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286. *The Hydrothermal Chemistry of Silicates. Part II.* Synthetic Crystalline Sodium Aluminosilicates.*

By R. M. Barrer and E. A. D. White.

The hydrothermal reactions of sodium aluminosilicate gels have been investigated between 150° and 450°. Crystal growth has been examined in absence and in presence of additional sodium compounds (NaCl, Na_2SO_4, Na_2CO_3, and NaOH) in the mother-liquors. Gel compositions were in the range $Na_2O,Al_2O_3,1$—$12SiO_2$.

The conditions employed gave rise to a felspar (albite); zeolites (analcite and mordenite); a mica (paragonite); felspathoids (nepheline, sodalite, nosean, and cancrinite), and α-quartz. Two hydrated phases of nepheline composition were synthesised, and also a range of crystalline phases related to the cancrinite, nosean, and sodalite structures, but without the usual interstitial salts. Rather large laminar crystals, of an apparently new hydrated silicate species, were formed in some preparations, and also large crystals of sodium silicate. Details of two new species obtained in minor yields are recorded.

All the compounds have been characterised by optical and *X*-ray methods, which in some cases reveal interesting differences between synthetic and naturally occurring forms of the mineral. Some ion-exchange reactions of cancrinite, nosean, and sodalite-type minerals, one of the minerals of nepheline composition, and one of the minor species were studied.

Despite the technical and scientific interest of many naturally occurring aluminosilicates, problems relating to their reproducible laboratory synthesis and their properties have as yet been solved very incompletely. The chemistry of mineral reactions can usually be inferred only in general outline from geochemical reasoning. Much of the earlier literature of hydrothermal reactions has been summarised by Morey and Ingerson (*Econ. Geol.*, 1937, **32**, 607), and Barrer (*Faraday Soc. Discussion*, 1949, **5**, 326) has discussed the principal synthetic methods in silicate mineral chemistry.

Recently, by direct synthesis from gels under carefully specified conditions, much new information on mineral formation has been obtained in this laboratory (Barrer, *J.*, 1948, 2158; 1950, 2342; H. W. Taylor, *J.*, 1949, 1253; Barrer and White, *J.*, 1951, 1167) and also by continental and American workers (Noll, *Neues Jahrb. Min.*, Beil. Bd., 1935, **70**, 65; Wyart, *Discuss. Faraday Soc.*, 1949, **5**, 323; Roy, Roy, and Osborne, *J. Amer. Ceram. Soc.*, 1950, **33**, 152; Friedman, *J. Geol.*, 1951, **59**, 19). In particular, Noll has been concerned with mixtures in which the ratio base : alumina in the parent aluminosilicate gel is varied and is usually less than unity, while the alumina : silica ratios are fixed in a few proportions only. Clay formation was one hydrothermal reaction in such mixtures (giving, for example, kaolinite, pyrophyllite, and montmorillonite). On the other hand, in the authors' work with the molar ratio base : alumina equal to or (by addition of excess alkali) rather greater than unity, and with systematic variation of the silica content, conditions were more alkaline. The compositions then crystallised as zeolites, felspars, felspathoids, quartz, and other species. In the present paper are given some new results obtained with gels $Na_2O,Al_2O_3,nSiO_2$,aq. ($n = 1$—12), which completes an earlier investigation where $8 < n < 12$ (Barrer, *J.*, 1948, 2158; *Nature*, 1946, **157**, 734) and which showed conditions necessary for the formation of analcite, mordenite, quartz, and other crystals.

The system Na_2O–Al_2O_3–SiO_2 has been investigated by other workers using pyrolytic and hydrothermal methods. Recently Friedman (*loc. cit.*) investigated part of this system hydrothermally and under rather specialised conditions. He obtained much information but few synthetic products.

Wyart (*loc. cit.*) has described crystallisations from the gels $Na_xK_{1-x}AlSiO_4$ ($0 < x < 1$), running from kaliophilite to nepheline in composition. Species reported included

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* Part I, *J.*, 1951, 1267.

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nepheline, cancrinite, and a sodalite-type mineral. Little information is given about these products, but it seems likely that they would prove similar to corresponding species reported in this paper.

EXPERIMENTAL

The apparatus and methods used were described in Part I (*loc. cit.*). Gels of composition $Na_2O,Al_2O_3,nSiO_2,mH_2O$, in which n varied from 1 to 12, were prepared by mixing the constituents in the necessary proportions when in aqueous suspension or solution. The mixtures were evaporated under various conditions (*e.g.*, over a steam-bath or in an air-oven at temperatures up to 120°), to creamy consistency and through intermediate stages up to dry gels.

The examination of the products of subsequent hydrothermal treatment of these gels has already been described (Part I). The larger size of many of the sodium aluminosilicate crystals now obtained enabled additional data to be determined from single crystal *X*-ray photographs, taken with a Unicam camera.

RESULTS

Products from gels of composition $Na_2O,Al_2O_3,nSiO_2$, treated hydrothermally at temperatures between 150° and 450°, are shown in Table 1. In many cases the addition of $\geqslant$100% excess of sodium hydroxide (in molar proportion) resulted in the formation of different minerals under otherwise similar experimental conditions. A slight excess only of sodium hydroxide enhanced the ease of crystallisation of the gels in almost all cases. Products in the same field, but grown in the presence of excess alkali hydroxide, are given in parentheses in Table 1.

Experiments were also made in which excess of sodium chloride, sulphate, or carbonate was added to the reaction mixtures. It was found that the products over almost the whole of the conditions of composition, pH, and temperature recorded in Table 1 were sodalite and nosean in the presence of chloride and sulphate respectively. In high-silica mixtures some albite and analcite were also observed. With insufficient added salt, a limited amount of sodalite or nosean was formed, together with crystals normally formed in that region in absence of added salts. The addition of sodium carbonate did not result in marked alteration of the usual products, but extended the conditions of formation of cancrinite (*i.e.*, formation at lower temperatures was observed), and improved the crystallisation of other appropriate species.

Crystallisation was more difficult from gels dried under rigorous conditions (*e.g.*, evaporated to dryness at 120° before hydrothermal treatment). Optimum crystallisation usually occurred when gels were evaporated to the consistency of a thick cream on the steam-bath. The effect of drying the gels was, however, counteracted when much alkali hydroxide was present in the mineralising mother-liquor, or when hydrothermal crystallisation was conducted at higher temperatures (>350°).

One may comment on the dominance of the zeolitic phase analcite over much of the field explored, although at higher temperatures albite (from high-silica gels) and paragonite (from low-silica gels) become dominant. At moderate temperatures the yield of analcite increased sharply at $n = 4$ with rising silica content of the gel $Na_2O,Al_2O_3,nSiO_2$, and then decreased slowly for still higher values of n. At temperatures approaching 300°, with increasing values of n small yields of mordenite appeared in the products, the yield rising to a maximum at $n = 10$. Some quartz was also formed in this region, and in increasing yield as n increased further (Barrer, *Nature*, 1946, **157**, 734). The addition of sodium carbonate in the high-silica region facilitated crystallisation of mordenite and quartz, but when the mother-liquor became very alkaline the initial precipitate of mordenite was attacked and recrystallised (cf. Barrer, *J.*, 1948, 2158).

Fig. 1, *a*—*g*, shows diagrammatically the regions of temperature and composition over which some important species were obtained, first at lower pH and then under highly alkaline conditions. Very high pH ($\geqslant$100% molar excess of sodium hydroxide) did not greatly influence the formation of the low-temperature phases. Above 300°, however, several new species appeared. From gels $Na_2O,Al_2O_3,2SiO_2 + NaOH,aq.$ at 450°, progressive increasing of pH gave, successively and in nearly 100% yields, paragonite, large nepheline crystals, cancrinite, and finally nosean-type phases. Moreover, at temperatures between 300° and 400° and over restricted ranges of composition (Fig. 1*f*) three new crystal species were grown. Two of them have the composition of nepheline, and since they are hydrated they are here designated as nepheline hydrates I and II. The third species (compound L) grew as plates up to 5 mm. across, but was not identified with any natural mineral. In general, these crystals were secondary products, although yields approaching 100% were occasionally noted.

