Chemistry of Soil Minerals. Part XIII.† Reactions of Metakaolinite with Single and Mixed Bases

By **R. M. Barrer** * and **D. E. Mainwaring**, Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

Low-temperature hydrothermal reactions of metakaolinite have been investigated, with and without additions of silica, by use of the bases LiOH, NaOH, RbOH, and CsOH and also the mixtures NaOH + LiOH, NaOH + KOH, KOH + LiOH, and NaOH + Me_4NOH. Over certain temperature and composition ranges reproducible crystallisation fields have been obtained for all the above bases and pairs of bases. Two hydrated non-zeolites were formed (nepheline hydrate I and a near-hectorite), and also a group of anhydrous phases. However under the conditions employed zeolitisation reactions were dominant, which are largely but not fully paralleled by similar reactions with aqueous alkaline aluminosilicate gels. A number of the products have been characterised by X-ray, d.t.a., t.g.a., and sorption studies, and in other ways. The most frequently occurring zeolite phases were those related to phillipsite, gismondite, gmelinite, chabazite, faujasite, Linde A type, sodalite and cancrinite hydrates, and two lithium zeolites and a sodium tetramethylammonium zeolite without natural counterparts.

STUDIES of crystallisation of aluminosilicate gels in the presence of mixed bases [1-8] have shown that the phases formed are sometimes specific to the mixture of bases chosen. It has also been observed that these phases for a given starting composition may vary according to the materials used (for example, gels, glasses, kaolinite + silica, metakaolinite + silica). Metakaolinite is a well known source of Linde zeolite A and of cracking catalysts containing faujasite-type crystals. It has also been shown that a range of zeolites and other aluminosilicates can be formed from metakaolinite (MTK) or metakaolinite plus silica with aqueous KOH, $Ba(OH)_2$, $Ba(OH)_2$ + KOH, and $Ba(OH)_2$ + tetramethylammonium hydroxide.[8] It was therefore of interest to examine further the mineralising action on metakaolinite or metakaolinite plus silica of other aqueous bases and mixtures of bases. As reported in this paper many interesting reactions were observed.

EXPERIMENTAL

Metakaolinite (oxide composition $Al_2O_3,2SiO_2$) was prepared from kaolinite by heating the latter to 600 °C for 12 h. Where desired metakaolinite was mixed with dry, powdered silica in known proportions. As bases AnalaR LiOH and NaOH were used, while RbOH and CsOH were prepared from pure $Ba(OH)_2$ by reaction (1). Tetramethylammonium hydroxide was obtained as its aqueous solution with 25% of the base.

$$M_2SO_4 + Ba(OH)_2 \longrightarrow 2MOH + BaSO_4\downarrow \quad (1)$$
$$(M = Rb \text{ or } Cs)$$

Syntheses below 100 °C were made as previously [8] in rotating polypropylene bottles. Stainless steel autoclaves were used above 100 °C. The crystalline products were examined by optical, electron, and scanning electron microscopy, by X-ray powder diffraction, and through ion exchange, differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.). Some of the porous crystals were analysed chemically and characterised as sorbents.

RESULTS AND DISCUSSION

Reactions with Single Bases.—The reaction products obtained by use of the single bases LiOH, NaOH, RbOH, and CsOH are summarised in Table 1. The letter designations are those employed previously in these laboratories as indicated by the reference numbers in the Table. The most diverse structural types were formed in aqueous sodium hydroxide.

TABLE 1

Crystalline products obtained with single bases

Base	Crystal designations	Crystal types
LiOH	Li-A [9]	Zeolite
	Li-H [9]	Zeolite
	Li-D [9]	Metasilicate
NaOH	Na-B [2]	Analcite
	Na-C [10]	Hydroxycancrinite (cancrinite hydrate)
	Na-J [10]	Nepheline hydrate I
	Na-P1 [2]	Pseudo-cubic near-gismondite
	Na-P2 [2]	Pseudo-tetragonal near-gismondite
	Na-P3 [2]	Pseudo-orthorhombic near-gismondite
	Na-Q [2]	Linde A type zeolite
	Na-R [2]	Near-faujasite
	Na-S [2]	Near-gmelinite
	Na-T [5]	Hydroxysodalite (sodalite hydrate)
RbOH	Rb-A [1]	Non-zeolite, like Cs-F [1]
	Rb-D [1]	Zeolite, like K-F [11]
	Rb-M	Zeolite, like K-M [11]
CsOH	Cs-D [12]	Zeolite, like K-F [11]
	Cs-F [1]	Non-zeolite, like Rb-A [1]
	Cs-G [1]	Pollucite

The Lithium-bearing Crystals.—Parts of the crystallisation fields of compositions within the ranges 1MTK + 2·5—45LiOH + $275H_2O$; 1MTK + $4SiO_2$ + 2·5—

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† *Previous Part*: ref. 8.

