36. *Hydrothermal Chemistry of the Silicates. Part VIII.* Low-temperature Crystal Growth of Aluminosilicates, and of Some Gallium and Germanium Analogues.*

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The hydrothermal method has been used to study the crystallisation of aluminosilicates from 60° to 250°. Hydrous gels of compositions $Na_2O,Al_2O_3,nSiO_2$ ($1 \leqslant n \leqslant 12$) in presence of excess of sodium hydroxide yielded analcite, mordenite, zeolites of the harmotome, faujasite and chabazite groups, Linde Molecular Sieve A, a zeolitic phase related to rhodesite, basic sodalite, basic nosean, and a phase related to nepheline hydrate. The species formed have been characterised by optical, *X*-ray, and chemical methods.

The corresponding crystallisation of mixed Na,K-aluminosilicate gels has been compared with that of the homoionic Na- and K-gels. From the mixed gels in the interval 60° to 250° phases in the analcite–leucite, the chabazite, harmotome–phillipsite, felspar, and kalsilite groups were prepared. In addition, boehmite, quartz, and a synthetic zeolite were obtained.

When Ga replaced Al and Ge replaced Si in Na-gels, crystallisation of alkaline gels at 100° yielded, as gallosilicate, a fibrous zeolite resembling thomsonite; as aluminogermanates, zeolites of faujasite type, and an analogue of Linde Sieve A and of harmotome; and as gallogermanates, zeolites again resembling thomsonite, faujasite, and Linde Sieve A. If Ga or Ge replace Al or Si, the unit cells of the crystalline phases become slightly larger.

Attention has been given to the mechanism of growth of diverse structural patterns from alkaline hydrothermal magmas.

THE lower-temperature crystallisation fields of aluminosilicates of lithium,[1] sodium,[2] potassium,[3] rubidium,[4] thallium,[5] and cæsium [4] were previously studied hydrothermally;

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* Part VII, *J.*, 1956, 2882.

[1] Barrer and White, *J.*, 1951, 1167.
[2] *Idem*, *J.*, 1952, 1561.
[3] Barrer and Baynham, *J.*, 1956, 2882.
[4] Barrer and McCallum, *J.*, 1953, 4029.
[5] Taylor, *J.*, 1949, 1253.

the chemistry and properties of some of the species obtained, among which were many zeolites, were investigated,[6-9] and certain aspects surveyed.[10]

Zeolites appear to be formed naturally at as low as 60° at Wairakei, New Zealand,[11] and in the temperature range 60—150° several potassium zeolites have been synthesised,[3, 8] for example, a series of chabazite phases and phases related to the harmotome–phillipsite group. Since the hydrothermal crystallisation of sodium aluminosilicates had been investigated at or above 150°, and had resulted in the synthesis of two zeolites only (analcite [2, 12-15] and mordenite [2, 16]), we have now studied the crystallisation field of sodium aluminosilicates down to lower temperatures. Zeolites are " filled " structures, the filler being water, and should be more readily formed the lower the temperature, owing to the volatility of the filler. The synthesis of additional synthetic zeolites, some of which are Na-rich, has already been indicated.[1-9]

Barrer, Hinds, and White [6] showed that mineral metamorphoses in hydrothermal media could take a course in mixed aqueous electrolytes, *e.g.*, sodium and potassium carbonates, different from that in either single electrolyte. Accordingly we have also studied the crystallisation of $(Na,K)_2O,Al_2O_3,nSiO_2,mH_2O$ gels containing two cations, in relation to crystallisation of these gels containing only one cation, Na or K. Finally, experiments have been made to see how readily one can replace Al by Ga and Si by Ge and still obtain the same structural types. Goldsmith [17, 18] showed that such replacements are possible in leucite and in felspars, and that a gallium-containing thomsonite can be synthesised hydrothermally from a gallium-containing glass. Similarly Eitel [19] demonstrated, by pyrolytic synthesis of phlogopite-micas, that analogous replacements of Si by Ge can occur in this layer-lattice mineral.

EXPERIMENTAL

(a) *Preparation of* Na-*gels, and Crystallisation Conditions.*—Silica was in the form of a stable dispersion " Syton 2-X " (Monsanto Chemicals Ltd.) and contained 30% (w/w) of SiO_2, had pH ~10, specific gravity 1·2, and average particle diameter 250 Å. There was a trace of chloride.

Alumina was initially introduced as aluminium hydroxide prepared by the action of cold water on lightly amalgamated aluminium foil.[20] Better crystallisations were achieved by using " Alfloc " sodium aluminate (Imperial Chemical Industries Limited) which contained ~87% (w/w) of $NaAlO_2$, a trace of iron, and the remainder free sodium hydroxide. Subsequent results refer to crystallisations achieved from gels containing " Alfloc."

Gels of compositions $Na_2O,Al_2O_3,nSiO_2$ ($1 \leqslant n \leqslant 12$) were prepared by dissolving " Alfloc " in water, filtering off the precipitated ferric hydroxide, and adding suitable quantities of " Syton." The SiO_2 gelatinised in presence of sodium cations and so continual stirring during the addition of the " Syton " and for about ½ hr. afterwards was necessary to disperse the silica evenly. " AnalaR " sodium hydroxide was added so that either 100%, 200%, or 300% molar excess of sodium hydroxide over that required for the ratio of base : alumina to be 1 : 1 was present.

Between 60° and 110° crystallisations were carried out in Pyrex glass tubes of ~1·25 cm.

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[6] Barrer, Hinds, and White, *J.*, 1953, 1466.
[7] Barrer, Baynham, and McCallum, *J.*, 1953, 4035.
[8] Barrer and Baynham, *J.*, 1956, 2892.
[9] Gard, Barrer, and Baynham, *J.*, 1955, 2480.
[10] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.
[11] Steiner, *Econ. Geol.*, 1953, **48**, 1.
[12] Friedman, *J. Geol.*, 1951, **59**, 14.
[13] von Nieuwenberg and Blumendahl, *Rec. Trav. chim.*, 1931, **50**, 989.
[14] Straub, *Ind. Eng. Chem.*, 1936, **28**, 113.
[15] Guyer, Ineichen, and Guyer, *Helv. Chim. Acta*, 1957, **40**, 1603.
[16] Barrer, *J.*, 1948, 2158.
[17] Goldsmith, *J. Geol.*, 1950, **58**, 518.
[18] *Idem, Mineralog. Mag.*, 1952, **29**, 952.
[19] Eitel, Proc. Int. Symp. on Reactivity of Solids, Gothenburg, 1954, Part I, 335.
[20] Weiser and Milligan, *J. Phys. Chem.*, 1937, **41**, 1029; *Chem. Rev.*, 1939, **25**, 1.

internal diam. Charges of ½ g. of gel, calculated as dry weight of the constituents, in 10 ml. of total mixture were sealed in the tubes so that the latter had an internal capacity of ~20 ml. At higher temperatures the glass was appreciably attacked by the gel, so stainless steel autoclaves of ~20 ml. capacity were employed.[21] The gels were heated in electrically heated ovens, thermostatically controlled to ±1°, and after any desired length of treatment the glass tubes were cooled in air, the steel autoclaves quenched in cold water, and the product filtered off, washed with hot water until free from alkali, and air-dried. Large-scale preparations were made in an electrically heated autoclave of 1 l. capacity (Chas. W. Cook and Sons Ltd.).

(b) *Preparation of Mixed* Na, K-*gels, and Crystallisation Conditions.*—Alumina, prepared as above from lightly amalgamated aluminium foil, was mixed with the appropriate amount of "AnalaR" potassium hydroxide solution. The product was then mixed with "Syton 2-X" with continuous stirring. Various aqueous gels were thus prepared, usually of oxide composition $K_2O,Al_2O_3,nSiO_2,mH_2O$ ($2 \leqslant n \leqslant 12$). To these gels various amounts of sodium hydroxide solution were then added, and the gel finally crystallised at various temperatures (see Tables 3 and 4) and for between 1 and 18 days as required.

(c) *Preparation of* Na-*gels containing* Ga *and* Ge, *and Crystallisation Conditions.*—Sodium gallosilicate, gallogermanate and aluminogermanate gels were prepared, by use of sodium aluminate ("Alfloc"), sodium gallate, silica sol ("Syton 2X"), and sodium germanate as appropriate components. The gallate and germanate were prepared as follows.