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TABLE 1. *Summary of results of crystallisation of gel compositions* $Na_2O,Al_2O_3,nSiO_2$.*

Temp.	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
150°	V. poor F 10·0 (Poor F)	Poor F & B 10·0 (Poor F & B)	Poor F, some B 10·0 (Poor F & B)	Poor B 10·0 (Good B)	V. poor B 10·0 (Good B)
180	V. poor F 10·5 (Poor F & B)	V. poor F 9·3 (Poor F & B)	V. poor F & B 9·0 (Poor B & F)	Poor B 10·0 (V. good B)	Poor B 9·3 (V good B)
210	V. poor F 10·0 (Mod. B & F)	Poor F 9·7 (Mod. B & F)	Poor F & B 9·3 (Good B)	Good B 9·0 (V good B)	Good B 9·3 (V. good B)
240	Mod. F & B 8·3 (Mod. B, some I)	Mod. F & B 8·7 (Mod. B, some I)	Mod. F & B 8·7 (Mod. B, some I)	V. good B 8·3 (V. good B)	V. good B 8·0 (V. good B)
270	Some F 8·7 (Mod. B, some J)	Mod. F, some B 8·7 (Mod. B, some J)	Mod. B, some F 9·0 (Mod. B, some J)	V good B 8·0 (Good B)	Good B 7·7 (Good B)
300	Some F 9·0 (Mod. F)	Mod, F, some B 9·4 (Mod. F, some J)	Mod. B 7·4 (Mod. F, some B)	Good B 7·4 (Mod. B, some A)	Good B 7·4 (Mod. B & A)
330	Some F 9·4 (Mod. F & I)	Mod. F, some I 9·7 (Mod. F & I)	Some F & I 9·0 (Mod. F, some B)	Mod. B 8·4 (Mod. B & A)	Mod. B 8·4 (Mod. A)
360	Poor G 7·4 (Good E & J)	Some G & B 8·3 (Good E, some J)	Poor B & G 8·0 (Mod. E, some J)	Mod. B, some C 8·4 (Good A, some B)	Mod. A, some B 7·7 (Mod. A & B)
390	Mod. G 7·4 (Mod. E)	Mod. G, some B 8·0 (Good K, some E)	Poor G 7·7 (Good K, some E)	Poor G, some B 7·4 (Mod. E & B)	Poor A 7·7 (Mod. B & A)
420	Good G 7·7 (Good E)	Good G 7·4 (V. good E)	Mod. G 7·7 (V. good E)	Poor G, some B 7·4 (Good E)	Poor G, some A 7·7 (Good B & A)
450	V. good G 7·4 (V. good E)	Good G 7·4 (V. good E)	Mod. G 7·4 (V. good E)	Mod. G 7·0 (V. good E)	Poor G 7·4 (Mod. E & A)

Temp.	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$
150	–10·0 (Good B)	–10·0 (Good B)	–10·0 (Good B)	–10·0 (Mod. B)	–10·0 (Mod. B)
180	Poor B 10·5 (V. good B)	Poor B 9·0 (V. good B)	Poor B 9·0 (Good B)	V poor B 9·0 (Good B)	V. poor B 10·0 (Mod. B)
210	Mod. B 9·7 (V. good B)	Mod. B 9·3 (V. good B)	Mod. B 9·7 (V. good B)	Mod. B, some D 10·0 (Good B)	Mod. B & D 9·0 (Good B)
240	Good B 8·3 (V good B)	Good B, some D 8·7 (V. good B)	Good B, some D 9·0 (V. good B)	Mod. B & D 9·0 (Good B)	Mod. D, some B 8·7 (Good B)
270	Good B 8·0 (Good B)	Good B 8·0 (Good B)	Good B, some D 7·7 (Good B)	Mod. D, some B 8·0 (Good B)	Good D 8·3 (Mod. B)
300	Good B 9·0 (Mod. B & A)	Good B 7·4 (Mod. B & A)	Mod. B & D 7·4 (Mod. B & A)	Good D, some B 7·4 (Mod. B & A)	V. good D, some B & H 8·0 (Poor B & A)
330	Mod. B, some A 8·0 (Good A)	Mod. B, some A 8·0 (Good A)	Mod. B, some D 7·7 (Good A)	Poor D & B 7·7 (Good A)	Mod. D 8·0 (Mod. A)
360	Mod. A 8·0 (Good A & B, some N)	Mod. A 8·4 (Good A, some B & N)	Mod. A 8·4 (Good A, some N)	Mod. A 8·4 (Good A)	Some A 8·7 (Good A)
390	Good A 8·4 (V. good A, some N)	Good A 8·0 (Good A, some N)	Mod. A 7·7 (Good A)	Mod. A 7·7 (Good A)	Poor A 7·4 (Good A)
420	Good A 8·0 (Good A, some B)	Good A 7·7 (Good A)	Good A 7·7 (Good A)	Mod. A 7·7 (Good A)	Mod. A 7·4 (Mod. A)
450	Poor G & A 7·7 (Good A)	Some G & A 7·7 (Good A, some B)	Poor A 7·4 (Good A)	Poor A 7·4 (Good A)	Some A 8·0 (Mod. A, some B)

* For significance of letters, see Table 2.

Note : Results in parentheses refer to growth in NaOH aq. ($\leqslant 100\%$ molar proportion). Figures refer to pH of cold mother-liquors.

TABLE 2.

Name	Ref. letter (Table 1)	Ideal empirical formula
Albite	A	$Na_2O,Al_2O_3,6SiO_2$
Analcite	B	$Na_2O,Al_2O_3,4SiO_2,2H_2O$
Cancrinite	C	$3(Na_2O,Al_2O_3,2SiO_2),Na_2CO_3$
Mordenite	D	$Na_2O,Al_2O_3,10SiO_2,6{\cdot}7H_2O$
Nepheline	E	$Na_2O,Al_2O_3,2SiO_2$
Nosean	F	$3(Na_2O,Al_2O_3,2SiO_2),Na_2SO_4$
Paragonite	G	$Na_2O,3Al_2O_3,6SiO_2,2H_2O$
Quartz	H	SiO_2
Sodalite	I	$3(Na_2O,Al_2O_3,2SiO_2),2NaCl$
Nepheline hydrate I	J	No natural counterpart, $Na_2O,Al_2O_3,2SiO_2,H_2O$
Nepheline hydrate II	K	,, ,, $Na_2O,Al_2O_3,2SiO_2,\frac{1}{2}H_2O$
Compound L	L	,, ,, $2Na_2O,Al_2O_3,6SiO_2,2H_2O$
Compound M	M	,, ,,
Compound N	N	,, ,,
Sodium silicate	O	Na_2O,SiO_2

