

299. *The Hydrothermal Chemistry of Silicates. Part III.*
Reactions of Analcite and Leucite.*

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Because of the readiness with which it may be synthesised (Part II) analcite ($\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$) has been used as a starting point for preparation, in high yield, of minerals and mineral-type compounds under reproducible and relatively accessible conditions. Analcite (or leucite, $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$) has been converted hydrothermally into nepheline, cancrinite, nosean, sodalite, barium feldspar, potash feldspar, kaliophilite, kalsilite, hieratite, α -eucryptite, and various species without naturally occurring counterparts. These include, *inter al.*, a lithium zeolite, $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 4\text{H}_2\text{O}$, described in Part I, a zeolitic compound, $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, 3\text{H}_2\text{O}$, and four mineral-type compounds containing intercalated potassium chloride or bromide, and barium chloride or bromide. The salt could usually be extracted hydrothermally, sometimes with recrystallisation. Conditions of formation, and optical and X-ray data, of these and other species have been given.

Many of the metamorphoses of analcite and leucite can be reversed under different conditions, so that various two-way reaction paths between these minerals and other species can be realised. Such paths have significance for the chemistry of zeolite and of granite formation and in the paragenesis of rock and soil-forming minerals.

ANALCITE, $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$, is readily synthesised in quantity and in high purity (Barrer, *Discuss. Faraday Soc.*, 1948, No. 5, 326; Barrer and White, Part II *).

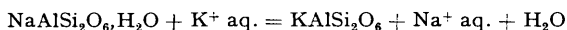
* Part II, *J.*, 1952, 1561.

It therefore provides a reproducible laboratory starting point for the study of further reactions of chemical and geochemical interest. It is as stable as most aluminosilicates, especially under mildly alkaline hydrothermal conditions, and shows both the sorptive and the ion-exchange properties of a normal zeolite. It can be converted by exchange of sodium for potassium into the feldspathoid leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$. This and other cation-exchange reactions have been studied elsewhere and show that analcite has ion-sieve as well as molecular-sieve properties (Barrer, *J.*, 1950, 2342). Despite the stability of the analcite type of framework it has been found that simple ion-exchange, under appropriate and often specific reaction conditions, can give place to complete recrystallisation (cf. Barrer, *J.*, 1948, 127). This earlier work is now extended and many new hydrothermal recrystallisation reactions are described. One may indeed obtain from analcite a notable variety of aluminosilicates, some representative of important mineral groups and others not identified with naturally occurring species.

EXPERIMENTAL

Analcite was synthesised from gels of composition $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 + aq.$ in the presence of a slight excess of sodium hydroxide. Crystallisation was effected at 180° in an autoclave of internal capacity about 1 l. 100-G. lots of high purity were formed under these conditions, although at higher temperatures in presence of 5*N*-sodium hydroxide the product consisted only of cancrinite with excess of silica and sodium silicate crystals (Part II).

Leucite was prepared from analcite by heating the latter with concentrated potassium chloride solution at 200° . Several treatments were given, all of 24 hours' duration and with a fresh supply of potassium chloride each time:



Samples of analcite or leucite were then heated at temperatures in the range 110 – 450° with various mineralising solutions. These included salts of lithium (Cl^- , NO_3^- , SO_4^{2-}), sodium (OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} , SeO_4^{2-}), potassium (OH^- , CO_3^{2-} , F^- , Cl^- , Br^- , I^- , SO_4^{2-} , NO_3^-), rubidium (Cl^-), thallium (Cl^-), lead (Cl^-), and barium (Cl^- , Br^-). The stainless-steel autoclaves and the heating methods used have been previously described (Barrer and White, Part I, *J.*, 1951, 1167). Where possible, "AnalaR" salts were employed.

The crystalline products were thoroughly washed, and after being dried in air, were examined by optical and X-ray methods. Chemical analyses were carried out only where approximately 100% yields were obtained.

RESULTS

Table 1 summarises the crystalline species obtained from analcite and leucite. For convenience the products are designated alphabetically. Among compounds of known composition it can be seen that the $Al_2O_3 : SiO_2$ ratio of 1 : 4 in the parent compound usually takes values 1 : 6, 1 : 4, and 1 : 2 in the metamorphic species. Where a change occurs from the ratio 1 : 4 in analcite and leucite, it is more usual to find silica rejected than alumina, so that the $Al_2O_3 : SiO_2$ ratio then decreases in the crystalline products. Reaction media were mostly on the alkaline side.

In the following sections we will describe the reactions of analcite with several types of salt, and will outline the properties of the metamorphic products.

Reactions with Carbonates.—Table 2 gives some results obtained, with sodium and potassium carbonate solutions as mineralisers. In all tables the symbols α , 2α , 3α , etc., denote respectively one, two, and three g. of analcite, and λ , 2λ , etc., denote similar weights of leucite. Where excess of salt is referred to it is understood throughout this paper that water is also present, but that the amount of salt is sufficient to give a saturated solution together with solid salt.

The cancrinites of Table 2 were identical with those synthesised from sodium aluminosilicate gels (Part II) and with those grown from hydroxide solutions (Table 3). The crystals usually appeared as thin hexagonal rods up to 50μ long, with a mean $n = 1.51$. X-Ray and optical data for cancrinite have been discussed in Part II. The yield of cancrinite from analcite improved with rising temperature, giving 100% conversion at 450° . As the yield grew, the crystal size often showed a parallel increase.

Kalsilite (Plate I) grew as small hexagonal plates $\sim 25 \mu$ across, although in treatments with KOH aq. crystals up to 250μ were obtained. The mineral was in all respects identical with natural kalsilite, and gave $\epsilon = 1.534$, $\omega = 1.541$. Complete conversion into kalsilite was

observed at 450°. Details of the formation of potash felspar from analcite have been given elsewhere (Barrer and Hinds, *Nature*, 1950, **166**, 562). X-Ray, optical data, and crystal habit are close to those for natural orthoclase (Table 8).

TABLE 1. *Alteration products from analcite and leucite.*

Species	Ref. letter	Probable ideal oxide formula
Cancrinite	A	$3(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)\text{X}^*$
Nosean	B	$3(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)\text{X}^*$
Sodalite	C	$3(\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2)\text{X}^*$
Leucite	D	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$
Kalsilite	E	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$
Potash felspar	F	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$
Kaliophilite	G	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$
Nepheline	H	$(\text{Na}, \text{K})_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$
Hieratite	I	K_2SiF_6
New species	J	Na, K aluminosilicate
Lithium zeolite	K	$\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 4\text{H}_2\text{O}$
α -Eucryptite	L	$\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$
New species	M	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, 3\text{H}_2\text{O}$
Potassium halide aluminosilicates	{	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, x\text{KCl}^\dagger$
	O	$\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, x\text{KBr}^\dagger$
Barium halide aluminosilicates	{	$\text{BaO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, y\text{BaCl}_2, z\text{H}_2\text{O}^\ddagger$
	Q	$\text{BaO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, y\text{BaBr}_2, z\text{H}_2\text{O}^\ddagger$
New species	R	Ba aluminosilicate
New species	S	Pb aluminosilicate
Barium felspar	T	$\text{BaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$
Near harmotome	U	$\text{BaO}, \text{Al}_2\text{O}_3, 5\text{SiO}_2, 6\text{H}_2\text{O}(?)$

* In these experiments X = $(m\text{NaOH} + n\text{H}_2\text{O})$, Na_2CO_3 , or Na_2SeO_4 for cancrinite; 2NaCl for sodalite; and $(m\text{NaOH} + n\text{H}_2\text{O})$ or Na_2SO_4 for nosean (see Part II for explanation of m and n).