3·75 g. of Ga_2O_3 (40 mequiv.) were dissolved in 25 ml. of aqueous sodium hydroxide (30%) and 50 ml. of water on the water-bath. The filtered solution was diluted to 400 ml. and acidified with hydrochloric acid (to pH ~1), and the hot solution finally neutralised with ammonia. The precipitated $Ga(OH)_3$ was filtered off, washed with hot water, and dissolved in 30 ml. of 2N-sodium hydroxide. Water was then added to make up 80 ml. An apparently colloidal, opaque alkaline dispersion was obtained, which may be regarded as a 0·5M-$NaGaO_2$ dispersion. [More than 3 NaOH per $Ga(OH)_3$ were necessary to obtain clear solutions.]

4·20 g. (40 mmoles) of GeO_2 were next dissolved in 20 ml. of aqueous sodium hydroxide (30%) on the water-bath, and the solution filtered after dilution with 50 ml. of water. The filtrate was acidified with concentrated hydrochloric acid, after which germanic acid gel was precipitated by adding aqueous ammonia (to pH ~6—7), and was washed thoroughly with hot water. The wet gel was then dissolved in 40 ml. of 2N-sodium hydroxide, and water added to make 80 ml. of 0·5M-sodium germanate solution.

"Syton 2X" was diluted to give a 1M-colloidal solution, and "Alfloc" was dissolved in a small amount of water and filtered to remove insoluble matter such as ferric hydroxide. It was then diluted to 1M, and a sample analysed. The excess of alkali corresponded to 0·25 mmole of sodium hydroxide per ml.

Measured amounts of the appropriate pairs of solutions or suspensions were then mixed with stirring to give reactant mixtures containing 0·5 g. of solid per 10 ml. No extra alkali was added since it was already in excess. The mixtures were then rotated in sealed glass tubes at 100° in thermostatic air-ovens. The crystallisations were allowed between 7 and 46 hr., after which the solid products were filtered off and washed thoroughly with hot water.

(d) *Examination of Products.*—A Leitz IIIC polarising microscope and a Vickers projection microscope were used to examine the products optically, but where the crystals were too small so to characterise their habit, electron micrographs were taken on a Metrovic EM3 by Dr. J. A. Gard of Aberdeen University. Refractive indices were determined to ±0·005 unit in white light.

X-Ray powder photographs were taken on 9 cm. Debye–Scherrer cameras and a "Nonius" Guinier camera, the Cu-K_α radiation used being generated by a Hilger HRX unit. Where possible, unit-cell dimensions were determined.

Products obtained in 100% yield were analysed by standard methods, the procedures followed being those recommended by Groves.[22]

Results.—*Crystalline sodium aluminosilicates.* The minerals observed are listed in Table 1, the reference letter being either that used in the previous higher-temperature investigation [2] or in a continuation of it.

The results of the crystallisations, the yields being determined by optical examination, are given in Table 2. The fields of growth of the major species are clarified in Fig. 1 (which includes

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[21] Barrer, *J.*, 1948, 127.

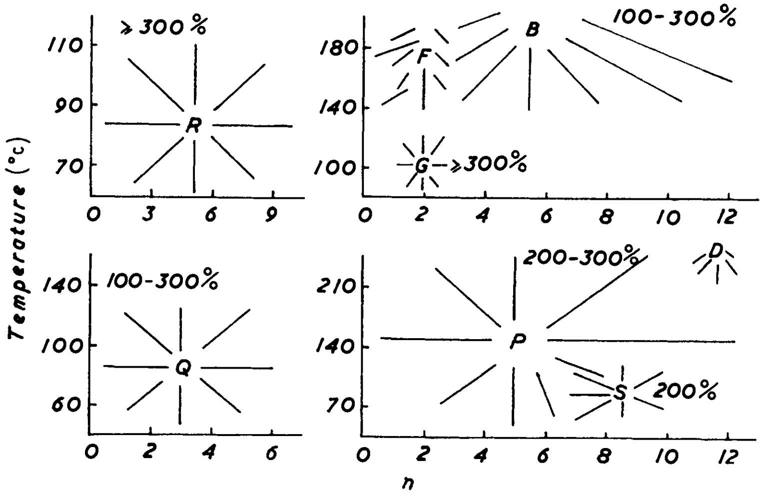
[22] Groves, "Silicate Analysis," Allen and Unwin, London, 1951.

experiments, particularly for Na-*R*, not recorded in Table 2), but it must be emphasised that only approximate areas of crystallisation can be delineated since no attempt was made to define the exact phase boundary of each species. Yields often diminish rather slowly along either the composition or the temperature axis.

Crystallisation was often very rapidly and easily accomplished. Thus 2 or 3 hr. were sufficient to obtain good yields of species *Q* at 85—110° from alumina-rich gels. Slightly longer was required as the silica content of the gel increased. Crystallisation was also better and more rapid from gels containing a large excess of sodium hydroxide (300%), the effect being especially marked at 60° and 85°.

The preparation and characteristics of individual species will now be considered.

FIG. 1. *Fields of growth of minerals synthesised from* $Na_2O,Al_2O_3,nSiO_2,mH_2O$ *gels with excess of sodium hydroxide added (percentages shown).*



Zeolites. Species *P*, related to the natural harmotome–phillipsite groups of zeolites, occurred as very small (~2 μ) irregular crystals (Plate 1) from gels $n = 1$ to $n = 12$ over the range 60—250°. The crystals exhibited no birefringence, but the refractive indices decreased from 1·493 for a sample grown from a gel of $n = 2$, through 1·475 for a gel of $n = 5$, to 1·455 for $n = 8$. Optimum yields were obtained after one day's treatment at 110° with 200% or 300% excess of alkali present, since under these conditions recrystallisation of species *Q*, which was usually the primary nucleation product, to this mineral was rapid.

TABLE 1. *Summary of crystalline species.*

Ref. letter	Name or natural counterpart	Oxide formula	Mineral class
B	Analcite	$Na_2O,Al_2O_3,4SiO_2,2H_2O$	Zeolite
D	Mordenite	$Na_2O,Al_2O_3,10SiO_2,6{\cdot}7H_2O$	Zeolite
F	" Basic " nosean	$Na_2O,Al_2O_3,2SiO_2,xNaOH,yH_2O$	Felspathoid
I	" Basic " sodalite	$Na_2O,Al_2O_3,2{\cdot}1SiO_2,2NaOH,1{\cdot}5H_2O$	Felspathoid
P	Phases of harmotome–phillipsite group	$Na_2O,Al_2O_3,3{\cdot}3SiO_2,4{\cdot}3H_2O$ to $Na_2O,Al_2O_3,5{\cdot}3SiO_2,5{\cdot}7H_2O$	Zeolites
Q	Species *Q*	$Na_2O,Al_2O_3,2SiO_2,4H_2O$	Zeolite
R	Phases of faujasite group	$Na_2O,Al_2O_3,2{\cdot}4SiO_2,6{\cdot}7H_2O$ to $Na_2O,Al_2O_3,3{\cdot}3SiO_2,7H_2O$	Zeolites
S	Phases of chabazite-gmelinite group	$Na_2O,Al_2O_3,5SiO_2,5{\cdot}4H_2O$	Zeolites
T	Nepheline hydrate III	$Na_2O,Al_2O_3,2SiO_2,xH_2O$?	Felspathoid
U	Species U	—	Zeolite (?)

The composition of the crystals varied from $Na_2O,Al_2O_3,3{\cdot}3SiO_2,4{\cdot}3H_2O$ to $Na_2O,Al_2O_3,5{\cdot}3SiO_2,5{\cdot}7H_2O$. Variations in the unit cell were also noted, some samples being cubic, $a = 10{\cdot}0$ Å, and others tetragonal, $a = 10{\cdot}0$ Å, $c = 9{\cdot}8$ Å, the *c* parameter also varying slightly between samples. *d*-Spacings are given in Table 3.

Plate 1. *Species P* × 4400.

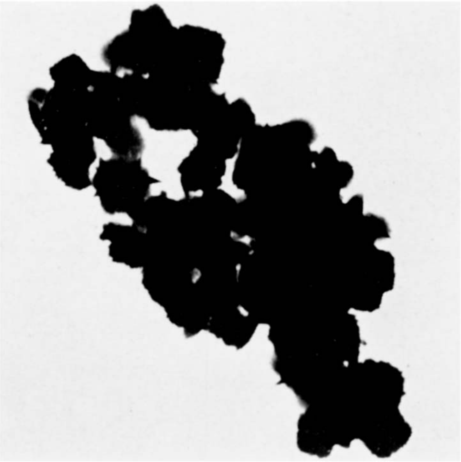


Plate 2. *Rhombohedral species P* × 628.