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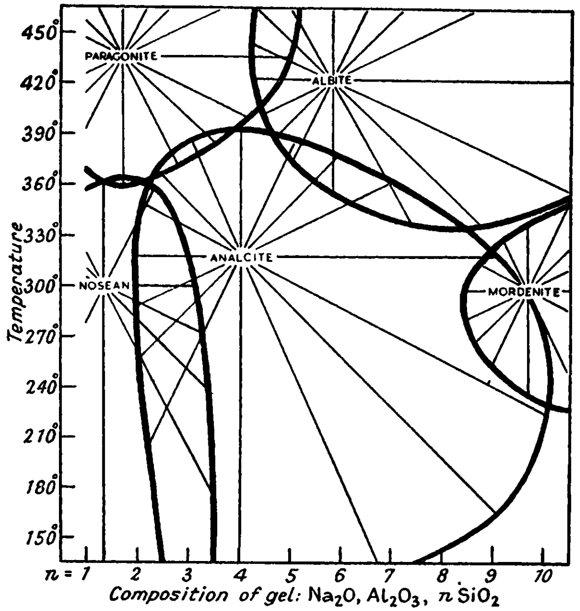
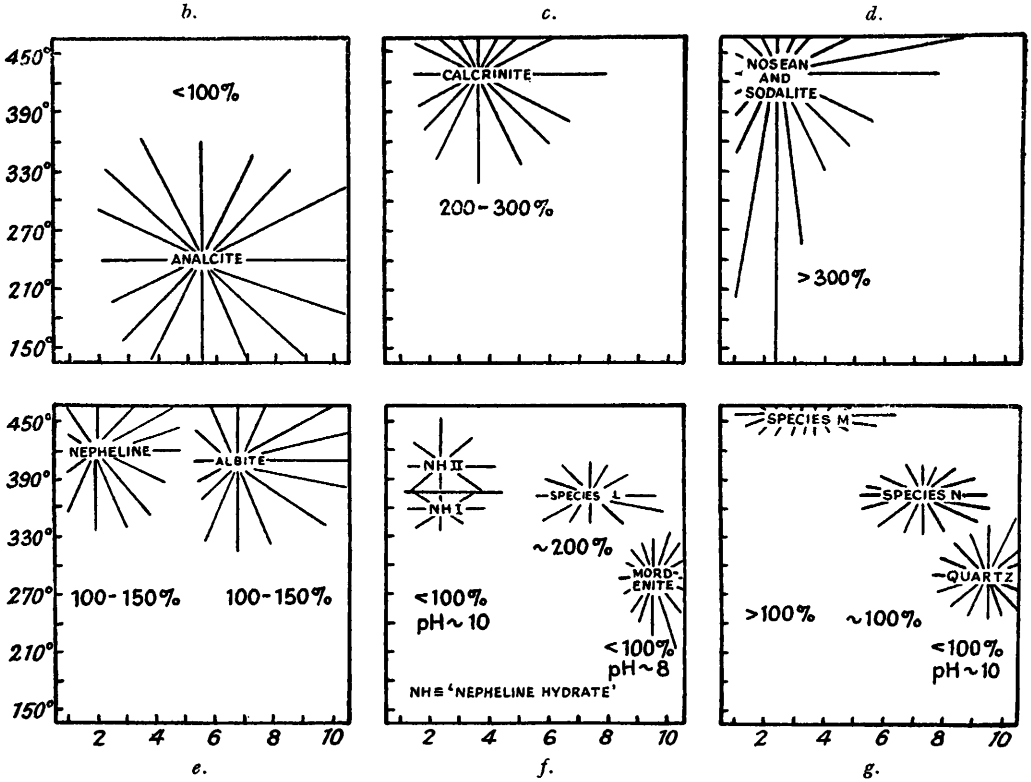


FIG. 1*a*. *Diagrammatic representation of the approximate areas of formation of the products obtained by crystallisation of the gels :* $Na_2O,Al_2O_3,nSiO_2 + aq.$ (*no excess* NaOH *added*).

The curves do not represent rigid boundaries; considerable overlapping of the products occurs. The mineral names are approximately located in the area where optimum formation occurs.

FIGS. 1*b*—*g*. *Digrammatic representation of the approximate areas of formation of products obtained by the crystallisation of gels in the presence of excess* NaOH.



Horizontal Scale : values of n *for* $Na_2O,Al_2O_3,nSiO_2$. *Vertical Scale : temperature* (° c).
Percentages refer to amounts of NaOH *added in excess of gel composition.*

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The principal species synthesised are given in Table 2 and some of their properties will now be described.

Zeolites.—The zeolites analcite and mordenite were readily obtained, analcite in 100% yield and mordenite often in major, but not 100% yield, from gels of their own composition.

Analcite was prepared in three habits: as spherulites, as ikositetrahedra, and as cubes with hemihedral faces (Plate I). The maximum crystal dimension was 0·5 mm., but more usually the crystals were much smaller (20—50 μ). It was possible to obtain 100% yields whether in 1-g. or 5-kg. quantities (Barrer, *Faraday Soc. Discussion*, 1949, **5**, 326). The crystals were isotropic and with unit-cell cube edge of 13·67 Å. The sorptive and ion-exchange properties of analcite have been studied elsewhere (Barrer, *Proc. Roy. Soc.*, 1938, *A*, **167**, 392, 406; Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195; Barrer, *J.*, 1950, 2342).

Mordenite grew as thin laths, usually in wheatsheaf-like clusters, up to ~25 μ in length. The crystals were weakly birefringent with a mean R.I. = 1·467, and were monoclinic. The conditions of growth of mordenite and its ion-exchange reactions have been described rather fully elsewhere (Barrer, *J.*, 1948, 2158). The temperature range of formation has been extended in the present work (Fig. 1*a*), as has the range of interchangeable cations which now includes the series Li^+, Na^+, K^+, Cs^+, Ag^+, NH_4^+, Tl^+, Ca^{++}, and Ba^{++}. The sorptive and molecular-sieve properties of dehydrated mordenite are noteworthy (Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555; *Quart. Reviews*, 1949, III, 293), and various ion-exchanged forms show the same type of sorptive behaviour as the parent mineral, modified to varying degrees by the cations present.

Hydrated Non-zeolitic Species.—Three hydrated, non-zeolitic phases were obtained: nepheline hydrate I, nepheline hydrate II, and compound L (Table 2).

Nepheline hydrate I (Plates II and III) occurred as complex hexagonal tablets, almost without exception showing mimetic twinning. Maximum dimensions were 150 μ. The optimum growth was observed at ~360° from gels $Na_2O,Al_2O_3,2$—$3SiO_2$ at pH values of ~10 (*i.e.*, slight excess of sodium hydroxide). It was usually a secondary phase to analcite, but yields approaching 100% were also obtained. The region of formation is comparatively restricted (Fig. 1*f*). The crystals showed moderate birefringence and straight extinction and belonged to the orthorhombic system, with $\alpha = 1·503$, $\beta = 1·506$, and $\gamma = 1·508$. Analysis gave a formula close to $Na_2O,Al_2O_3,2SiO_2,H_2O$. Dehydration of the crystals did not render them capable of sorbing ammonia. The compound may be the "hydronephelite" prepared by Thugutt (*Z. anorg. Chem.*, 1892, **2**, 64, 113) but he did not give identifying physical data.

Nepheline hydrate II (Plate IV) occurred as twinned hexagonal plates in a restricted region indicated in Fig. 1*f*. It grew best from gels $Na_2O,Al_2O_3,2SiO_2$ at ~420° in the presence of a slight excess of sodium hydroxide (pH ~10). These crystals were identical in appearance with the twinned hexagonal plates of nepheline hydrate I (Plate III), but were of higher refractive index ($\alpha = 1·548$, $\beta = 1·546$, $\gamma = 1·534$). They also showed straight extinction and belonged to the orthorhombic system. The maximum diameter of the hexagonal plates was ~250 μ. This species was found in close association with nepheline. For example, Plate IV shows typical crystals of nepheline hydrate II, from the centres of which protrude hexagonal prisms of nepheline. The moisture content was lower than for nepheline hydrate I, and a nepheline composition being assumed, it corresponded nearly to $Na_2O,Al_2O_3,2SiO_2,\frac{1}{2}H_2O$. *X*-Ray powder photographs of the two hydrates (Table 6) showed no particular resemblance either *inter se* or with nepheline. Nevertheless, there may be some structural similarities: nepheline hydrate II and nepheline must have a lattice arrangement along the 001 plane similar enough to permit overgrowth; the refractive indices along the *c* axes are identical.

