562. *The Hydrothermal Chemistry of the Silicates. Part VII.** *Synthetic Potassium Aluminosilicates.*

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In an attempt to prepare zeolites and other mineral species containing potassium as the only interstitial cation, which have not been found in Nature, a series of potassium aluminosilicate gels of composition $K_2O,Al_2O_3,nSiO_2$ ($1 < n < 12$) were prepared and subjected to hydrothermal crystallisation. The effect of temperature and time of crystallisation on the products, and the behaviour of the latter in ion-exchange and sorption experiments, have been studied.

MUCH early work on the synthesis of aluminosilicates suffers from a lack of sufficient information on the conditions of crystal growth and the products.[2] Recent research has remedied this, to some extent, for the aluminosilicates of Group IA and IIA metals.[1,3]

Many successful syntheses of naturally occurring potassium aluminosilicates have been reported.[4] However, apart from the work of Müller and Koenigsberger,[5] no systematic study of the hydrothermal chemistry of the potassium aluminosilicates has been reported.

Few "pure" potassium framework aluminosilicates are known to occur in Nature. One of the most widely distributed minerals in the lithosphere is a potassium felspar, orthoclase. There are two further modifications of the felspar (sanidine and microcline), three modifications of $KAlSiO_4$ (hexagonal and orthorhombic kaliophilite and kalsilite), and two modifications of leucite (cubic and tetragonal). However, none of the naturally occurring zeolites is known to contain only potassium as the interstitial cation, although many of them, chabazite and phillipsite *inter alia*, may contain potassium along with other metals. Müller and Koenigsberger [5] claimed to have synthesised potassium zeolites but their products were crystallised from material containing both sodium and potassium. Previous studies in these laboratories [1a-1e] have shown that the non-occurrence in Nature of zeolites or other aluminosilicates of a particular metal does not necessarily preclude the possibility of their synthesis in the laboratory under suitable conditions. This study might then be expected to yield "pure" potassium zeolites or synthetic aluminosilicates if the correct conditions for crystallisation are achieved.

EXPERIMENTAL

"AnalaR" potassium hydroxide was used. Aluminium hydroxide was obtained by the action of water on lightly amalgamated aluminium foil.[6] It was necessary to cool the reaction mixture to avoid crystallisation of hydrated alumina, usually bayerite ($Al_2O_3,3H_2O$). The silica was obtained from two sources. (*a*) Hydrothermal extraction of B.D.H. silica gel (containing approximately 15% of SiO_2) at 200° yielded a mother-liquor free from common inorganic anions. (*b*) A very fine silica dispersion containing approximately 30% by weight of SiO_2 was supplied as Syton 2-X by Monsanto Chemicals Ltd. This dispersion had specific gravity 1·2, pH$\simeq$10·0, and contained a trace of chloride.

A series of gels of composition $K_2O,Al_2O_3nSiO_2$, where $1 \leqslant n \leqslant 12$, was made by mixing the constituents in the required ratios. Latterly no attempt was made to evaporate off any of the moisture since this preliminary ageing was found to inhibit crystallisation below 200°.

The autoclaves used for the hydrothermal crystallisation[7] had an internal capacity of 20 ml.;

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* Part VI, *J.*, 1955, 2480.

[1] Parts I—VI: Barrer and White, (*a*) *J.*, 1951, 1167; (*b*) 1952, 1561; (*c*) Barrer, Hinds, and White, *J.*, 1953, 1466; (*d*) Barrer and McCallum, *J.*, 1953, 4029; (*e*) Barrer, Baynham, and McCallum, *J.*, 1953, 4035; (*f*) Ghard, Barrer, and Baynham, *J.*, 1955, 2480.

[2] Cf. review by Morey and Ingerson. *Econ. Geol.*, 1937, 607.

[3] Noll, *F.I.A.T.* Rev. of German Science, Inorganic Chemistry, Part III, p. 87; Kruger, *ibid.*, Part V, p. 202; Roy, Roy, and Osborne, *J. Amer. Ceram. Soc.*, 1950, **33**, 152.

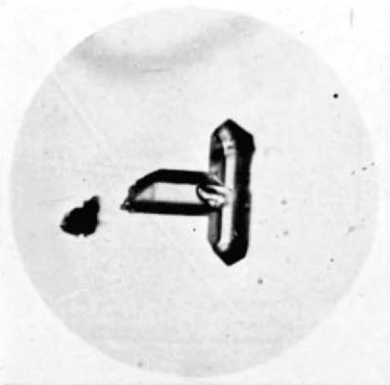
[4] *E.g.*, Baur, *Z. anorg. Chem.*, 1914, **84**, 31; Wyart, *Compt. rend.*, 1947, **225**, 944; Barrer and Hinds, *Nature*, 1950, **166**, 562; Part III, ref. 1.

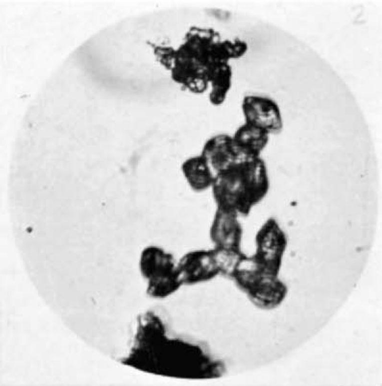
[5] Müller and Koenigsberger, *Z. anorg. Chem.*, 1918, **104**, 1.

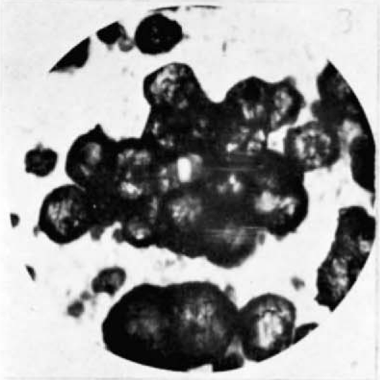
[6] Weiser and Milligan, *Chem. Rev.*, 1939, **25**, 1.

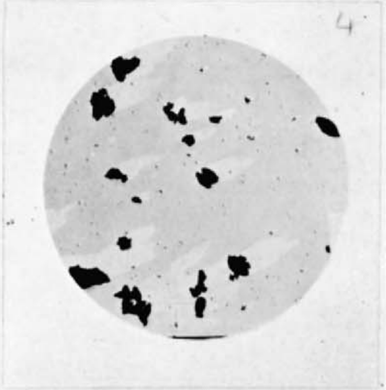
[7] Barrer, *J.*, 1948, 127.

