH), as well as H_2O.

FIGURE K

The Fluid Phase Analyses

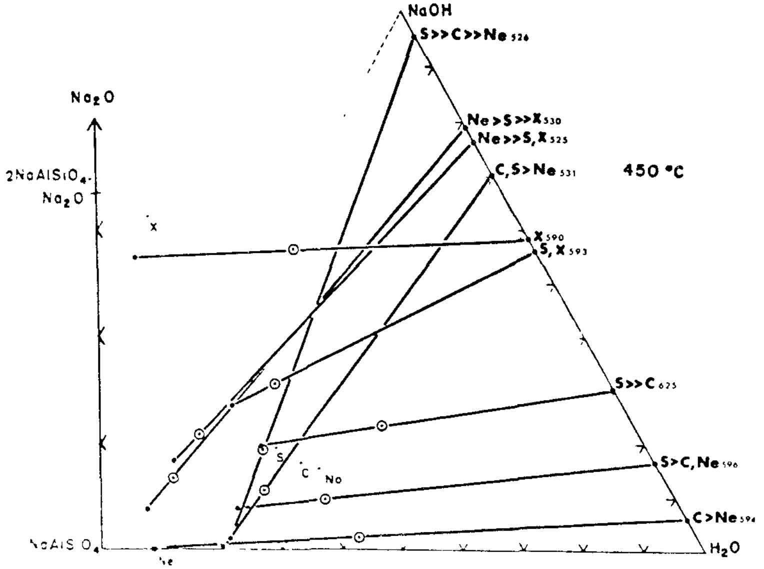
The method of analysis is described in Appendix I, section 1, and the numerical data is in table App.-5. The results of the sodium and water determinations are shown as points on the $NaOH-H_2O$ join; to the left of each of these points, the crystalline assemblage and number of the charge is shown. The bulk compositions of the charges are indicated, as are the "bulk compositions of the solid phases", the latter being obtained by subtracting the sodium and water content of the fluid phase from the bulk compositions of the charges. The three points for each charge are connected by a straight line, which has no other significance. Those charges for which the "bulk compositions of the solid phases" are plotted off the left hand sides of the diagrams, showed a greater loss of weight, on dehydration, than the weight of water originally in the capsule. The excess of water was very small, in all such cases, and probably represents a slight uptake of water during the reaction. The fluid phase compositions should not be noticeably affected.

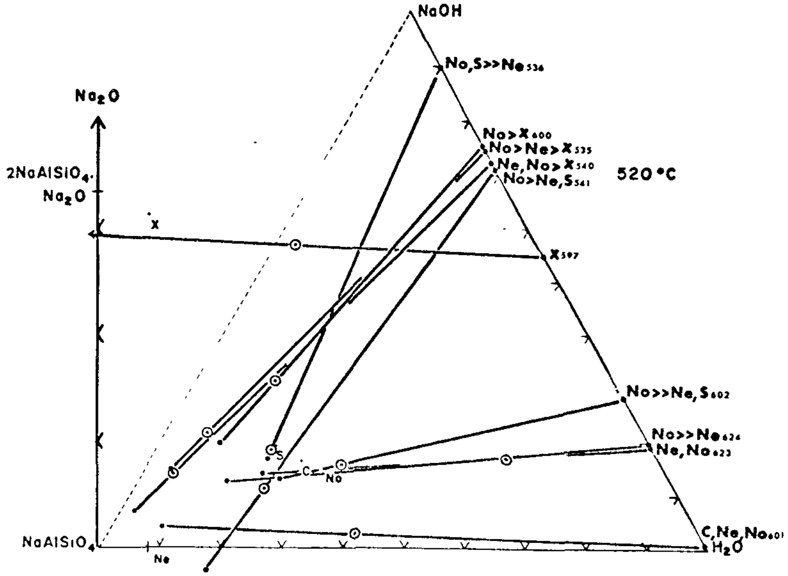
Key:

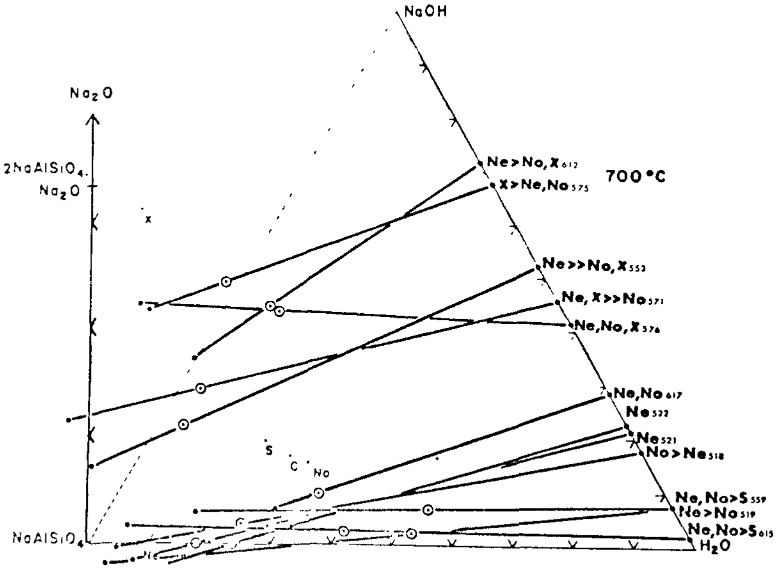
⊙ .... Bulk composition of the charge

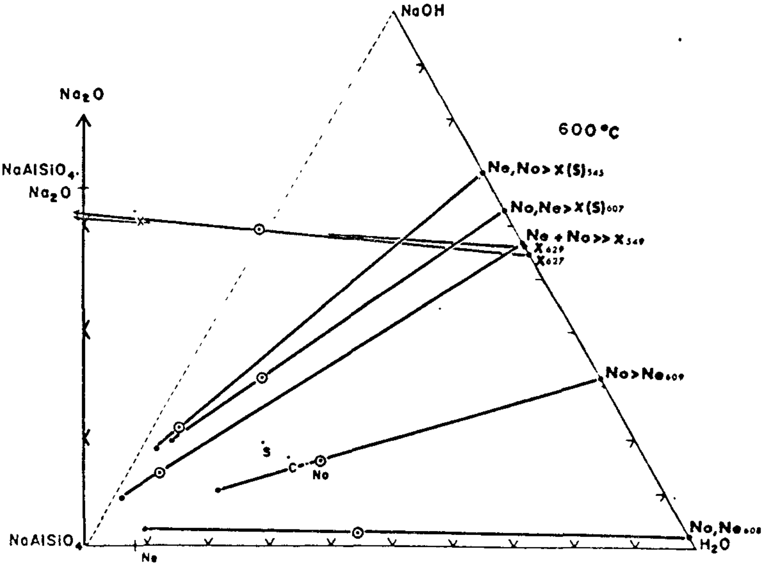
● .... "Bulk composition of the crystalline phases"

● .... Analysed compositions of the fluid phases, from figure E.


450 °C
NaOH
Na_2O
$2NaAlSiO_4 \cdot Na_2O$
$NaAlSiO_4$
H_2O
S>>C>>Ne$_{526}$
Ne>S>>X$_{530}$
Ne>>S,X$_{525}$
C,S>Ne$_{531}$
X$_{590}$
S,X$_{593}$
S>>C$_{625}$
S>C,Ne$_{596}$
C>Ne$_{594}$
X
S
C
No
Ne


520 °C
NaOH
Na_2O
$2NaAlSiO_4 \cdot Na_2O$
$NaAlSiO_4$
H_2O
No,S>>Ne$_{536}$
No>X$_{600}$
No>Ne>X$_{535}$
Ne,No>X$_{540}$
No>Ne,S$_{541}$
X$_{597}$
No>>Ne,S$_{602}$
No>>Ne$_{624}$
Ne,No$_{623}$
C,Ne,No$_{601}$
X
S
C
No
Ne


700 °C
NaOH
Na_2O
$2NaAlSiO_4 \cdot Na_2O$
$NaAlSiO_4$
H_2O
Ne>No,X$_{612}$
X>Ne,No$_{575}$
Ne>>No,X$_{553}$
Ne,X>>No$_{571}$
Ne,No,X$_{576}$
Ne,No$_{617}$
Ne$_{522}$
Ne$_{521}$
No>Ne$_{518}$
Ne,No>S$_{559}$
Ne>No$_{519}$
Ne,No>S$_{615}$
X
S
C
No


600 °C
NaOH
Na_2O
$2NaAlSiO_4 \cdot Na_2O$
$NaAlSiO_4$
H_2O
Ne,No>X(S)$_{545}$
No,Ne>X(S)$_{607}$
Ne + No>>X$_{549}$
X$_{629}$
X$_{627}$
No>Ne$_{609}$
No,Ne$_{608}$
X
S
C
No
Ne

The fluid phase analyses suffer from the obvious defect, that alumina and silica were not determined. The actual analytical procedures tended to underestimate the amount of water present; these amounts of water were, moreover, often near the limits of precision of the five-place balance used.

Some of the water determined may have been intracrystalline, at 15,000 p.s.i., and not a part of the fluid phase, and some sodium may have been leached from the crystalline phases[1].

Despite these uncertainties, the fluid phase analyses are generally consistent with the other findings. The bulk compositions of the solid phases, calculated from the fluid phase analyses, should correspond with the compositions of the analysed crystalline specimens, or should lie between the latter compositions, when more than one crystalline phase is present. To a first approximation, the two sets of analyses do correspond, and the agreement is very good, in some cases.

The most important information derived from the fluid phase analyses bears on the presence or absence of a fluid phase, in some charges. The analytical results indicate fluids with high NaOH contents, for charges containing the solid assemblages nepheline + nosean + X, nepheline + sodalite + X, and nepheline + sodalite + cancrinite. The water, determined in these cases, was a small quantity, and may represent:

---

[1] This would be contrary to the findings of Barrer and Falconer (1956), for cancrinite and sodalite; these authors found that there is no exchange of hydrogen for sodium, when hydroxyl sodalite and hydroxyl cancrinite are placed in distilled water.

a. Fluid remaining, due to incomplete reaction. This is not considered likely, since the amounts of water obtained at 600°C and 700°C were greater than those from comparable charges at 450°C and 520°C; at the higher temperatures, reaction should be faster and more complete.

b. Intracrystalline water. This, also, is contradicted by the greater amounts of water obtained at higher temperatures, from charges of similar compositions and identical assemblages. A given crystalline species is usually less hydrous at higher temperature.

c. An equilibrium fluid. This explanation is consistent with the larger amounts of water found at the higher temperatures, since for given charge composition, the fluid phase should be a greater proportion of the charge, at higher temperatures.

It is therefore concluded that there was a liquid present in all charges, and that this liquid was an equilibrium liquid (or a close approximation to an equilibrium liquid; see chapter VI). This indicates that the plane $NaAlSiO_4$-$NaOH$-H_2O is quaternary in part, since the addition of a fluid to the fields of three crystalline phases results in fields of four phases; four phase assemblages are possible only on univariant lines, in ternary systems at equilibrium.