† A small amount of Na^+ is probably present. The value of x is ~ 2 .

‡ A small amount of Na^+ is probably present. y and z may vary, depending on conditions of formation. Representative values are $y \sim \frac{2}{3}$, $z \sim 2$ (Barrer, *J.*, 1948, 127).

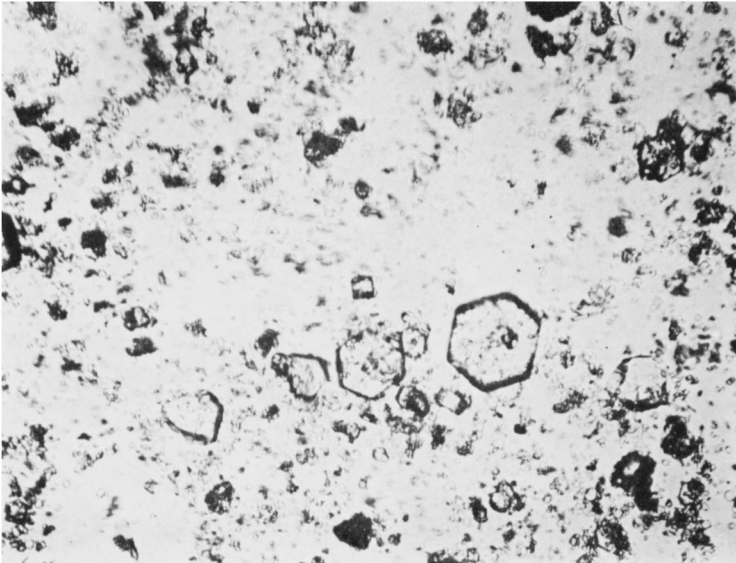
TABLE 2. *Reactions with carbonates.*

Reaction mixture	Time (days)	Temp. (c)	Product
$2x + 10$ c.c. $2N\text{-Na}_2\text{CO}_3$	4	260°	Analcite + little <i>cancrinite</i>
" "	4	300	Analcite + more <i>cancrinite</i>
" "	4	360	Analcite + moderate <i>cancrinite</i>
" "	4	410	Good yield <i>cancrinite</i>
$2x + 10$ c.c. $8N\text{-Na}_2\text{CO}_3$	4	450	<i>Cancrinite</i> only
$3x + 10$ c.c. $5N\text{-K}_2\text{CO}_3$	1	280	<i>Leucite</i>
" "	1	360	<i>Leucite</i> + some <i>potash felspar</i>
$2x + \text{excess K}_2\text{CO}_3 + 1$ g. $\text{KOH} + 10$ c.c. H_2O	2	220	<i>Leucite</i> + some <i>kalsilite</i>
$2x + 10$ c.c. $8N\text{-K}_2\text{CO}_3$	4	450	<i>Kalsilite</i> only
$\lambda + \text{sat. } (\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3)$ aq.	14	110	Some <i>species J</i>
" " "	14	110	" " " "
" " "	3	160	Good " yield of <i>species J</i>
" " "	7	160	" " " "
" " "	7	180	" " " "
" " "	0.67	195	$\sim 95\%$ Conversion into <i>potash felspar</i>
" " "	0.67	200	Smaller yield of <i>potash felspar</i>
$\lambda + \text{sat. K}_2\text{CO}_3$ aq.	3	160	No recrystallisation
" " "	7	160	" " " "
" " "	3	200	" " " "

Species J was found as small rectangular or sometimes rhombohedral tablets up to $\sim 20 \mu$ in length. They belonged to the monoclinic system, exhibiting considerable birefringence in some orientations; $\alpha = 1.532$, $\beta = 1.501$, $\gamma = 1.495$. The compound was grown also in the presence of mixed sodium and potassium fluoride solutions (Table 4). Since it did not usually appear in major yield analytical data were not obtained. It could not be identified with any minerals and may be a new sodium-potassium aluminosilicate.

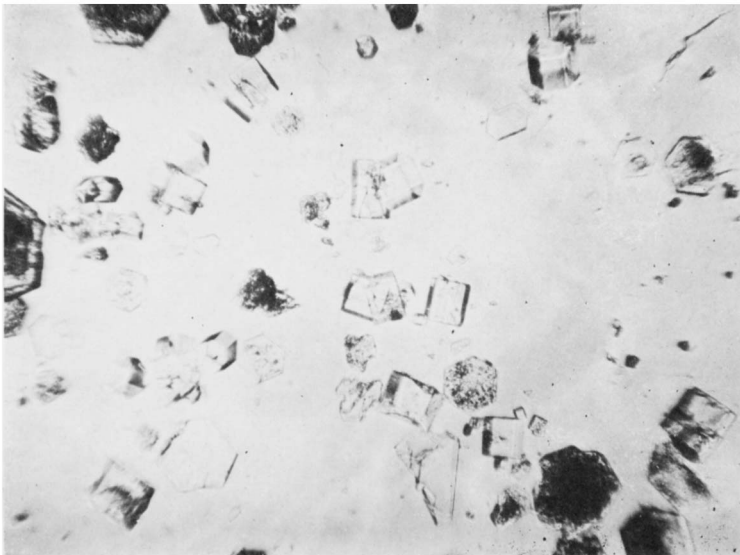
Reactions with Hydroxides.—In Table 3 reactions observed between hydroxide solutions and analcite or leucite are summarised. Both nosean and cancrinite were formed from analcite at 450°. In general, nosean was obtained only when the mineralising solution was very highly alkaline ($\sim 4N\text{-NaOH}$). The products are the "basic" nosean and cancrinite described in Part II and then grown from gels. The introduction of potassium into the mineralising solution resulted at first in the formation of nepheline, but as the potassium content increased the yield

PLATE I.