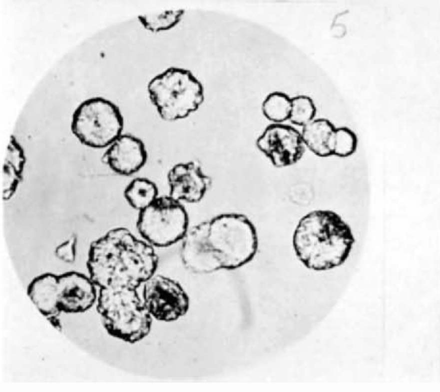
PLATES 1—6.











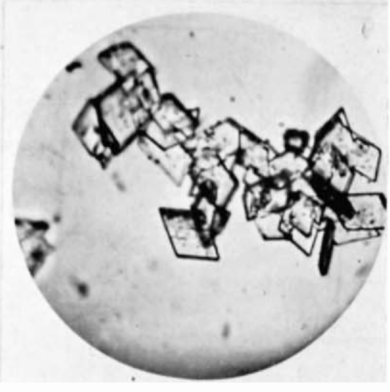
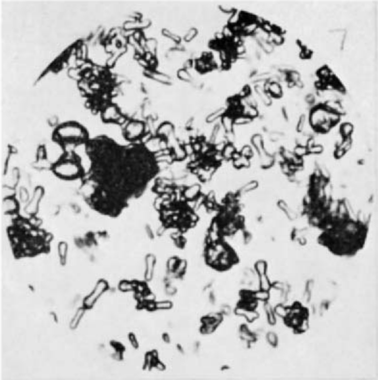


PLATE 1. K–*B* (× 300).
PLATE 2. K–*A* (× 300).
PLATE 3. K–*C* (× 300).
PLATE 4. K–*D* (×1800).
PLATE 5. K–*E* (× 130).
PLATE 6. K–*N* (×300).

[*To face p.* 2882.

PLATES 7—10.



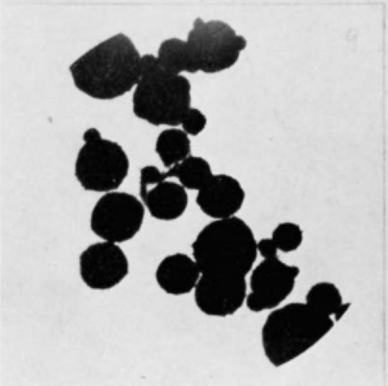
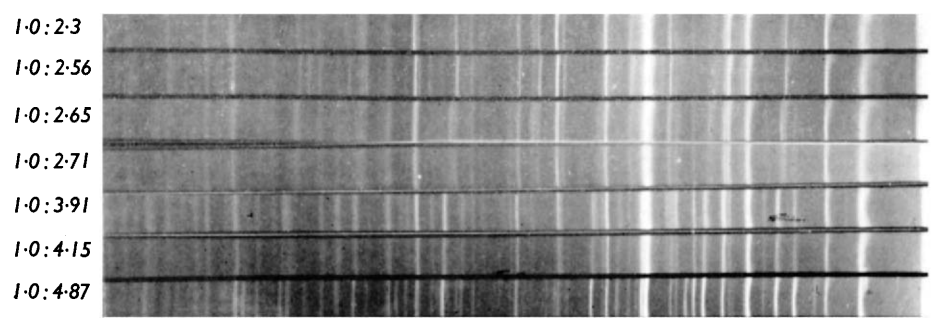


PLATE 7. K–*M* (× 300). PLATE 8. K–*M* (× 1066).
PLATE 9. K–*G* (× 2000). PLATE 10. K–*G* (× 5330).

FIG. 5. *Comparison of* X-*ray powder patterns of* K–*G with that of the natural chabazite* (bottom member of the series).



the charge in each was wet gel corresponding to 0·5 g. dry weight of the constituents together with 15 ml. of solution. The autoclaves were kept at a uniform temperature for the allotted time, then quenched, the products filtered off, and the pH of the cold mother-liquor was measured (±0·5 unit). The product was then thoroughly washed. For crystallisations below 150° sealed Pyrex-glass tubes were convenient; their walls suffered no corrosion at the relatively low temperatures employed.

The time required for crystallisation in high yield increased as the temperature was lowered. Not more than 16 hours sufficed at and above 300°, but 3—4 days were required for some crystallisations at temperatures below 150°, even with very reactive gels.

Examination of Products.—The products were examined optically by using a Leitz polarising and a Vickers projection microscope. The refractive indices were measured in white light to within ±0·005 unit, but owing to the small size of the crystallites no other optical properties were determined. Further examinations of crystal habit and purity were made with a Metrovic EM III electron microscope.

The powders were also studied by *X*-ray diffraction methods, Cu-K_α radiation from a Hilger HRX unit equipped with 9-cm. cameras being used. Where possible the unit-cell dimensions were determined.

Ion Exchange.—Ion-exchange reactions of the products of crystallisation were studied by using the chlorides and nitrates of Li^+, Na^+, Rb^+, Cs^+, and Ca^{++}. The hydrothermal method, which involves heating the crystals with a saturated solution of the desired salt in a sealed tube, was employed. Temperatures from 110° to 200° were used. For one species the vapour-phase method using ammonium chloride was also employed to achieve exchange to the NH_4^+ form. The ion-exchange products were washed free from exchanging salt, dried at 120°, and allowed to come to equilibrium in air before being examined optically and by *X*-ray methods. The amount of exchange was determined either by analysis of the crystals or by the difference in weight of the ignited crystals before and after exchange.

Analyses of the products obtained in 100% yield were carried out by standard methods, minerals with an $Al_2O_3 : SiO_2$ ratio not lower than about 1 : 4 being decomposed by repeated treatments on the water-bath with concentrated hydrochloric acid.[8]

Sorption.—This was studied by using the static gas-volumetric method in an apparatus of standard design, ammonia and permanent gases being used as sorbates. Ammonia was prepared as described earlier,[9] and the gases were supplied in the pure state by the British Oxygen Co.

Results.—The products from gels of composition $K_2O,Al_2O_3,nSiO_2$, in which $1 \leqslant n \leqslant 12$, are listed in Table 2, and in Table 3 are given the products obtained from the same gels when excess of potassium hydroxide had been added. For convenience, in Table 1, the products are given alphabetical symbols. The products listed in Table 2 were all obtained from gels evaporated to a milky consistency on the water-bath. This method of gel preparation rendered crystallisation more difficult even in the presence of excess of alkali. However, gels obtained simply by mixing the constituents in the desired ratios, although lowering the temperature limit of crystallisation in the presence of excess of alkali, failed to crystallise when no excess of alkali was added. The extent of crystallisation as given in Tables 2 and 3 was estimated by optical examination. Only in the case of species K–*D* was any doubt cast on the reproducible formation of the product.

TABLE 1.