THE PSEUDO-TERNARY NATURE OF THE PLANE. In the more hydrous areas, and at the lower temperatures investigated, the plane $NaAlSiO_4$-$NaOH$-H_2O approximates quite well to a ternary system, as the compositions of the analysed crystalline phases all lie near to it. The liquids, however, probably have an Al:Si ratio somewhat higher than that of the solids. At S.T.P., alumina is more soluble than is silica, in NaOH solutions with a pH of nine or greater; this tendency may persist qualitatively, at higher pressures and temperatures. There is evidence of preferential solution of alumina by the fluid phase, from the compositions of the solids. Only the sodalite and nosean analysed have Al:Si approximately equal to 1. Despite the slight alumina excesses in the reagent gels, the other crystalline phases are aluminum-deficient, as were the sodalite and cancrinite reported by Barrer and Falconer. When the liquid coexisting with such aluminum-deficient crystals is a small proportion of the total assemblage, this liquid must contain a large excess of alumina, to satisfy the condition that Al:Si = 1, in the bulk composition of the charge.

At the higher temperatures and less hydrous compositions, the plane $NaAlSiO_4$-$NaOH$-H_2O, together with that part of the $NaAlSiO_4$-Na_2O-$NaOH$ join shown in figures G, H. I, and J, is quaternary. This is concluded from the fluid phase analyses, and from the appearance of nepheline at the highly-sodic parts of the liquidus. The four components are probably Na_2O, Al_2O_3, SiO_2 and H_2O, with departures from the ternary plane being restricted to differences of the ratio Al:Si in the several phases of a given assemblage.

<u>SPECIFIC RELATIONSHIPS AT THE FOUR TEMPERATURES</u>. Figures L, M, N and O are equilibrium diagrams referring to the four temperatures investigated. They are based primarily on the experimental results, but contain interpretive elements, where these results were considered to be ambiguous. All the diagrams are drawn for a ternary system; that is, the maximum number of phases shown is three, for divariant conditions, although the system is somewhat quaternary at 600°C, and distinctly so, at 700°C.

The fields of the pure crystalline phases, shown in the diagrams, are small. The actual extents of these fields may be larger (or, even smaller); there is little evidence bearing on this point, except in the case of nepheline.

Specific comments on the individual diagrams accompany the figures.

FIGURE L

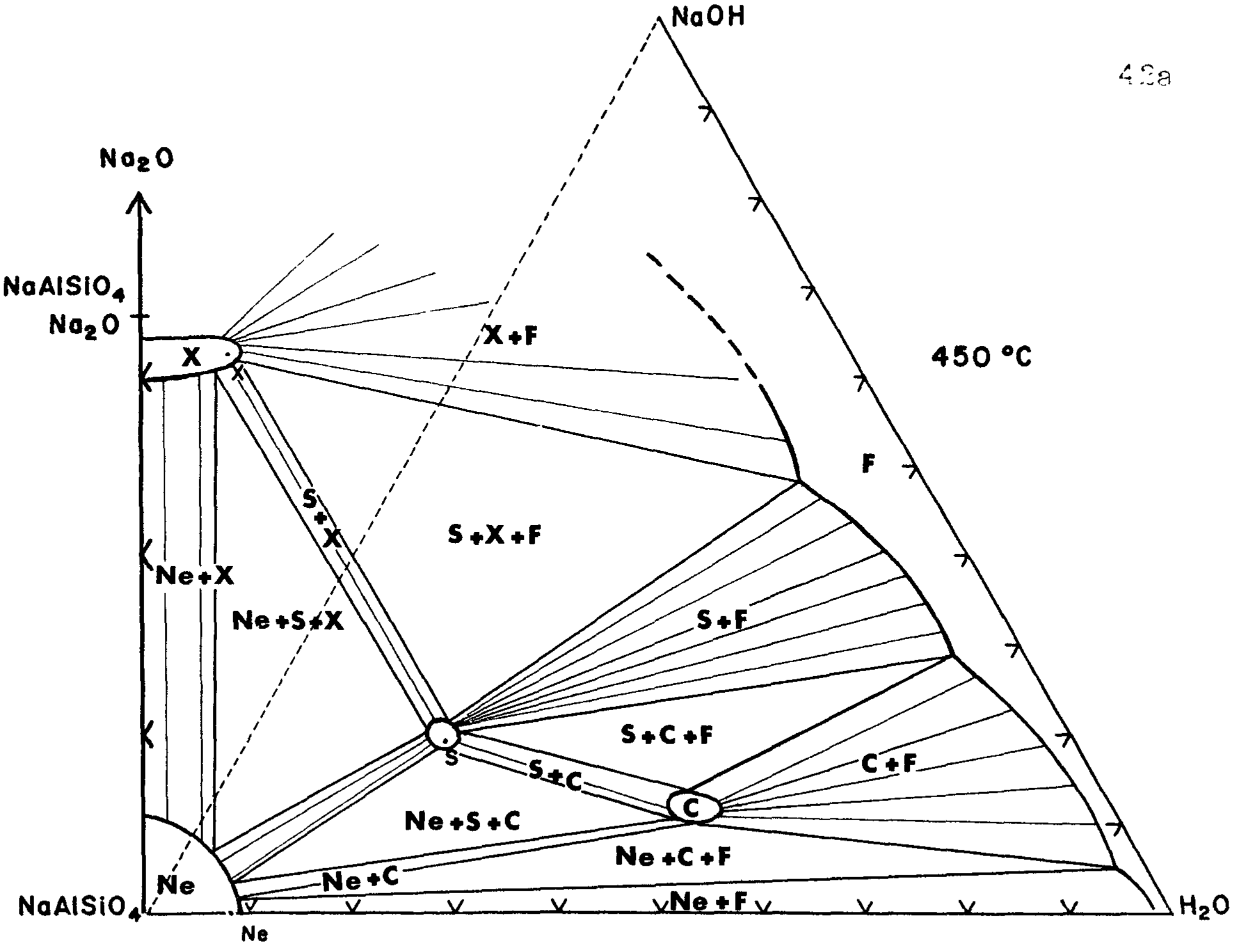
Inferred Relationships at 450°C

The results at 450°C, 15,000 p.s.i. total pressure (figure G) indicate the relationships shown. To give the best fit with the experimental data, cancrinite is placed at a much higher water content than that indicated by the analysis (figure E). The experimental results do not indicate the composition of the fluid of the assemblage nepheline + cancrinite + fluid.

FIGURE M

Interpretation of the Results at 520°C

The experimental results are shown in figure H. The most problematic aspect of this section is the relationship of nosean and cancrinite. Cancrinite strongly favours the area near the H_2O vertex. The presence of cancrinite in charges with such sodic compositions as those of charges nos. 468 and 473 (figure H) is difficult to explain, except on the basis of metastability. The possible polymorphic relationship shown in the diagram could account for a tendency to metastable formation and persistence of nosean and cancrinite, near the transition point.


NaOH
Na₂O
2 NaAlSiO₄
Na₂O
450 °C
X
X
X + F
F
S
X
S + X + F
Ne + X
Ne + S + X
S + F
S + C + F
S
S + C
C + F
C
Ne + S + C
Ne + C + F
Ne
Ne + C
Ne + F
NaAlSiO₄
Ne
H₂O

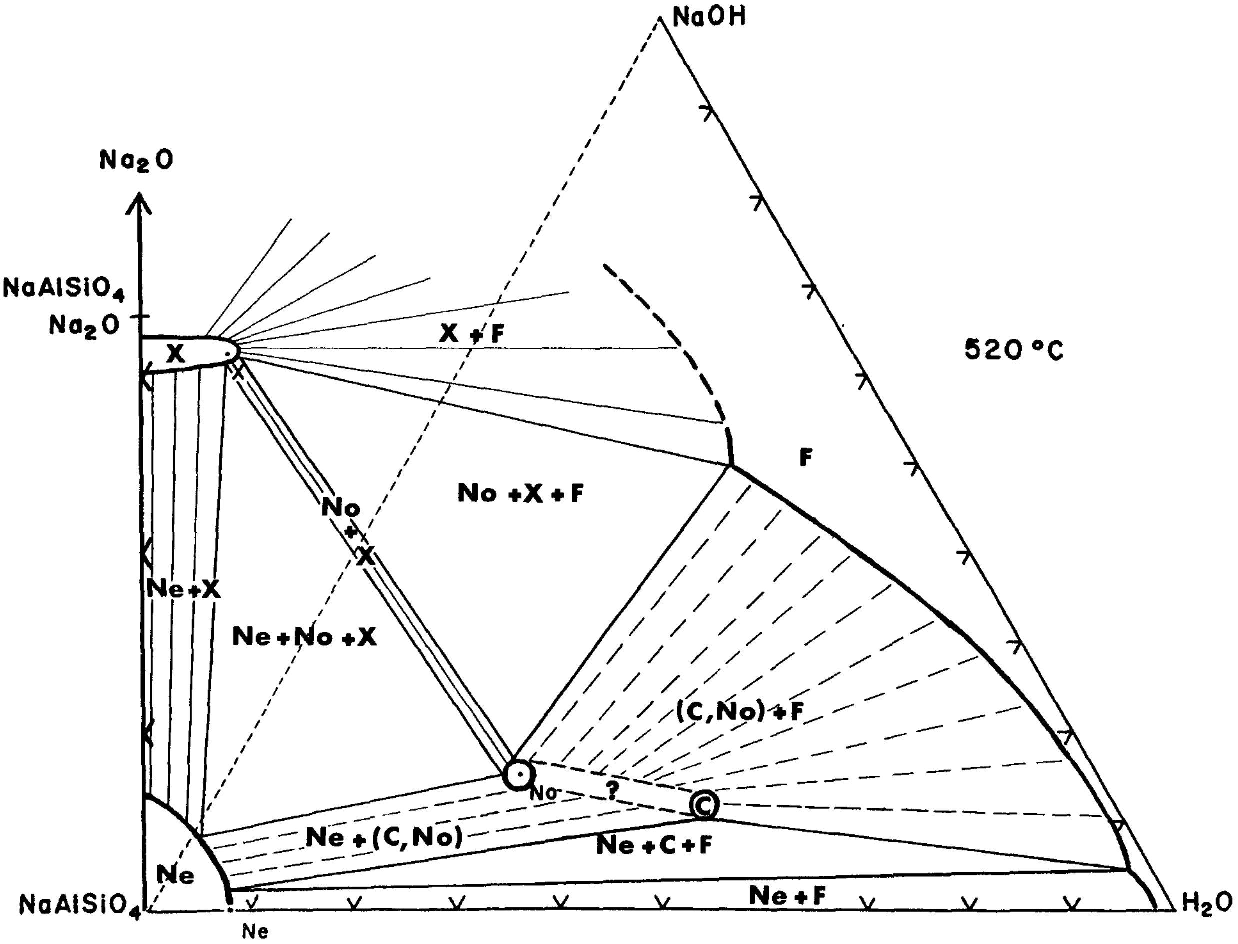

NaOH
Na₂O
2 NaAlSiO₄
Na₂O
520 °C
X
X
X + F
F
No
X
No + X + F
Ne + X
Ne + No + X
(C, No) + F
No
?
C
Ne + (C, No)
Ne + C + F
Ne
Ne + F
NaAlSiO₄
Ne
H₂O