Kalsilite. ($\times 120.$)

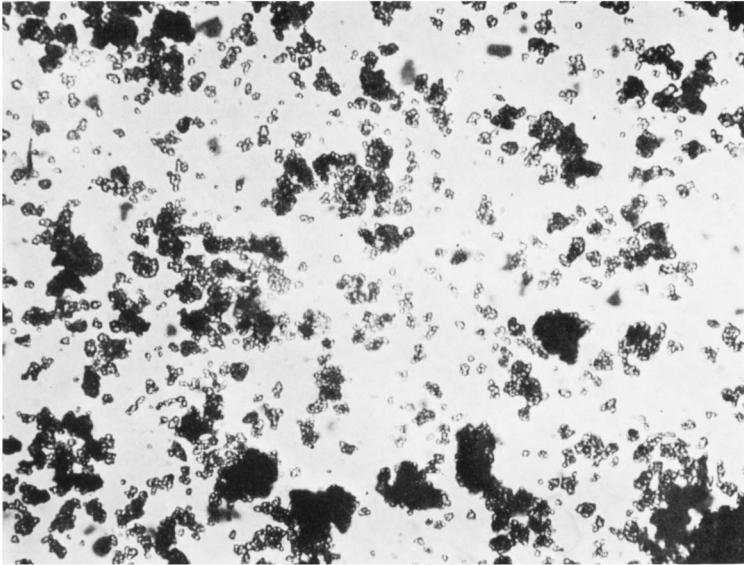
PLATE II.



Nepheline (grown in presence of K^+). ($\times 75.$)

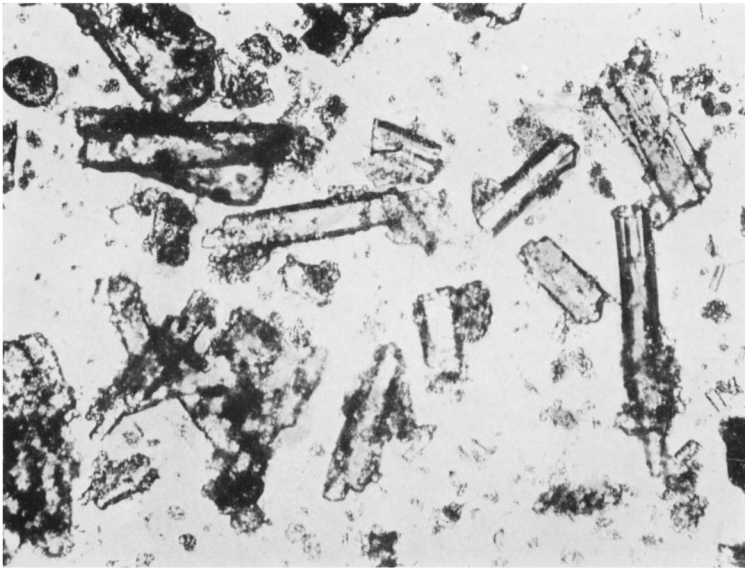
[To face p. 1468.]

PLATE III.



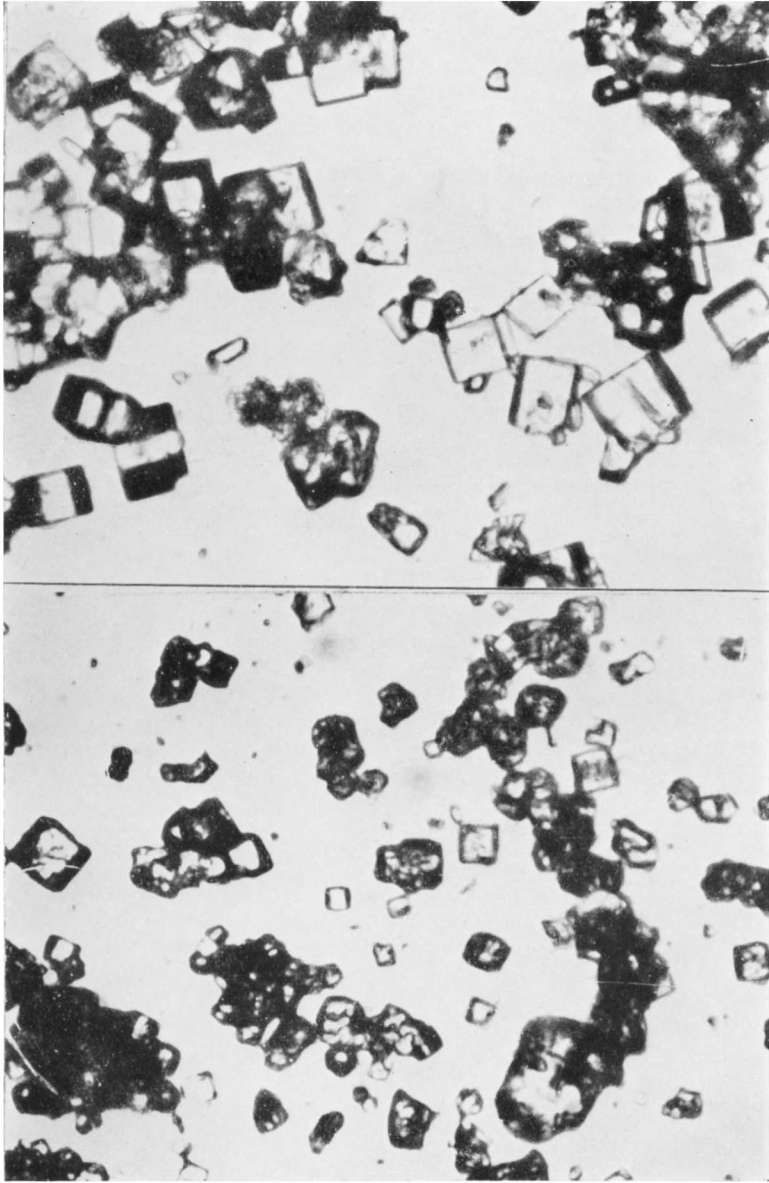
Kaliophilite. ($\times 120$.)

PLATE IV.



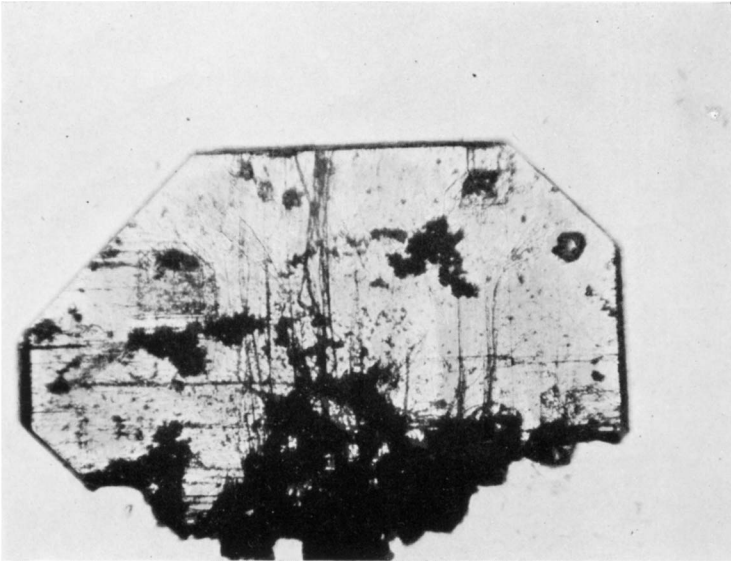
Species M obtained by hydrothermal treatment of compounds N and O. ($\times 120$.)

PLATE V.