Species ref. letter	Mineral name or class	Idealised oxide formula	Species ref. letter	Mineral name or class	Idealised oxide formula
K–*A*	Sanidine	$K_2O,Al_2O_3,6SiO_2$	K–*G*	K-Zeolite (ψ-chabazite)	$K_2O,Al_2O_3,nSiO_2,xH_2O$ $(2{\cdot}3 \leqslant n \leqslant 4{\cdot}15)$
K–*B*	α-Quartz	SiO_2	K–*H*	Bayerite	$Al_2O_3,3H_2O$
K–*C*	Leucite	$K_2O,Al_2O_3,4SiO_2$	K–*I*	Boehmite	Al_2O_3,H_2O
K–*D*	Kaliophilite	$K_2O,Al_2O_3,2SiO_2$	K–*M*	K-Zeolite (ψ-phillipsite)	$K_2O,Al_2O_3,3SiO_2,3H_2O$
K–*E*	K-Analcite	$K_2O,Al_2O_3,4SiO_2,H_2O$	K–*N*	Kalsilite	$K_2O,Al_2O_3,2SiO_2$
K–*F*	K-Zeolite	$K_2O,Al_2O_3,2SiO_2,3H_2O$			

Figs. 1 and 2 show the distribution of the species obtained with variation of temperature and gel composition, both with and without excess of alkali. The addition of alkali drastically reduced the time required for crystallisation, and so lowered the temperature limit of

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[8] Murata, U.S. Geol. Survey Bull. No. 950, 1946, p. 25.

[9] Barrer and Rees, *Trans. Faraday Soc.*, 1954, **50**, 852.

crystallisation that a number of low-temperature hydrated species were synthesised. The properties of these and other principal species obtained will now be described.

Quartz (K–*B*) (Plate 1).—This was obtained, usually in minor yield, along with the felspar from gels rich in silica. However it was formed in major yield at 300° from gels of composition $K_2O,Al_2O_3,nSiO_2$, where $8 \leqslant n \leqslant 12$, in a liquor of pH > 10·5. The product grew as hexagonal prisms of relatively large dimensions ($\sim$30 μ long) showing moderate birefringence, straight extinction, and with $\varepsilon = 1·550$ and $\omega = 1·540$. The *X*-ray spacings (Table 4), along with the optical data, identify the product as α-quartz.

Alumina.—*Species* K–*H*. This species occurred both in the initial preparation of alumina[10] and as a product from the hydrothermal crystallisation of gels of composition $K_2O,Al_2O_3,nSiO_2$, where $2 \leqslant n \leqslant 10$, when excess of alkali was present. The species crystallised in small stout rods showing some birefringence and having $n \sim 1·560$. The *X*-ray data identify the species as bayerite, $Al_2O_3,3H_2O$. Bayerite was never obtained above 120°, although below this temperature the crystallisation field under alkaline conditions penetrated even into the silica-rich region (Fig. 2*a*).

TABLE 2.

$K_2O,Al_2O_3,nSiO_2$	250°	300°	350°	400°	450°
$n = 1$	Poor yield of K–*M*, pH $\sim$10·0	Poor yield of K–*M*, pH $\sim$8·0	Poor yield of K–*M* + K–*A*, pH $\sim$8·0	Poor yield of K–*A* + K–*M*, pH $\sim$8·0	Poor yield of K–*M*, pH $\sim$8·0
$n = 2$	Moderate yield of K–*M*, pH $\sim$10·0	Poor yield of K–*M*, pH $\sim$8·0	Moderate yield of K–*A* + some K–*M*, pH $\sim$8·0	Moderate yield of K–*A* + K–*M*, pH $\sim$8·0	Moderate yield of K–*M*, pH $\sim$8·0
$n = 3$	Moderate yield of K–*M* and K–*I*, pH $\sim$10·0	Poor yield of K–*M* + K–*A*, pH $\sim$7·0	Moderate yield of K–*A* + some K–*M*, pH $\sim$8·0	Moderate yield of K–*A* + some K–*M*, pH $\sim$8·0	Moderate yield of K–*M* + K–*E*, pH $\sim$8·0
$n = 4$	No crystn., pH $\sim$9·5	Poor yield of K–*A* + trace K–*M*, pH $\sim$10·0	Moderate yield of K–*A*, pH $\sim$8·0	Moderate yield of K–*A*, pH $\sim$8·0	Moderate yield of K–*M*, and K–*E*, pH $\sim$8·0
$n = 5$	V. poor yield of K–*I*, pH $\sim$10·0	V. poor yield of K–*A*, pH $\sim$8·5	Moderate yield of K–*A*, pH $\sim$9·0	Good yield of K–*E* + some K–*A*, pH $\sim$10·0	Good yield of K–*E* + some K–*A*, pH $\sim$9·0
$n = 6$	V. poor yield of K–*A*, pH $\sim$8·5	V. poor yield of K–*A* + K–*I*, pH $\sim$9·0	Good yield of K–*A*, pH $\sim$8·0	Moderate yield of K–*A*, pH $\sim$8·0	Good yield of K–*A*, pH $\sim$7·5
$n = 7$	V. poor yield of K–*A*, pH $\sim$9·0	V. poor yield of K–*A*, pH $\sim$10·0	Good yield of K–*A*, pH $\sim$8·5	Good yield of K–*A*, pH $\sim$8·0	Good yield of K–*A*, pH $\sim$8·0
$n = 8$	No crystn., pH $\sim$9·0	V. poor yield of K–*A*, pH $\sim$10·0	Good yield of K–*A*, pH $\sim$8·0	Good yield of K–*A*, pH $\sim$8·0	Good yield of K–*A*, pH $\sim$8·0
$n = 9$	No crystn., pH $\sim$9·0	Moderate yield of K–*A*, pH $\sim$8·0	Good yield of K–*E* + K–*A*, pH $\sim$8·5	Moderate yield of K–*A*, pH $\sim$9·0	Moderate yield of K–*A*, pH $\sim$8·0
$n = 10$	No crystn., pH $\sim$9·0	Poor yield of K–*A*, pH $\sim$7·5	Moderate yield of K–*A*, pH $\sim$9·0	Moderate yield of K–*A*, pH $\sim$8·0	Poor yield of K–*A*, pH $\sim$9·0
$n = 11$	No crystn., pH $\sim$9·0	Poor yield of K–*A*, pH $\sim$8·0	Poor yield of K–*A*, pH $\sim$9·0	Poor yield of K–*A*, pH $\sim$9·0	Poor yield of K–*A*, pH $\sim$8·0
$n = 12$	No crystn., pH $\sim$9·0	Poor yield of K–*A*, pH $\sim$8·0	Poor yield of K–*A*, pH $\sim$8·5	Poor yield of K–*A*, pH $\sim$8·0	Poor yield of K–*A*, pH $\sim$8·0

Species K–*I*. This species crystallised from gels of composition $K_2O,Al_2O_3,nSiO_2$, where $3 \leqslant n \leqslant 6$, when the cold mother-liquor had a final pH $\leqslant$10·0. The product crystallised in relatively large crystals ($\sim$20 μ long) showing strong birefringence and having $\alpha = 1·645$ and $\gamma = 1·670$. The *X*-ray spacings identify this species as boehmite.[1b]

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[10] Cf. ref. 6.