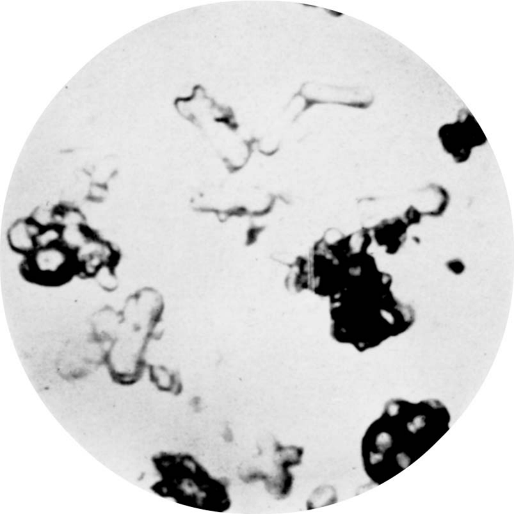


Plate 3. *Species Q* × **3000**.

Plate 4. *Species R* × **13**,000.

[*To face p.* **198.**

Plate 5. *Species S* × 628.

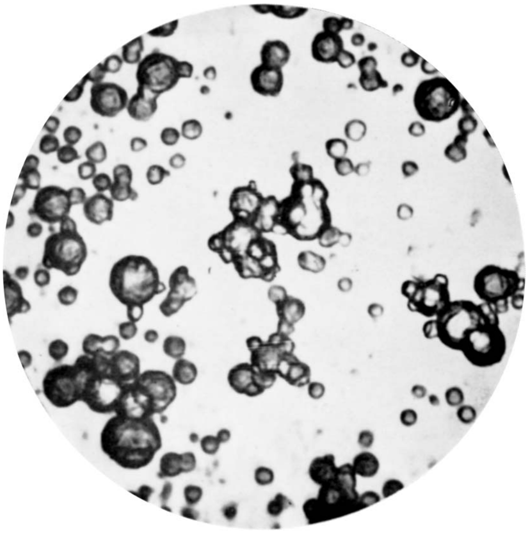


Plate 6. *Species U* × 4000.

Two preparations, having orthorhombic unit cells, $a = 14{\cdot}1$, $b = 14{\cdot}0$, $c = 9{\cdot}8$, were grown at 250° from gels $n = 5$ with about 200% excess of alkali but syntheses were not reproducible. These orthorhombic forms grew in a variety of crystal habits, the most common being rods slightly thickened at each end which occasionally exhibited cross twinning (Plate 2). This resembles the mode of growth of species K-M [3], which also had a very similar X-ray powder pattern (Table 3). The inter-relations of the unit cells of these phases will be discussed in another paper.[24]

Species Q is a purely synthetic zeolite with no natural counterpart but its X-ray pattern identifies it with the synthetic zeolite type A described by Breck *et al.*[25, 26] It grew as very

TABLE 2. *Products of crystallisation of sodium aluminosilicate gels.*

In all cases pH of mother-liquor >10·5.
No brackets = 100% molar excess of NaOH, *i.e.*, gel was $2Na_2O,Al_2O_3,nSiO_2$.
( ) = 200% molar excess of NaOH, *i.e.*, gel was $3Na_2O,Al_2O_3,nSiO_2$.
[ ] = 300% molar excess of NaOH, *i.e.*, gel was $4Na_2O,Al_2O_3,nSiO_2$.
$Q \longrightarrow P$ signifies that species Q recrystallised to species P very readily.

Temp.	$n = 1$	$n = 2$	$n = 3$	$n = 4$
60°	Moderate Q (Moderate Q) [Moderate Q]	Poor Q (Moderate Q) [Moderate Q]	Poor Q (Moderate Q) [Moderate Q]	No crystallisation (Moderate Q) [Moderate Q]
85°	Good Q (Good Q) [Good Q]	Good Q (Good Q) [Good Q]	Poor Q (Good Q) [Good Q]	No crystallisation after 1 day (Poor Q) [Moderate Q]
110°	Good F + some Q (Good F + some Q) [V. good P + some Q]	Good $Q \longrightarrow P$ (Good $Q \longrightarrow P$) [V. good P]	Good $Q \longrightarrow P$ (Good $Q \longrightarrow P$) [V. good P]	Good $Q \longrightarrow P$ (V. good P) [V. good P]
150°	Good F (Good F) [Good F]	Good F + some B (Good $B + F$) [Good F]	Good $F + B$ (Good $F + B$) [Good F + some P]	Good B + some P (Good B) [Good B]
200°	Good F (Good F) [Good F]	Good F (Good $B + F$) [Good B + some F and T]	Good F + some B and P (Good F + some P) [Good B]	Good B + some F (V. good B) [V. good B]
250°	Good F (Good F + some B and P) [Good F + some P]	Good $B + F$ (Good $B + F$) [Good $B + F$]	Good F + some P and B (Good B and F + some P) [Good $P + F$]	Good $B + F + P$ (Good B + some F and P) [V. good B]
	$n = 5$	$n = 6$	$n = 7$	$n = 8$
60°	No crystallisation (Moderate Q) [Good $Q + R$]	V. poor Q (Poor Q) [Poor P + some R]	No crystallisation (No crystallisation) [Poor S + some R]	No crystallisation observed even with 300% excess of NaOH
85°	Poor Q (Poor Q) [Poor Q]	Moderate Q (Moderate Q) [Good P]	No crystallisation (No crystallisation) [Moderate P]	No crystallisation (No crystallisation) [Good S]
110°	Good Q (Good P) [Good P]	Moderate Q (Good P) [Good P]	No crystallisation (Good P) [Good $P + S$]	Good S + some P (Good $P + S$) [Good $P + S$]
150°	Good B + some P (Good B) [Good B]	Good P (Good B) [Good B + some P]	Good $B + P$ (Good P) [Good $B + P$]	Good B (Good B) [Good $B + P$]
200°	Good $B + P$ (Good B + trace P) [Good $B + P$]	Good B (Good B) [Good B]	Good $B + P$ (Good B) [Good $B + P$]	Good B (Good B) [Good $B + P$]
250°	Good B (Good B) [Good B]	Good $B + P$ (Good $B + P$) [Good $B + P$]	Good $B + P$ (Good B) [Good $B + P$]	[Good $B + P$] (Good B) [Good $B + P$]

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[23] Strunz, *Neues Jb. Min.*, 1956, **11**, 250.
[24] Barrer, Bultitude, and Kerr, unpublished work.
[25] Breck, Eversole, Milton, Reed, and Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 5963.
[26] Reed and Breck, *ibid.*, p. 5972.

TABLE 2. (*Continued.*)

Temp.	$n = 9$	$n = 10$	$n = 11$	$n = 12$
60°	No crystallisation even with 300% excess of NaOH	No crystallisation even with 300% excess of NaOH	No crystallisation even with 300% excess of NaOH	No crystallisation even with 300% excess of NaOH
85°	No crystallisation (Poor *S*) [Moderate *S*]	No crystallisation (Poor *S*) [Poor *S*]	No crystallisation even with 300% excess of NaOH	No crystallisation even with 300% excess of NaOH
110°	Good *S* (Good *S*) [Good *S*]	No crystallisation (Good *S*) [Good *S*]	No crystallisation even with 300% excess of NaOH	No crystallisation even with 300% excess of NaOH
150°	No crystallisation (Moderate *B* + *P* and some *S*) [Good *B* + *P*]	Poor *B* (Good *P* and some *B*) [Good *B* + *P*]	No crystallisation (Moderate *P* + some *B*) [Good *P* + some *B*]	No crystallisation (Poor *B*) [Good *B* + some *P*]
200°	Good *B* + *P* (Good *B*) [Good *B*]	Moderate *B* (Moderate *B* + *P*) [Good *B*]	No crystallisation (Good *B*) [Good *B*]	Moderate *B* + some *P* (Good *B*) [Good *B*]
250°	Moderate *B* + *P* (Moderate *B* + *P*)· [Moderate *B* + *P*]	Moderate *B* + some *P* (Moderate *B* + *P*) [Good *B* + some *P*]	Poor *B* + *P* (Moderate *B* + *P*) [Moderate *B* + some *P*]	Poor *B* (Poor *B*) [Good *B* + *D*]

small cubic crystals with a maximum size of ~3 μ (Plate 3), isotropic, and having a refractive index of ~1·472. Its range of growth was from gels with $n = \frac{1}{2}$ to $n = 6$ over the range of 60—110°, only 2—3 hr. being required for virtually 100% yields with 200% or 300% excess of sodium hydroxide present at the upper temperature. Under these conditions recrystallisation of species *Q* to species *P* was, however, rapid. At 85° the pattern of species *P* appeared on the *X*-ray photographs only after 5 days' heating of the gel with 300% excess of sodium hydroxide, but at 110° with 200% excess of base conversion into the harmotome-like mineral was complete after 1 day. The recrystallisation could be brought about by treating species *Q* with a normal solution of sodium hydroxide at 100°. In very concentrated gels species *Q* recrystallised to basic sodalite (see species *I* below).