[1] R. M. Barrer and N. McCallum, *J. Chem. Soc.*, 1953, 4029.

[2] R. M. Barrer, J. W. Baynham, F. W. Bultitude, and W. M. Meier, *J. Chem. Soc.*, 1959, 195.

[3] R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 1961, 983.

[4] S. P. Zhdanov, in 'Molecular Sieves,' Soc. Chem. Ind., London, 1968, p. 62.

[5] R. Aiello and R. M. Barrer, *J. Chem. Soc. (A)*, 1970, 1470.

[6] A. Pereyron, J.-L. Guth, and R. Wey, *Compt. rend.*, 1971, **272**, 181.

[7] A. Pereyron, J.-L. Guth, and R. Wey, *Compt. rend.*, 1971, **272**, 1331.

[8] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 1259.

[9] R. M. Barrer and E. A. D. White, *J. Chem. Soc.*, 1951, 1267.

[10] R. M. Barrer and E. A. D. White, *J. Chem. Soc.*, 1952, 1561.

[11] R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.

[12] R. M. Barrer, J. F. Cole, and H. Sticher, *J. Chem. Soc. (A)*, 1968, 2475.

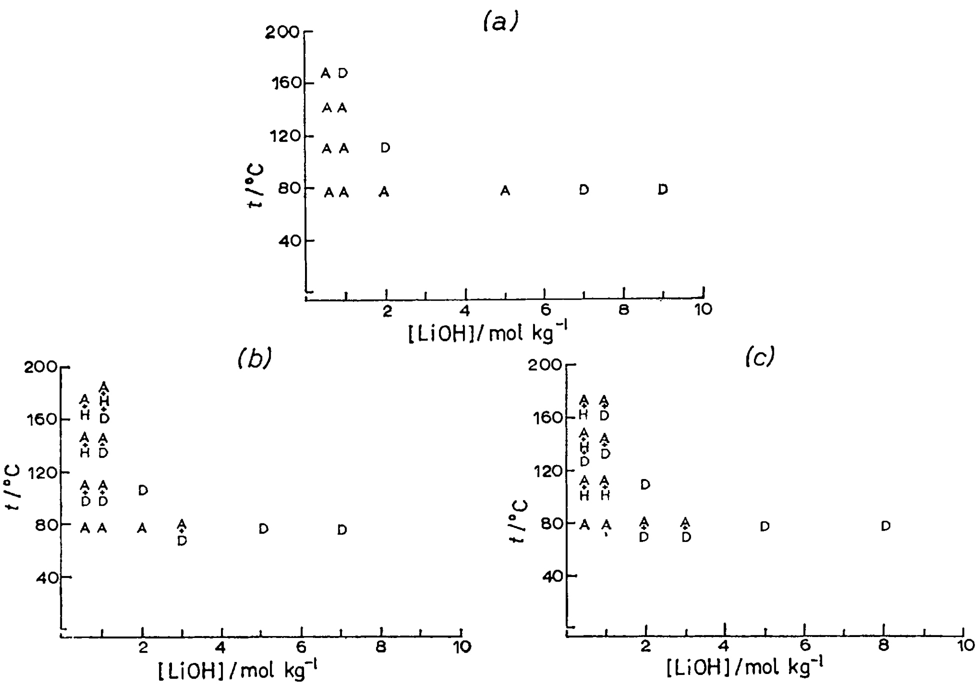

FIGURE 1 Crystallisations from the compositions (a) 1MTK + 2·5—45LiOH + 275H_2O; (b) 1MTK + 4SiO_2 + 2·5—45LiOH + 275H_2O; and (c) 1MTK + 8SiO_2 + 2·5—45LiOH + 275H_2O showing dependence on temperature and alkalinity