TABLE 3.

Gel composition $K_2O,Al_2O_3,nSiO_2$. pH $>$10·5 in all cases.

Temp.	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
60°	V. poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + trace K–*H*
85	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*	Moderate yield K–*G* + trace K–*H*	Poor yield of K–*G* + K–*H*	Poor yield of K–*G* + K–*H*
120	Poor yield of K–*F*	Moderate yield of K–*F*	Moderate yield of K–*F*	Good yield of K–*F*	Moderate yield of K–*F*	Poor yield of K–*G*
150	Moderate yield of K–*F*	Moderate yield of K–*F*	Moderate yield of K–*F* or K–*G* (depending on xs. KOH)	Good yield of K–*G*	Good yield of K–*G*	Good yield of K–*G*
200	Moderate yield of K–*M*	Moderate yield of K–*M*	Poor yield of K–*M*	Good yield of K–*M*	Poor yield of K–*A* + K–*M*	Poor yield of K–*A* + K–*M*
250	Good yield of K–*M*	Moderate yield of K–*M*	Moderate yield of K–*M*	Good yield of K–*M* + K–C	Moderate yield of K–*A*	Good yield of K–*A* + trace K–*M*
300	Good yield of K–*N*	Good yield of K–*N* + some K–*C*	Good yield of K–*C* + some K–*A*	Good yield of K–*N*	Moderate yield of K–*A* + some K–*N*	Good yield of K–*A* + some K–C
350	Good yield of K–*N*	Good yield of K–*N* + some K–*C*	Good yield of K–*N* + some K–*C*	Good yield of K–*A* + some K–*C*	Good yield of K–*A*	Good yield of K–*A*
400	Good yield of K–*N*	Good yield of K–*N* + some K–*C*	Good yield of K–*N* + trace K–*C*	Good yield of K–*N* + K–*A*	Good yield of K–*C*	Excellent yield of K–*A*
450	Good yield of K–*N*	Good yield of K–*N*	Good yield of K–*N*	Moderate yield of K–*N*	Moderate yield of K–*A*	Good yield of K–*A*

Temp.	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$
60°	Poor yield of K–*H* + some K–*G*	Poor yield of K–*H*	V. poor yield of K–*H*	V. poor yield of K–*H*	V. poor yield of K–*H*	V. poor yield of K–*H*
85	Good yield of K–*M* + K–*G*	Good yield of K–*M* + K–*G*	V. poor yield of K–*H*	V. poor yield of K–*H*	V. poor yield of K–*H*	V. poor yield of K–*H*
120	Good yield of K–*M* + some K–*F* and K–*G*	Good yield of K–*M* + some K–*H*	Poor yield of K–*H*	Poor yield of K–*M* + some K–*H*	Poor yield of K–*H*	Poor yield of K–*H*
150	Good yield of K–*M*	Good yield of K–*M*	Moderate yield of K–M + K–*H*	Moderate yield of K–*M*	Poor yield of K–*A* and K–*B*	Poor yield of K–*A* and K–*B*
200	Poor yield of K–*A*	Poor yield of K–*A* + trace K–*M*	Poor yield of K–*A* + trace K–*M*	Moderate to poor yield of K–*B*	Poor yield of K–*B* + K–*A*	Poor yield of K–*B* + K–*A*
250	Good yield of K–*A*	Moderate yield of K–*A*	Moderate yield of K–*A*	Poor yield of K–*B* + K–*A*	Poor yield of K–*B* + K–*A*	Poor yield of K–*B* + K–*A*
300	Good yield of K–*A* + some K–*B* and K–*C*	Moderate yield of K–*B* + some K–*A*	Good yield of K–*B* + some K–*A*	Excellent yield of K–*B* + trace K–*A*	Excellent yield of K–*B* + some K–*A*	Excellent yield of K–*B* + some K–*A*
350	Moderate yield of K–*N* + K–*C*	Poor yield of K–*A* + K–*B*	Moderate yield of K–*A* + K–*B*	Moderate yield of K–*A* + K–*B*	Moderate yield of K–*A* + some K–*B*	Moderate yield of K–*A* + some K–*B*
400	Moderate yield of K–*A*	Moderate yield of K–*A* + K–*B*	Moderate yield of K–*A* + K–*B*	Moderate yield of K–*B* + K–*A*	Good yield of K–*B* + K–*A*	Good yield of K–*B* + K–*A*
450	Good yield of K–*A* + some K–*B*	Good yield of K–*A* + some K–*B*	Moderate yield of K–*A* + some K–*B*	Poor yield of K–*A* + K–*B*	Moderate yield of K–*B* + K–*A*	Moderate yield of K–*B* + K–*A*

TABLE 4.

Natural sanidine		K–*A*		Leucite[11]		K–*C*		Kaliophilite[13]		K–*D*	
I	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'
vw	6·62	mw	6·56	—	3·45	vs	3·42	w	6·21	ms	6·22
vw	5·95	m	5·62	—	3·26	vs	3·23	m	5·75	—	—
s	4·22	s	4·23	—	2·91	s	2·89	w	4·51	mw	4·50
vw	3·96	w	3·96	—	2·81	s	2·83	m	4·26	m	4·24
s	3·80	s	3·78	—	2·64	m	2·64	ms	3·56	—	—
w	3·60	vw	3·61	—	2·38	s	2·37	m	3·41	—	—
ms	3·48	ms	3·45	—	2·30	w	2·30	s	3·10	vvs	3·07
vvs	3·27	vvs	3·29	—	2·14	ms	2·14	ms	2·79	w	2·82
—	—	vs	3·23	—	2·06	mw	2·06	m	2·69	vvw	2·68
ms	2·99	ms	2·99	—	1·72	m	1·72	ms	2·61	s	2·60
m	2·91	ms	2·90	—	1·66	s	1·66	m	2·23	vw	2·21
m	2·77	m	2·77	—	1·63	m	1·62	w	2·07	w	2·05
ms	2·59	ms	2·59	—	1·58	m	1·58				
m	2·17	m	2·17	—	1·53	m	1·53				
mw	2·11	mw	2·11	—	1·48	ms	1·48				
mw	2·06	mw	2·06								
m	1·92	m	1·92								
ms	1·80	s	1·79								