Compound L (Plate IV) was obtained in moderate yield from gels $Na_2O,Al_2O_3,6$—$10SiO_2$ at 350° in presence of a large excess of sodium hydroxide (~300%). The crystals grew as tablets up to 5 mm. in length and could easily be separated by hand-picking or sieving. They were usually a secondary phase, and conditions of formation were restricted (Fig. 1*f*) although they were reproducibly formed. The crystals were obtained as irregular hexagonal tablets, easily cleavable into thin sheets. They were of low birefringence, biaxial positive, with a mean R.I. = 1·49; they belong to the monoclinic system having a unit cell of $a = 8·10$, $b = 6·10$, $c = 4·88$ Å, $\beta = 105° 20$. Great resistance to attack by concentrated acids was shown, and on ignition the crystals readily fused to a glass with 7% loss in weight. On dehydration *in vacuo* they showed no sorptive power towards ammonia. *X*-Ray spacings are given in Table 6.

Nepheline hydrates I and II and compound L appear to have no natural counterparts, although the last shows similarities to the mineral ussingite ($2Na_2O,Al_2O_3,6SiO_2,H_2O$). Analysis of hand-picked crystals showed compound L to have composition close to $2Na_2O,Al_2O_3,6SiO_2,2H_2O$. Refractive indices of the two compounds are also similar (for

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ussingite, *n* ~1·50) but the *X*-ray powder-diffraction patterns of the two materials are not related.

Micaceous Products.—The only mica obtained was paragonite, which formed from gels $Na_2O,Al_2O_3,2SiO_2$, aq. at 420° and at low pH (~7). Yields approached 90% and the product comprised very small anhedral crystals (~5 μ) present in masses. The crystals showed high birefringence with maximum and minimum R.I. of 1·579 and 1·573. Natural paragonite is of rather rare geochemical occurrence.

Albite. The felspar albite was obtained in two characteristic habits (Plate V). Optimum growth occurred from gels of albite composition at 420° and at pH ~10 (the pH was not critical, however). The crystals, up to 50 μ in length, were frequently twinned, monoclinic, of low birefringence, and in some orientations gave oblique extinction; $\alpha = 1{\cdot}529$, $\beta = 1{\cdot}532$, $\gamma = 1{\cdot}537$. Some differences from the natural compound were observed from the *X*-ray powder photographs (Table 6), but identity was apparent with albite obtained by ignition from synthetic analcite (Table 4), and it is probably the high-temperature modification of albite (Tuttle and Bowen, *J. Geol.*, 1950, **58**, 572; Friedman, *ibid.*, 1951, **59**, 19).

Felspathoids. Felspathoids obtained were nepheline, cancrinite, nosean, and sodalite. Excellent growth was observed in all cases from gels $Na_2O,Al_2O_3,2SiO_2$ in the presence of varying quantities of excess of sodium hydroxide (see Figs. 1*b*—*g*).

Nepheline (Plate VI) was usually formed as elongated hexagonal prisms with pyramidal ends, terminated by basal pinacoids, but occasionally it occurred as thick hexagonal tablets. The larger crystals were 1—2 mm. in length, and under crossed Nicols showed a cross-hatched structure, presumably due to complex twinning. Best growth was found at 420° in the presence of 100—150% excess of sodium hydroxide, yields of 100% then being recorded. As in the case of natural and synthetic albite, some differences in *X*-ray powder spacings were noted (Table 6) when compared with natural nepheline. Of moderate birefringence and straight extinction, the crystals had R.I. of $\varepsilon = 1{\cdot}537$, $\omega = 1{\cdot}534$, which are slightly lower than those of natural nepheline ($\varepsilon = 1{\cdot}542$, $\omega = 1{\cdot}538$, according to I.C.T., **1**, 153). The hexagonal unit-cell had dimensions $a = 4{\cdot}95$, $c = 8{\cdot}37$ Å.

Normal sodalite was found as spherulites up to 200 μ in diameter, but usually much smaller. The crystals were obtained in presence of excess of sodium chloride over the whole range of temperatures 150—450°, in yields up to 100%. They were isotropic with $n = 1{\cdot}488$, and belonged to the cubic system with unit-cell edge = 8·87 Å.

In addition, similar crystals of " basic " sodalite were grown at temperatures between 350° and 420° in the complete absence of sodium chloride but in the presence of a large excess (~300%) of the hydroxide. It was occasionally admixed with analcite, but was grown in 100% yields from analcite by treatment with aqueous sodium hydroxide at 400—450°. The cubic cell edges of these crystals varied between 8·77 and 8·90 Å, and although the intensities of the *X*-ray powder reflections were extremely similar to those of natural sodalite (Plate IX), yet small regular shifts in spacings occur. The R.I. of the more collapsed specimens was somewhat higher, with *n* reaching a limit of 1·495. Barth (*Z. Krist.*, 1932, **83**, 409) gave $a = 8{\cdot}89$ Å for natural sodalite.

Normal and " basic " noseans (Plate VII) were formed under conditions of temperature and pH rather like those found effective for the sodalites. Normal nosean formed as spherulites up to 20 μ in diameter in presence of excess of sodium sulphate over the range 150—450°. The isotropic crystals had $n = 1{\cdot}486$ and a cubic cell edge of 9·10 Å. Basic nosean was grown as rhombic dodecahedra, often distorted, to a maximum dimension of 2 mm. 100% Yields were obtained at 450° in the presence of a great excess of sodium hydroxide (400—600%), and in the complete absence of the sulphate. It was also obtained in varying yields over a wide temperature and considerable pH range. *X*-Ray intensities were identical with those of natural nosean, but again shifts in the spacings occurred (Plate IX) corresponding to variations in the cubic cell edge between 9·03 and 9·10 Å. The isotropic crystals had R.I. which varied from 1·486 to 1·494. Mixtures of spherulites having nosean, sodalite, and analcite structures were grown from gels $Na_2O,Al_2O_3,1$—$3SiO_2$ at temperatures between 130° and 300°, in the presence of a small excess of sodium hydroxide (<100%). These compounds were usually of the collapsed type.

Normal cancrinite formed as thin rods, usually ~30 μ in length, when the gel $Na_2O,Al_2O_3,2SiO_2$ was treated with excess of aqueous sodium carbonate in the temperature interval 300—420°. Birefringence was moderate, with $\varepsilon = 1{\cdot}497$, $\omega = 1{\cdot}500$, and the system hexagonal, with unit cell dimensions of $a = 12{\cdot}63$, $c = 5{\cdot}18$ Å. " Basic " cancrinites (Plate VIII) were grown in complete absence of carbonate ion, but in the presence of excess of

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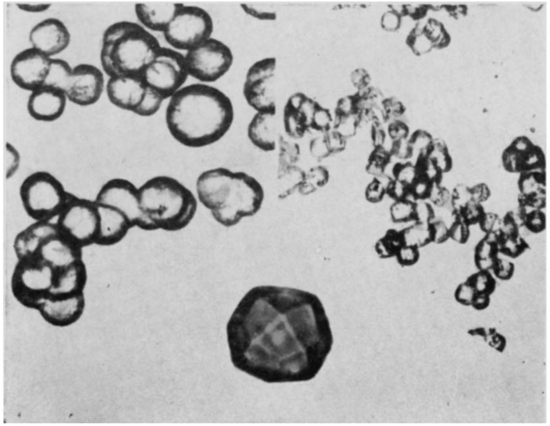
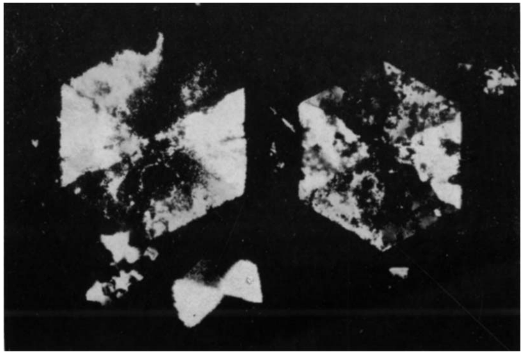
PLATE I.