FIGURE N

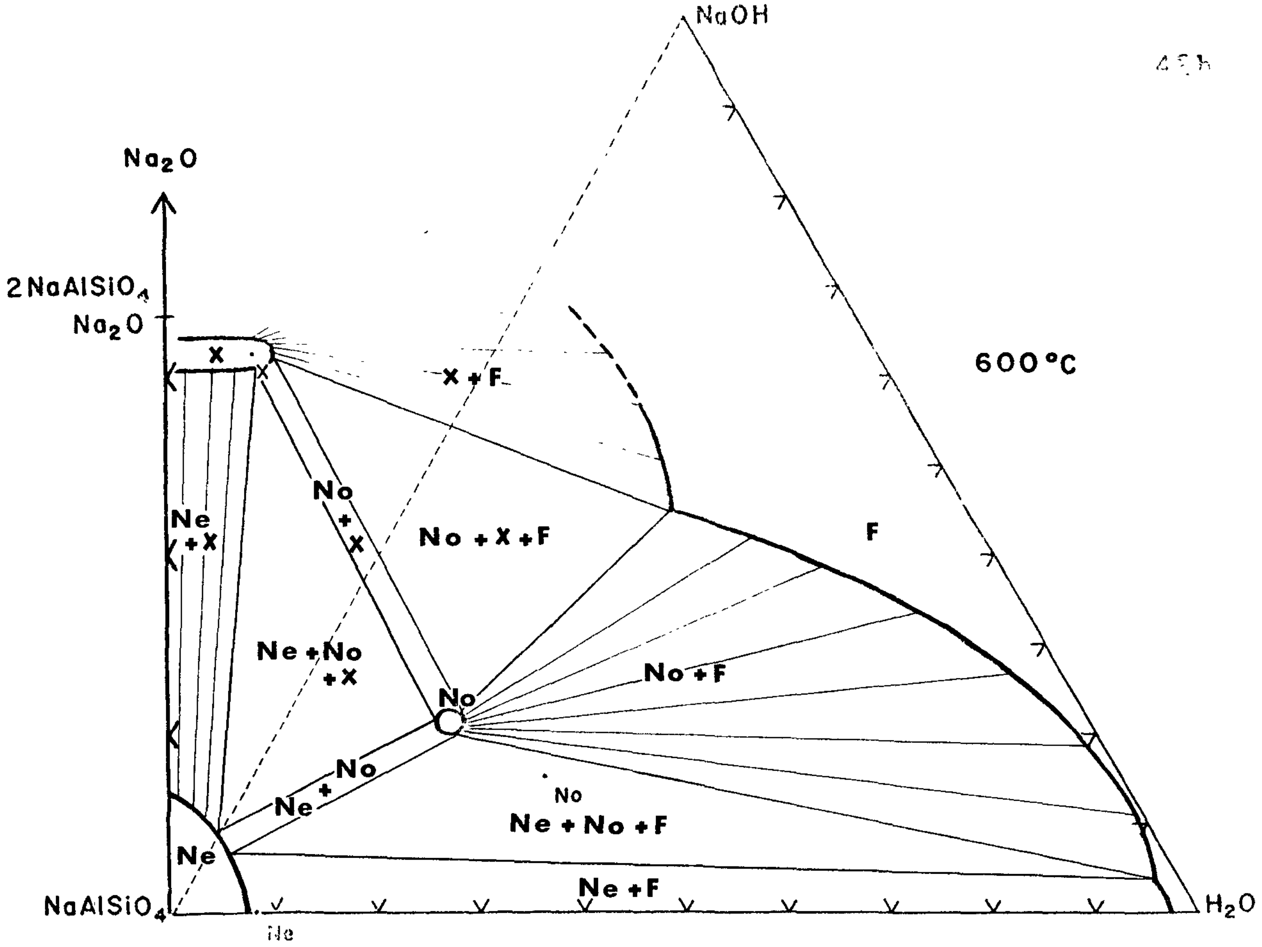
Inferred Relationships at 600°C

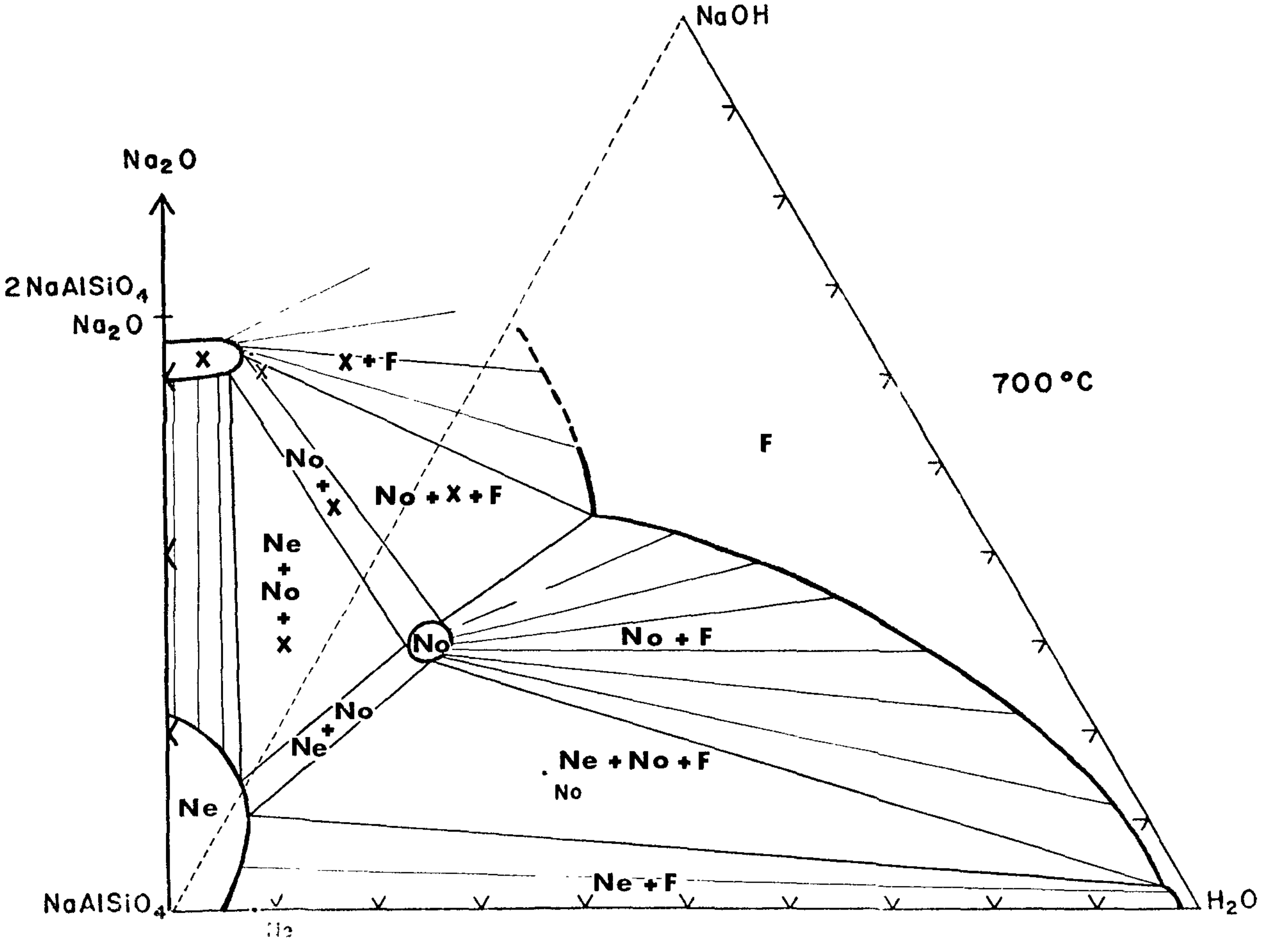
The experimental results are shown in figure I. The section is shown as a ternary system, but the appearance of small quantities of nepheline at (or very near to) the sodium-rich parts of the liquidus shows that the system is somewhat quaternary, at this temperature.

FIGURE O

Interpretation of the Results at 700°C

The results at 700°C are shown in figure J. The system is quaternary at this temperature, with nepheline appearing in all charges except those containing fluid, or X + fluid only. In view of the unusual nature of the nepheline formed at high NaOH concentrations (similar nepheline has not been reported from systems other than the present one), and the apparent absence of X from geological systems, the ternary representation is probably more directly comparable with analogous systems, such as $NaAlSiO_4$-$NaCl$-H_2O. There is no reason to suspect that the latter system is quaternary.


NaOH
Na₂O
2NaAlSiO₄
Na₂O
600°C
X
X + F
No + X
No + X + F
F
Ne + X
Ne + No + X
No
No + F
Ne + No
No
Ne + No + F
Ne
Ne + F
NaAlSiO₄
Ne
H₂O


NaOH
Na₂O
2NaAlSiO₄
Na₂O
X
X + F
700°C
F
No + X
No + X + F
Ne + No + X
No
No + F
Ne + No
Ne + No + F
No
Ne
Ne + F
NaAlSiO₄
Ne
H₂O

CHAPTER VI

DISCUSSION

EQUILIBRIUM IN THE EXPERIMENTAL RESULTS. Although stable equilibrium is probably never attained in studies involving silicate crystallisation, a reasonably close approach to these conditions is essential to any investigation such as the present one, if the results are to have any meaning. It is, however, practically impossible positively to demonstrate stable equilibrium in these experiments, and the investigator usually must be content with negative results to tests for disequilibrium. The most commonly used criteria involve the application of the phase rule, and tests to establish that reactions at postulated phase boundaries are not irreversible.

The use of the phase rule entails the correct choice of the number and characters of the components. Thus, the field at 700°C of nepheline + nosean + X + fluid could be interpreted as representing ternary disequilibrium, or quaternary equilibrium. The latter was chosen largely on the evidence of the fluid phase analyses. In fact, none of the results of the present study violate the phase rule for quaternary systems.

Testing for the reversibility of reactions was not formally attempted in the present study, since those most in need of such examination, and on which other direct evidence could not be brought to bear, were isobaric, isothermal reactions.[1] On the other hand, there was incidental breakdown of pre-formed sodalite and nepheline structures in many of the charges, establishing the instability of these structures under certain conditions.

Many of the charges clearly failed to reach equilibrium, in that sodalite persisted to a variable degree at temperatures above its field of stability. This is a special case of disequilibrium, resulting from isolation of the sodalite from the fluid phase. The persistence of sodalite probably caused little other change to the equilibrium assemblage, since sodalite and the nosean which apparently replaces it are of very similar compositions.

Near the $NaAlSiO_4$-H_2O join, the charges at 450°C and 520°C afforded visual evidence of incomplete reaction, and were largely disregarded. Near the H_2O vertex, at all four temperatures, the excessive width of the fields of nepheline + cancrinite + fluid, and nepheline + nosean + fluid, are also assumed to represent disequilibrium (see figures L and N). This phenomenon may be causally related to that found by Litvin and Dem'yanets (1962); in charges of natural nepheline + carbonate ion + water, either nepheline or cancrinite crystallised, depending only on which structure was present as a seed

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[1] Examples are the reactions nepheline + nosean + fluid + NaOH $\rightleftarrows$ nosean + fluid, and cancrinite + nepheline + fluid + NaOH $\rightleftarrows$ cancrinite + fluid, both near the $NaAlSiO_4$-H_2O join, and nosean + fluid + H_2O $\rightleftarrows$ cancrinite + fluid. Adequate supplies of the pure phases, necessary for such isobaric, isothermal tests, were not available.

crystal.[1] It appears that the $NaAlSiO_4$-H_2O join is very prone to the development of non-equilibrium assemblages.