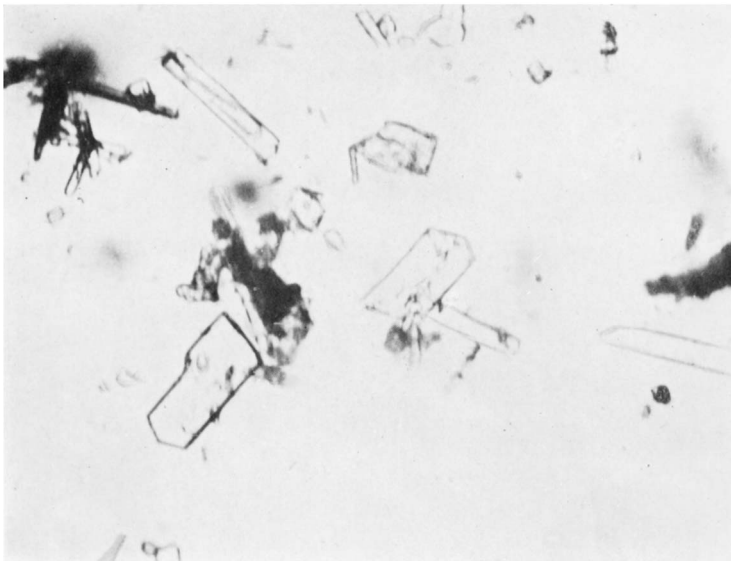
Species P (below) and O (above). (×475.)

PLATE VI.



Species R. ($\times 75$.)

PLATE VII.



Compound S. ($\times 250$.)

of nepheline diminished and at a ratio NaOH : KOH = 1 : 5 (by wt.) in the solution the product consisted mainly of kalsilite. The nosean and cancrinite were identical with the same species grown from gels (Part II).

The nepheline grew as hexagonal tablets as much as 400 μ wide (Plate II). They belonged to the hexagonal system with $\epsilon = 1.541$ and $\omega = 1.545$, the X-ray powder photographs being indistinguishable from that of natural nepheline. It is interesting that nepheline grown in the presence of potassium differs somewhat in n , habit, and X-ray powder photographs from nepheline grown from sodium aluminosilicate gels (Part II). Although nepheline can contain potassium, continuous replacement of sodium by potassium over the whole range $\text{NaAlSi}_3\text{O}_8$ to KAlSi_3O_8 with retention of the nepheline structure did not often occur. Especially at higher

TABLE 3. *Reactions with hydroxides.*

Reaction mixture	Time (days)	Temp. (c)	Products
2 α + 15 c.c. 2N-NaOH	2	330°	Cancrinite and some analcite
2 α + 10 c.c. 3N-NaOH	2	360	Cancrinite and little analcite
2 α + 10 c.c. 5N-NaOH	4	450	Cancrinite only
2 α + 1 g. NaOH + 0.2 g. KOH + 10 c.c. H ₂ O	2	450	Cancrinite 100%. Large crystals
2 α + 0.6 g. NaOH + 0.6 g. KOH + 10 c.c. H ₂ O	2	450	Nosean only
2 α + 0.2 g. NaOH + 1.0 g. KOH + 10 c.c. H ₂ O	2	450	Large nepheline crystals only
λ + 10 c.c. N/100-KOH	4	190	Kalsilite and some nepheline
λ + 10 c.c. N/10-KOH	2.5	200	Leucite unchanged
λ + 10 c.c. N/4-KOH	2	200	Leucite and some species M
$\frac{1}{2}\lambda$ + 6 c.c. N/2-KOH	2	200	" " "
$\frac{1}{2}\lambda$ + 6 c.c. N-KOH	2	200	" " "
$\frac{1}{2}\lambda$ + 5 c.c. 2N-KOH	2	200	Good yield of species M, some kaliophilite and little leucite
$\frac{1}{2}\lambda$ + 5 c.c. 3.6N-KOH	2	206	Excellent yield kaliophilite
$\frac{1}{2}\lambda$ + 5 c.c. 5N-KOH	2	206	Kalsilite only
$\frac{1}{2}\lambda$ + 5 c.c. 3N-KOH	2	250	" "
$\frac{1}{2}\lambda$ + 5 c.c. 4N-KOH	2	250	" "
$\frac{1}{2}\lambda$ + 5 c.c. 5N-KOH	2	250	Much leucite and some species M (autoclave leaked)
2 λ + 10 c.c. 3N-KOH	2	350	Kalsilite only
2 λ + 10 c.c. 5N-KOH	2	400	" "
2 λ + 10 c.c. 5N-KOH	1	450	" "

temperatures one observed instead the precipitation of nepheline and kalsilite together from potassium-rich mixtures.

Kaliophilite has the composition of potassium nepheline and was at low temperatures sometimes obtained as very small laminar crystals of indefinite outline and about 5 μ diameter (Plate III). The mean value of n was 1.54₁, and birefringence was low. The crystals gave X-ray data in agreement with those in the "Alphabetical Index of X-ray Data" (American Society for Testing Materials), although minor differences in intensity and spacing were also noted (Table 8).

Dilute solutions of potassium hydroxide (<N/4) at low temperatures (~200°) had little effect upon leucite, although isolated rectangular prisms of species M were observed. The yield at 200° increased with potassium hydroxide concentration, although some kaliophilite was also formed. Above 250° kaliophilite and species M gave place to kalsilite. The compound M was on occasions found as one layer of a zoned crystal consisting of inner and outer prisms. The mean refractive index of the outer layer (compound M) was 1.496. The system may be orthorhombic or tetragonal, but no complete indexing of the X-ray spacings for a tetragonal unit cell was obtained. Species M was also found as an alteration product after extraction of compounds N and O hydrothermally; (Plate IV); and again as very much finer elongated crystallites when gels K₂O, Al₂O₃, 3SiO₂ were treated hydrothermally with excess of potassium hydroxide (unpublished work by R. M. Barrer and J. W. Baynham). The crystals grown from gels were sometimes in high yield, and analysis then gave the formula K₂O, Al₂O₃, 3SiO₂, 3H₂O. The mineral was zeolitic and when outgassed could sorb ammonia at 200°. X-Ray spacings are given in Table 8 and further determinations of refractive index gave $\epsilon = 1.490$ and $\omega = 1.494$. The compound could not be identified with any natural zeolite such as thomsonite, natrolite, or scolecite, or with any potassium aluminosilicate.

Reactions with Halides.—The mineralising action of fluorides, chlorides, and bromides has

now been studied in some detail, using analcite, leucite and, as reported earlier, aluminosilicate gels (Barrer, *J.*, 1948, 127). The present work is in part an extension of that carried out previously, and the experiments are summarised in Table 4. Hieratite, species J, α -eucryptite, and one of the lithium zeolites of Part I were all identified by X-ray photography, and kalsilite was identified optically.

Among conversions in which fluorides were used it was noteworthy that mixed NaF-KF solutions are more effective than either salt alone (cf. p. 1474). Hieratite was not formed above 300°, probably being too soluble for deposition above this temperature. The crystals were small (~5 μ) and isotropic.

TABLE 4.