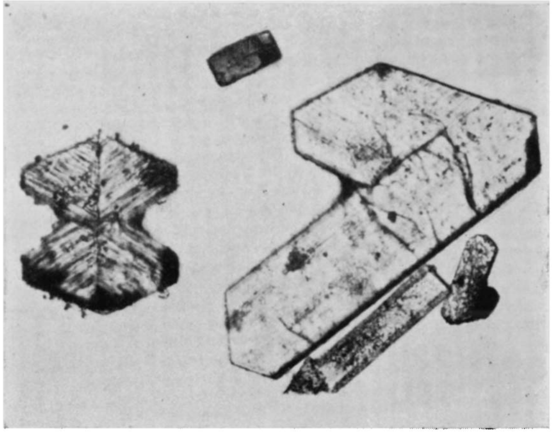
Analcite, showing three characteristic habits : spherulites (× 325) ; *cubes* (× 325) ; *and an ikositetrahedron* (× 522).

PLATE II.



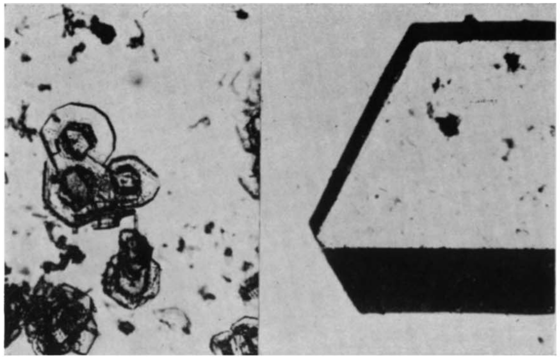
Left : *Nepheline hydrate I* (× 89). Right : *Nepheline hydrate II* (× 60). *Taken under crossed Nicols, and showing similarity in twinning.*

PLATE III.



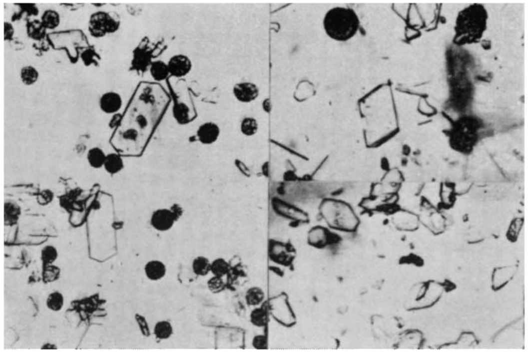
Nepheline hydrate I (left, × 125 ; right, × 100). *Characteristic crystals showing twinning. These crystals are of the* Ag^+ *ion-exchanged form ; the striations shown, particularly on the left-hand crystal, are not visible in the* Na^+ *form.*

PLATE IV.



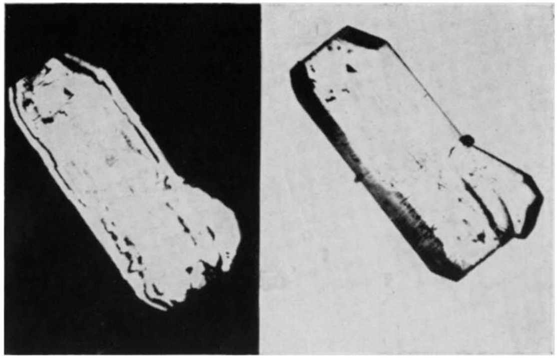
Left : *Plates of nepheline hydrate II overgrown on central hexagonal prism of nepheline* (× 120). Right : *Part of a crystal of compound* L (× 37·5).

PLATE V.



Characteristic forms of albite, together with some analcite spherulites. (Left, × 95 ; right, × 200.)

PLATE VI.



Nepheline crystal under crossed Nicols and in ordinary light. Internal irregularities in the crystal are clearly demonstrated in the left-hand photograph.

[*To face p.* 1566.

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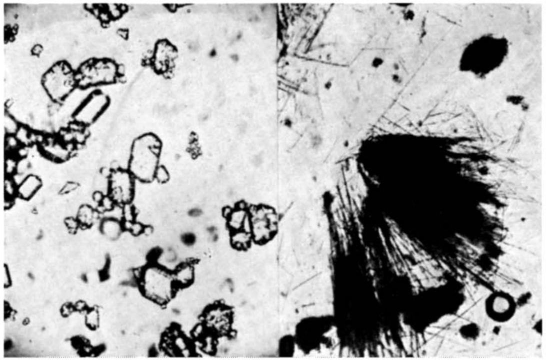
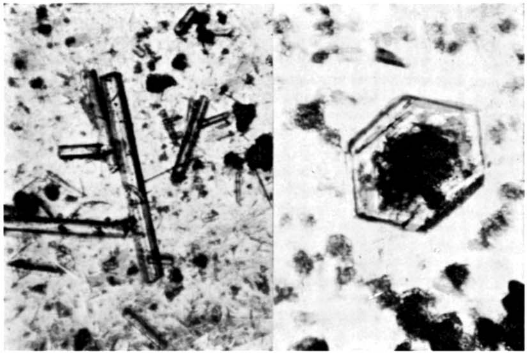
Plate VII.



Left: "*Basic*" *nosean* (× 140). Right: *Compound* N (× 125).

Plate VIII.



Left: "*Basic*" *cancrinite* (× 85). Right: *Compound* M (× 85). *The terraced structure is visible near the edges and causes the dark central portion.*

Plate IX.

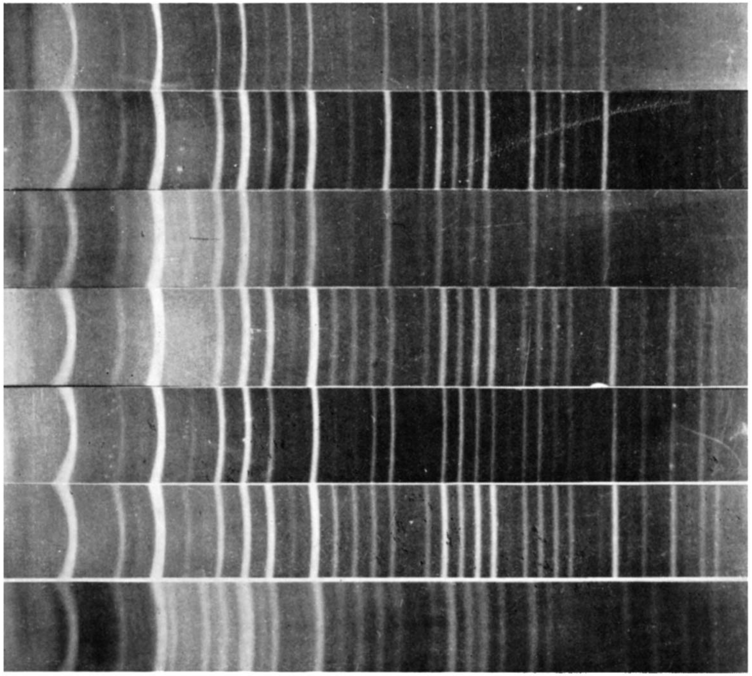
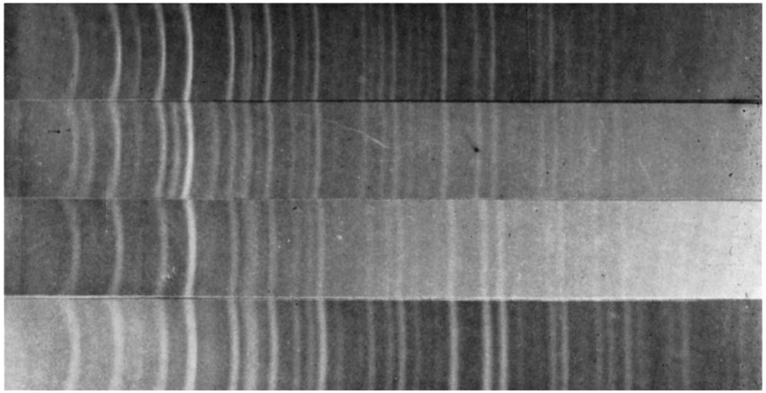


Plate X.