Analcite[14]		K–*E*		α-Quartz[1a]		K–*B*		Rb-aluminosilicate[1d]		K–*F*	
I	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'
s	5·59	vvs	5·67	ms	4·26	s	4·28	m	7·95	vvs	7·45
m	4·85	m	4·92	vs	3·35	vs	3·37	—	—	vw	4·78
vvs	3·43	vvs	3·46	m	2·46	m	2·47	—	—	m	3·98
s	2·93	vs	2·94	m	2·28	mw	2·29	—	—	m	3·47
m	2·69	m	2·68	w	2·24	w	2·25	—	—	m	3·29
m	2·50	ms	2·51	m	2·13	m	2·13	vs	3·25	vs	3·09
mw	2·42	m	2·42	w	1·98	mw	1·98	s	3·11	s	2·97
m	2·22	ms	2·22	s	1·82	ms	1·82	s	2·96	vs	2·82
m	1·90	s	1·90	m	1·67	m	1·67	vw	2·42	mw	2·35
m	1·86	ms	1·87	ms	1·54	ms	1·54	vw	2·35	w	2·20
ms	1·74	vs	1·74	vw	1·45	mw	1·45	—	—	m	2·11
m	1·42	s	1·41	vw	1·42	mw	1·44	vw	1·90	m	1·85
m	1·36	s	1·36	ms	1·37	ms	1·38	mw	1·79	m	1·74
								vw	1·74	mw	1·68
								vw	1·63	m	1·59
								vw	1·59	m	1·56

Phillipsite		K–*M*		Ba-aluminosilicate[18]		Phillipsite		K–*M*		Ba-aluminosilicate[18]	
I	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'
—	—	ms	8·26	s	8·18	m	2·94	ms	2·97	w	2·95
vs	7·64	s	7·15	s	7·16	ms	2·71	s	2·73	m	2·70
m	5·24	m	5·37	—	—	m	2·52	m	2·54	w	2·55
m	4·98	ms	5·05	vw	4·96	m	2·40	m	2·42	—	—
ms	4·25	m	4·32	—	—	m	1·78	s	1·77	w	1·78
		vs	3·25	—	—	m	1·72	ms	1·72	w	1·72
s	3·18	vs	3·18	s	3·18						

Natural kalsilite		K–*N*		Synthetic kalsilite[13]		Natural kalsilite		K–*N*		Synthetic kalsilite[13]	
I	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'
ms	4·37	ms	4·37	vw	4·33	m	1·58	ms	1·58	m	1·57
vs	3·97	vs	3·99	s	3·96	s	1·49	s	1·49	s	1·48
vvs	3·12	vvs	3·12	s	3·10	—	—	m	1·34	w	1·33
vs	2·58	vs	2·59	vs	2·57	w	1·29	m	1·29	m	1·29
m	2·47	m	2·47	m	2·45	ms	1·26	ms	1·26	w	1·26
mw	2·22	m	2·22	m	2·21	m	1·23	m	1·23	w	1·23
ms	2·18	ms	2·17	m	2·16	m	1·21	m	1·21	w	1·21
m	1·66	m	1·66	m	1·65	m	1·19	m	1·19	m	1·19
m	1·62	m	1·62	w	1·62						

Aluminosilicates.—*Felspar* (K–*A*) (Plate 2). The potassium felspar, $K_2O,Al_2O_3,6SiO_2$, crystallised mainly in hexagonal plates showing moderate birefringence with a mean refractive index of 1·525. The crystals formed reproducibly over a wide range of temperature and composition (Figs. 1 and 2*c*). The optimum conditions for growth were at 350° from a gel of composition $K_2O,Al_2O_3,6SiO_2$ in a mother-liquor with a final pH $>10·5$. The refractive indices and the *X*-ray spacings (Table 4) identify the product as sanidine, the monoclinic, high-temperature modification of the potassium felspar.

Felspathoids.—Species K-*C* (Plate 3). This species crystallised principally along with K-*N* (kalsilite) but was also obtained in major yield at 300° from a gel of composition $K_2O,Al_2O_3,3SiO_2$ + 135% molar excess of KOH in aqueous solution when the mother-liquor had a final pH >10·5. Spherulitic crystals were obtained showing moderate birefringence with mean refractive index of 1·510. In Table 4 the *X*-ray spacings are compared with figures for a natural[11] leucite and a synthetic[12] leucite. The dimensions of the unit cell of K-*C* (*a* = 12·92 Å; *c* = 13·70 Å) are smaller than those quoted by Naray-Szabo[11] for a natural leucite (*a* = 13·01 Å; *c* = 13·82 Å) but correspond closely to those given by Wyart[12] for his synthetic leucite (*a* = 12·95 Å; *c* = 13·74 Å).

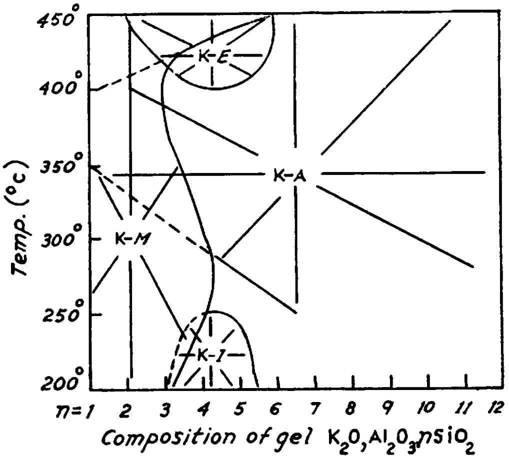

FIG. 1. *Diagrammatic representation of the approximate areas of formation of the products of crystallisation of gels* $K_2O,Al_2O_3,nSiO_2$ + aq. (*no excess* KOH *added*).