The occurrences of nosean and cancrinite, at 520°C, are difficult to explain in detail, on the basis of equilibrium relationships, and, to a limited extent, probably represent disequilibrium. In view of the compositional similarity of these two phases, the metastable presence of one or the other should not disturb the other phase relationships.

It is clear, from the foregoing, that the results near the $NaAlSiO_4$-H_2O join, the persistence of sodalite at 520°C and above, and some of the charges containing nosean and cancrinite, are all expressions of disequilibrium. The rest of the results are most easily interpreted in terms of equilibrium, ternary and quaternary. Any undetected disequilibrium phenomena that may be present, must be very consistent; within the conditions of experimentation, the results were reproducible, with few, or no, exceptions.

THE RELATIONSHIP OF HYDROXYL NOSEAN AND HYDROXYL CANCRINITE. According to chemical analyses, hydroxyl nosean and hydroxyl cancrinite have almost identical compositions (see figure E), but the obvious preference of cancrinite for the area of the H_2O vertex indicates that this phase tends to be more hydrous than does nosean, at the conditions of reaction. Cancrinite may, in fact, behave in a manner analogous to that of a

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[1] The temperature of the experiments was 300°C to 400°C, and the pressure was less than 1 kilobar. A temperature gradient was maintained in the system, which was not at equilibrium. These authors also report a cancrinite of the composition $3NaAlSiO_4.2NaOH$, apparently formed in the system natural nepheline + water.

sponge. There are relatively large channels (Pauling, 1930); Jarchow, 1966; Barrer and Falconer, 1956) traversing cancrinite, circumscribed by twelve-membered rings of Al-O and Si-O tetrahedra. The corresponding cavities of nosean are smaller, being surrounded by six-membered rings. Both species have about the same cell volume,[1] and the same number of $NaAlSiO_4$ units per cell; in both, the openings in the frameworks contain the NaOH and H_2O of the chemical formulae. In nosean, there is more than enough NaOH and H_2O to fill the two cavities per cell. The larger openings of cancrinite may be able to accommodate relatively large quantities of structurally unimportant water, under hydrothermal conditions, but with loss of this water, on release of the pressure. Such behaviour would explain the apparent contradiction of the similarity of the analysed compositions, and the obvious stabilisation of cancrinite by higher water concentrations.

The stabilisation of hydroxyl nosean, relative to hydroxyl cancrinite, by increase of temperature, is in accord with the findings of Edgar and Burley (1961, 1963), who pointed out that some other types of cancrinite give way to nosean structures, with rising temperature.

In the section at 520°C (figure M), it was suggested that the composition fields of hydroxyl nosean and hydroxyl cancrinite may join. A polymorphic relationship was suggested by Edgar and Burley (Ibid.)

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[1] The analysed cancrinite has a cell volume of about 715 $\mathring{A}^3$, and that of the nosean is about 730 $\mathring{A}^3$. Cancrinite and nosean have 6 $NaAlSiO_4$ per cell, with two additional cation valencies, and two additional anion valencies.

for carbonate and bicarbonate forms of nosean and cancrinite; in the present study, such a relationship would account for the confused relationships[1] indicated in figure H, the experimental data at 520°C.

THE RELATIONSHIP OF HYDROXYL NOSEAN AND HYDROXYL SODALITE. The present study has reaffirmed the fact that hydroxyl sodalite and hydroxyl nosean are distinct phases, but has not yielded positive information on the nature of the differences, other than that of cell size, between the two phases. Sodalite was found to be unstable at and above 520°C, and stable at 450°C, the reverse being true for nosean.

Sodalite can persist, for a period of days or longer, at temperatures up to 700°C. The alteration of sodalite to nosean appears to take place at the surface of the grains, and to be impeded by isolation from the fluid phase. These factors suggest either a significant difference of composition between the two, or different arrangements of the aluminosilicate frameworks. Chemical analyses of the two have shown the chemical compositions to be very similar, with the possible exception of the water contents, and Barrer and Falconer (1956) have shown that water and sodium are quite mobile in the hydroxyl sodalite structure, at 300°C to 400°C. Thus, some difference of the aluminosilicate frameworks seems, from this data, to be more likely. This is apparently confirmed in a very recent publication (von Lons and Schulz, 1967), in which the

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[1] The occurrence of cancrinite on the sodium-rich side of the field of nepheline + nosean (charges nos. 468 and 473) is difficult to explain, except by metastability. Near the conditions of a polymorphic transition, metastable persistence of one or other phase is very likely.

structure of a chloride sodalite is described. The aluminum and silicon are largely ordered, in contrast with the reported structures of nosean and hauyne (see, for example, Saalfeld, 1959, 1961). The space group of the chloride sodalite is $P\bar{4}3n$, while that of sulphate nosean is $P\bar{4}3m$. It appears, from a preliminary single-crystal study of the hydroxyl forms of the present investigation, that a similar space group difference exists. This study, by Dr. C. Calvo, of the Materials Sciences Department, McMaster University, is continuing.

The results of earlier work (Anderson, 1963) at 440°C to 540°C are shown in figure C. The crystalline phases were not analysed at that time, and the data were taken to indicate that nosean was of a more sodic composition that sodalite. In view of the compositional similarity now evident, the field of sodalite + nosean (+ fluid), in figure C, may be the spurious result of kinetic factors, and the transformation of hydroxyl sodalite to hydroxyl nosean could be isothermal and polymorphic. The earlier results are now interpreted as showing that the alteration of hydroxyl sodalite to hydroxyl nosean, at 15,000 p.s.i., takes place at a temperature, or at temperatures, between 460°C and 480°C.

THE APPLICATION OF THESE RESULTS. As was stated in the early chapters, the purpose of this study has been, to provide a basis of information, regarding felspathoid phase relationships, which would be useful in studies of those multi-component systems in which the natural felspathoids occur. Whether or not this goal has been realised, will be shown only when the more complex systems are attempted.

The effects of the addition of certain ionic or molecular species, to the system $NaAlSiO_4$-$NaOH$-H_2O, are readily predictable from previous information. Chloride ion stabilises the sodalite structure over a large temperature range. Carbonate ion stabilises the cancrinite structure at lower temperatures, and the nosean structure at higher temperatures; similar effects are to be expected of the sulphate ion. The effects of mixtures of these, and other, ions, are not so predictable, and it is in such cases as these, that the present results should be of value.

The stabilisation of cancrinite, by very high water concentrations, may be an important factor in some equilibria. The work of von Eckermann was cited in chapter II; he concluded that the reaction,

$$\text{nepheline} + \text{calcite} \rightleftharpoons \text{cancrinite}$$

is pushed to the right, by high partial pressures of CO_2. Several other variables could influence this equilibrium, but the results of the present study indicate that particular attention should be paid to variations of the partial pressure of water.

The high-NaOH form of nepheline is interesting in itself, but does not appear to be a form found in rocks. Slow cooling of this substance should permit the observed structural changes to proceed further, so that the low temperature structure, or structures, could be identified.

SUMMARY. At 15,000 p.s.i. total pressure, in the system $NaAlSiO_4$-$NaOH$-H_2O, the hydroxyl felspathoids have stability fields as outlined in figures L, M,N and O. Sodalite is stable from below 450°C to a temperature just below 520°C, and the range of stability of cancrinite extends from below

450°C to a temperature between 520°C and 600°C. Nosean is stable from a temperature between 450°C and 520°C, to above 700°C. The effects of temperature and pressure are crucial in determining which of the hydroxyl felspathoids will form, at given composition of the isolated system, as the compositions of these phases all approximate to $3NaAlSiO_4.NaOH.xH_2O$, with x varying from less than 1, to at least 1.5. Analyses of hydroxyl cancrinite probably indicate much lower water content than was present under hydrothermal conditions; cancrinite is clearly favoured over the other phases by highly aqueous compositions.

Two other crystalline phases occur over the whole temperature range 450°C to 700°C: sodic nepheline, including an abnormal form of higher than normal sodium content, and phase X. The latter appears to be an unreported phase, with composition close to $Na_4Al_2Si_2O_9$.

The system $NaAlSiO_4$-$NaOH$-H_2O is distinctly quaternary at 600°C and 700°C, probably with the ratio Al:Si differing from one phase to another.

REFERENCES CITED

Anderson, P.A.M., 1963. The system $NaAlSiO_4$-$NaOH$-H_2O, at 1 kilobar and 440°C to 540°C. M.Sc. Thesis, McMaster University.

Aramaki, S. and Roy, R., 1962. Revised phase diagrams for the system SiO_2-Al_2O_3. Jour. Amer. Ceram. Soc., 45, p. 229.

Barnes, H.L. and Ernst, W.G., 1963. Ideality and ionisation in hydrothermal fluids: the system MgO-H_2O-$NaOH$. Amer. Jour. Sci., 261, p. 129.

Barth, T.F.W., 1932a. The structures of the minerals of the sodalite family. Zeit. Krist., 83, p. 405.

________ 1932b. The chemical composition of noselite and hauyne. Amer. Min., 17, p. 466.

Barrer, R.M. and Falconer, J.D., 1956. Ion exchange in felspathoids as a solid state reaction. Proc. Roy. Soc., A, 236, p. 227.

________ and White, E.A., 1952. The hydrothermal chemistry of silicates. Part II, synthetic crystalline alumino-silicates. Jour. Chem. Soc., 286, p. 1561.

Borchert, W. and Keidel, J., 1949a. Beitrage zur Reaktionsfahigkeit der Silikate bei niedrigen Temperaturen. I. Mitteilung. Reaktionen zwischen Kaolin und NaOH. Heidelberger Beitrage zur Min. Petr., 1, p. 2.

Borchert, W. and Keidel, J., 1949b. Beitrage zur Reaktionsfahigkeit der Silikate bei neidrigen Temperaturen. II. Mitteilung. Die Strukturen Na_2O-reicher Carnegieite. Heidelberger Beitrage zur Min. Petr., 1, p. 17.

Burnham, C.W. and Jahns, R.H., 1958. Experimental studies of pegmatite genesis: The solubility of water in granitic magmas. Bull. Geol. Soc. Amer., 69, p. 1544.

Cruft, E.F., Ingamells, C.O. and Muysson, J., 1965. Chemical analysis and the stoichiometry of apatite. Geochim. et Cosmochim. Acta, 29, p. 581.

Deer, W.A., Howie, R.A. and Zussman, J., 1963. Rock-forming Minerals, vol. 4. Framework Silicates. Longmans, London.

Donnay, G., Schairer, J.F. and Donnay, J.D.H., 1959. Nepheline solid solution. Min. Mag., 32, p. 93.

Eckermann, H. von, 1948. The alkaline district of Alno Island. Sveriges Geol. Undersok., ser. Ca., No. 36.

Edgar, A.D., 1961. Mineral chemistry of some synthetic cancrinites. M.Sc. Thesis, McMaster University.

________ and Burley, B.J., 1963. Studies on cancrinites. I-Polymorphism in sodium carbonate-rich cancrinite-natrodavyne. Canad. Min., 7, p. 631.