Print of X-ray powder photographs of different forms of "*basic*" *cancrinite* (1, 3, *and* 4), *and of natural sulphatic cancrinite* (2).

Plate IX.

Print of X-ray powder photographs demonstrating the lattice changes in synthetic noseans and sodalites.

(1) *and* (2) *Basic nosean.*
(3) *Nosean* (*with* SO_4^{--}).
(4) *and* (5) "*Basic*" *sodalites.*
(6) *Sodalite* (*with* Cl^-).
(7) "*Basic*" *Sodalite, with some analcite present.*

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sodium hydroxide (200—300%), at ~390°. They occurred as small crystallites in masses and sometimes as hexagonal prisms up to 500 μ long. Although the *X*-ray powder photographs were almost identical with that of natural cancrinite, yet slight alterations in lattice spacing (Plate X) were found corresponding to expanded and contracted forms; variations in the unit-cell dimensions of these forms were $a = 12{\cdot}47$—$12{\cdot}71$ Å and $c = 5{\cdot}07$—$5{\cdot}20$ Å. Furthermore, the optical properties of different preparations showed a comparable variation (Table 4). The mean R.I. was ~1·50.

These remarkable " basic " noseans, sodalites, and cancrinites have not been observed in Nature. All three species are based upon a similar type of aluminosilicate framework (Bragg, " Atomic Structure of Minerals," Cornell Univ. Press, 1937), and it is noteworthy that these " basic " forms have been made by using the same gels ($n\mathrm{Na_2O,Al_2O_3,2SiO_2}$,aq.) in all cases, and by varying only the amounts of excess of sodium hydroxide. As shown in Plate IX, compounds intermediate between a collapsed nosean and an expanded sodalite have been prepared, and it is likely that a continuous range of compounds is possible between the collapsed sodalite and expanded nosean structures, the formation of such a range being directly dependent upon the amount of sodium hydroxide present in the reacting mixture.

Other Products.—Two other crystal species were prepared in yields usually <50%. These are compounds M and N of Table 2. The former grew as hexagonal plates up to 250 μ across, and usually having a curious " terraced " structure (Plate VIII). Optimum yields were produced at 450° from the gel $\mathrm{Na_2O,Al_2O_3,2SiO_2}$, with excess of sodium hydroxide present (>100%). The crystals were often a secondary phase in nosean preparations and could be separated by hand-picking. Belonging to the orthorhombic system, the crystals had a mean R.I. ~1·635, and unit-cell dimensions of $a = 11{\cdot}75$, $b = 5{\cdot}81$, $c = 8{\cdot}52$ Å.

Compound N was produced as very thin needles in bunches, single crystals often having a length : thickness ratio of ~300 : 1 (Plate VII). They grew in varying yields as a secondary phase, from gels $\mathrm{Na_2O,Al_2O_3,6}$—$\mathrm{8SiO_2}$ at ~360° in the presence of a moderate excess of sodium hydroxide (~100%). Refractive indices were $\varepsilon = 1{\cdot}616$ and $\omega = 1{\cdot}612$, the probable system being hexagonal. On treatment with aqueous silver nitrate at 110°, ion-exchange occurred and the product had a mean R.I. > 1·77. Attempts at separation of these crystals were unsucessful and *X*-ray data were not obtainable.

Large acicular crystals, almost 1 cm. long, were found attached to the autoclave stoppers after some experiments with gels of high silica content and a large excess of sodium hydroxide (>300%) at temperatures of ~390°. On *X*-ray examination these proved to be of anhydrous $\mathrm{Na_2SiO_3}$.

Exchange Reactions with Dry Hydrogen Chloride.—The basic noseans, sodalites, and cancrinites could contain only $\mathrm{H_2O}$ or NaOH in place of the usual intercalated $\mathrm{Na_2SO_4}$, NaCl, or $\mathrm{Na_2CO_3}$. Little water was liberated by outgassing at 300—350°, however, so the interstitial compound was thought to be sodium hydroxide. To test this, the crystals were thoroughly outgassed and then exposed to dry hydrogen chloride at temperatures >100°. A steady irreversible sorption was observed, the more rapid the higher the temperature. If the temperature was high enough, water was simultaneously liberated and condensed on the walls of the apparatus. The amounts of hydrogen chloride sorbed are shown in Table 3. Thus a reaction such as

$$\mathrm{HCl(gas)} + \mathrm{NaOH(intracrystalline)} \longrightarrow \mathrm{H_2O(intracrystalline)} + \mathrm{NaCl(extracrystalline)}$$

had occurred, and must involve migration of $\mathrm{H^+}$ into the crystals and equivalent migration of $\mathrm{Na^+}$ out of the crystals. The presence of solid sodium chloride was revealed by *X*-ray powder photographs of the hydrogen chloride-treated material. The original reflection intensities of the aluminosilicates were weakened and there was also increased background scattering, suggesting some breakdown during the exchange, probably associated with a second type of reaction (with hydrogen chloride) described below.

The $\mathrm{Na^+} \rightleftharpoons \mathrm{H^+}$ exchange diffusion recalls the behaviour of the glass electrode; the use of dry hydrogen chloride, however, is an extension of Clarke and Steiger's method of effecting ion exchange by using gaseous ammonium chloride (*Amer. J. Sci.*, 1902, **13**, 27; *Z. anorg. Chem.*, 1902, **29**, 338). Like $\mathrm{NH_4^+}$, $\mathrm{H^+}$ readily migrates into the lattice but the larger $\mathrm{Cl^-}$ ion remains outside the crystal.

Barth (*loc. cit.*) assigns to sodalite and nosean structures in which *all* $\mathrm{Na^+}$ ions occupy nearly equivalent positions in the lattice. Thus the sodium hydroxide is present as $\mathrm{Na^+}$ and $\mathrm{OH^-}$ ions, and, moreover, there seems no reason why exchange of $\mathrm{Na^+}$ for $\mathrm{H^+}$ should be limited to a number

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of such ions equal to the number of OH^- ions present; rather, *all* the Na^+ ions should be able to exchange, but with possible different results (see below). To investigate exchange of other Na^+ ions, crystals of analcite and particles of a silicate glass containing 16% of sodium oxide were exposed to dry hydrogen chloride. Both reacted to a considerable extent (Table 3), and *X*-ray examination showed solid sodium chloride to be formed in each case. The reaction here must be represented as

$$\geqslant \mathrm{Si{-}O^-} \ldots \mathrm{Na^+} + \mathrm{HCl\ (gas)} \longrightarrow \geqslant \mathrm{Si{-}OH} + \mathrm{NaCl\ (extracrystalline)}$$

On heating to ~250° some water was liberated, so that further reaction occurs :

$$\geqslant \mathrm{Si{-}OH} + \mathrm{HO{-}Si} \leqslant \longrightarrow \geqslant \mathrm{Si{-}O{-}Si} \leqslant + \mathrm{H_2O}$$

This reaction forms a collapsed silica glass coating round the particles, and may be expected to prevent or retard exchange diffusion, as well as to account for the *X*-ray evidence of partial decomposition of the H^+-ion exchanged sodalite, nosean, and cancrinite (see above).