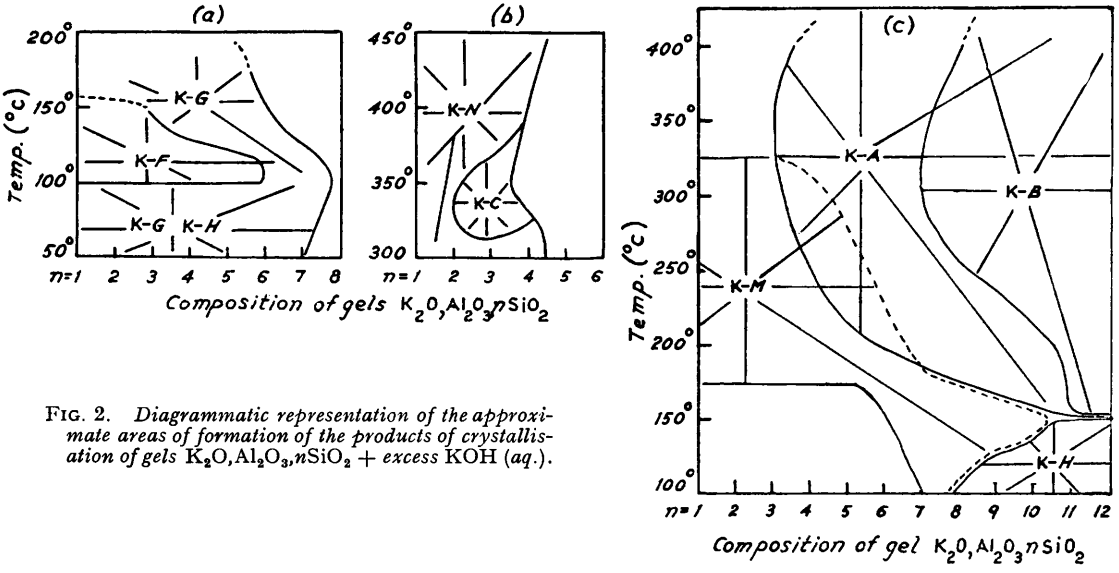

FIG. 2. *Diagrammatic representation of the approximate areas of formation of the products of crystallisation of gels* $K_2O,Al_2O_3,nSiO_2$ + *excess* KOH (*aq.*).

Species K-*D* (Plate 4). Kaliophilite, $K_2O,Al_2O_3,2SiO_2$, was obtained in only one preparation. This species occurred as very small lenticular crystals showing moderate birefringence with ε = 1·530; ω = 1·535. The *X*-ray spacings (Table 4) identity the product as kaliophilite

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[11] Naray-Szabo, *Z. Krist.*, 1942, **104**, 39.
[12] Wyart, *Compt. rend.*, 1941, **212**, 365.

but whether of the low-temperature hexagonal or the high-temperature orthorhombic form remains in doubt.

Species K-*N* (Plate 6). Kalsilite, $K_2O,Al_2O_3,2SiO_2$, occurred mainly in hexagonal plates and occasionally as stout rods showing moderate birefringence with $\varepsilon = 1{\cdot}535$; $\omega = 1{\cdot}540$. The optimum conditions for growth were from a gel of composition $K_2O,Al_2O_3,3SiO_2$ + 135% molar excess of KOH in a mother-liquor of final pH >10·5. Its formation was severely restricted to high temperatures and from silica-poor gels (Fig. 2*b*). In Table 4 the *X*-ray spacings are compared with those of a natural kalsilite and another synthetic kalsilite.[13]

Zeolitic Species.—*Species* K–*E* (Plate 5). This is a hydrated potassium analcite occurring in well-formed spherulites showing no birefringence and with a variable refractive index depending on the temperature of crystallisation. Species K–*E* was obtained at 400—450° from a gel of composition $K_2O,Al_2O_3,5SiO_2$. However, an isolated synthesis was obtained at 200° from a gel of composition $K_2O,Al_2O_3,6SiO_2$ in a mother-liquor with a final pH $\simeq$8·0. The latter product had $n \sim 1{\cdot}490$. The *X*-ray spacings in Table 4 identified the product as an expanded analcite-type structure with a unit cell edge of $a = 13{\cdot}79$ Å compared with $a = 13{\cdot}70$ Å for analcite[14] and $a = 13{\cdot}40$ Å for cubic leucite.[15] The crystals lost water when heated to 450° and gave a contracted structure with $a = 13{\cdot}70$ Å and $n \sim 1{\cdot}420$. A preparation at 450° also had a unit cell edge of $a = 13{\cdot}70$ Å but a refractive index of $\sim 1{\cdot}485$. This product on ignition lost 6·92% by weight. On sintering of the 200° preparation at 800° some transformation to the K-felspar occurred which was completed on sintering and quenching at 1000°.

FIG. 3.

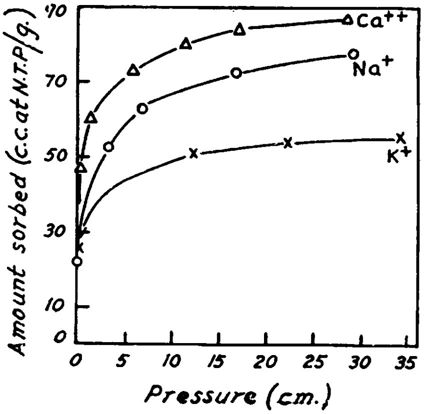
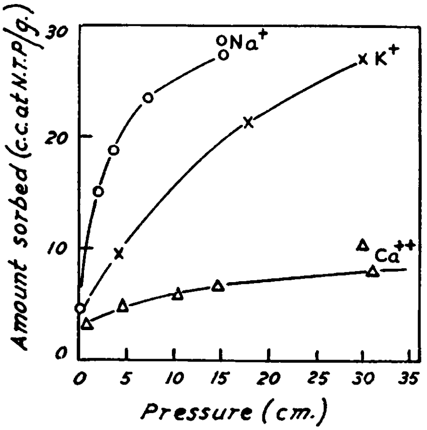


FIG. 4.



Species K–*F*. This is a new zeolitic species, $K_2O,Al_2O_32SiO_2,3H_2O$, which has not been identified with any naturally occurring mineral. The species crystallised at or below 150° in small rods showing very weak birefringence with a mean *n* of 1·500. Maximum yields and reproducibility were obtained at 120° from a gel of composition $K_2O,Al_2O_3,4SiO_2$ + 130% molar excess of KOH in a mother-liquor of final pH >10·5. The product lost 12·5% by weight on ignition at 1000° and had a sufficiently rigid structure to remain unaltered on outgassing at ~300°. When heated to 600° for 3 days and quenched, the species was transformed into kaliophilite.

Cationic exchange was carried out at 110°, and the Na- and Ca-forms obtained. *X*-Ray diffraction showed that no appreciable alteration occurred in the lattice when these cations were introduced. The Na- and Ca-forms lost 15·8% and 16·2%, respectively, by weight on ignition at 1000°.

The K^+-, Na^+-, and Ca^{++}-forms were not able to occlude oxygen or argon at 90° K, after the crystals had been outgassed at 350°. However, ammonia was sorbed very slowly at 293° K. At 473° K the Na^+- and K^+-forms sorbed ammonia fairly readily but the Ca^{++}-form still sorbed this gas slowly (Fig. 4). The latter behaviour was explained by the breakdown of the structure,

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[13] Rigby and Richardson, *Min. Mag.*, 1947, **28**, 75.
[14] Taylor, *Z. Krist.*, 1930, **74**, 1.
[15] Wyart, *Bull. Soc. franç. Min.*, 1938, **61**, 228.

as shown by general scattering on the *X*-ray powder photograph of the sample after use. The weights of sorbent in Fig. 4 refer to their hydrated state.