Analysis of species *Q* gave Na_2O, 16·3; Al_2O_3, 28·0; SiO_2, 33·5; H_2O, 22·1%, equivalent to

TABLE 3. X-*Ray data.* d-*Spacings* (Å) *and intensities.**

Species *P*										
Cubic form $a = 10{\cdot}0_1$ Å			Tetragonal form $a = 10{\cdot}0_1$ Å, $c = 9{\cdot}8_8$ Å			Orthorhombic form $a = 14{\cdot}1$ Å, $b = 14{\cdot}0$ Å, $c = 9{\cdot}8$ Å			K-*M*[a]	
hkl	*d*	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*
—	—	—	—	—	—	001	9·5	m	9·4	mw
—	—	—	—	—	—	101	8·2	mw	8·2	m
110	7·1	s	110	7·1	s	200	7·2	s	7·1	s
—	—	—	—	—	—	020	7·0	mw	7·0	w
—	—	—	111	5·8	vw	201	5·6	mw	5·6	w
—	—	—	—	—	—	211	5·4	w	5·4	m
200	5·0	m	200	5·0	m	220	5·0	s	4·97	m
—	—	—	002	4·94	m	102	4·68	w	4·68	w
—	—	—	102	4·44	vvw	310	4·50	w	4·45	mw
—	—	—	—	—	—	112	4·34	s	4·34	mw
—	—	—	—	—	—	—	—	—	4·28	mw
112	4·10	s	211	4·09	s	311	4·08	s	4·08	mw
—	—	—	112	4·07	vw	—	—	—	—	—
—	—	—	—	—	—	212	3·88	mw	3·86	w
—	—	—	220	3·65	vw	400	3·58	m	3·64	w
220	3·45	vw	202	3·50	vvw	222	3·45	m	—	—
—	—	—	212	3·32	mw	312	3·35	m	—	—
—	—	—	003	3·26	w	013	3·24	m	3·24	vs
310	3·18	vvs	310	3·18	s	420	3·19	vs	3·17	vs
—	—	—	103	3·11	s	—	—	—	—	—
—	—	—	311	3·02	w	—	—	—	—	—
—	—	—	113	2·96	vw	203	2·93	s	2·94	s
222	2·90	vw	—	—	—	—	—	—	2·87	w
—	—	—	203	2·73	vw	223	2·73	m	2·72	mw
321	2·68	s	312	2·68	ms	422	2·68	m	2·67	mw
—	—	—	213	2·65	m	313	2·60	m	2·58	w
400	2·52	vw	400	2·52	w	—	2·51	m	2·48	w
410, 322	2·41	vw	410	2·42	w	—	2·42	vvw	2·42	vw
411, 330	2·36	w	330	2·38	vw	—	—	—	2·38	w
204	2·23	vw	420	2·24	vw	—	2·24	vw	—	—

* s = strong, w = weak, d = diffuse, m = medium, v = very. In certain columns numerals are used, and these are defined as in the original references, the strongest being given as either 10 or 100.

TABLE 3. (*Continued.*)

Species *S*				K-*G*[2]		Chabazite[23]		Gmelinite[22]	
Hexagonal $a = 13{\cdot}72$ Å	$c = 10{\cdot}00$ Å			$a = 13{\cdot}85$ Å	$c = 15{\cdot}50$ Å	$a = 13{\cdot}78$ Å	$c = 14{\cdot}97$ Å	$a = 13{\cdot}72$ Å	$c = 9{\cdot}95$ Å
hkil	$d_{obs.}$	$d_{calc.}$	*I*	*d*	*I*	*d*	*I*	*d*	*I*
$10\bar{1}0$	11·8	11·9	ms	—	—	—	—	11·9	7
0001	~9·5	10·0	vd	9·5	ms	9·3	7	9·3	6
	—	—	—	—	—	—	—	7·63	4
$11\bar{2}0$	6·85	6·86	s	6·94	m	6·92	3	56·86	4
	—	—	—	—	—	—	—	0·99	1
	—	—	—	5·55	vvw	5·47	6	5·51	4
0002	5·01	5·00	s	5·24	m	4·96	5	5·01	6
	—	—	—	4·78	vvw	—	—	—	—
$21\bar{3}0$	4·46	4·49	mw	—	—	4·60	1	4·58	1
	—	—	—	4·32	s	4·29	8	4·33	5
$30\bar{3}0$	3·962	3·961	mw	3·95	ms	—	—	4·08	5
	—	—	—	—	—	3·82	3	3·85	1
	—	—	—	3·68	mw	3·56	5	3·59	4
$22\bar{4}0$	3·431	3·430	s	3·45	mw	3·39	3	3·40	4
$31\bar{4}0$	3·280	3·296	vvw	—	—	—	—	—	—
$10\bar{1}3$	3·167	3·211	vw	3·18	mw	3·187	3	3·209	5
$30\bar{3}2$		3·106							
$40\bar{4}0$	2·970	2·971	m	—	—	—	—	—	—
$20\bar{2}3$	2·900	2·908	mw	2·93	vvs	2·907	9	2·912	8
$22\bar{4}2$	2·829	2·828	mw	—	—	—	—	—	—
	—	—	—	—	—	2·675	1	2·683	5
$41\bar{5}0$	2·595	2·593	s	2·59	ms	2·578	4	2·585	4
	—	—	—	—	—	2·481	4	2·495	2
$20\bar{2}4$	2·284	2·305	w	2·29	ms	2·287	2	2·292	2
	—	—	—	2·17	m	—	—	2·201	1
$32\bar{5}3$	2·113	2·112	w	2·10	mw	—	—	—	—
$30\bar{3}4$		2·116							
$33\bar{6}2$	2·083	2·081	s	2·07	w	2·076	3	2·080	4
	—	—	—	—	—	2·006	1	—	—
$11\bar{2}5$	1·901	1·919	m	1·89	vw	1·910	1	1·933	1
$40\bar{4}4$		1·915							
	—	—	—	1·84	mw	1·852	2	1·848	1
$41\bar{5}4$	1·800	1·800	s	—	—	1·797	5	1·797	5
$44\bar{8}0$	1·716	1·715	s	1·72	s	1·716	4	1·716	4
$70\bar{7}0$	1·687	1·697	m	—	—	—	—	—	—
0006	1·667	1·667	m	—	—	1·675	1	1·669	1
$10\bar{1}6$	1·646	1·647	w	—	—	—	—	—	—
$62\bar{8}0$		1·648							
$11\bar{2}6$	1·636	1·620	w	1·64	m	1·631	4	1·631	1