Reaction mixture	Time (days)	Temp. (° C)	Products
<i>Reactions with fluorides.</i>			
4 α + 6 g. KF + 7 c.c. H ₂ O	2	250	Hieratite with leucite
2 α + 4 g. KF + 7 c.c. H ₂ O	2	350	Kalsilite with leucite
" " " "	2	450	" "
α + excess (Na,K)F	14	110	Hieratite and "species J"
λ + excess (Na,K)F	1	200	Hieratite and less of species J
<i>Reactions with chlorides.</i>			
α + excess LiCl	4	220	Li-zeolite (Li ₂ O,Al ₂ O ₃ ,2SiO ₂ ,4H ₂ O) and analcite
α + excess NaCl	2	360	Unaltered analcite
" "	3	400	Analcite and some sodalite
" "	4	450	Sodalite
α + excess NaCl + 10 c.c. 2N-NaOH... ..	4	350	" "
2 α + 1—6 g. KCl + 5 c.c. H ₂ O *	4	360	} Leucite and some species N
2 α + 1—6 g. KCl + 10 c.c. H ₂ O *	4	360	
2 α + 1—4 g. KCl + 15 c.c. H ₂ O *	4	360	
2 α + 4 g. KCl + 7 c.c. H ₂ O	2	400	} Leucite and more species N
" " " "	2	450	} Leucite and better yield species N
$\frac{1}{2}\alpha$ + excess RbCl	1	360	Rb-analcite
$\frac{1}{2}\alpha$ + excess TlCl	1	360	Tl-analcite
2 α + excess (Na,K)Cl	2	450	Mainly sodalite (containing some K)
α + excess PbCl ₂	7	400	Mainly species S
α + excess BaCl ₂ †	2—4	~200	Species P (yield decreasing with increasing H ₂ O in mixture)
3·4 α + 10 g. BaCl ₂ + 15 c.c. H ₂ O	2	225	Species P and little analcite
2 λ + 8 g. BaCl ₂ + 10 c.c. H ₂ O	2	220	Species P
α + excess BaCl ₂ ‡	2	350	} Species P, very small crystals
" "	2	400	
" "	2	450	
<i>Reactions with bromides.</i>			
2 α + excess KBr + 5—15 c.c. H ₂ O †... ..	4	200—250	Some conversion into species O
2 α + 6 g. KBr + 7 c.c. H ₂ O	4	300	Species O in higher yield
" " " "	1	360	} Very good yield species O. Trace of kalsilite
" " " "	1	400	
" " " "	1	450	
α + excess BaBr ₂ †	2—3	194—209	Species Q; yield increases as amount of H ₂ O decreases
3·4 α + 10 g. BaBr ₂ + 15 c.c. H ₂ O	3	225	Species Q; excellent yield
2 α + excess BaBr ₂	2	350	} Species Q; crystals small
" "	2	400	
" "	2	450	

* Results of a series of experiments. † Results of a series of experiments in which proportions of solids and water were varied (Barrer, *J.*, 1948, 127). ‡ Six treatments of α with excess of BaCl₂ at 210° gave species P only.

The compounds N, O, P, and Q (see Plate V for P and O) had been prepared by Barrer (*J.*, 1948, 127), N and O in minor, and P and Q in major yields. We have now obtained high yields of N and O, extended the range of conditions for forming all the species, and characterised them more fully. The formation of species N and O proceeded only to a very limited extent at 250° and the yield did not vary much with changing proportions of analcite, potassium chloride or bromide, and water. Repeated treatments with fresh charges of chloride or bromide also failed to give noticeably increased yields. It seems likely that the leucite which is also formed by ion-exchange during the first treatment with the potassium salts is then stable at 250° and that Na⁺

in the analcite lattice is necessary for reaction. On the other hand treatment of analcite with a 1 : 1 mixture of sodium and potassium chlorides produced a partly ion-exchanged sodalite. Yields of species N never exceeded about 25%, but compound O was obtained in major yield at 450°. Species N was, however, obtained in higher yield by direct synthesis (Table 6).

Reactions of Analcite with Miscellaneous Salts.—Salts other than hydroxides, carbonates, chlorides, and bromides were sometimes very successful mineralisers (Table 5). Reaction

TABLE 5.

Reaction mixtures	Time (days)	Temp. (c)	Products
α + excess KNO_3 + little H_2O	1	360°	<i>Leucite</i>
α + excess LiNO_3 + 10 c.c. H_2O	2½	250	Analcite and Li-zeolite ($\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 4\text{H}_2\text{O}$)
α + excess LiNO_3 + 8 c.c. H_2O	3	270	Li-zeolite in high yield
α + excess LiNO_3 + 7 c.c. H_2O	6	310	α - <i>Eucryptite</i> and Li-zeolite
4α + 8 g. KNO_3 + 8 c.c. H_2O	2	250	<i>Leucite</i>
α + excess Na_2SO_4 + little H_2O	1	360	Analcite
α + excess Na_2SO_4 + 2N-NaOH	1	360	Analcite; some alteration
2α + excess Na_2S + little H_2O	3	400	<i>Sodalite</i> as large crystals
α + excess Na_2SeO_4 + 5 c.c. N-NaOH	2	360	<i>Cancrinite</i>
2α + 4 g. K_2SO_4 + 7 c.c. H_2O	3	400	<i>Leucite</i>

products obtained with LiNO_3 aq. (α -eucryptite and the zeolite $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 4\text{H}_2\text{O}$) were also obtained by using LiCl aq. (Table 4) and by direct synthesis (Part I). The sodalite, prepared as 0.5-mm. crystals by using sodium sulphide aq., was identical with the "basic" sodalite of Part II. There was no evidence of occlusion of sodium sulphide in the lattice. The cancrinite formed by use of alkaline sodium selenate solution gave an X-ray pattern indistinguishable from that of a natural sulphatic cancrinite. "Basic" cancrinites prepared as in Part II showed various minor differences in the X-ray photographs from sulphatic cancrinite. Thus the identity between the selenatic and sulphatic cancrinite may result from intercalation, not of sodium hydroxide, but of sodium selenate in place of sodium sulphate. Qualitative analysis of the selenatic cancrinite showed the presence of considerable selenium in the mineral.

Some Properties of the Mineral-type Compounds N, O, P, and Q.—The results shown in Table 4 and Barrer's earlier experiments (*J.*, 1948, 127) show that the species N, O, P, and Q are readily formed in presence of potassium chloride or bromide or barium chloride or bromide from analcite or leucite. The compounds P and Q were also grown by Barrer from gels with addition of excess of barium chloride or bromide and some water. The experiments summarised in Table 6 show that N and O may be grown in like manner from gels of composition $\text{Al}_2\text{O}_3, 4\text{SiO}_2$, when treated with excess of potassium chloride or bromide in presence of potassium hydroxide solution.