Gittins, J., 1961. Nephelinisation in the Haliburton-Bancroft district, Ontario, Canada. Jour. Geol., 69, p. 291.

Hahn, T. and Buerger, M.J., 1955. The detailed structure of nepheline, $KNa_3Al_4Si_4O_{16}$. Zeit. Krist., 106, p. 308.

James, R.S., 1965. The properties of sodalite and its petrogenesis at the Princess Quarry, Bancroft, Ontario. M.Sc. Thesis, McMaster University.

Jarchow, O. von, 1966. Atomanordnung und Strukturverfeinerung von Cancrinit. Zeit. Krist., 122, p. 407.

Koster van Groos, A.F., 1966. The effect of NaF, NaCl and Na_2CO_3 on the phase relationships in selected joins of the system Na_2O-CaO-Al_2O_3-SiO_2-H_2O at elevated temperatures and pressures. Ph.D. Thesis (published), University of Leiden.

________ and Wyllie, P.J., 1966. Liquid immiscibility in the system Na_2O-Al_2O_3-SiO_2-CO_2 at pressures to 1 kilobar. Amer. Jour. Sci., 264, p. 234.

Kozu, S. and Takane, K., 1933. Crystal structure of cancrinite from Dodo, Korea. Proc. Imp. Acad. Tokyo, 9, pp. 56-69, 105-108.

Litvin, B.N. and Dem'yanets, L.N., 1962. Hydrothermal synthesis of monocrystals of nepheline. Soviet Physics, Crystallography, 7, p. 519. (Consultants Bureau translation.)

Lons, von J. and Schulz, H., 1967. Strukturverfeinerung von Sodalith, $Na_8Al_6Si_6O_{24}Cl_2$. Acta. Crist., 23, p. 434.

Morey, G.W. and Hesselgesser, J.M., 1951. The solubility of some minerals in superheated steam at high pressures. Econ. Geol., 46, p. 821.

Nithollon, P., 1955. Structure cristalline de la cancrinite. Publications scientifiques et techniques du ministère de l'air, France, N.T. 53. (Abstract: Structure Reports 19, p. 480.)

Nystrom, E.T., 1927. Some alkaline rocks of Shansi province, N. China. Bull. Geol. Inst. Uppsala, 22, p. 59.

Pauling, L., 1930a. The structure of sodalite and helvite. Zeit. Krist., 74, p. 213.

________, 1930b. The structure of some sodium and calcium aluminosilicates. Proc. Nat. Acad. Sci., 16, p. 453.

Peteghem, J.K. van, 1961. Studies pertaining to the mineral chemistry of sodalite, nosean and hauyne. M.Sc. Thesis, McMaster University.

________ and Burley, B.J., 1962. Studies on the sodalite group of minerals. Trans. Roy. Soc. Canada, Vol. LVI, ser. III, Sec. III, p. 37.

________ and Burley, B.J., 1963. Studies on solid solution between sodalite, nosean and hauyne. Can. Min., 7, p. 808.

Saalfeld, H., 1959. Unterschungen uber die Nosean-Struktur. Neues Jahrb. Min., Monatshefte, p. 38.

________, 1961. Struktur besonderheiten des Hauyngitters. Zeit. Krist., 115, p. 132.

Saha, P., 1961. The system $NaAlSiO_4$(nepheline)-$NaAlSi_3O_8$(albite)-H_2O. Amer. Min., 46, p. 859.

Sand, L.B., Roy, R. and Osborn, E.F., 1957. Stability relations of some minerals in the Na_2O-Al_2O_3-SiO_2-H_2O system. Econ. Geol., 52, p. 169.

Schairer, J. F. and Bowen, N.L., 1956. The system Na_2O-Al_2O_3-SiO_2. Amer. Jour. Sci., 254, p. 129.

Shapiro, L. and Brannock, W.W., 1956. Rapid analysis of silicate rocks. U.S. Geol. Surv. Bull. 1036-C.

Smith, J.V. and Tuttle, O.F., 1957. The nepheline-kalsilite system. I: X-ray data for the crystalline phases. Amer. Jour. Sci., 255, p. 282.

Tuttle, O.F. and Smith, J.V., 1958. The nepheline-kalsilite system. II: Phase relations. Amer. Jour. Sci., 256, p. 571.

Yoder, H.S., 1958. Effect of water on the melting of silicates. Carnegie Inst. Washington, Ann. Rept. Dir. Geophys. Lab., 1957-58, p. 189.

APPENDIX I

SECTION 1 - EXPERIMENTAL METHOD

GENERAL. Phase stability was determined by synthesis from gels, using gold containers in heated pressure vessels. This chapter will describe: A. the reactant gels; B. execution of the reactions; C. treatment of the reaction products; D. optical examination of the products; E. X-ray examination of the products; F. analytical procedures.

A. THE REACTANT GELS

Because of the difficulties of handling and purifying sodium hydroxide, gels were used as starting reagents. SiO_2 was used in the form of a dry gel (Cab-O-Sil M5, The Cabot Chemical Co.); the Al_2O_3 and Na_2O were weighed as the nitrates (Analytical Grade Reagents). Water was added to the weighed silica and nitrates, and stirred to a thick, cream-like consistency. Concentrated NH_4OH (S.G.=0.88) was then added, the aluminum gelling as $Al(OH)_3$. The mixtures were evaporated to dryness, ground, fired at 800°C to decompose the nitrates, ground again, and stored over potassium hydroxide.

Analyses were made of the eight prepared gels (see F., below) and showed that the sodium contents were, in four cases, well below those intended (analysis results are in table App.-1). Two gels were rejected; one because of excessively low sodium, the other, because of low Al_2O_3 content. The accepted gels contain some excess Al_2O_3 and CO_2. The low Na_2O content probably arose from failure to use plastic beakers in the first stage of preparation; some of the dried gels remained in the glassware uses, and must have contained a disproportionate amount of sodium.

The analyses were taken to represent the true compositions of the dry mixtures. Two of the gels used (nos. 7 and 8) were made by mixing calculated quantities of two other gels.

The gels were examined optically and by x-ray diffraction, immediately after they were made, and at the end of the whole set of experiments. On both occasions, they showed no optical evidence of crystalline structure, and the initial set of x-ray diffraction patterns showed no long-range structure. The concluding set of diffraction patterns, made two and one-half years after the first, indicated the formation of appreciable quantities of nepheline and sodalite structures; the somewhat diffuse reflections could also have resulted, in part, from the presence of cancrinite or nosean structures.

B. EXECUTION OF THE REACTIONS

Gold tubes of 2½mm. I.D., 3mm. O.D. and 25mm. length were welded closed at one end and weighed. Water was inserted, using a ten microlitre syringe, and the capsule reweighed; the dry reagent was then added quickly via a small electric vibrating funnel, and the capsule again was weighed. The open end of the capsule was welded shut, inspected for leaks under a microscope, and the capsule weighed once more.

Reaction was accomplished in periods of two to four weeks in $\frac{1}{2}$ inch I.D., 2 inches O.D. bombs of 12 inches length, heated in cylindrical furnaces of 3 inches I.D. These furnaces were temperature controlled with an electronic multi-channel controller (Thermoelectric Co. Ltd.), using chromel-alumel thermocouples in the furnace windings. Temperatures were monitored using chromel-alumel thermocouples inserted in small wells in the bombs, near the charges; the potential was read from a manually-operated potentiometer with a precision of ±0.02 mV (about $\frac{1}{2}$°C, using chromel-alumel couples).

The measured temperatures normally varied less than ±2°C from the mean, for any given charge; these means were within 2°C of the set temperatures, and were probably within 3°C of the absolute values. The manufacturer of the bombs, Tem-Pres Research, Inc., state that the temperature of that part of the bomb in which the capsules were placed, is normally within 5°C of the temperature of the thermocouple well. If errors from the last-mentioned source are approximately constant, the temperatures quoted have an internal consistency of 2°C, and an absolute accuracy of ±10°C. Pressures were read from a Bourdon type gauge (American Instrument Co.), with a presumed overall accuracy of ±5 per cent.

The bombs, at the end of the reaction, were cooled to 450°C by an air blast (taking up to 90 seconds for this), then cooled to room temperature with a bucket of water. The end of the bomb could be held in the hand within two minutes, from any starting temperature.

After heating in the bombs, the capsules were weighed; those capsules which had changed by more than 0.03 per cent in weight were considered to have opened during the reaction. Some sets of capsules were considered to have remained closed, despite a weight change of 0.1 per cent, but this only when all capsules of the set showed similar behaviour.

A few larger capsules, of 1/3 inch I.D. and 1½ inches long, were used for synthesis of analysable quantities of the various compounds.

The weighings mentioned above were carried out on a four-place balance.

C. TREATMENT OF THE REACTION PRODUCTS

The capsule was opened, and part or all of the charge removed and washed in water. After drying with acetone, the sample was ready for examination. About one third of the capsules were treated otherwise; the contents were analysed for residual water and free sodium ion.

Those capsules of which the contents were chemically analysed were held, before opening, in a Bunsen flame, for a few seconds; the internal steam pressure expanded the capsules to a nearly-cylindrical shape, at which point they were immediately quenched in water. After drying, the capsule was weighed on a five-place balance, pierced at one end with a pin, and re-weighed. They were then dried to constant weight in an oven or vacuum desiccator at 125°C to 200°C, the loss in weight being, presumably, all water.[1] After dehydration, the capsules were opened under water, and the capsule and contents were carefully washed off, with light grinding of the contents. The washings from capsules and contents were filtered into 250 ml. graduated flasks, together with 25 ml. of 5000 p.p.m. Li^+ solution, and 25 ml. of normal HCl solution. The flasks were made up to volume, and the solutions compared with suitable standard solutions of NaCl, using a Perkin-Elmer model 303 atomic absorption spectrophotometer. The readings were made by J.R. Muysson, with probable accuracy of ±1 per cent (absolute).

D. OPTICAL EXAMINATION OF THE REACTION PRODUCTS

Optical examination of the reaction products was carried out using white light, at various magnifications from 20X to 675X. Refractive index determinations were made by observation of the Becke line, the immersion oils being calibrated at intervals of 0.002 units. The refractive indices of the oils were found to deviate from the rated values by less than 0.0007 units, upon checking with an Abbé refractometer at 25°C, in sodium light. No correction was made, when examining the reaction products, for temperature or wavelength of light.

E. X-RAY EXAMINATION OF THE REACTION PRODUCTS

For general identification purposes, X-ray diffraction patterns were made with a Norelco diffractometer of the geiger-counter type. The

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[1] Dehydrations of capsules numbered 576 or higher were effected in a vacuum desiccator. Other dehydrations were carried out in a drying oven, and some CO_2 may have been absorbed during drying, leading to an improperly low value for the water content.

normal scan rate used was 1° of the angle 2θ per minute; with a chart paper speed of one inch in eight minutes, the resulting record showed eight degrees of 2θ per inch. Slower scanning rates were used when more detailed examination was necessary. Nickel-filtered copper radiation was used for all determinations.