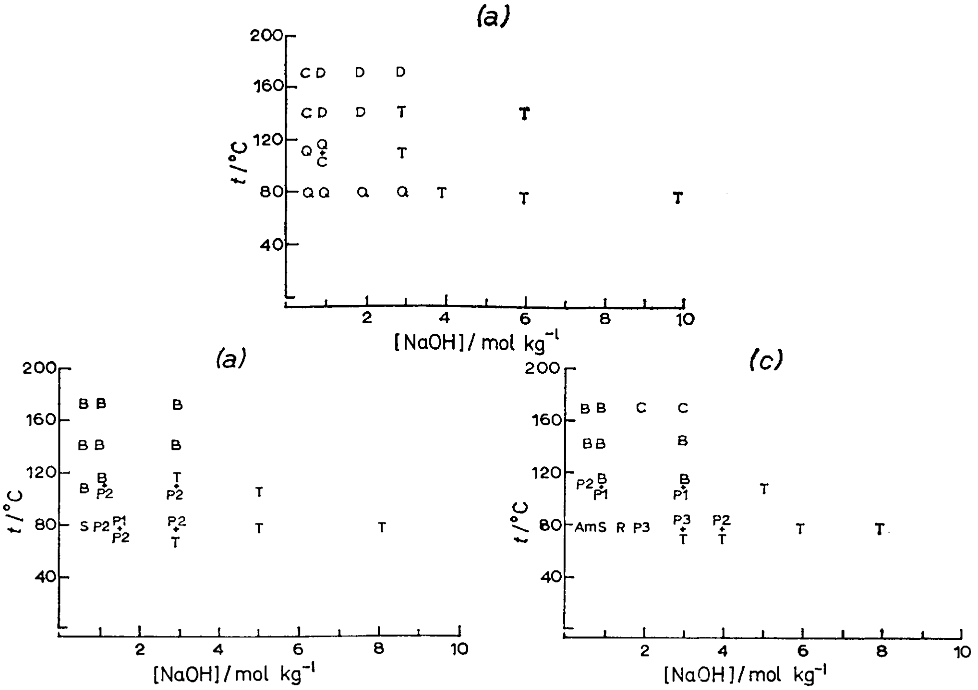

FIGURE 2 Crystallisations from the compositions (a) 1MTK + 1·0—50NaOH + 275H_2O; (b) 1MTK + 4SiO_2 + 2·5—50NaOH + 275H_2O; and (c) 1MTK + 8SiO_2 + 2·5—50NaOH + 275H_2O, showing dependence on temperature and alkalinity

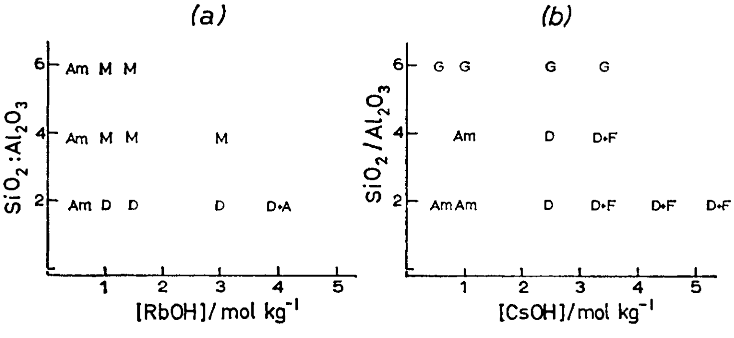

FIGURE 3 Crystallisations of (a) Rb-aluminosilicates and (b) Cs-aluminosilicates at 80 °C as functions of the ratios $SiO_2 : Al_2O_3$ and of alkali concentration

45LiOH + 275H_2O; and 1MTK + 8SiO_2 + 2·5—45LiOH + 275H_2O, normally after a period of 7 days, are shown in Figure 1(a), (b), and (c) respectively. From metakaolinite without added silica the aluminous zeolite Li-A of Barrer and White[9] and Li-metasilicate (Li-D) were the only products [Figure 1(a)]. The higher the temperature the lower the alkali concentration at which the products appeared, but the metasilicate required a higher concentration of LiOH than the zeolite. When 4 mol of SiO_2 were added to each mol of metakaolinite the siliceous zeolite Li-H[9] also appeared in admixture with Li-A or Li-D. With 8 mol of SiO_2 per mol of metakaolinite, Li-H was already observed a few degrees above 100 °C [Figure 1(c)].

Li-A forms from kaolinite[12] as well as from metakaolinite, or from gels.[9] In all these or other[7,13,14] Li-aluminosilicate syntheses it is of interest that bikitaite, the only naturally occurring Li-zeolite, has not so far been observed, although this zeolite has been reported as a hydrothermal transformation product of Li-gmelinite.[15]

The Sodium-bearing Crystals.—Figures 2(a), (b), and (c) show crystallisation areas, usually after 7 days, from the compositions: 1MTK + 1·0—50NaOH + 275H_2O; 1MTK + 4SiO_2 + 2·5—50NaOH + 275H_2O; and 1MTK + 8SiO_2 + 2·5—50NaOH + 275H_2O. From these compositions hydroxysodalite always formed as a low-temperature product under the most alkaline conditions. At the higher experimental temperatures hydroxycancrinite, nepheline hydrate I, and analcite were most common. Other low-temperature products were the zeolites Na-Q (Linde Sieve A type), Na-S (gmelinite-type) Na-P (gismondite-type), and Na-R (faujasite-type). Na-Q was the only one of these zeolites to appear from metakaolinite alone, but was not found in significant amounts when $SiO_2 : Al_2O_3$ = 6 or 10. At 80 °C and after 7 days the appearance sequences of crystals in order of increasing molalities of alkali (given in parentheses) were as shown in Table 2.