The cubic crystals obtained in presence of potassium fluoride (Table 6) were shown from X-ray photographs to be of the same type as species N (or O). Hieratite (K_2SiF_6) obtained

TABLE 6. *Direct hydrothermal synthesis of N and O from gels.*

Reaction mixture : 2 g. of gel plus	Time (days)	Temp. (c)	Products
0.6 g. KOH + excess KCl	2	300°	Some <i>species N</i> , much <i>kalsilite</i>
0.5 g. KOH + 0.1 g. NaOH + excess KCl ...	1	400	<i>Kalsilite</i>
0.5 g. KOH + excess KCl	1	450	Moderate yield of N
0.2 g. KOH + excess KBr	1	360	Some <i>species O</i> , mainly <i>leucite</i> , and <i>kalsilite</i>
0.6 g. KOH + excess KBr	1	400	Mainly <i>species O</i> , some <i>kalsilite</i>
0.6 g. KOH + 0.5 g. KF	1	360	<i>Cubic crystals</i> like N, and some <i>leucite</i>
0.6 g. KOH + 1 g. KF	1	400	<i>Cubic crystals</i> like N, and some <i>kalsilite</i>

at lower temperatures from analcite or leucite in presence of potassium fluoride (Table 4) was not precipitated above 300°. Table 6 also shows that species N and O were frequently less in amount than *kalsilite* or *leucite*. Wyart (*Discuss. Faraday Soc.*, 1949, 5, 324) has reported a difficulty in obtaining leucite by hydrothermal reaction.

In Barrer's earlier work (*J.*, 1948, 127) it was suggested that the compounds, N, O, P, and Q were all based upon one aluminosilicate framework. This was shown to be true of P and Q, but the substances N and O could not then be obtained in large enough yield for adequate X-ray study. Considerable amounts of both phases have now been prepared and it has been

found that, while N and O are based upon a single aluminosilicate framework, this is not identical with the framework characteristics of P and Q (see Table 8).

The crystals of N and O grew as well-defined cubes, showing moderate birefringence normal to all faces. They were orthorhombic, with $\alpha = 1.525$, $\beta = 1.523$, and $\gamma = 1.518$ for species N; $\alpha = 1.542$, $\beta = 1.539$, and $\gamma = 1.534$ for species O, although small variations from these values were sometimes noted. Optimum yields were obtained at 450°, at which temperature yields of compound O reached 100%. Individual crystals measured as much as 200 μ along the cube edge.

Both N and O when treated with water at 250° for a day recrystallised to a mixture containing orthoclase, leucite, and as principal species large prismatic crystals of compound M. Hydrothermal extraction of species O at 170° removed potassium bromide, at first without lattice collapse or recrystallisation but with progressive decreases in refractive index. After 4–5 extractions, each of a day, the amount of potassium bromide removed at 170° became very small. The mother-liquors during the first extractions were extremely alkaline (pH \sim 14). This extracted material was outgassed but then proved inert as a sorbent towards ethane at -78° and to ammonia at 0°. It was thus contrasted with the extracted pseudomorph of compound P (Barrer and Riley, *J.*, 1948, 133). Attempts to remove potassium bromide from O by percolation at 100° were not successful, but treatment with saturated aqueous silver nitrate at 120° gave a Ag^+ ion-exchanged form having a mean value of $n = \sim 1.69$.

Compounds P and Q grew as small isotropic cubes of $n = 1.587$ for P and 1.597 for Q, although variations were noted between different preparations. The best crystals were formed at about 220°. Although good yields (as shown by X-ray photography) were obtained up to 450° the crystals became very small above 300°. The crystals belonged to the cubic system, the unit cell edge being 13.2₀ Å for P and 13.2₈ Å for Q.

Hydrothermal extraction of compound P at $\sim 200^\circ$ gives a yield of gas-sorbing zeolitic crystals pseudomorphous with P, together with some recrystallisation (Barrer, *J.*, 1948, 127). Extraction has now been followed by X-ray photography. The mineral Q (containing barium bromide) showed a greater tendency to recrystallise, giving after thirteen extractions of one day each at 220°, a good yield of species U (see below, also Table 8 and Barrer, *J.*, 1948, 127, Plate 6). At 250° one hydrothermal extraction of P gave a slight lattice shrinkage only; but after the sixth extraction recrystallisation to species T (see below and Table 8) was extensive.

Both compounds P and Q showed ion-exchange properties. The silver forms were obtained by treatment with saturated aqueous silver nitrate at 120°, and the ammonium form by heating with ammonium chloride vapour at 330°. Unlike species N and O the silver ion-exchanged form has a refractive index close to that of the original phase (~ 1.59), although changes in the X-ray powder photographs were observed. The effect of thermal treatment of the crystals was

TABLE 7. Comparison of three types of synthetic aluminosilicate.

Property	Species N & O	Species P & Q	Synthetic sodalite-nosean crystals
Crystal system	Orthorhombic	Cubic	Cubic
Crystal habit	Cuboids	Cubes	Rhombohedral dodecahedra
Ion-exchange	Yes	Yes	Yes
Intercalated salts	KF, KCl, KBr	BaCl ₂ , BaBr ₂	NaCl, Na ₂ SO ₄ , NaOH, etc.
Probable formula	(Na, K) ₂ O, Al ₂ O ₃ , 4SiO ₂ , 2KX	(Na, Ba)O, Al ₂ O ₃ , 4SiO ₂ , 0.67BaX ₂ , 2–3H ₂ O *	3(Na ₂ O, Al ₂ O ₃ , 2SiO ₂), 2NaCl
Crystallisation from gels	Yes	Yes	Yes
Thermal stability	Stable to > 550°	Stable to > 550°	Stable to > 550°
X-Ray pattern	Phases containing KCl and KBr show same spacings	Small but definite expansion of phase containing BaBr ₂ compared with that containing BaCl ₂	Range of structures possible between noseans and sodalites (Part II)
Crystal chemical nature	All are robust three-dimensional aluminosilicate framework structures		
Hydrothermal extraction at 200°	Removes intercalated salt; extensive recrystallisation	Removes intercalated salt: less recrystallisation	No extraction without decomp.
Sorptive properties of crystals when extracted	Not a general sorbent	Excellent molecular sieve sorbent †	Non-sorbent

* There is some evidence of variable halide and water content (Barrer, *J.*, 1948, 127).

† Sorptive properties have been studied by Barrer and Riley (*J.*, 1948, 133).

TABLE 8. Summary of principal X-ray spacings (Å).