	Species *R*				Natural faujasite (Sasbach, Kaiserstuhl)				Nepheline hydrate		Nepheline hydrate		Species *Q*			Na-Zeolite.	
	94·96 †		24·83 †		24·65 †												
	1 : 2·4 ‡		1 : 3·3 ‡		1 : 4·7 ‡		Species *T*		I[2]		H[2]		Cubic $a = 12{\cdot}30$ Å			Type *A*[25]	
hkl	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*
111	14·52	vs	14·25	vs	14·25	vs	8·2	mw	8·3	ms	—	—	100	12·36	vs	12·294	100
220	8·84	ms	8·75	s	8·70	s	7·6	mw	7·4	ms	—	—	110	8·77	s	8·706	69
311	7·56	ms	7·51	s	7·38	s	—	—	6·4	mw	6·3	mw	111	7·15	s	7·109	35
331	5·74	s	5·71	vs	5·66	vs	5·6	m	5·5	m	5·5	m	200	6·35	w	—	—
511	4·81	m	4·78	m	4·76	s	4·85	w	—	—	—	—	210	5·52	s	5·508	25
440	4·42	ms	4·39	s	4·36	s	4·66	mw	4·72	vvw	4·67	s	211	5·03	w	5·031	2
531	4·20	vvw	—	—	4·16	w	4·46	ms	4·39	vs	4·34	ms	220	4·36	m	4·357	6
620	3·954	w	3·931	m	3·90	w	—	—	4·11	vw	4·07	vs	300, 221	4·102	s	4·107	36
533	3·813	ms	3·789	s	3·76	vs	—	—	—	—	3·84	w	310	3·899	w	—	—
622	3·769	mw	3·746	mw	—	—	—	—	3·61	vw	3·67	vs	311	3·712	s	3·714	53
444	3·621	vvw	3·580	w	—	—	—	—	3·40	vvs	3·40	ms	320	3·413	m	3·417	16
551	3·515	vvw	3·475	w	3·44	w	3·25	m	3·22	vw	3·20	s	321	3·287	ms	3·293	47
642	— §	—	3·321	m	3·29	s(d)	3·17	m	—	—	3·16	w	400	3·072	vw	—	—
731	—	—	3·231	w	3·19	w	2·93	s	2·95	vs	2·95	vvs	410, 322	2·982	vs	2·987	55
733	3·048	m	3·034	mw	3·01	w	2·84	w	2·84	ms	2·84	mw	411, 330	2·900	m	2·904	9
660	2·941	m	2·926	m	2·93	s(d)	2·72	w	—	—	2·74	mw	420	2·751	m	2·754	12
555	2·881	s	2·867	ms	2·81	s	2·58	w	2·60	s	2·59	m	421	2·681	mw	2·688	4
480	2·790	m	2·775	m	2·75	m	2·39	w	2·43	s	2·44	w	332	2·623	s	2·626	22
753	2·745	w	2·729	w	—	—	2·34	w	2·30	vw	2·30	w	422	2·512	mw	2·515	5
842	2·725	vw	2·711	vvw	2·69	w	2·27	w	—	—	2·27	w	430, 500	—	—	2·464	4
664	2·662	m	2·650	m	2·61	m	2·23	w	2·19	mw	2·20	w	431, 510	2·410	w	—	—
931	2·617	mw	2·603	mw	2·58	mw	—	—	2·11	w	2·13	mw	511, 333	2·369	mw	2·371	3
844	2·545	mw	2·534	w	2·51	w	—	—	—	—	2·08	vw	520, 432	—	—	2·289	1
1022	2·403	m	2·391	mw	2·37	ms	2·02	w	2·05	vw	2·04	mw	521	2·247	w	2·249	3
1040	— §	—	— §	—	2·29	w	—	—	1·97	vw	1·97	vw	440	2·174	m	2·177	7
880	2·206	m	2·193	mw	2·17	m	—	—	—	—	1·91	w	441	2·143	mw	2·144	10
955	2·181	m	2·168	mw	2·15	w	1·89	w	1·86	m	1·88	vw	433, 530	2·109	mw	2·113	3
													531	2·078	mw	2·083	4
													600, 442	2·050	m	2·053	9

† Unit cell edge in Å. ‡ Ratio of $Al_2O_3 : SiO_2$.
§ Obscured by lines at 3·343 and 2·282 Å of quartz which was used as an internal standard.

an oxide formula of $Na_2O,Al_2O_3,2{\cdot}0SiO_2,4{\cdot}6H_2O$. The *X*-ray pattern could be indexed to primitive cubic with $a = 12{\cdot}30$ Å (Table 3). An electron-diffraction study by Dr. J. A. Gard showed that this may be a pseudo-cell, the true cell being face-centred cubic with $a \sim 24{\cdot}6$ Å. This conclusion has been firmly established by *X*-ray diffraction [27] by use of the alumino-germanate analogue whose synthesis is here recorded.

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[27] Barrer and Meier, *Trans. Faraday Soc.*, 1958, **54**, 1074.

Species *R*, as shown by *X*-ray powder photographs, is a synthetic zeolite related to natural faujasite and to Linde Molecular Sieve X. It was synthesised as very small isotropic crystals (~1 μ) with a cubic crystal habit shown in the electron microphotograph (Plate 4). The refractive index was very difficult to measure but was about 1·46, varying slightly between samples. Its method of preparation varied slightly from that of other species. The concentration of gel used was approximately 1 g. in a total volume of 14 ml. of mixture (with 300% or greater excess of alkali added). About 50 g. of gel were heated in the 1 l. autoclave, stirred at about two revolutions per min. The temperature was raised at ~6° per hr. to between 70° and 80°. This temperature was not critical since some samples were prepared at above 100°. Heating was continued for about two days. The gels used ranged from $n = 1$ to $n = 10$.

The composition of the products varied from $Na_2O,Al_2O_3,2{\cdot}4SiO_2,6{\cdot}7H_2O$ to $Na_2O,Al_2O_3,3{\cdot}3SiO_2,7H_2O$. The cubic face-centred unit cell decreased from 24·96 Å for the most aluminous sample to 24·83 Å at the silica-rich end of the series. This compares with 24·65 Å for a natural faujasite of composition $Na_2O,Al_2O_3,4{\cdot}7SiO_2,9{\cdot}1H_2O$ calculated from an analysis by Damour.[28] *X*-Ray data are in Table 3.

Species *S* was a synthetic sodium analogue of the chabazite–gmelinite natural zeolites. It grew as spherulitic and lenticular crystals with irregular surfaces. These may be aggregates of very tiny crystals. The crystal diameter was usually about 1 μ although one sample was obtained which had crystals of ~12 μ (Plate 5). No birefringence was detected. The refractive index was ~1·458.

This mineral grew from gels $n = 7$ to $n = 10$ and over the range 60—110° with preferably 200% to 300% excess of sodium hydroxide present. The concentration of gel was 1 g. in ~10 ml. of mixture. Best yields were obtained from a gel with $n = 9$ with 300% excess of alkali heated for two days at 100° with continuous vigorous stirring. Analysis of one sample: Na_2O, 10·4; Al_2O_3, 18·1; SiO_2, 54·0; H_2O, 17·5%, which is equivalent to an oxide formula of $Na_2O,Al_2O_3,5{\cdot}1SiO_2,5{\cdot}4H_2O$. *X*-Ray powder data of Table 3 indicated a hexagonal unit cell $a = 13{\cdot}7_2$ Å, $c = 10{\cdot}0_0$ Å.

TABLE 4. *Crystallographic data for* Na-*U*, *rhodesite, and erionite.*

Crystal	Symmetry	Unit-cell dimensions (Å)				Cleavage
Na-*U*	Orthorhombic	Pseudo-cell:	23·5 ± 1·0	6·5	7·0	(100)
	A-centred	True-cell:	23·5 ± 1·0	13·0	14·0	Elongation *C*
Rhodesite	Orthorhombic	Pseudo-cell:	23·8	6·54	7·05	(100)
	A-centred	True-cell:	23·8	13·1	14·1	Elongation *C*
Erionite *	Orthorhombic	Pseudo-cell:	23·0	13·26	7·55	—
	C-centred	True-cell:	23·0	13·26	15·12	Elongation *C*

* The unit cell of erionite is hexagonal, $a = 13{\cdot}26$, $c = 15{\cdot}12$ Å. In the Table the equivalent orthorhombic cell is given.

Species *B* is a zeolite practically identical with natural analcite. It grew as spherulitic and cubic crystals, refractive index ~1·486. The lowest temperature of synthesis was 150°, *i.e.*, it did not grow at temperatures lower than those previously investigated. Its conditions of growth and cation-exchange, chemical, and sorptive properties have been investigated.[2, 6, 7, 29, 30, 31]

Species *D*, synthetic mordenite, has also been investigated fully.[1, 16] It was synthesised as typical wheatsheaf-shaped crystals, but again only in the temperature range observed previously.[1, 16]

Species *U* (Plate 6) was shown optically to grow as needles or fibres from gels with $n = 5$ to $n = 12$ at 250° with 100% to 300% excess of base added. These were usually associated with analcite, but although appearing in some cases to be in almost 20% yield, no reflections other than those due to analcite or the harmotome-like mineral, Na-*P*, were noted on the *X*-ray photographs. However, electron diffraction studies of single crystals by Dr. Gard showed it

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[28] Damour, *Ann. Mines*, 1848, **14**, 67.

[29] Barrer, *J.*, 1950, 2342.

[30] *Idem*, *Proc. Roy. Soc.*, 1938, *A*, **167**, 392, 406.

[31] Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 206.

to have an orthorhombic cell resembling that of a new zeolitic silicate mineral, rhodesite.[33] There is also a more superficial resemblance to erionite. These relations are tabulated (Table 4) from information supplied by Dr. Gard. Species *U* is probably of the rhodesite family.

Felspathoids. " Basic " nosean occurred at temperatures of 150° or more from gels with $n = 1$ to $n = 3$ with 100% to 300% excess of alkali. The optical properties, unit-cell dimensions and range of growth have been defined by Barrer and White.[1]

" Basic " sodalite was grown from very concentrated $Na_2O,Al_2O_3,2SiO_2$ gels containing originally 1 g. of gel in 8 ml. of mixture but these were allowed to become more concentrated by evaporation at ~100° (water-bath). Maximum yields were obtained with 300% excess of sodium hydroxide. After about 1 day on the water-bath, lines of species *Q* were also evident on the *X*-ray photograph but after 4—5 days conversion into sodalite was complete. Spherulitic and cubic crystals were observed, of maximum size ~13 μ. The crystals were isotropic, the refractive index varying between 1·468 and 1·493. The unit cell of one sample was calculated as cubic, $a = 8{\cdot}9_4$ Å and analysis [32] showed it to have the composition $Na_2O,Al_2O_3,2{\cdot}1SiO_2,2NaOH,1{\cdot}5H_2O$.