TABLE 2

$SiO_2 : Al_2O_3$ = 2	Na-Q (0·2 to 3); Na-T (4 to 10)
$SiO_2 : Al_2O_3$ = 6	Na-S (0·5); Na-R (1·0); Na-P (1 to 3); Na-T (5 to 8)
$SiO_2 : Al_2O_3$ = 10	Na-S (0·5 to 1); Na-R (1·5); Na-P (2 to 4); Na-T (3 to 8)

Rubidium- and Caesium-bearing Crystals.—The crystal-

TABLE 3

Crystalline products obtained with mixed bases

Bases	Crystal designations	Crystal types
NaOH + KOH	(Na,K)-D,*Kal* *	Kaliophilite
	(Na,K)-F	Like zeolite K-F[11]
	(Na,K)-G	Chabazite type
	(Na,K)-M	Like zeolite K-M[11]
	(Na,K)-P1	Pseudo-cubic, gismondite-like
	(Na,K)-P2	Pseudo-tetragonal, gismondite-like
	(Na,K)-Q	Linde A type
	(Na,K)-S	Gmelinite type
	(Na,K)-T	Hydroxysodalite
NaOH + LiOH	(Na,Li)-A	Like zeolite Li-A[9]
	(Na,Li)-C	Hydroxy cancrinite
	(Na,Li)-D	Metasilicate[9]
	(Na,Li)-F	Like zeolite K-F[11]
	(Na,Li)-P1	Pseudo-cubic, gismondite-like
	(Na,Li)-P2	Pseudo-tetragonal, gismondite-like
	(Na,Li)-R	Near-faujasite
	(Na,Li)-S	Gmelinite type
	(Na,Li)-T	Hydroxysodalite
	(Na,Li)-U	Layer silicate, like hectorite
KOH + LiOH	(K,Li)-A	Like Li-A[9]
	(K,Li)-D	Metasilicate[9]
	(K,Li)-D,*Kal* *	Kaliophilite
	(K,Li)-F	Like K-F[11]
	(K,Li)-G	Chabazite type
	(K,Li)-M	Like K-M[11]
	(K,Li)-S	Gmelinite type
	(K,Li)-U	Layer silicate, like hectorite
NaOH + NMe_4OH	(Na,Me_4N)-C	Hydroxycancrinite type
	(Na,Me_4N)-P1	Pseudo-cubic, gismondite type
	(Na,Me_4N)-Q	Like Linde A
	(Na,Me_4N)-R	Faujasite-type
	(Na,Me_4N)-T	Hydroxysodalite type
	(Na,Me_4N)-V	Like Linde zeolite N[19]

* To distinguish this phase from (K,Li)-D (metasilicate), *Kal* is added to the original letter designation,[11] to indicate the kaliophilite structure.

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[13] H. Borer, and W. M. Meier, in 'Molecular Sieve Zeolites,' Advances in Chemistry Series, No. 101, Amer. Chem. Soc., 1971, 123.

[14] C. Ruiz-Menacho and R. Roy, *Bull. Geol. Soc. Amer.*, 1959, **70**, 1666.

[15] H. Hoss and R. Roy, *Beitr. Mineral. u. Petrog.*, 1960, **7**, 389.

lisation fields from the compositions in which $SiO_2 : Al_2O_3 = 2$, 4, and 6 are shown in Figure 3(a) and (b). As compared with reactions with NaOH at 80 °C crystallisations when RbOH or CsOH were the bases required higher concentrations [$\geqslant$0·5 molal (m) with RbOH and $\geqslant$1 m with CsOH]. The similarity between some of the reactions of RbOH and of CsOH with the reaction mixtures and those of KOH with the same compositions [16] suggests that the absence in nature of Rb-rich aluminosilicates (except a Rb-rich felspar [17]) or Cs-aluminosilicates (except pollucite) is largely a consequence of their low concentration in the lithosphere. Natural phillipsite is selective for the large ions K^+, Rb^+, and Cs^+ in preference to Na^+.[18] However, the phillipsite-type zeolite, M, formed at 80 °C with KOH and RbOH but not with CsOH.