Species K–*G*. (Plates 9 and 10; Table 5). A number of phases of varying alumina : silica ratio crystallised in lenticular habit showing moderate birefringence. The ragged edges of the lenticular crystals shown in the electron micrographs suggest that they are aggregates of tiny crystals. The optimum conditions for growth were at 150° from a mother-liquor of pH >10·5.

A series of specimens was prepared and analysed. The chemical composition and refractive indices are given in Table 6. The gradual increase in silica content is accompanied by a decrease in the refractive indices, which are, however, also influenced by a variation in the water content. In Fig. 5 the *X*-ray powder patterns are compared *inter se* and with that given by a natural chabazite (Bay of Fundy, Nova Scotia) cation-exchanged to a potassium-rich form. This Figure shows the most siliceous sample to be almost identical with the natural mineral. However, the more aluminous samples give patterns with some differences at higher angle reflections. The clearest difference resides in the number of diffuse reflections shown by the aluminous

TABLE 5.

K–*G* (1)		K–*G* (2)		K–*G* (3)		K–*G* (4)		K–*G* (5)		K–*G* (6)		Natural chabazite (K-form)	
I	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'	*I*	'*d*'
ms	9·47	s	9·58	ms	9·52	ms	9·45	ms	9·40	ms	9·38	vs	9·47
—	—	—	—	—	—	—	—	—	—	m	8·02	—	—
m	6·90	ms	6·90	m	6·94	m	6·94	mw	7·05	mw	7·00	mw	6·93
—	—	—	—	—	—	vvw	5·55	w	5·54	mw	5·60	m	5·55
m	5·22	m	5·25	m	5·22	m	5·24	m	4·99	m	5·11	m	5·02
—	—	—	—	—	—	vvw	4·78	—	—	w	4·66	—	—
s	4·32	s	4·27	s	4·33	s	4·32	s	4·33	s	4·34	s	4·32
ms	3·97	s	3·95	ms	3·94	ms	3·95	ms	3·90	ms	3·92	ms	3·89
w	3·70	mw	3·73	mw	3·68	mw	3·68	ms	3·59	m	3·61	ms	3·57
w	3·46	—	—	vw	3·45	mw	3·45	—	—	mw	3·47	ms	3·34
mw	3·11	mw	3·16	mw	3·17	mw	3·18	ms	3·22	mw	3·21	mw	3·16
vvs	2·93	vvs	2·92	vvs	2·93	vvs	2·93	vvs	2·92	vvs	2·93	vvs	2·91
w	2·80	w	2·80	—	—	mw	2·79	—	—	—	—	—	—
s	2·59	ms	2·58	ms	2·59	ms	2·59	m	2·57	m	2·61	m	2·59
s	2·29	ms	2·29	ms	2·30	ms	2·29	m	2·30	mw	2·31	m	2·30
ms	2·19	m	2·19	mw	2·17	m	2·17	—	—	—	—	—	—
m	2·09	mw	2·09	m	2·09	mw	2·10	mw	2·08	mw	2·10	m	2·08
w	1·90	w	1·90	w	1·90	vw	1·89	mw	1·87	w	1·86	m	1·87
m	1·84	m	1·85	m	1·84	mw	1·84	ms	1·81	m	1·82	s	1·80
vw	1·75	w	1·75	—	—	—	—	vw	1·76	—	—	—	—
s	1·71	ms	1·72	s	1·72	ms	1·71	m	1·72	m	1·73	ms	1·72
m	1·63	mw	1·64	m	1·64	m	1·64	m	1·64	mw	1·65	m	1·65
ms	1·57	m	1·58	m	1·57	mw	1·57	mw	1·56	mw	1·56	m	1·56
—	—	vw	1·52	w	1·53	mw	1·52	mw	1·52	mw	1·52	—	—
w	1·48	mw	1·48	w	1·48	w	1·48	w	1·48	w	1·49	—	—
w	1·45	mw	1·46	—	—	—	—	—	—	—	—	—	—
w	1·44	w	1·44	m	1·43	m	1·43	ms	1·42	mw	1·42	—	—
ms	1·32	ms	1·32	ms	1·32	mw	1·32	m	1·32	mw	1·32	—	—
w	1·30	vw	1·30	vw	1·30	—	—	mw	1·29	—	—	—	—
m	1·28	w	1·28	mw	1·28	vw	1·28	—	—	w	1·28	—	—
m	1·23	ms	1·23	w	1·23	—	—	w	1·23	vw	1·23	—	—

TABLE 6.

Sample no.	Gel composition	Excess of alkali (KOH) added (%)	Ultimate gel composition	Refractive indices		Molar proportions (Al_2O_3 = 1·00)		
				α	γ	K_2O	SiO_2	H_2O
1	$K_2O,Al_2O_3,3SiO_2$	150	$2{\cdot}5K_2O,Al_2O_3,3SiO_2$	1·480	1·485	0·92	2·30	3·40
2	$K_2O,Al_2O_3,4SiO_2$	140	$2{\cdot}4K_2O,Al_2O_3,4SiO_2$	1·490	1·495	1·11	2·56	2·62
3	$K_2O,Al_2O_3,4SiO_2$	275	$3{\cdot}75K_2O,Al_2O_3,4SiO_2$	1·475	1·480	0·99	2·65	3·72
4	$K_2O,Al_2O_3,5SiO_2$	310	$4{\cdot}1K_2O,Al_2O_3,5SiO_2$	1·465	1·470	0·95	2·72	3·94
5	$K_2O,Al_2O_3,5SiO_2$	150	$2{\cdot}5K_2O,Al_2O_3,5SiO_2$	1·460	1·465	1·00	3·91	4·63
6	$K_2O,Al_2O_3,6SiO_2$	150	$2{\cdot}5K_2O,Al_2O_3,6SiO_2$	1·470	1·475	1·03	4·15	4·38

samples. The small particle size of the specimens might be thought to create some diffuseness, but the crystals of the more siliceous samples are not observably larger and do not exhibit the diffuse reflections. Again, not all reflections in the aluminous crystals are diffuse, suggesting that disorder or imperfection is occurring only in certain lattice planes.