Species *T* only occurred once. It appeared from a gel with $n = 2$ in presence of 300% excess of alkali after being heated for 1 day at 200°. Analcite and nosean were also present, but the *X*-ray powder pattern of species *T* was easily differentiated from these, being closely similar to those of the nepheline hydrate minerals obtained earlier [1] although identical with neither (Table 3). Its temperature of synthesis was lower than that reported for hydrates I and II although the gel composition was similar.

Crystallisation of mixed Na–K *gels.* We first consider the effect of increasing amounts of sodium hydroxide upon the crystallisation for 4 days at 150° of an aqueous gel of composition $K_2O,Al_2O_3,4SiO_2,mH_2O$. The results (Table 5) indicate that the products depend in a striking way on the Na : K ratios, and probably on the $(Na_2 + K_2)O : Al_2O_3$ ratios.

TABLE 5.

Gel composition, excluding H_2O				Crystallisation products	
Na_2O	K_2O	Al_2O_3	SiO_2		
0	1·00	1·00	4·00	K-*G* [3]	(chabazite-type zeolite)
0·286	1·00	1·00	4·00	K, Na-*G*	(chabazite-type zeolite)
0·572	1·00	1·00	4·00	K, Na-*M*	(phillipsite-type zeolite)
0·858	1·00	1·00	4·00	Na, K-*I* *	(sodalite-type phase)
1·716	1·00	1·00	4·00	Na, K-*P*	(harmotome-type zeolite)
1·00	0	1·00	4·00	Na-*B* [2]	(analcite)

* The autoclave leaked during the experiment, and the product was dry.

In a second, more extended series of experiments we investigated the effect of temperature, and of molar proportions of silica, upon the crystallisation processes. In Table 6 the crystalline phases derived from Na-, (Na, K)-, and K-gels are compared, the nomenclature [3] of the relevant potassium minerals being: K-*A*, Sanidine; K-*B*, α-quartz; K-*C*, leucite; K-*F*, K-zeolite; K-*G*, K-zeolite; K-*H*, bayerite; K-*M*, K-zeolite; K-*N*, kalsilite. The phases obtained from mixed gels are classified on the basis of *X*-ray data according as they are structurally related to the potassium phases above, or the sodium phases previously discussed. In a phase such as (K, Na)-*M* the sequence (K, Na)- indicates that *M* refers to the potassium mineral nomenclature. Similarly in (Na, K)-*P* the sequence (Na, K)- indicates that *P* refers to the sodium mineral nomenclature already indicated (Table 1). Crystallisations from homoionic Na-gels refer to the conditions given in Table 2, *i.e.*, to conditions in which additional sodium hydroxide is added so that the ratio $Na_2O : Al_2O_3$ exceeds unity in the aqueous gels. Similarly the homoionic K-gels are those crystallised as described previously [3] from aqueous media containing additional potassium hydroxide. The significance of the description of composition of the mixed gels can be shown by an illustration: in the mixed gel having the ratio $Al_2O_3 : SiO_2 = 1 : 6$, the figures in parentheses (Table 6) associated with Na_2O and K_2O mean that the overall molar proportions of the components were $Na_2O : K_2O : Al_2O_3 : SiO_2 = 1{\cdot}82 : 1{\cdot}00 : 1{\cdot}00 : 6{\cdot}00$, together with about 10 ml. of water. About 0·5 g. of solid gel were crystallised in each experiment.

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[32] Barrer and Falconer, *Proc. Roy. Soc.*, 1956, *A*, **236**, 227.
[33] Gard and Taylor, *Mineralog. Mag.*, 1957, **31**, 611.

Comparison of the results in Table 6 covering the temperatures 60—250° leads to the following conclusions:

(i) There is widespread occurrence of phases related to the phillipsite–harmotome group (Na-*P*, K-*M*), whether from homoionic or mixed gels. In the sodium field, Na-*B*(analcite) is prominent above 150°.

TABLE 6. *Comparison of modes of crystallisation of* Na-, (Na,K)-, *and* K-*gels.*

Temp.	1 : 2 = $Al_2O_3 : SiO_2$				1 : 3 = $Al_2O_3 : SiO_2$		
	Na-gel	$Na_2O + K_2O$ (1·03) (2·00)	$Na_2O + K_2O$ (1·00) (2·00)	K-gel	Na-gel	$Na_2O + K_2O$ (1·25) (1·00)	K-gel
60°	Na-*Q*, Na-*P*	(Na, K)-*P*, (K, Na)-*F*	—	K-*G*, K-*H*	Na-*P*, Na-*Q*	—	K-*G*, K-*H*
85	Na-*Q*, Na-*R*	(Na, K)-*P*	—	K-*G*, K-*H*	Na-*P*, Na-*Q*	(K, Na)-*M*	K-*G*, K-*H*
110	Na-*Q*, Na-*P*	(Na, K)-*P*	(Na, K)-*P*	K-*F*	Na-*P*, Na-*Q*	—	K-*F*
150	Na-*F*, Na-*B*	(K, Na)-*G*, (K, Na)-*M*	—	K-*F*	Na-*F*, Na-*B*	(K, Na)-*M*	K-*F*, K-*G*
200	Na-*F*	(K, Na)-*F*	—	K-*M*	Na-*F*, Na-*B*	(Na, K)-*B*	K-*M*
250	Na-*F*, Na-*B*	—	—	K-*M*	Na-F, Na-*B*	(K, Na)-*N*	K-*M*

Temp.	1 : 4 = $Al_2O_3 : SiO_2$				1 : 5 = $Al_2O_3 : SiO_2$		
	Na-gel	$Na_2O + K_2O$ (1·43) (1·00)	$Na_2O + K_2O$ (1·00) (2·00)	K-gel	Na-gel	$Na_2O + K_2O$ (1·63) (1·00)	K-gel
60	Na-*P*, Na-*Q*	(K, Na)-*M*	—	K-*G*, K-*H*	Na-*Q*, Na-*P*, Na-*R*	(K, Na)-*M*	K-*G*, K-*H*
85	Na-*P*, Na-*Q*	(K, Na)-*M*	—	K-*G*, K-*H*	Na-*Q*, Na-*P*	(K, Na)-*M*	K-*G*, K-*H*
110	Na-*P*, Na-*Q*	(K, Na)-*M*	(Na, K)-*P*	K-*F*	Na-*Q*, Na-*P*	(K, Na)-*M*	K-*F*
150	Na-*B*	(K, Na)-*M*	—	K-*G*	Na-*B*	(K, Na)-*M*	K-*G*
200	Na-*B*	Na-*J*, (Na, K)-*B* or (K, Na)-*N*	—	K-*M*	Na-*B*	(Na, K)-*P*	K-*A*, K-*M*
250	Na-*B*	Na-*J*, (Na, K)-*B* or (K, Na)-*N*	—	K-*M*, K-*C*	Na-*B*	(K, Na)-*A*	K-*A*

Temp.	1 : 6 = $Al_2O_3 : SiO_2$			1 : 7 = $Al_2O_3 : SiO_2$			
	Na-gel	$Na_2O + K_2O$ (1·82) (1·00)	K-gel	Na-gel	$Na_2O + K_2O$ (2·02) (1·00)	$Na_2O + K_2O$ (1·00) (1·00)	K-gel
60	Na-*P*, Na-*Q*, Na-*R*	(K, Na)-*M*	K-*G*, K-*H*	Na-*P*, Na-*S*, Na-*R*	K-*H*	—	K-*H*, K-*G*
85	Na-*P*, Na-*Q*	(K, Na)-*M*	K-*G*, K-*H*	Na-*P*	K-*H*	—	K-*M*, K-*G*
110	Na-*P*, Na-*Q*	(K, Na)-*M*	K-*G*	Na-*P*	—	(Na, K)-*P*	K-*M*, K-*F*, K-*G*
150	Na-*B*	(K, Na)-*M*	K-*G*	Na-*B*	K-*H*	—	K-*M*
200	Na-*B*	(K, Na)-*M*	K-*A*, K-*M*	Na-*B*	(K, Na)-*A*	—	K-*A*
250	Na-*B*	(Na, K)-*B*, (K, Na)-*M*	K-*A*, K-*M*	Na-*D*, Na-*B*	(K, Na)-*A*	—	K-*A*