Synthetic potash felspar		Natural ortho- clase		Species T		Species S		Synthetic kalsilite		Synthetic kalio- phillite		Natural kalio- phillite*	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
6.69	vw	6.38	m	6.5	m	14	vs	4.36	mw	6.22	ms	—	—
6.00	vw	—	—	—	—	7.5	m	3.97	s	4.49	mw	—	—
5.55	vw	5.60	mw	—	—	6.2	m	3.11	vvs	4.24	m	4.24	40
4.65	w	4.64	mw	4.63	vwv	4.25	s	2.58	vs	3.99	m	3.92	40
4.26	m	4.20	s	—	—	3.80	s	2.47	w	—	—	3.72	40
3.97	m	4.00	w	3.99	s	3.60	m	2.43	vw	—	—	3.46	40
3.78	m	3.80	ms	3.78	s	3.31	m	2.22	w	—	—	3.40	60
3.68	vw	3.66	ms	3.60	mw	3.21	mw	2.17	m	3.07	vvs	2.86	100
3.47	ms	3.47	s	3.47	mw	3.10	vw	1.98 ₅	vw	2.82	w	2.79	40
3.31	vs	3.35	vw	3.29	vvs	3.00	vs	1.95 ₀	vwv	—	—	2.69	40
3.25	vs	3.25	vvs			2.89	w	1.93 ₀	vwv	2.68	vwv	2.59	20
3.10	w	—	—	—	—	2.76	w	1.76 ₉	vw	2.60	s	2.50	80
3.00	mw	2.99	m	2.97	vvs	2.69	vw	1.65 ₉	mw	2.49	m	2.45	40
2.92	mw	2.90	m			2.64	w	1.62 ₁	mw	—	—	2.41	20
2.76	vw	2.76	mw	2.76	mw	2.48	(diff.) mw	1.57 ₃	m	—	—	2.39	20
2.68	vw	—	—	—	—	2.39	vwv	1.55 ₇	vw	2.39	mw	2.34	20
2.59	mw	2.60	mw	2.58	s	2.27	vwv	1.49 ₀	m	—	—	2.24	20
—	—	2.53	mw	—	—	2.22 ₆	vwv	1.46 ₁	vw	2.26	w	2.21	20
—	—	2.42	w	—	—	2.14 ₈	vwv	1.373	vw	—	—	2.18	40
2.31	vwv	2.33	vw	2.38	(diff.) w	2.10 ₆	vwv	1.332	vwv	2.21 ₃	vw	3.09	20
2.21	vw	2.23	vwv	—	—	2.06 ₀	mw	1.291	w	2.16 ₆	vwv	2.16	20
2.17	vw	2.15	m	2.21	(diff.) m	2.02 ₂	mw	1.265	mw	2.11 ₁	m	2.13	50
2.13	vw	2.11	vw	—	—	1.96 ₃	vwv	1.228	mw	2.05 ₂	w	2.06	20
2.03	vwv	2.04	vwv	2.07	vw	1.91 ₅	vwv	1.211	mw	1.98 ₉	vw	1.97	20
1.98	vwv	1.98	vw	—	—	1.85 ₉	vw	1.192	mw	1.91 ₅	mw	1.93	40
1.93	vwv	1.92	vw	—	—	1.79 ₃	vwv	1.138	vw	1.87 ₀	mw	1.86	20
1.88 ₈	vwv	1.90 ₁	vw	—	—	1.74 ₂	vwv	—	—	—	—	1.82	20
1.84 ₇	vwv	1.85 ₃	vw	1.85 ₂	w	—	—	—	—	—	—	1.80	20
1.79 ₆	mw	1.79 ₇	m	1.79 ₉	m	—	—	—	—	1.76 ₀	mw	1.76	40
—	—	—	—	1.63 ₃	vwv	—	—	—	—	—	—	1.67	20
—	—	—	—	1.58 ₇	w	—	—	—	—	1.67 ₀	m	1.65	60
—	—	—	—	1.52 ₉	vwv	—	—	—	—	—	—	—	—
—	—	—	—	1.50 ₃	vw	—	—	—	—	—	—	—	—

Species J		Species M		Species O †		Species P		Species Q		Species R		Species U	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
6.27	mw	7.2	w	6.88	w	13.2	vs	13.3	vs	4.95	vw	9.7	w
5.22	ms	4.27	w	5.43	w	—	—	9.5	mw	4.01	vw	8.2	w
4.07	mw	3.28	vs	4.98	mw	—	—	6.0	w	3.53	ms	7.2	w
3.90	s	2.96	s	4.23	w	4.41	s	4.42	mw	3.33	m	6.5	ms
3.41	s	2.82	vw	3.92	w	4.17	m	4.20	mw	3.12	mw	5.11	ms
3.27	w	2.74	ms	3.77	w	4.00	w	4.00	w	2.88	m	4.49	vw
3.15	vvs	2.42	mw	3.62	w	3.81	ms	3.82	s	2.64	vwv	4.22	vw
3.00	mw	2.17	m	3.45	vs	3.63	vw	3.66	vwv	2.48	vs	4.10	vs
2.91	w	1.86 ₃	m	3.27	ms	3.50	vw	3.50	vw	2.23	vw	3.87	m
2.82	w	1.79 ₃	ms	3.06	vvs	3.33	w	3.33	w	2.11	vwv	3.66	mw
2.70	m	1.73 ₀	m	2.95	ms	3.20	m	3.20	vs	1.94 ₉	vwv	3.26	mw
2.62	w	1.67 ₃	m	2.80	ms	3.03	vs	3.04	vs	1.76 ₀	m	3.02	mw
2.48	mw	1.63 ₃	mw	2.71	m	2.92	vwv	—	—	1.70 ₃	w	2.85	m
2.37	w	1.59 ₁	mw	2.59	vwv	2.81	s	2.81	s	1.57 ₆	vwv	2.77	m
2.31	vw	1.48 ₈	mw	2.43	vw	—	—	2.64	ms	1.50 ₃	vwv	2.69	m
2.24	mw	1.28 ₂	vw	2.37	w	2.54	ms	2.54	m	1.43 ₂	vwv	2.59	w
2.20	mw	1.26 ₁	vw	2.29	mw	2.37	vwv	2.33	vw	1.40 ₆	vwv	2.48	w
2.13 ₀	vw	—	—	2.24	mw	2.30	m	2.30	ms	1.24 ₈	vwv	2.39	w
2.11 ₀	mw	—	—	2.17	vw	2.12 ₃	vwv	2.10 ₈	vwv	1.10 ₇	vwv	—	—
2.02 ₉	w	—	—	2.12 ₇	vw	2.00 ₅	vwv	2.02 ₄	vwv	—	—	—	—
1.95 ₁	w	—	—	2.08 ₄	w	1.79 ₄	vwv	—	—	—	—	—	—
1.84 ₀	w	—	—	1.95 ₁	w	1.74	vw	1.74 ₈	w	—	—	—	—
1.71 ₈	mw	—	—	1.91 ₆	w	1.69 ₃	vwv	1.69 ₈	vwv	—	—	—	—
1.66 ₅	vwv	—	—	1.88 ₂	w	1.64 ₉	w	1.64 ₉	vw	—	—	—	—
1.63 ₇	vw	—	—	1.83 ₈	w	1.61 ₃	vw	1.61 ₀	vw	—	—	—	—
1.61 ₃	w	—	—	1.81 ₂	w	1.55 ₆	vw	—	—	—	—	—	—
1.56 ₆	w	—	—	1.77 ₉	vwv	1.42 ₆	w	—	—	—	—	—	—
1.52 ₃	vw	—	—	1.72 ₆	m	1.38 ₅	vw	—	—	—	—	—	—
1.47 ₉	vw	—	—	1.67 ₀	vwv	—	—	—	—	—	—	—	—
1.44 ₁	vw	—	—	1.62 ₃	vwv	—	—	—	—	—	—	—	—
1.35 ₇	vw	—	—	—	—	—	—	—	—	—	—	—	—

* Spacings from A.S.T.M. index.