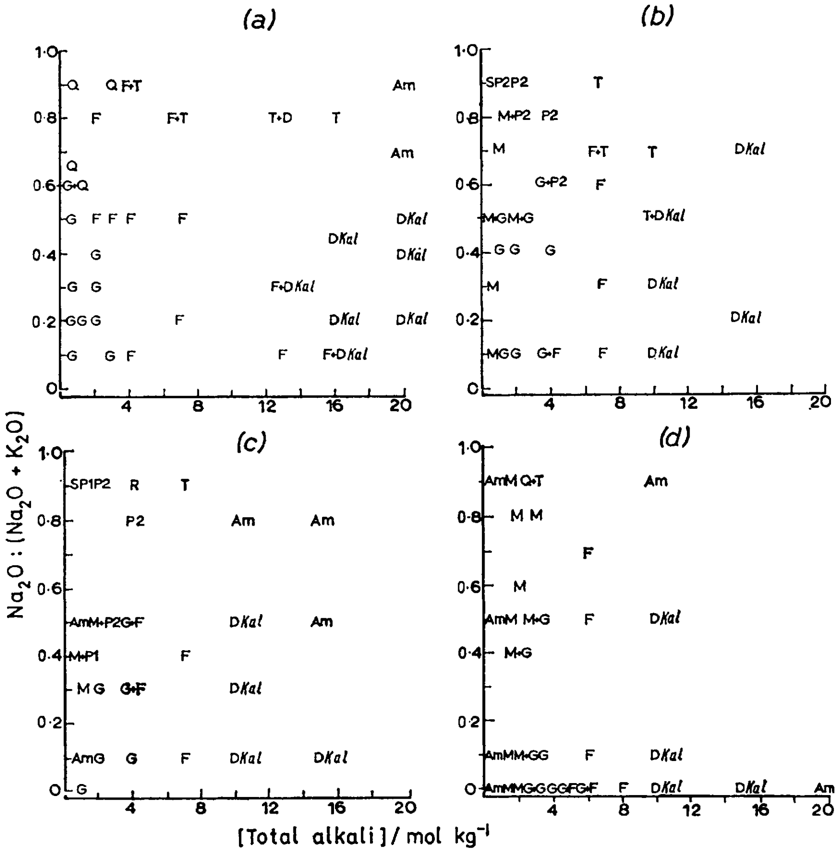

FIGURE 4 Crystallisation at 80 °C of aluminosilicates from mixed NaOH + KOH as a function of cation fraction of Na^+, $SiO_2 : Al_2O_3$, ratio and total alkali concentration. The compositions were (a) 1MTK + 2·8—100[mKOH + (1 − m)NaOH] + $275H_2O$; (b) 1MTK + 2·8—75[mKOH + (1 − m)NaOH] + $4SiO_2$ + $275H_2O$; (c) 1MTK + 2·8—75[mKOH + (1 − m)NaOH] + $6SiO_2$ + $275H_2O$; (d) 1MTK + 2·8—100[mKOH + (1 − m)NaOH] + $8SiO_2$ + $275H_2O$; m varies in the range 0 to 1

Crystallisation Reactions with Mixed Bases.—Reactions of metakaolinite, with and without added silica, with the base pairs NaOH + KOH, NaOH + LiOH, KOH + LiOH, and NaOH + NMe_4OH yielded the products [9,11,19] given in Table 3. Crystallisation fields at low temperatures are shown for the four pairs of bases in Figures 4, 5, 6, and 7 respectively, in which the cation fraction of one ion of each pair is plotted against the total base concentration. These Figures therefore show how both these variables influenced the reactions. For example, from Figure 4, (Na,K)-Q required high cation fractions of Na (X_{Na}) and low total alkali concentration; (Na,K)-T also required high X_{Na} but this time high total alkali concentration. From Figure 6 the layer silicate, (K,Li)-U, required high X_{Li}, as did (K,Li)-A. Various other examples of this behaviour can be seen from the Figures. Structure-directing influences of the cations of the four base pairs are clearly evident. Thus P1, P2, Q, R, and T did not normally form in absence of Na^+; G, M, and D, *Kal* similarly required K^+; A, C, D, and U did not form in absence of Li^+; while zeolite V appeared only in presence of Me_4N^+. Zeolites F and S appeared with all pairs save NaOH + Me_4NOH.

Characterisation of the Products.—The crystalline phases of Tables 1 and 3 fall into three classes. These are *non-zeolite hydrated phases, anhydrous non-zeolites,*

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[16] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton* 1972, 1254.

[17] O. J. Adamson, *Geol. För. Förh.* (*Stockholm*), 1942, **64**, 19.

[18] R. M. Barrer and B. Munday, *J. Chem. Soc.* (*A*), 1971, 2904.

[19] N. A. Acara, 1968, U.S.P. 3,414,602 to Union Carbide Corp.

and many *zeolites*. Some of these phases are described below.