Cell parameters of the isometric compounds were determined in two ways: firstly, one sample each of nosean and sodalite were examined using a powder camera of radius 5.7 cm.; reflections up to 170° of 2θ were read easily, and the cell parameters were determined from the mean of the function $\sin^2\theta$ for the five highest-angled reflections read from the film. Secondly, when mixtures of the various compounds rendered the high-angled reflections confusing, diffractometer traces were made of the range $2\theta=42°$ to $2\theta=44.5°$, with a scan rate of 1/4° of 2θ per minute and chart speed of one inch in 8 minutes, and oscillating through one forward-and-backward cycle. The (411/330) reflection of nosean occurs at 44.2° to 44.5° 2θ; that of sodalite at about 43° 2θ. $SrCO_3$ was used as an internal standard, having a reflection at 44.012° 2θ. The absolute accuracy of the latter method cannot be expected to be good, but it was satisfactory for purposes of comparison; replicate determinations agreed to within ±0.05 per cent.

The cell parameters of cancrinite were determined from powder photograph data, with the aid of an I.B.M. 7040 computer, and a program written by Dr. H.D. Grundy and revised by the writer. This program generates the indices and the angle 2θ, for all possible reflections of a crystal of known cell parameters and Bravais lattice. The cell parameters and space group of phase X were determined by Dr. H.D. Grundy, using rotation and Weissenberg photographs. Reflections of the crystalline phases are listed in table App.-3.

F. ANALYTICAL PROCEDURES

REAGENTS. The reagent gels were analysed by Mr. J.R. Muysson, using the standard "Rapid Method" of Shapiro and Brannock (1956), with slight modifications, for Na_2O, SiO_2, CO_2 and Al_2O_3. Water was determined by the method described by Ingamells, Cruft and Muysson (1965). These analyses are shown in table App.-1.

ANALYSIS OF PRODUCTS. Nepheline, "X", nosean and cancrinite were hand-picked from mixtures of phases synthesised for this purpose in larger tubes; the quantities of the mixtures available varied from 0.7 gm. to 2 gm. The quantity of picked sample varied from 10 mg. (for "X") to 40 mg. (for nosean). Water was determined by dehydration for one hour at 700°C, and soda, alumina and silica were determined by the same "Rapid Method" procedures used for the gels, except for: a. modification of the standardisation methods, because of the small sample size; b. the use of a Perkin-Elmer model 303 atomic absorption spectrophotometer, instead of the flame photometer used by Brannock and Shapiro.

Sodalite was not synthesised with grain-size large enough for hand separation, so was partially separated from the contaminating cancrinite by floatation in a heavy liquid, before analysis. The cancrinite content of the 365 mg. sample was estimated by point-count of about 800 points, using a petrographic microscope and automatic counting stage; the analysed composition of the sample was corrected for the amount of cancrinite present (10.7 volume per cent), using the analysed composition of cancrinite for this purpose. The impure sodalite sample was analysed by the same method used for the reagent gels, with the substitution of the atomic absorption spectrophotometer for the flame photometer. Analyses of the crystalline phases are shown in table App.-2. Weighings of small samples of nepheline, nosean, cancrinite and X, were carried out by the writer, using a microgram balance, as were the dehydrations, which are probably the greatest source of error in the determinations. No suitable standard was available to check on the completeness of dehydration for 1 hour, at 700°C. Higher temperature and longer dehydration time might have resulted in serious sodium loss.

The analytical accuracy, estimated, by Mr. Muysson, by analysis of National Bureau of Standards standard granite, was:

Oxide	Analyses of reagent gels	Analysis of sodalite
Na_2O	± 0.3 per cent	± 0.1 per cent
Al_2O_3	0.2	0.15
SiO_2	0.2	0.1
H_2O	0.1	0.1

The accuracy of the analyses of nepheline, cancrinite, nosean and X samples is difficult to establish. The totals for these determinations vary from 95.5 to 98.01, and constitute the principal source of doubt, concerning accuracy. The water determinations were the most obviously inadequate; alumina and silica, being determined from the same solution, are probably in the correct ratio, to the limits of the analysis of sodalite. Sodium was determined from a separate solution. The analyses of nepheline, cancrinite and nosean, together with that of sodalite, corresponding well with the formulas expected, by analogy with natural examples. In the opinion of the writer, all of the analyses, as plotted on figure IV-B, are correct to within two per cent, in terms of the ratio $NaAlSiO_4$:NaOH plotted on the $NaAlSiO_4$-NaOH join. The water content of the cancrinite is probably rather low, but the sample may have lost water before analysis.

SECTION 2 - DETAILED EXPERIMENTAL RESULTS

GENERAL. The detailed experimental results are given in five tables, showing: the analyses of the reagent gels (table App.-1) and crystalline phases (table App.-2); x-ray data for the crystalline phases (table App.-3); the compositions and phase assemblages of the individual charges (table App.-4); results of the fluid phase determinations (table App.-5). The last two are the output of the computer program mentioned in the previous section, and require some explanation.

THE COMPOSITIONS AND REACTION PRODUCTS OF THE CHARGES. In table App.-4, the charges are listed in order of ascending reaction temperatures, the charges at any one temperature being in numerical order. The charge numbers were assigned arbitrarily. The charge compositions are stated as molecular percentages, in terms of the components $NaAlSiO_4$, NaOH and H_2O, so that charges with compositions in the system $NaAlSiO_4$-NaOH-Na_2O are shown with negative water content. In the latter cases, the molecular percentages of $NaAlSiO_4$ and NaOH were recalculated to 100, and the charge composition was plotted on the diagrams (figures E, G, H, I, J) by producing the straight line from the H_2O vertex through the appropriate point on the $NaAlSiO_4$-NaOH join, and marking off the indicated negative percentage of water. A key to the symbols used is given with the table.

THE RESULTS OF THE FLUID PHASE ANALYSES. (Table App.-5). The charges are listed in numerical order. The results of the sodium and water determinations are expressed in molecular percentages of NaOH, as points on the NaOH-H_2O join.[1] The "bulk compositions of the solid phases", computed as, (charge composition)-(Na and H_2O of the fluid phase), are given as molecular percentages of the components $NaAlSiO_4$, NaOH and H_2O, for points within that system. In the cases in which NaOH or H_2O were negative, relative to that system, the compositions of the solid phases are expressed as the inverse lever ratios, referring to the plotted compositions of the charges and fluid phases. This is further explained in table App.-5.

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[1] The NaOH content was taken to be the same as the determined sodium ion content. In fact, however, part of this sodium is associated with the alumina and silica content of the fluid. The true fluid phase compositions would presumably be better represented by points of the calculated water percentage, but lying on the liquidus of figures L, M, N and O, and by operation of the lever principle, the bulk compositions should be more sodic than they are shown to be, in the figures. Such representation could, however, be misleading, in the absence of accurate data on the position of the liquidus, or of the true NaOH, Al_2O_3 and SiO_2 contents of the fluid phases.

TABLE App.-1

Analyses of the Reagent Gels*

Weight per cent:

Gels no.	1	2	3	4	5	6	7**	8**
SiO_2	36.85	30.78	33.67	35.14	40.82	41.76	38.22	39.48
Al_2O_3	32.67	26.86	28.93	30.51	35.28	36.10	33.59	34.41
Na_2O	27.21	39.14	33.33	28.48	22.15	20.32	25.61	23.88
H_2O	2.46	2.20	2.71	5.49	1.45	0.89	2.13	1.80
CO_2	0.45	0.92	0.95	0.71	0.43	1.03	0.45	0.44
TOTALS	99.64	99.90	99.59	100.33	100.13	100.10	100.00	100.01

Molecular per cent:

$NaAlSiO_4$	67.7	49.7	56.4	54.2	85.6	86.9	72.9	79.0
Na_2O	14.6	35.7	25.9	15.5	2.24	0.0	11.0	6.82
H_2O	15.1	11.85	15.2	28.2	10.1	6.54	13.54	12.0

Contaminants:

Al_2O_3	1.54	0.71	0.35	0.63	0.81	3.49	1.36	1.08
CO_2	1.10	2.01	2.18	1.49	1.23	3.10	1.16	1.19

* Analysed by J.R. Muysson

** Gels nos. 7 and 8 were not analysed, being mixtures of gels nos. 1 and 5.

TABLE App.-2

Analyses of the Synthetic Crystalline Phases*

Phase:	Hydroxyl sodalite	Hydroxyl cancrinite	Hydroxyl nosean	Nepheline	Phase X
Quantity analysed:	365 mg.**	33 mg.	32 mg.	15 mg.	8 mg.
Wt. per cent,					
SiO_2	37.38	36.27	35.90	42.21	34.36
Al_2O_3	32.09	28.93	31.64	31.94	26.74
Na_2O	25.35	24.06	23.57	20.76	35.10
H_2O	5.50	6.24	6.90	2.30	1.39
Total	100.32	95.50	98.01	97.21	97.59

* Analysed by J.R. Muysson and P.A.M. Anderson.

** The sodalite sample contained 10.7 volume per cent of cancrinite, as determined by counting about 800 points.

TABLE App.-3

X-ray Reflections of the Crystalline Phases

The reflections of the crystalline phases, for copper Kα radiation, are given on the following five pages. The data for phase X was obtained with a Norelco diffractometer, while that for the other phases is from powder photographs taken on a camera of radius 5.7 cm. The intensities were estimated visually from the powder photographs, and the intensities given for phase X are the peak heights.

For the isometric phases, the quantity N, equal to $(h^2 + k^2 + l^2)$, is given for each reflection. The other phases were only partially indexed.

TABLE App.-3

X-ray Reflections of the Crystalline Phases

HYDROXYL NOSEAN

I	2θ	N
vw	12.5	?
vs	13.85	2
m	19.75	4
m	21.4	?
w	21.85	?
vs	24.15	6
vw	27.95	8
vs	31.30	10
vs	34.45	12
m	37.30	14
w	39.95	16
s	42.55	18
w	49.60	24
s	51.70	26
w	55.85	30
ms	57.85	32
ms	59.80	34
ms	61.75	36
ms	63.60	38
vvw	65.40	40
w	67.30	42
m	69.15	44
w	71.0	46
w	72.70	48
vw	74.40	50
m	77.90	54
$\alpha 1$		
	125.45	108
	127.50	110
	131.95	114
	134.20	116
	136.60	118
	147.65	126
	150.85	128
	164.25	134

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a=9.001 Å, determined by averaging the values of a for the eight highest reflections. The sample is from charge no. 623.

TABLE App.-3 (continued)

HYDROXYL SODALITE

I	2θ	N
vs	14.00	2
vw	20.00	?
w	21.45	?
vw	23.85	?
vs	24.45	6
w	25.15	?
w	28.40	8
w	29.35	?
s	31.75	10
s	35.00	12
m	37.90	14
w	44.10	?
w	45.60	20
w	47.80	22
m	50.25	24
m	52.55	26
m	58.70	32
m	60.60	34
m	62.65	36
w	64.50	38
w	68.15	42
w	70.10	44
w	73.65	48
m	79.00	54
w	82.50	58
vw	89.40	66
vw	98.00	76
α1		
	110.40	90
	116.00	96
	118.00	98
	120.00	100
	126.20	106
	128.25	108
	130.55	110
	135.15	114
	137.75	116
	140.35	118
	146.05	122
	152.90	126
	157.00	128
	161.90	130

A=8.890 Å, obtained by averaging the values for the seven highest reflections. The sample is from charge no. 490.