TABLE 3. *Exchange sorption of dry* HCl *by several crystals.*

Mineral	HCl sorbed (c.c. at N.T.P./g.)	Max. temp. reached	% Total Na^+ ions exchanged in mineral	Refractive indices Before exchange	After exchange
Analcite	28·5	360°	~28	1·487	1·455
Cancrinite (formed in absence of CO_3^{--}) ...	125	250	66·3	1·50 (mean)	1·460
Nosean (formed in absence of SO_4^{--})	50·1	250	26·5	1·494	1·365
Nosean (formed in presence of SO_4^{--})	30·8	250	17·1	1·486	~1·46
Sodalite (formed in absence of Cl^-)	99·1	250	52·5	1·488	~1·47
Silicate glass	25·7	200	18·2	—	—

Dehydrated chabazite also gave some reaction with dry hydrogen chloride, although in this case, before reaction, *molecular* hydrogen chloride was absorbed and sodium and calcium chlorides were produced interstitially, and could be extracted hydrothermally (Barrer and Brook, in preparation). One may conclude that a substantial degree of exchange of Na^+ by H^+ can occur in a variety of minerals. It is most marked for the " basic " cancrinites, sodalites, and noseans of the previous section, probably because these contain reactive sodium hydroxide intercalated in place of the usual salts.

Optical and Other Properties of " Basic " Cancrinites.—A number of preparations of cancrinites were carried out from gels $Na_2O,Al_2O_3,2SiO_2$ but with variable amounts of sodium hydroxide and carbonate in the mother-liquors. These cancrinites were investigated by *X*-rays and optically, with the results shown in Table 4.

TABLE 4. *Some properties of synthetic cancrinite.*

Growth medium	Refractive indices ε	ω	Elongation	Lattice type compared with a natural cancrinite
NaOH aq.	1·504	1·501	+	Slightly expanded
Na_2CO_3 + NaOH aq.	1·498	1·502	—	Considerably collapsed
NaOH aq.	1·497	1·500	—	Identical
NaOH aq.	1·498	1·494	+	Slightly collapsed
NaOH aq.	1·504	1·498	+	Slightly collapsed
Na_2CO_3 aq.	1·498	1·501	—	Slightly collapsed

TABLE 5. *Ignition products.*

Species	Ignition loss, %	Product	Species	Ignition loss, %	Product
Albite	Negligible	Albite	Basic sodalite	3·3	Carnegieite
Analcite	8·3	Albite	Mordenite	13·5	Glass
Normal cancrinite ...	7·9	Glass	Nepheline	Negligible	Nepheline
Basic cancrinite	5·9	Nepheline	Paragonite	4·3	Mullite
Normal nosean	10·8	Nepheline	Compound L	7	Glass
Basic nosean	14·2	Carnegieite	Nepheline hydrate I ...	9·6	Nepheline
Normal sodalite	7·4	Nepheline	Nepheline hydrate II	2·0	Nepheline

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TABLE 6. X-*Ray data for typical species (spacings in* Å).

Synthetic albite		Natural albite		Synthetic nepheline		Natural nepheline		Nepheline hydrate I	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
w	6·49	w	6·40	mw	4·68	—	—	ms	8·3
w	4·27	vw	4·33	w	4·30	—	—	ms	7·4
mw	4·03	ms	4·05	ms	4·16	s	4·18	mw	$6{\cdot}3_8$
mw	3·76	m	3·78	s	3·83	vw	3·83	m	$5{\cdot}5_2$
w	3·63	m	3·69	mw	3·66	—	—	vw	$4{\cdot}7_2$
ms	3·35	mw	3·36	vs	3·26	s	3·27	vs	4·39
vs	3·18	vs	3·19	—	—	w	3·17	vw	4·11
mw	2·92	ms	2·94	vs	3·00	vvs	3·00	vw	3·61
vw	2·83	vvw	2·84	w	2·88	s	2·88	vvs	3·40
vvw	2·75	vvw	2·74	w	2·73	—	—	vw	3·22
vw	2·64	vw	2·65	mw	2·57	m	2·57	vs	2·95
mw	2·50	w	2·55	mw	2·49	mw	2·49	ms	2·84
vvw	2·45	vvw	2·44	mw	2·41	w	2·39	s	2·60
mw	2·28	vw	2·32	w	2·34	ms	2·34	s	2·43
vvw	2·21	vw	2·19	mw	2·30	mw	2·30	vw	2·30
w	2·12	vw	2·12	w	2·13	vw	2·12	mw	2·19
w	2·09	vw	2·07	w	2·09	mw	2·08	w	2·11
vw	1·87	w	1·89	mw	1·98	vvw	1·98	vw	2·05
mw	1·82	w	1·83	w	1·93	m	1·93	vw	1·97
w	1·78	vw	1·78	vvw	1·88	mw	1·88	m	1·86
vw	1·606	vw	1·603	vw	1·85	vw	1·84	vw	1·84
vw	1·571	vvw	1·561	vw	1·79	mw	1·79	w	1·80
—	—	vw	1·509	vw	1·75	vvw	1·76	vw	1·74
—	—	vw	1·465	w	1·70	w	1·70	w	1·70
				—	—	mw	1·62	vw	1·61
				w	1·59	w	1·60	vw	1·58
				m	1·56	ms	1·56	w	1·57
				—	—	w	1·52	vw	1·52
				vw	1·46	vw	1·46		

Nepheline hydrate II		Synthetic paragonite		Natural paragonite *		Species L		Species M	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
mw	6·27	m	9·5	60	9·3	s	5·97	vvs	9·7
vw	5·49	—	—	40	4·97	m	4·30	vw	5·94
s	4·67	vw	4·77	30	4·72	ms	3·96	w	4·10
ms	4·34	ms	4·39	100	4·39	w	3·77	w	3·96
vs	4·07	w	4·21	—	—	ms	3·62	ms	3·56
w	3·84	vw	4·01	60	4·01	w	3·21	mw	3·46
s	3·67	—	—	70	3·74	m	3·06	w	3·33
ms	3·40	—	—	60	3·65	s	2·97	ms	3·19
s	3·24	w	3·50	—	—	mw	2·67	w	2·97
w	3·16	—	—	50	3·27	m	2·58	mw	2·84
vvs	2·95	s	3·18	70	3·14	ms	2·43	mw	2·73
mw	2·84	mw	3·03	40	2·93	w	2·34	mw	2·65
mw	2·74	—	—	60	2·87	w	2·27	ms	2·42
m	2·59	vw	2·79	50	2·77	w	2·14	vw	2·37
mw	2·49	vs	2·51	100	2·52	w	2·07	vw	2·31
w	2·44	m	2·41	70	2·41	mw	1·89	w	2·27
w	2·30	w	2·34	60	2·33	ms	1·82	vw	2·21
w	2·27	w	2·17	60	2·16	vw	1·78	ms	2·07
w	2·20	m	2·08	70	2·09	w	1·75	w	1·97
mw	2·13	mw	1·92	60	1·90	vw	1·70	w	1·90
vw	2·08	vvw	1·82	40	1·83	vw	1·67	vw	1·79
mw	2·04	w	1·67	60	1·67	mw	1·61	m	1·61
vw	1·97	mw	1·60	60	1·60	w	1·58	w	1·56
w	1·91	vvw	1·55	40	1·57	vw	1·55	m	1·51
vw	1·88	vvs	1·48	100	1·47			w	1·48
vw	1·84	vvw	1·37	20	1·37			mw	1·42
w	1·76	vw	1·34	50	1·34			mw	1·40
vw	1·70	vw	1·31	50	1·30			mw	1·38
		vw	1·28	60	1·28			m	1·35
		vvw	1·25	50	1·25				
		vw	1·23	60	1·23				

* " Alphabetical Index of *X*-Ray Data " (American Soc. Testing Materials).