Temp.	1 : 8 = $Al_2O_3 : SiO_2$			1 : 9 = $Al_2O_3 : SiO_2$		
	Na-gel	$Na_2O + K_2O$ (2·22) (1·00)	K-gel	Na-gel	$Na_2O + K_2O$ (2·41) (1·00)	K-gel
60	Na-*P*	K-*H*	K-*H*	Na-*P*, Na-*S*	K-*H*	K-*H*
85	Na-*P*	K-*H*	K-*M*, K-*G*	Na-*P*, Na-*S*	—	K-*H*
110	Na-*P*	—	K-*M*, K-*H*	Na-*P*, Na-*S*	—	K-*H*
150	Na-*B*	—	K-*M*	Na-*B*	K-*H*	K-*M*, K-*H*
200	Na-*B*	(K, Na)-*A*	K-*A*, K-*M*	Na-*D*, Na-*B*	(K, Na)-*A*	K-*A*, K-*M*
250	Na-*B*	—	K-*A*	Na-*B*, Na-*D*	—	K-*A*

Temp.	1 : 10 = $Al_2O_3 : SiO_2$			1 : 12 = $Al_2O_3 : SiO_2$		
	Na-gel	$Na_2O + K_2O$ (2·61) (1·00)	K-gel	Na-gel	$Na_2O + K_2O$ (3·00) (1·00)	K-gel
60	No crystn.	K-*H*	K-*H*	No crystn.	K-*H*	K-*H*
85	Na-*S*	K-*H*	K-*H*	No crystn.	K-*H*	K-*H*
110	Na-*S*	—	K-*H*	No crystn.	—	K-*H*
150	Na-*S*, Na-*B*, Na-*P*	K-*H*	K-*A*, K-*B*	Na-*B*, Na-*P*	K-*H*	K-*A*, K-*B*
200	Na-*B*, Na-*P*, Na-*D*	(Na, K)-*B*, (K, Na)-*N*	K-*B*, K-*A*	Na-*B*, Na-*P*	(K, Na)-*A*, (K, Na)-*B*	K-*B*, K-*A*
250	Na-*B*, Na-*P*, Na-*D*	—	K-*B*, K-*A*	Na-*B*, Na-*D*	—	K-*B*, K-*A*

(ii) It is sometimes possible to predict the crystals grown from mixed gels from those grown from homoionic gels, *e.g.*, the phases related to the phillipsite–harmotome groups. However, such predictions refer to a situation where mineral-type compounds of this group are grown from both corresponding homoionic gels under like experimental conditions.

(iii) Some Na-phases had no crystalline analogue derived from the corresponding potassium gels, and conversely (*e.g.*, *F*, *I*, *Q*, *R*, and *D* in the Na-species, and *F* and *N* in the K-species). The phases formed from mixed gels are then not readily predictable. Thus phases analogous to Na-*D*, Na-*F*, Na-*I*, Na-*Q*, and Na-*R* were absent from the mixed crystallisates, although analogues of K-*N* and K-*F* were noted and also analogues of Na-*B*. K-*G* (a compound of the chabazite family) was less often formed from the mixed gels than from corresponding K-gels. Na-*S* (also of the chabazite family) did not appear as a product from the mixed gel.

(iv) The frequent occurrence of K-*H* (bayerite, $Al_2O_3,3H_2O$) from K-gels and mixed (Na, K)-gels is considered to be due primarily to the mode of formation of these gels, in all of which freshly prepared aluminium hydroxide was used. The Na-gels on the other hand were made by use of sodium aluminate and silica sol. Thus the mode of preparation of the gel may influence the products.

The foregoing investigation of crystallisation of mixed (Na,K)-gels is adequate as far as the temperature is concerned, up to 250°, but does not cover a wide range of Na : K ratios. It is possible that new products would appear over an increased range in this ratio.

Crystalline phases containing gallium and germanium. Crystallisations were carried out at one temperature, 100°. The crystalline species obtained were:

Gallosilicates	Na-*V*	(Thomsonite-type zeolite)
Aluminogermanates	Na-*R*	(Faujasite-type zeolite)
	Na-*Q*	(Analogue of Linde Sieve A)
	Na-*P* *	(Analogue of harmotome)
Gallogermanates	Na-*V*	
	Na-*R*	
	Na-*I*	(Analogue of basic sodalite)

* By recrystallisation of the Na-*Q*.

Some details of the crystallisation conditions are given in Table 7. Evidently replacement of Al by Ga, or both Al and Si by Ga and Ge, makes easy the synthesis of a zeolite closely related to thomsonite (one of the fibrous zeolites). This zeolite has not been synthesised in the many experiments we have conducted with gels of Li, Na, K, Rb, and Cs. Moreover it is possible to prepare the important molecular-sieve zeolites Na-*R* and Na-*Q* (which are analogous

TABLE 7. *Crystallisation of aluminogermanates, gallosilicates, and gallogermanates at* 100°.

Ratio $Al_2O_3 : GeO_2$ in gel	Excess of NaOH (mol. %)	Time (hr.)	Products	Ratio $Ga_2O_3 : SiO_2$ or : GeO_2 in gel	Excess of NaOH (mol. %)	Time (hr.)	Products
	Aluminogermanates				*Gallosilicates*		
3 : 2	90	15	Na-*Q*	1 : 0·67	50	26	(Na-*V*) *
1 : 1	125	15	Na-*Q*	1 : 1	50	26	(Na-*V*)
1 : 2	225	15	Na-*Q*	1 : 1·33	50	26	Na-*V*
1 : 3	325	15	Na-*Q*	1 : 2	50	26	Na-*V*
1 : 4	425	15	(Na-*Q*) *	1 : 4	50	26	Na-*V*
1 : 6	625	15	Na-*R*	1 : 4	50	26	Na-*V*
1 : 1	125	40	Na-*R* and Na-*Q*	1 : 5	50	26	Na-*V*
1 : 4	425	40	Na-*R* and Na-*Q*	1 : 6	50	26	Na-*V*
1 : 2	225	7	Na-*Q*				
1 : 6	625	22	Na-*R*		*Gallogermanates*		
1 : 2	225	22	Na-*R* and Na-*Q*	1 : 1	150	40	Na-*R*
1 : 1	125	46	Na-*R*	1 : 1	150	40	Na-*I*
1 : 2	225	46	Na-*R* and (Na-*Q*)	1 : 2	250	40	(Na-*R*)
1 : 2	225	46	Na-*R* and (Na-*Q*)	1 : 2	250	40	(Na-*V*)
1 : 4	425	46	(Na-*R* and Na-*Q*)	1 : 4	450	40	Na-*V*
1 : 1	125	46	Na-*R* and Na-*Q*	1 : 5	550	40	(Na-*V*)
1 : 2	225	46	Na-*R*	1 : 6	650	40	—
1 : 2	225	46	Na-*R*				
1 : 4	425	46	(Na-*R* and Na-*Q*)				
1 : 1	125	31	Na-*R* and Na-*Q*				

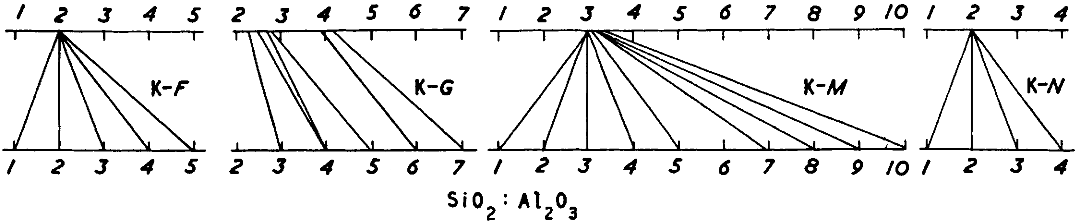
* Parentheses indicate minor yields only.

to Linde Molecular Sieves A and X) with Ga replacing all the Al; and in the case of Na-R with full replacement of Al by Ga and of Si by Ge. This full isomorphous replacement by Ga and Ge is likewise found in the very characteristic sodalite-type phase Na-*I*. We thus have phases structurally analogous to certain aluminosilicates, but free from both Al and Si. The important ionic radii are: Al^{3+}, 0·57; Si^{4+}, 0·37; Ga^{3+}, 0·62; Ge^{4+}, 0·44 Å, and differ most for the pair Ga–Si. The unit cells (Å) of the aluminosilicate phases and of those containing Ge or Ga and Ge were measured:

	Al, Si	Al, Ge	Ga, Ge
Na-*I* (sodalite-type)	8·94	—	9·09
Na-*Q* (analogue to Linde Sieve A)	12·30	12·35	—
Na-*R* (analogue to faujasite and Linde Sieve X)	$24{\cdot}8_5$	$25{\cdot}0_0$	$25{\cdot}2_5$

These unit-cell dimensions clearly reflect the different ionic radii, and suggest that the structural tetrahedra SiO_4^{4+}, GeO_4^{4+}, AlO_4^{5-}, and GaO_4^{5-} differ in dimensions. Just as the Al–Si form of Na-*Q* recrystallised readily to Na-*P*, the harmotome-like phase, so also the Al–Ge form of Na-*Q* recrystallised to the germanium-containing analogue of Na-*P*. This change could be brought about by treatment of the Na-*Q* for 3 days with N-sodium hydroxide at 100°.