TABLE App.-3 (continued)

HYDROXYL CANCRINITE

(hkl)	I	2θ
110	s	14.00
210	s	21.60
300	s	24.20
211	s	27.55
301	w	29.90
400	s	32.60
311	m	34.40
102	w	35.90
401	s	37.05
	m	39.80
411	m	41.55
330	s	42.85
501	w	45.00
402	m	48.35
430	m	50.60
	m	52.00
431	w	53.85
	w	55.10
	vw	56.25
	s	58.10
	vw	59.05
	m	61.90
	s	63.95
323	vw	65.75
	w	69.60
	m	71.10
	vw	73.00
	w	75.05
	w	76.50
	w	78.40
	vw	80.00
	vw	85.25
	vw	91.95
	vw	96.85
	α1	
		120.20
		126.45
		138.00
		149.00
		152.55
		158.80

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a=12.6$_8$, c=5.1$_4$, calculated from reflections up to 50° only. The sample is from charge no. 619.

TABLE App.-3 (continued)

NORMAL NEPHELINE			HIGH-NaOH NEPHELINE	
(hkl)	I	2θ	2θ	I
100	vw	10.40		
101	vw	14.60		
	vw	19.00		
200	w	20.75	20.45	m
002	w	21.30[1]	21.00 21.75	s vs
201	m	23.45	23.10 23.65	s vs
210	ms	27.35	27.25 27.75	s vs
211	m	29.20		
202	vs	29.65	29.60 30.05	vs vs
			31.40	vw
	m	32.81	32.05 33.00	vw vw
			34.85	vw
	m	33.35		
			35.2	w
	w	39.15	38.75 39.40	m m
	w	42.15	42.45	vw
320	vw	45.0	43.55	vw
			46.10	vw
	m	47.50	47.50	vw
	w	53.75	51.35	vw
	w	59.25	59.45	m
	vw	61.30	65.05	vw
	vw	63.55		
	vw	68.65	68.6	vw
			69.4	vw

Cell dimensions not calculated.

The indices are from Smith and Tuttle (1957). Charge no. 623.

Cell dimensions not calculated.

The sample is from charge no. 509.

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[1] Several pairs of reflections of high NaOH nepheline appear to result from the splitting of normal nepheline reflections. This relationship is indicated by the lines drawn in the table.

TABLE App.-3 (continued)

PHASE X

(hkl)	I	2θ
110	5	9.55
120	20	14.55
210	35	15.62
220	30	19.16
111	4	19.98
130	12	20.35
201	15	22.72
211	6	23.58
230	10	23.90
040	2	25.52
031	3	26.05
140	80	26.52
311	10	28.67
?	70	28.92
240	100	29.40
410	25	29.58
231	10	29.78
321	5	30.80
420	5	31.62
?	5	31.95
150	20	32.80
	α1	
340	20	33.65
?	12	34.02
411	15	34.65
?	12	35.10
002	30	35.50
?	10	36.45
341	3	38.12
351	15	42.98
232	6	43.36
450	6	43.64
360	6	44.66
?	6	45.30
620	45	46.04
242	10	46.75
?	10	46.85
?	6	49.55

From single crystal photographs, the cell dimensions are: a=12.3 Å, b=14.0 Å, c=5.0 Å. The sample is from charge no.508.

TABLE App.-4

Compositions and Reaction Products of the Charges

Symbols:

RUN .. Charge number

T'C .. Reaction temperature

PHASES, XRAY + OPT .. The phases formed, denoted thus:

C .. Hydroxyl cancrinite

NE .. Nepheline; LNE .. Nepheline with (100) and (110) reflections;

HNE .. Nepheline without these reflections.

NO .. Hydroxyl nosean

S .. Hydroxyl sodalite

X .. Phase X

L .. Glassy fluid, seen optically

GT .. "more abundant than"

VGT .. "much more abundant than"

Q .. "query"; e.g. "QS" denotes that inconclusive evidence of the presence of sodalite was seen

H2O.T .. The molecular percentage of water in the charge

NEP.T .. The molecular percentage of nepheline

NAOH.T .. The molecular percentage of sodium hydroxide

DC .. The charge composition lies in the system $NaAlSiO_4$-$NaOH$-Na_2O

DS .. The "bulk composition of the solid phases" is shown, by fluid phase analysis, to lie in the system $NaAlSiO_4$-$NaOH$-Na_2O.

TABLE APP.-4.

RUN	T'C	PHASES, XRAY + ØPT.	H2Ø.T P.CENT	NEP.T P.CENT	NAPH.T P.CENT	RUN	
333	450	X	0.4	40.9	58.7	333	
335	450	S GT X	25.5	47.4	27.1	335	
337	450	NE VGT C	11.0	84.6	4.4	337	
330	450	NE GT X	42.6	57.4	0.0	330	
367	450	X	-18.9	41.0	59.0	367	DC
369	450	S GT X	-4.4	52.1	47.9	369	DC
370	450	S VGT C VGT X	-13.6	63.6	36.4	370	DC
397	450	LNE	89.0	10.4	0.5	397	
398	450	LNE VGT C	53.4	44.3	2.3	398	
399	450	NE VGT C	71.7	26.9	1.4	399	
400	450	NE GT C	27.8	68.6	3.6	400	
401	450	LNE,C	16.5	79.3	4.2	401	
402	450	LNE	92.9	7.1	0.0	402	
403	450	LNE VGT C	73.5	26.5	0.0	403	
404	450	LNE GT C	54.8	45.2	0.0	404	
405	450	LNE GT C	25.4	74.6	0.0	405	
406	450	LNE,C	13.8	86.2	0.0	406	
459	450	S GT C	50.7	34.4	14.9	459	
457	450	S VGT C	18.7	56.8	24.5	457	
458	450	S GT C	27.2	50.9	22.0	458	
460	450	NE GT C	69.6	21.2	9.2	460	
461	450	C VGT NE	91.9	5.7	2.5	461	
462	450	S GT C	28.3	45.6	26.1	462	
463	450	S GT C	34.7	41.5	23.7	463	
464	450	C + S	54.7	28.9	16.5	464	
465	450	C VGT NE	71.1	18.4	10.5	465	
466	450	C VGT NE	90.6	6.0	3.4	466	
487	450	X	-21.9	41.0	59.0	487	DC
488	450	X	-9.6	41.0	59.0	488	DC
489	450	S GT X.	30.2	28.7	41.2	489	
490	450	S	54.4	18.7	26.9	490	
491	450	C,NE.	86.2	5.6	8.1	491	
492	450	X + S	80.7	10.0	9.2	492	
493	450	X + S	17.6	43.0	39.5	493	
494	450	S VGT C.	48.2	27.0	24.8	494	
495	450	S GT C.	61.5	20.1	18.5	495	
496	450	C VGT NE	88.2	6.1	5.6	496	
525	450	NE GT S VGT X	5.0	72.9	22.1	525	
526	450	S VGT C VGT NE	17.1	63.6	19.3	526	
527	450	C,S GT NE	46.5	41.1	12.4	527	
528	450	C GT NE	68.4	24.2	7.3	528	
529	450	C VGT NE	89.2	8.3	2.5	529	
530	450	NE VGT S GT X	5.3	80.8	14.0	530	
531	450	C,S GT NE	21.1	67.2	11.6	531	
532	450	C GT S,NE	50.5	42.2	7.3	532	
533	450	C + NE	91.4	7.4	1.3	533	
534	450	C GT NE	69.3	26.2	4.5	534	
590	450	X	3.7	39.5	56.8	590	DS
591	450	S GT X	5.6	49.2	45.2	591	
592	450	S GT L	51.6	11.2	37.2	592	
593	450	S ENCLØSES X	13.0	55.3	31.6	593	
594	450	L GT C GT NE	41.8	55.3	2.9	594	

TABLE APP.-4 (CONTINUED)

RUN	T°C	PHASES, XRAY + OPT.	H2O.T P.CENT	NEP.T P.CENT	NAOH.T P.CENT	RUN	
595	450	S VGT C	30.8	53.1	16.1	595	
596	450	S GT C,NE	32.7	57.4	9.9	596	
625	450	S VGT C	34.6	41.6	23.8	625	
632	450	S GT C	34.6	41.6	23.8	632	
633	450	S GT C	34.8	41.5	23.7	633	
634	450	S GT C	35.0	41.4	23.6	634	
340	520	NE,NO GT X	19.4	56.3	24.3	340	
344	520	NE + NO	10.0	57.3	32.7	344	
358	520	NO GT NE,X	4.5	66.7	28.8	358	
365	520	LNE VGT C	15.7	84.3	0.0	365	
408	520	LNE VGT NO GT C	52.5	45.1	2.4	408	
410	520	NE GT C	28.4	68.0	3.6	410	
411	520	NE VGT C.	16.8	79.1	4.1	411	
413	520	LNE VGT C	71.0	29.0	0.0	413	
414	520	LNE VGT C	55.0	45.0	0.0	414	
415	520	LNE + C	25.4	74.6	0.0	415	
416	520	NE,C	12.7	87.3	0.0	416	
467	520	NO GT X, QS	16.4	57.0	24.6	467	
468	520	NO GT C GT S	27.4	50.7	21.9	468	
469	520	NO VGT NE	52.9	32.9	14.2	469	
470	520	NE GT C.	67.8	22.5	9.7	470	
471	520	NE GT C	90.2	6.8	3.0	471	
472	520	NO VGT S	28.3	45.6	26.1	472	
473	520	C GT NO GT S	35.8	40.8	23.3	473	
474	520	NO VGT NE	53.3	29.7	17.0	474	
475	520	C GT NE	69.1	19.7	11.2	475	
476	520	C VGT NE	90.3	6.1	3.5	476	
497	520	X	-21.6	41.0	59.0	497	DC
498	520	X	-8.9	41.0	59.0	498	DC
499	520	X GT NO	52.8	44.9	2.4	499	
500	520	NO VGT S,L	55.1	18.4	26.5	500	
501	520	C GT NE	86.6	5.5	7.9	501	
502	520	X VGT NO	-4.5	52.1	47.9	502	DC
503	520	NO GT X GT S,L	17.8	42.8	39.3	503	
504	520	NO GT S,L	48.7	26.8	24.6	504	
505	520	NO VGT NE,S	62.0	19.8	18.2	505	
506	520	NE GT C	87.3	6.6	6.1	506	
535	520	NO GT NE GT X, QS	6.9	71.5	21.6	535	
536	520	NO,S VGT NE	18.8	62.3	18.9	536	
537	520	NO GT NE,S GT C	45.7	41.7	12.6	537	
538	520	C GT NE	66.0	26.1	7.9	538	
540	520	NE,NO GT X	5.3	80.8	14.0	540	
541	520	NO GT NE,S	21.1	67.3	11.6	541	
542	520	NO GT NE,S GT C	49.6	43.0	7.4	542	
543	520	C GT NE	69.3	26.2	4.5	543	
597	520	X VGT L	4.0	39.4	56.6	597	DS
598	520	X,NO VGT S	5.6	49.2	45.2	598	
599	520	L	53.2	10.0	36.8	599	
600	520	NO GT X GT S	13.0	55.3	31.6	600	
601	520	NE,NO GT C	40.3	56.7	3.0	601	
602	520	NO VGT NE,S	31.8	52.4	15.8	602	
603	520	NO VGT NE	34.4	56.0	9.7	603	