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The optical character is seen to be variable and could not apparently be correlated with any one factor. Ion exchange of Ag^+ for Na^+ also gave products, differing optically *inter se*, when made from the above variable forms of cancrinite. Of two specimens treated under identical conditions with saturated silver nitrate solution at 110°, one gave a crystalline product almost isotropic and with R.I. = 1·647, while the other yielded crystals with very high birefringence, having $\varepsilon \sim 1{\cdot}640$ and $\omega \sim 1{\cdot}670$. The *X*-ray powder photographs of both showed them to be ion-exchanged cancrinites with, however, some intensity differences between them.

Wyart (*loc. cit.*) has recorded a cancrinitic phase which had a composition approximating to $Na_2O,Al_2O_3,2SiO_2,2H_2O$, together with a small amount of sodium carbonate. This cancrinite gave $\varepsilon = 1{\cdot}489$ and $\omega = 1{\cdot}492$, and may be in part analogous to the preparations here described. Our "basic" cancrinites are, moreover, rather similar in *X*-ray spacings to the "phase X" grown by Friedman (*loc. cit.*), for which the analysis corresponds to $13Na_2O,9Al_2O_3,22SiO_2,H_2O$. One has thus further reason to formulate these basic cancrinites as $3(Na_2O,Al_2O_3,2SiO_2),xNaOH,yH_2O$, where x and y may be variable and possibly interrelated. One might by analogy with natural cancrinites assume than when $x = 2$, $y = 0$, and, considering Wyart's cancrinitic phase, that if $x = 0$, $y = 2$.

The reason for the occurrence of these variable basic cancrinites or, under somewhat different conditions, basic noseans and sodalites, remains, however, obscure. It may be that, by changing the pH, the proportions of sodium hydroxide and of water which are intercalated are modified progressively, and that these changes are accompanied at certain stages by modifications in the aluminosilicate framework.

Ignition Products.—The crystalline products were ignited in a platinum crucible over a Meker burner at ~1150° (measured by Pt/Pt–Rh thermocouple). Ignition losses and products identified by *X*-ray powder photography are given in Table 5. The formation of carnegieite can be ascribed to slightly increased ignition temperature; the nepheline–carnegieite inversion occurs at ~1250° for compositions $Na_2O,Al_2O_3,2SiO_2$. Minerals obtained on ignition are well-known refractory materials.

Ion-exchange Reactions.—The relatively open framework structures of cancrinite, sodalite, and nosean should enable them to show cation exchange similar to that in zeolites. Saturated silver nitrate solution at 110° was found after 2 days to effect exchange with each mineral, as demonstrated by changes in refractive indices and *X*-ray powder diffraction patterns and by analysis. Similar attempts to introduce Ag^+ ions into albite, nepheline, and paragonite were on the other hand unsuccessful, although Silber (*Ber.*, 1881, **14**, 941) has claimed that one-third of the Na^+ in nepheline can be exchanged by Ag^+ under similar conditions.

Crystals of nepheline hydrate I were found to exchange Na^+ readily for Tl^+ or Ag^+ under mild hydrothermal conditions, whereas nepheline hydrate II was in this respect inert. This suggests that nepheline hydrate I has the more open frame-work structure, and is compatible with its lower refractive indices.

DISCUSSION

Analcite occurs over a very wide range of temperature and composition, at moderate pH (~9). Friedman (*loc. cit.*) nevertheless considers that analcite is a metastable phase and that even at 400° true equilibrium is not established in less than about 10 days in contact with the mother-liquor. However, except at the higher temperatures this view is not supported in the present work. Recrystallisation of analcite was not observed when these crystals were kept for abnormal periods in contact with the crystallisation media. Although many metamorphoses of this zeolite were possible, special conditions were usually required for such transformations (Barrer, Hinds, and White, in preparation). Moreover, by using gels as starting materials for hydrothermal crystallisation rather than homogenised glasses, crystal growth is more rapid, and can be studied to much lower temperatures, so that equilibrium conditions may be more quickly approached.

However, the preparation of the most stable phases only was not the full objective of the present research: often the most interesting properties are associated with metastable crystals; mordenite, for example, when grown in media of high pH soon disproportionates to give other phases such as analcite (Barrer, *loc. cit.*). Nevertheless, it may be reproducibly formed.

A feature of the aluminosilicate chemistry both of lithium (Part I, *loc. cit.*) and of sodium (this paper) has been the preparation of species without natural counterparts, or

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which are variants of naturally occurring minerals. Moreover, the basic cancrinites, noseans, and sodalites reported here, with stoicheiometric and physical differences from their natural counterparts, by no means complete the limits of adaptability possessed by this type of aluminosilicate framework. Sodalite-type crystals have also been prepared where the intercalated salts are sodium bromide and nitrate (Flint, Clarke, Newman, Shartis, Bishop, and Wells, *J. Res. Nat. Bur. Stand.*, 1945, **36**, 63). With only minor structural changes it would appear that replacements are possible in the sodalite-nosean framework covering at least NaCl, NaBr, NaOH, Na_2CO_3, $NaNO_3$, and H_2O, while with cancrinite the replacements Na_2SO_4, Na_2CO_3, NaOH, and H_2O are found. Such exchanges are not effected directly, but by hydrothermal synthesis of the various forms.

One may note that this kind of replacement (through direct synthesis, not by ion-exchange) is observed among other aluminosilicate minerals. It is well shown among the felspars ($K \rightleftharpoons Na \rightleftharpoons Ca \rightleftharpoons Ba$; also $Al \rightleftharpoons Ga$ and $Si \rightleftharpoons Ge$) (Goldsmith, *J. Geol.*, 1950, **58**, 518), while with synthetic mica an extraordinary degree of diadochic replacement has been discovered (Hatch, Eitel, and Humphrey, U.S. Naval Res. Report on Synthetic Micas, 1949). Similarly, by direct synthesis, a number of diadochic forms have been prepared based on the analcite structure (Barrer and McCallum, in preparation). In each such series of crystals the permanent aluminosilicate frameworks show considerable powers of adjustment, but always as variants of a pattern characteristic of the series.

Although some of the species grown under these alkaline conditions were not of robust three-dimensional network type (*e.g.*, paragonite at lower pH), by far the greater proportion of the crystals were of this kind. It seems that alkaline mother-liquors and 1 : 1 ratio between Na_2O and Al_2O_3 in the gel lead preferentially to framework aluminosilicates. A problem unsolved by this study concerns the conditions of growth for the fibrous aluminosilicates, such as natrolite ($Na_2O,Al_2O_3,3SiO_2,2H_2O$). Despite claims in the earlier literature (Thugutt, *Neues Jahrb. Min.*, Beil. Bd., 1894, **9**, 554; Friedel and Grandjean, *Bull. Soc. Min.*, 1909, **32**, 150; Gruner, *Z. anorg. Chem.*, 1929, **182**, 319), no natrolite was observed among the numerous species formed in the present work. It is possible that at least some of the earlier claims may have referred to cancrinite, which grows as acicular crystals comparable with natrolite in form and refractive index (for natrolite, $n \sim 1{\cdot}49$; for cancrinite, $n \sim 1{\cdot}50$).

Although the compounds described here were grown only in small amounts, there seems no reason why many of them could not be obtained in quantity. The average size of individual crystals in the sodium aluminosilicate field usually exceeded that of the lithium aluminosilicate crystals (Part I, *loc. cit.*). In a single preparation, and without growing on seeds, crystals of 1—5 mm. were sometimes obtained. If the pH of the mother-liquor is properly adjusted, it is possible, by using a seed crystal and, as feed material, small synthetic crystals of the same species grown as described in this paper, that still larger crystals could be made. The method of deposition on the seed by using a moderate thermal gradient and placing the seed in the colder part of the alkaline mother-liquor, has for example proved successful in growing large quartz crystals (Brown, Kell, Thomas, Wooster, and Wooster, *Nature*, 1951, **167**, 940), and is probably of some general applicability.

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