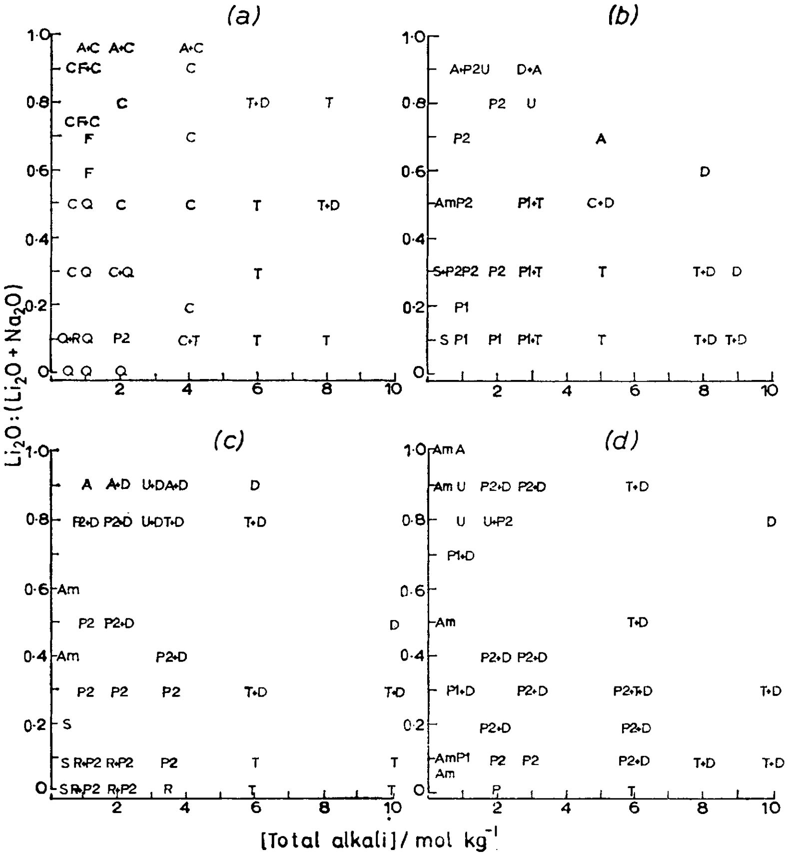

FIGURE 5 Crystallisation at 80 °C of aluminosilicates from mixed NaOH + LiOH as a function of cation fraction of Li^+, $SiO_2 : Al_2O_3$, ratio and total alkali concentration; (a) 1MTK + 2·5—40[*m*NaOH + (1 − *m*)LiOH] + $275H_2O$; (b) 1MTK + 2·5—45[*m*NaOH + (1 − *m*)LiOH] + $4SiO_2$ + $275H_2O$; (c) 1MTK + 2·5—50[*m*NaOH + (1 − *m*)LiOH] + $6SiO_2$ + $275H_2O$; (d) 1MTK + 2·5—50[*m*NaOH + (1 − *m*)LiOH] + $8SiO_2$ + $275H_2O$; *m* varies in the range 0 to 1

Hydrated Non-zeolites.—Nepheline hydrate I. Na-J was made hydrothermally from gels in 1952.[10] In the present work it was the main product from metakaolinite above 140 °C [Figure 2(a)]. The composition was $Na_2O,Al_2O_3,2SiO_2,H_2O$. The water was lost in the t.g.a. trace in a two-step dehydration where *ca.* 1% was lost below 200 °C and *ca.* 4% between 200 and 400 °C. Above this temperature there was no further weight loss, but lattice breakdown had occurred by 500 °C. A sample heated to 350 °C failed to re-imbibe water. In accord with the two-step water loss the d.t.a. trace showed two endothermal stages. The unit cell of nepheline hydrate I was indexed according to the orthorhombic unit cell suggested by Edgar.[20] This led to the calculated and observed *d*-spacings of Table 4. Although for most *d*-spacings agreement is excellent some discrepancies (*e.g.*, for *d* = 4·72, 4·39, and 2·602 Å) may mean that Edgar's suggestion does not represent the true unit cell.

The layer silicates (Na,Li)-U *and* (K,Li)-U. These phases crystallised at 80 °C from compositions in which the aqueous alkali was from 1 molal upwards (Figures 5 and 6). The *X*-ray powder pattern showed the broad, diffuse bands characteristic of smectites, and the *d*-spacings are compared with those of hectorite in Table 5. The products were obtained as very small aggregates of

TABLE 4

Calculated and observed *d*-spacings/Å of Na-J, for the orthorhombic cell *a* = 8·21, *b* = 7·47, and *c* = 5·23 Å

Intensity	Indices	d_{obs}	d_{calc}
m	100	8·3	8·21
m	010	7·47	7·47
mw	110	5·52	5·52
w	101	4·72	4·41
s	011	4·39	4·28
w	200	4·10	4·10
w	111	3·79	3·80
w	210	3·61	3·60
s	120	3·401	3·400
w	201	3·225	3·229
s	211	2·961	2·964
m	121	2·848	2·850
ms	002	2·602	2·615
s	221	2·443	2·443
w	311	2·304	2·306
w	320	2·200	2·207
w	131	2·172	2·168
w	212	2·111	2·115

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[20] A. D. Edgar, *Amer. Mineralogist*, 1964, **49**, 1139.

crystals. Li^+, the cation essential for this layer silicate, is probably present in interlayer as well as octahedral sites. It promotes the growth of layer silicates in solutions much more alkaline than those from which smectites are usually synthesised.