These phases could all be indexed on the rhombohedral crystal system with a unit cell edge of $a = 9{\cdot}52$ Å which remained constant despite the variations in chemical composition.[16] Since the Al–O bond length is greater than the Si–O bond length, distortions must occur in a structure as the aluminium content is increased if the unit cell edge remains constant. These distortions may be localised, or the strain may distort the complete rhombohedral unit cell, *e.g.*, by altering the angle of the rhomb. The angle of the rhombohedron of the aluminous samples is $\alpha = 93° 20'$ compared with 94° for the siliceous samples and 94° 24′ given by Wyart[16] for natural chabazite.

Species K–*G* appears, then, to consist of a number of chabazite-like phases of different composition, the varying alumina : silica ratio and hence cation density causing slight differences in the *X*-ray diffraction patterns and other properties. Each member of the series undergoes ready cation exchange and the Li^+-, Na^+-, NH_4^+-, Rb^+-, Cs^+-, and Ca^{++}-forms were all obtained.

Species K–*M* (Plates 7 and 8). This was a major species in many crystallisations from mother-liquors of final pH both less than and greater than 10·0. Species K–*M*, $K_2O,Al_2O_3,3SiO_2,3H_2O$, crystallised in characteristic "wheatsheaf bundles" and spherulites composed of fibres radiating from the centre which showed moderate birefringence with $\alpha = 1{\cdot}490$; $\gamma = 1{\cdot}495$. The habit shown on Plate 8 also occurred. The lowest temperature recorded for the synthesis of the species was 85°, and optimum conditions of growth were at 250° from a gel of composition $K_2O,Al_2O_3,3SiO_2$. The *X*-ray spacings (Table 4) identify the species with another synthetic potassium aluminosilicate[1c] and show the structure to be similar to that of a natural phillipsite and of a synthetic calcium aluminosilicate.[17] A barium aluminosilicate found in Nature with kalsilite[18] also has a comparable *X*-ray powder pattern. This species occurred in acicular bundles with $n \sim 1{\cdot}500$ and may be wellsite.

Species K–*M* readily underwent cation-exchange at 110° to the Na^+- and Ca^{++}-forms without showing any appreciable alteration in the lattice. The K^+-, Na^+-, or Ca^{++}-forms did not show any appreciable sorptive powers towards oxygen or argon at 90° K when dehydrated at 350°. However, at 293° K all the dehydrated forms sorbed ammonia quite rapidly, equilibrium being reached in a few hours (Fig. 3).

DISCUSSION

Alumina crystallises at room temperature to either bayerite or boehmite.[19] We have also observed bayerite to be the product from an aged alumina gel. This pre-crystallisation rendered the aluminosilicate gels less reactive and was avoided by the use of freshly prepared alumina in all gels. Species K–*H* and K–*I*, bayerite and boehmite respectively, as shown in Figs. 1 and 2*a*, were crystallised under the specified conditions and were not products of pre-crystallisation.

The distribution of species K–*B* (α-quartz) clearly illustrates the fact that alkali acts as a selective mineraliser of quartz only from gels rich in silica.[20] The quartz was crystallised from these highly reactive aluminosilicate gels at the comparatively low temperature of 150°.

The potassium felspar was obtained as the monoclinic, high-temperature form. However, the synthesis of high-temperature modifications under low-temperature hydrothermal conditions is in line with recent work.[21] A recent study of the naturally occurring potassium felspars[22] has suggested that most of these potassium felspars crystallised as the monoclinic modification and the presence in Nature of the microclines (triclinic) is largely due to inversion and not growth. Again, sanidine, the monoclinic modification,

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[16] Cf. natural chabazite, Wyart, *Bull. Soc. franç. Min.*, 1933, **56**, 81.
[17] Barrer, unpublished work.
[18] Bannister and Hey, *Min. Mag.*, 1941/43, **26**, 218.
[19] Noll, *Neues Jahrb. Min., Beil. Bd.*, 1935, **70**, 65.
[20] Barrer, *Nature*, 1946, **157**, 734.
[21] Cf. ref. 1*b*; Goldsmith, *Amer. Min.*, 1949, **34**, 471.
[22] Goldsmith and Laves, *Geochim. Cosmochim. Acta*, 1954, **6**, 100.

is regarded as having the highest degree of Al–Si disorder. The crystallisation of highly reactive gels is likely to occur rapidly from a high degree of supersaturation. In these circumstances the ordered incorporation of aluminium and silicon into the aluminosilicate framework is unlikely. It is not then surprising that sanidine, although not thermodynamically the most stable under the conditions employed, is the product of crystallisation from gels of suitable composition. This potassium felspar was successfully crystallised at the relatively low temperature of 150° and, in agreement with the results of Goldsmith and Laves,[22] this suggests that the potassium felspars should not be used in geological thermometry.

The potassium felspar occurred as a minor species in the preparation of a hydrated potassium analcite at 400—450°. When the pH of the mother-liquor was raised by addition of potassium hydroxide solution, a potassium felspar crystallised in an analcitic habit. This suggests the initial crystallisation of an analcite-type structure with subsequent transformation to the felspar. The hydrated potassium analcite, in contrast to leucite, is metastable to the felspar structure at high temperatures and in this way behaves similarly to analcite.[1b]

Wyart[23] stated that he succeeded in preparing kalsilite and orthoclase by hydrothermal methods, but never the product of intermediate composition, leucite. This has not been our experience, since leucite was the final product when the time factor was varied from one to five days provided the other conditions for optimum yield were maintained. However, both above and below 300° leucite was metastable to kalsilite under similar conditions.

The occurrence of a chabazite-like series of variable alumina : silica ratio is particularly interesting. It appears directly to corroborate Winchell's theory[24] of the existence of isomorphous series in the zeolitic class. Study of sorption by these phases yields further information on the relationships between them and the natural chabazite and will be discussed in another paper.

The occurrence of a near-phillipsite is widespread in the crystallisation field of the potassium aluminosilicates. The stability of the structure is emphasised by its being unaltered when the material was heated at 650° for 3 days, and quenched. There was, however, transformation to leucite at 1025°. It may then seem surprising that a " pure " potassium phillipsite has not been found in Nature. However, the low-temperature preparation of the very stable felspar structure (~150°) may offer some explanation of this.

Phillipsite is common in deep-sea deposits where its formation is due to the action of ions in solution with sedimentary material.[25] Crystallisation must take place at very low temperatures under these conditions, although the lower limit achieved by us was 85°. Indeed, crystallisation at this temperature only occurred from a liquor of very high pH such as would not be expected on the ocean bed. However, one cannot hope to emulate the time factor involved in the growth of crystalline species in Nature.

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[23] Wyart, *Discuss. Faraday Soc.*, 1949, **5**, 323.

[24] Winchell, *Amer. Min.*, 1925, **10**, 145.

[25] Mason, " The Principles of Geochemistry," Wiley & Sons Inc., New York, 1952, p. 170.