† Species N is identical.

followed by *X*-ray studies up to 550°. No changes in the lattice could be detected, but water up to 6% (by weight) was evolved.

Analyses have shown that the compounds P and Q have somewhat variable halide and water content. From several analyses Barrer (*J.*, 1948, 127) adduced an ideal formula $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 0.67\text{BaCl}_2 \cdot 2-3\text{H}_2\text{O}$ for the chlorine-containing phase.

It is of interest to compare the behaviour of N and O, of P and Q, and of synthetic sodalite-nosean minerals, because these three types of compound show certain resemblances (Table 7).

Compounds R, S, T, and U.—From Table 4 it is seen that hydrothermal treatment of analcite at 450° with excess of barium bromide produced a few crystals of the phase R. These grew as micaceous plates up to 1 mm. across (Plate VI). They were feebly birefringent, of straight extinction, and showed pleichroism, the colour varying between blue and purple. They gave a biaxial negative interference figure, the optic axial angle being very small, and they probably belonged to the monoclinic system. The mean value of *n* was ~1.67. A small amount of the pure substance was collected by sieving and hand-picking, and *X*-ray data were obtained (Table 8). The substance could not be identified with any barium aluminosilicate. Although yields were small, formation was reproducible.

During attempts to prepare lead analcite from analcite and lead chloride at temperatures between 250° and 400° the recrystallisation of part of the analcite was observed. Two metamorphic products appeared of which one, species S, was most abundant (Plate VII). *X*-Ray spacings of S are given in Table 8. The crystal habit recalls that of albite, and the spacings show a superficial resemblance to those of potash feldspar, although there are some considerable differences also. Kohler (*Anz. Akad. Wien., Math.-naturw. Klasse*, 1935, 72, 123) has made a synthetic lead feldspar.

Crystals of species T appeared after the fifth extraction of compound P (prepared at 450°) with distilled water at 250° (*J.*, 1948, 127). *X*-Ray spacings in Table 8 show a correspondence with potash feldspar sufficient to indicate that T belongs to the feldspar group. It may be a celsian, but the crystals were too small for adequate optical characterisation. The mean refractive index of ~1.56 is lower than that of celsian. This may be due to the presence of some sodium in both P and T, derived from the parent mineral analcite.

Species U was derived principally from the compound Q, although it was also found as an alternative product from P (cf. Barrer, *J.*, 1948, 127, Fig. 6). It appeared as elongated prisms up to 150 μ long and often eroded. One specimen, when outgassed at ~330° and tested as a sorbent, still retained its characteristic *X*-ray spacings (Table 8). The powder photographs showed resemblances to, but some differences from, a natural harmotome. Species U gave a mean value of *n* ~1.517.

DISCUSSION

In general, at low temperatures, leucite and analcite showed ion-exchange alone (Barrer, *J.*, 1950, 2342). Recrystallisations set in with saline solutions only at more elevated temperatures. Exceptions arise, however, with *mixed* sodium and potassium salt solutions. Thus potash feldspar was formed at 195–200° from leucite and saturated, mixed sodium and potassium carbonates (cf. Barrer and Hinds, *Nature*, 1950, 166, 562). The aluminosilicate J was formed under similar conditions at 160°; and hieratite (K_2SiF_6) grew at temperatures as low as 110° with saturated, mixed sodium and potassium fluoride solutions as mineraliser. On the other hand in the presence of solutions of one of the carbonates alone recrystallisation required temperatures of at least 300°, and usually gave rise to different phases. These phenomena may be of general occurrence. If so, geologically significant low-temperature interconversions of minerals may be possible, because mixed solutions will be common under natural conditions. Knowledge of synthetic mineralogy may also be improved by investigating the hydrothermal growth of aluminosilicates from mixed gels. To a limited extent this has been attempted by Wyart and Mille Michel-Levy (*Compt. rend.*, 1949, 229, 131) for the system $\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$ ($0 < x < 1$).

A notable feature of the aluminosilicate syntheses recorded in Parts I and II and this paper has been that slight but distinct structural and optical differences may arise between synthetic minerals and their naturally occurring counterparts (*e.g.*, potash feldspar, kaliophilite, nepheline, albite, α -eucryptite). Such differences may be explained at least in part by the fact that the synthetic form is often a chemically pure end-member. Natural aluminosilicate crystals frequently contain, by isomorphous replacements,

appreciable amounts of other elements. Nepheline grown by us in presence of solutions containing both K⁺ and Na⁺ was, in accordance with this idea, indistinguishable from a natural nepheline, but differed slightly from the pure synthetic sodium nephelines.

The ease of formation and the persistence of analcite in the hydrothermal sodium aluminosilicate field has already been commented upon (Part II). In the present work it has been shown that analcite and leucite can in turn give high yields of various minerals (Table 1). To these may be added albite, formed from analcite by sintering (Part II) and kaolinite, made from analcite or leucite under somewhat acid conditions (Norton, *Amer. Min.*, 1941, **26**, 1; Schwarz and Trageser, *Z. anorg. Chem.*, 1933, **215**, 190). In their turn, however, many of these rock and soil-forming minerals can be re-converted by mineralising solutions at least in part into analcite. This is true of leucite, nepheline, potash felspar (adularia and microcline), albite, okenite, muscovite, eucryptite, and kaolin (Barrer, *J.*, 1950, 2342; von Nieuwenberg and Blumendahl, *Rec. Trav. chim.*, 1931, **50**, 989; Stevenson, *J. Geol.*, 1916, **24**, 180; Doelter, *Neues Jahrb. Miner.*, 1890, I, 118; Friedel, *Bull. Soc. Miner. franç.*, 1896, **19**, 5; Barrer and White, Part I; Lemberg, *Z. deut. geol. Ges.*, 1887, **39**, 559). Similar relations arise between leucite and other species, so that both analcite and leucite figure in a variety of two-way paths by which they may be generated from, or give rise to, diverse important species. Leucite has been reported as being formed from kaliophilite, kaolin, feldspars, mica, and analcite (von Nieuwenberg and Blumendahl, *loc. cit.*; Lemberg, *loc. cit.*; Friedel and Friedel, *Bull. Soc. Miner. franç.*, 1890, **13**, 129; Barrer, *J.*, 1950, 2342). In turn it may give rise to analcite, orthoclase, kaolinite, and sericite (Barrer, *J.*, 1950, 2342; von Nieuwenberg and Blumendahl, Schwarz and Trageser, and Norton, *loc. cit.*). Leucite is a relatively common pyrolytic mineral, although its low-temperature hydrothermal synthesis has also been noted (cf. Table 6). Analcite is a hydrothermal mineral, but there is the possibility that it can be formed in deep-seated rocks as a primary mineral (Scott, *Trans. Geol. Soc., Glasgow*, 1916, **16**, 34; Yoder, *Amer. J. Sci.*, 1950, **248**, 312).

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