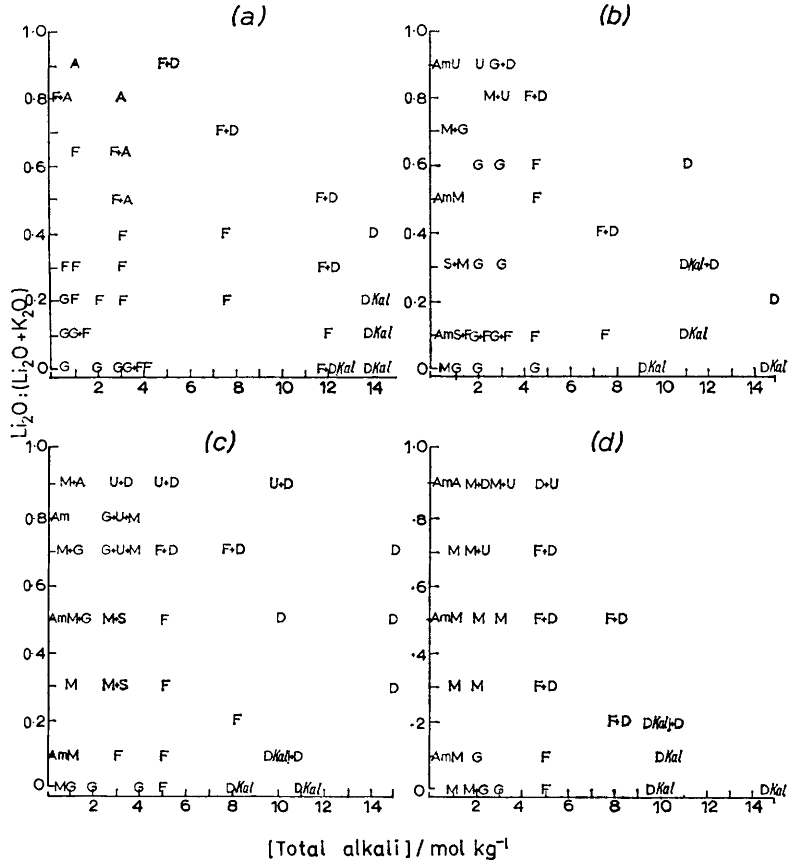

FIGURE 6 Crystallisation at 80 °C of aluminosilicates from mixed KOH + LiOH as a function of cation fraction of Li^+, $SiO_2:Al_2O_3$ ratio and total alkali concentration; (a) 1MTK + 2·5—90[mKOH + $(1-m)$LiOH] + $275H_2O$; (b) 1MTK + 2·5—75[mKOH + $(1-m)$LiOH] + $4SiO_2$ + $275H_2O$; (c) 1MTK + 2·5—75[mKOH + $(1-m)$LiOH] + $6SiO_2$ + $275H_2O$; (d) 1MTK + 2·5—50[m KOH + $(1-m)$LiOH] + $8SiO_2$ + $275H_2O$; m varies in the range 0 to 1