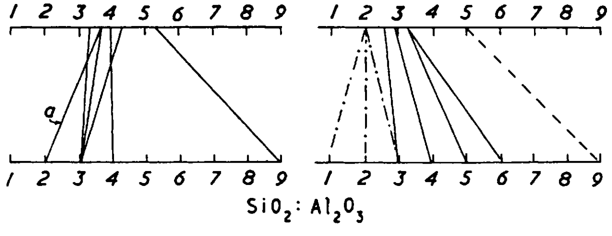
FIG. 2. *Composition changes when potassium alumino-silicate gels are crystallised.*



Horizontal scales give values of $SiO_2 : Al_2O_3$ in the parent gels (lower) and products (upper).

Composition change in crystallisation from gels. In Fig. 2 are shown changes in the ratio $SiO_2 : Al_2O_3$ which occur during the crystallisation of potassium aluminosilicate gels, under conditions described earlier.[8] The crystallisations are of K-*F* (zeolite), K-*G* (chabazite-type zeolite), K-*M* (phillipsite-type zeolite), and K-*N* (kalsilite). Fig. 3 shows the changes in $SiO_2 : Al_2O_3 = n$ during crystallisations of sodium aluminosilicate gels (this paper) leading to Na-*P* (harmotome-like zeolite), Na-*R* (faujasite-type zeolite), Na-*Q* (zeolite), and Na-*S* (chabazite-type zeolite).

FIG. 3. *Composition changes observed during crystallisations of sodium aluminosilicate gels.*



Horizontal scales give values of $SiO_2 : Al_2O_3$ in mineral (upper) and gel (lower). In the left hand portion the crystallisation product is Na-*P*.
a, Na-*P*, from species *Q* by treatment with N-sodium hydroxide. In the right-hand portion full lines represent species *R*, dashed lines species *S*, and dots and dashes species *Q*.

In the formation of K-*F*, K-*N*, and Na-*Q* from gels of any composition, the $SiO_2 : Al_2O_3$ ratio changes to 2 : 1. For gels yielding K-*G*, the trend is for the crystals to be more aluminous than the gel, and this is true also of K-*M* provided $n > 3$ in the gel, of Na-*R* at least for $3 < n < 6$, and of Na-*S* for $n = 9$. In the case of Na-*P*, gels having $2 < n < 9$ yield crystals with $3{\cdot}3 < n < 5{\cdot}3$. According to Loewenstein's rule,[34] in all aluminosilicates with frameworks

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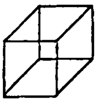
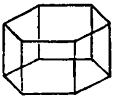
[34] Loewenstein, *Amer. Min.*, 1954, **39**, 92.

built from $(Al,Si)O_4$ tetrahedra, no Al–O–Al bonds can form, and consequently all gels having $n < 2$ must yield more siliceous species, with $n \geqslant 2$. However, if $n > 2$ the larger its value the greater is the tendency of the crystalline phase to be more aluminous than the parent gel.

DISCUSSION

The formation of diverse kinds of structural framework leads to questions as to the mechanism of growth. The phases are often obtained reproducibly in yields nearing 100% and the free-energy balance between the many possible aluminosilicate nuclei must be delicate. The development of elaborate and continued space patterns by progressive additions of single $(Al,Si)O_4$ tetrahedra is difficult to imagine, particularly in the case of very open zeolite structures. The formation of these frameworks is, however, much more easily visualised if in the aqueous crystallising magma there are secondary building units in the form of rings of tetrahedra, or polyhedra. These may pack in various simple co-ordinations to yield different aluminosilicates. Table 8 indicates some possible anions, from which more complex ones can be formed. Thus, appropriate linking of six 4-ring anions can give the cubo-octahedral unit so characteristic of the nosean–sodalite family. It may be considered that the high anionic charges given in Table 8 make the real existence of such complex anions unlikely. However there is no reason why full ionisation should be realised, since the oxygen atoms linked only to one Al or Si atom may not be $-O^-$ groups but may exist partly as un-ionised –OH groups, freely available for condensation-polymerisation, by which mechanism more complex units form.

TABLE 8. *Some complex aluminosilicate anions.*

Anion type	Compositions possible (Al and Si)	Maximum charge	Total no. of configurations	Anion type	Compositions possible (Al and Si)	Maximum charge	Total no. of configurations
Ring of 3 tetrahedra	0Al,3Si (1) *	−6	2	Double 4-ring:	0Al,8Si (1)	−8	6
	1Al,2Si (1)	−7			1Al,7Si (1)	−9	
Ring of 4 tetrahedra	0Al,4Si (1)	−8	3		2Al,6Si (2)	−10	
	1Al,3Si (1)	−9			3Al,5Si (1)	−11	
	2Al,2Si (1)	−10			4Al,4Si (1)	−12	
Ring of 5 tetrahedra	0Al,5Si (1)	−10	3	Double 6-ring (or three 4-rings):	0Al,12Si (1)	−12	25
	1Al,4Si (1)	−11			1Al,11Si (1)	−13	
	2Al,3Si (1)	−12			2Al,10Si (7) †	−14	
Ring of 6 tetrahedra	0Al,6Si (1)	−12	5		3Al,9Si (8) ‡	−15	
	1Al,5Si (1)	−13			4Al,8Si (6) †	−16	
	2Al,4Si (2)	−14			5Al,7Si (1)	−17	
	3Al,3Si (1)	−15			6Al,6Si (1)	−18	

* Figures in parentheses denote the number of distinguishable configurations of the particular composition given.

† Two pairs of these configurations are non-superposable mirror images.

‡ Three pairs of these configurations are non-superposable mirror images.

In all the zeolites whose structures have been determined, except heulandite,[35] each $(Al,Si)O_4$ tetrahedron is a member of at least one 4-ring. Also, even-numbered rings of 4, 6, 8, or 12 tetrahedra are more usual than odd-numbered rings. This could indicate in part a tendency of Al–O–Si bonds to be preferred to Si–O–Si bonds (cf. Figs. 2 and 3), since structures containing odd-numbered rings must contain Si–O–Si bonds. All zeolites and other framework aluminosilicates having $SiO_2 : Al_2O_3 = 2 : 1$ (and in which therefore only Al–O–Si bonds should occur) should be built only from even-numbered ring units (*e.g.*, Na-*Q*, K-*F*, K-*N*). The more siliceous zeolites could in principle have 5-rings (*e.g.*, heulandite), or other odd-numbered rings, in the structural motif, although not many odd-numbered rings have been recorded.

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[35] Ventriglia, *Periodico Miner.*, *Rome*, 1955, **24**, 49.

The frequent occurrence of 4-rings in the structural pattern suggests that this unit leads to very stable patterns. The nucleation of aluminosilicates may in such species be initiated from 4-ring anions. If two of these join together a cubic anion results (Table 8), and these cubes may be stacked in 8-fold co-ordination to give Na-*Q* (Linde Sieve A).[26] It is particularly interesting that this structure may be so visualised, for it can equally well be regarded as formed by an appropriate stacking of cubo-octahedral anions[36] in 6-fold co-ordination. Another mode of arranging the cubic anions of Table 8 in 8-fold co-ordination leads to Na-*P*, K-*M*, and other zeolites of the harmotome–phillipsite group.[24]

Again, if three 4-rings are appropriately linked by oxygen bridges, the double 6-ring anion of Table 8 is formed. The faujasite type of zeolite (faujasite, Na-*R*, Linde Sieve X) then results if these units are joined in six-fold co-ordination. This mode of building the framework is alternative to a four-fold co-ordination of cubo-octahedral units.[37]

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[36] Barrer, Report on " Physical Chemistry of some Non-Stoicheiometric Phases," 10th Solvay Council, Brussels, May 1956, p. 21.

[37] Barrer, Bultitude, and Sutherland, *Trans. Faraday Soc.*, 1957, **53**, 1111.