TABLE APP.-4 (CONTINUED)

RUN	T'C	PHASES, XRAY + OPT.	H2O.T P.CENT	NEP.T P.CENT	NAPH.T P.CENT	RUN	
619	520	C + NE	68.9	19.8	11.3	619	
622	520	C + NE	69.0	19.7	11.3	622	
623	520	NE + NO	53.3	29.7	17.0	623	
624	520	NO VGT NE	53.3	29.7	17.0	624	
349	600	NO GT NE GT X	18.0	57.3	24.7	349	
352	600	NO VGT NE,S VGTX	12.5	45.6	41.9	352	
353	600	NO VGT NE	13.9	54.8	31.3	353	
355	600	NE GT NO	31.3	65.2	3.4	355	
356	600	NE+NO	33.0	63.6	3.3	356	
374	600	NO GT NE,X, QS	4.9	66.4	28.7	374	
376	600	NO VGT NE	-19.8	41.0	59.0	376	DC
378	600	NO,X GT NE,S	-15.2	63.6	36.4	378	DC
380	600	NE VGT NO, QS	12.5	83.1	4.4	380	
417	600	NE	15.2	84.8	0.0	417	
419	600	LNE GT HNE	54.8	45.2	0.0	419	
422	600	NE VGT NO, QS	18.0	77.9	4.1	422	
424	600	NE GT NO	72.8	25.8	1.4	424	
477	600	NO VGT S,L	19.1	56.5	24.4	477	
478	600	NO VGT S,L	26.8	51.1	22.1	478	
479	600	NO GT NE, QS	53.6	32.4	14.0	479	
480	600	NE GT NO VGT S	64.5	24.8	10.7	480	
482	600	NO VGT S,L	28.7	45.4	25.9	482	
483	600	NO VGT S,L	29.4	44.9	25.7	483	
484	600	NO GT L	52.5	30.2	17.3	484	
508	600	X	-7.4	41.0	59.0	508	DC
509	600	L GT NO GT NE	27.0	29.9	43.0	509	
510	600	NO,L GT S	52.0	19.7	28.3	510	
512	600	NO,X GT S	-6.6	52.1	47.9	512	DC
513	600	NO GT NE,S VGT X	18.8	42.3	38.9	513	
514	600	NO GT S,L	48.7	26.7	24.6	514	
515	600	NO VGT NE GT L	66.1	17.6	16.2	515	
545	600	NE,NO GT X GT S	4.4	73.4	22.2	545	
546	600	NE,NO,S.	16.5	64.1	19.4	546	
547	600	NO GT NE GT S	47.6	40.2	12.2	547	
548	600	NO. GT NE.	67.5	25.0	7.5	548	
549	600	NO GT NE GT X	5.3	80.8	14.0	549	
550	600	NE,NO VGT S 20 DAY	20.1	68.1	11.8	550	
551	600	NE,NO.	51.5	41.4	7.2	551	
552	600	NO GT NE	69.8	25.7	4.4	552	
604	600	X VGT L	6.5	38.4	55.1	604	
605	600	X GT NO GT S GT L	4.3	49.9	45.8	605	
606	600	L	66.9	-0.2	33.3	606	
607	600	NO,NE GT S GT X	13.0	55.3	31.6	607	
608	600	NO + NE, QS	42.8	54.3	2.8	608	
609	600	NO GT NE	30.3	53.5	16.2	609	
627	600	X	-1.4	41.0	59.0	627	DCDS
628	600	X	-1.4	41.0	59.0	628	DCDS
629	600	X	-1.3	41.0	59.0	629	DCDS
638	600	NE, NO GT S 1HR	20.7	67.6	11.7	638	
640	600	NO,NE GT S 3HR	20.4	67.9	11.7	640	
641	600	NE,NO GT S 3HR	21.0	67.3	11.6	641	
644	600	NE,NO GT S 18HR	20.0	68.2	11.8	644	

TABLE APP.-4 (CONTINUED)

RUN	T'C	PHASES, XRAY + OPT.	H2O.T P.CENT	NEP.T P.CENT	NAPH.T P.CENT	RUN	
646	600	NE,NO GT S 4DAY	20.8	67.5	11.7	646	
647	600	NE,NO GT S 4DAY	21.1	67.2	11.6	647	
518	700	NO GT NE	23.4	72.8	3.8	518	
519	700	NE GT NO, QS	52.1	45.5	2.4	519	
521	700	NE	12.9	87.1	0.0	521	
522	700	NE	23.9	76.1	0.0	522	DS
553	700	NE VGT NO,X	4.5	73.3	22.2	553	DS
554	700	NE GT NO	18.7	62.4	18.9	554	
555	700	NE + NO	50.1	38.3	11.6	555	
557	700	NE.	5.3	80.8	14.0	557	
558	700	NE + NO	20.1	68.1	11.8	558	
559	700	NE,NO GT S	52.8	40.3	7.0	559	
560	700	NE GT NO	70.1	25.5	4.4	560	
571	700	NE,X VGT NO	3.7	67.3	29.1	571	DS
572	700	NE,NO GT L GT X	14.6	59.7	25.8	572	DS
573	700	NE,NO GT S,(L)	50.3	34.7	15.0	573	
575	700	X GT NE,NO, QS	-2.6	52.1	47.9	575	DCDS
576	700	NE,NO,X, QS	9.4	47.2	43.4	576	DS
577	700	NO GT S GT NE GT L	47.9	27.2	25.0	577	
578	700	NO GT S GT L GT NE	58.4	21.7	19.9	578	
579	700	X.	-21.9	41.0	59.0	579	DC
580	700	L GT NO VGT NE	29.4	29.0	41.6	580	
581	700	X VGT L	-6.8	41.0	59.0	581	DC
582	700	NO,S VGT NE	57.8	17.3	24.9	582	DS
583	700	NE GT NO GT L	13.0	55.3	31.6	583	
584	700	NE,NO GT S VGT L	25.2	47.6	27.2	584	DS
585	700	NE,NO GT S, QL	49.9	31.9	18.2	585	
611	700	X,L	4.5	39.2	56.3	611	
612	700	NE GT NO,X	7.8	48.0	44.1	612	DS
613	700	L	48.9	13.2	37.9	613	
614	700	NE GT NO,L	13.0	55.3	31.6	614	
615	700	NE,NO GT S	40.7	56.4	3.0	615	
617	700	NE + NO	33.3	56.8	9.8	617	
635	710	GLASS	30.8	28.4	40.8	635	
636	710	GLASS	30.2	28.6	41.2	636	

TABLE App.-5

Results of the Fluid Phase Analyses

Symbols:

RUN .. Charge number

T'C .. Reaction temperature

NA.FL P.CENT .. The molecular percentage of NaOH in the fluid phase, determined as Na ion.

H20.S 0R LR .. The molecular percentage of water in the solid phases, <u>or</u>, the "lever" ratio for the solid phase compositions*, for compositions outside the system $NaAlSiO_4$-NaOH-H_2O; in such cases, the last two columns are empty.

NEP.S P.CENT .. The molecular percentage of nepheline in the solid phases.

NA0H.S P.CENT .. The molecular percentage of NaOH in the solid phases.

* The "lever" ratio (LR) was used thus:

x was measured, and y was calculated by the relationship,

$$y = x(LR)$$

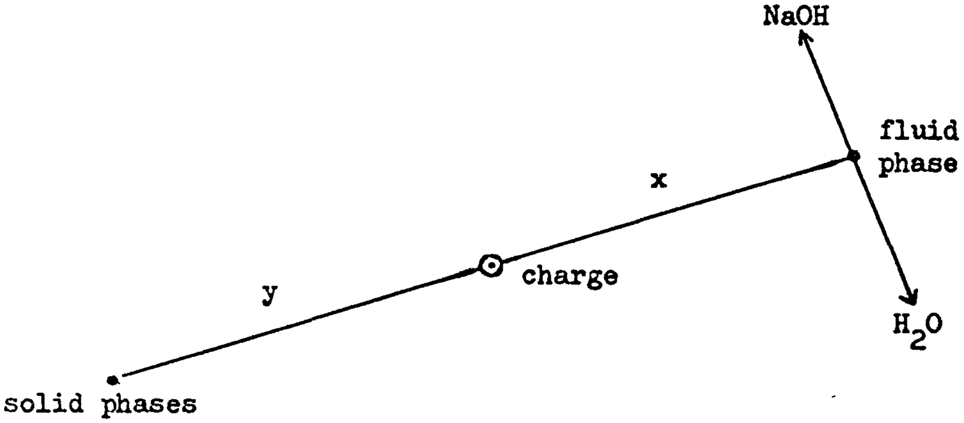

TABLE APP.-5.

RUN	T'C	NA.FL P.CENT	H20.S 0R LR	NEP.S P.CENT	NA0H.S P.CENT
518	700	18.04	-0.07	******	******
519	700	7.81	0.49	******	******
521	700	21.61	-0.29	******	******
522	700	22.68	-0.19	******	******
525	450	77.69	3.43	79.60	16.96
526	450	96.09	19.96	77.42	2.62
527	450	34.11	0.55	******	******
529	450	10.24	6.70	******	******
530	450	79.39	4.04	87.20	8.76
531	450	70.79	19.61	79.83	0.56
532	450	30.10	0.56	******	******
533	450	8.05	7.91	******	******
534	450	23.86	1.51	******	******
535	520	74.83	4.52	80.63	14.85
536	520	90.56	0.02	******	******
537	520	45.01	0.53	******	******
538	520	19.04	1.44	******	******
540	520	72.62	2.55	90.68	6.77
541	520	71.69	-0.02	******	******
542	520	38.60	0.53	******	******
545	600	70.21	2.35	79.25	18.40
549	600	57.06	1.34	89.19	9.48
553	700	52.55	-0.13	******	******
559	700	7.79	14.51	79.32	6.16
571	700	45.94	-0.09	******	******
572	700	47.97	0.03	******	******
575	700	67.86	0.05	******	******
576	700	41.44	0.19	******	******
577	700	26.49	4.43	73.17	22.40
582	700	22.10	1.96	******	******
584	700	35.14	0.23	******	******
585	700	15.17	12.70	65.85	21.45
590	450	58.99	0.30	******	******
593	450	56.71	8.03	64.47	27.50
594	450	6.42	7.72	91.70	0.58
596	450	16.57	18.45	73.50	8.04
597	520	55.11	0.30	******	******
600	520	75.69	10.02	70.07	19.91
601	520	0.72	8.33	87.47	4.19
602	520	28.36	23.00	63.93	13.07
607	600	63.34	4.30	75.76	19.94
608	600	2.38	8.05	88.81	3.14
609	600	31.61	16.47	72.95	10.58
612	700	72.08	0.17	******	******
614	700	28.61	0.06	******	******
615	700	2.07	4.72	91.77	3.51
617	700	28.15	0.16	******	******
623	520	19.37	19.92	66.04	14.04
624	520	19.88	14.77	72.38	12.84
625	450	30.84	16.50	63.39	20.11
627	600	55.03	0.23	******	******
628	600	66.12	0.23	******	******
629	600	56.72	0.23	******	******