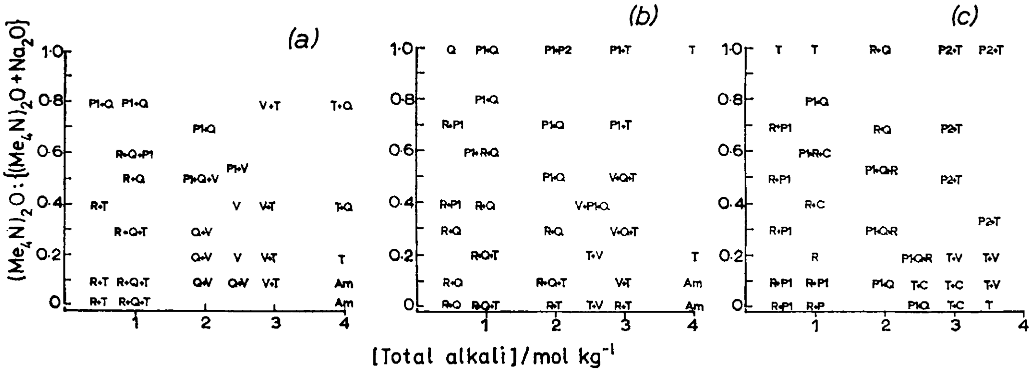

FIGURE 7 Crystallisation at 85 °C of aluminosilicates from mixed NaOH + Me_4NOH as a function of cation composition, $SiO_2:Al_2O_3$ ratio and total alkali concentration; (a) 1MTK + 2—10[mNaOH + $(1-m)Me_4NOH$] + $275H_2O$; (b) 1MTK + 2·8—20[m(NaOH + $(1-m)Me_4NOH$] + $4SiO_2$ + $275H_2O$; (c) 1MTK + 2·8—18[mNaOH + $(1-m)Me_4NOH$] + $8SiO_2$ + $275H_2O$; m varies in the range 0 to 1

The Anhydrous Phases.—The anhydrous species will not be considered further. The main interest of this group is the very low temperature at which it is possible to prepare anhydrous aluminosilicates and silicates in hydrothermal systems. Such species are sometimes considered as relatively high-temperature, often pyrolytically formed, products.

The Zeolites.—Li-A, (Na,Li)-A, *and* (K,Li)-A. The structure of this zeolite, first grown from gels in 1951,[9] has no relation with that of Linde Sieve A, nor does it have any natural counterpart. It was a major low-temperature product with LiOH as base under not too alkaline conditions (Figure 1). The best crystalline product in this work was obtained at 110 °C. The *d*-spacings and intensities of the preparations of the present work were in agreement with those of the earlier preparations.[9,12]

TABLE 5

d-Spacings/Å of U and of hectorite

(K,Li)-U	*hkl*	Hectorite
13	001	12
4·5	020, 110	4·6
3·2	004	3·2
2·55	200, 130	2·6
1·70	150, 240, 310	1·72
1·50	330, 060	1·51

Li-H. This silica-rich zeolite co-crystallised with Li-A from the compositions in which $SiO_2 : Al_2O_3 = 6$ and 10, but was not obtained pure. The *d*-spacings and intensities corresponded with those of the original preparation [9] made from gels. Like Li-A, Li-H has no natural counterpart and the structure is unknown.

Phases with Analcite Structure: Na-B *and* Cs-G.—Preparations of Na-B, made between 110 and 170 °C, were well crystallised in the habit shown in Plate 1(a). The *X*-ray powder patterns were almost identical with that of a natural analcite. Two preparations made under identical conditions, except for the concentration of NaOH, had the unit cell dimensions and volumes given in Table 6. The analcite made from 1·0N-NaOH had the larger unit cell, in accord with the observation that the higher the alkali concentration the more aluminous the phase which crystallises.[21]

TABLE 6

Concn. of NaOH	Cell edge/Å	Cell volume/Å^3
0·5N	13·694 ± 0·004	2568 ± 2·0
1·0N	13·723 ± 0·002	2584 ± 0·5

A sample was heated in a Guinier–Lenné camera to 800 °C. The film was measured and the unit cells were found to change with temperature as shown in Table 7. The t.g.a. curve showed that the unit-cell changes tended to follow the weight loss, while the d.t.a. curve indicated the main endothermic dip to be at *ca.* 440 °C. The water loss occurred in the range 300—500 °C. These are high temperatures for zeolitic dehydration and are due to a low mobility of water in the restricted channels in the analcite framework.[22]

TABLE 7

t/°C	Cubic cell edge/Å
25	13·78
275	13·77
360	13·73
420	13·67
590	13·63

Cs-G, the synthetic analogue of pollucite, is isostructural with analcite. The synthetic phase, Cs-G, was anhydrous, like that made at 165 °C from CsOH(aq) and aluminosilicate gels.[1] It had a cubic cell with $a = 13{\cdot}7$ Å and was the only crystalline phase observed at 80 °C when the parent mixture had $SiO_2 : Al_2O_3 = 6$. It was not observed when this ratio was 4 or 2 (Figure 3). The phase is notable for its great thermal stability.[1]

The Cancrinite-type Phases Na-C, (Na,Li)-C, *and* (Na,Me_4N)-C.—When NaOH was the only base, cancrinite hydrate appeared in 100% yields at 170 °C to give perfectly shaped hexagonal rods such as those in Plate 1(b). From sodium aluminosilicate gels hydrothermal growth of cancrinite hydrate was restricted to high temperatures of *ca.* 330 to 450 °C,[10] but by addition of certain salts to the kaolinite + NaOH system cancrinite hydrate could be formed even at 80 °C.[23] In the present work syntheses at 80 °C were also effected by replacing NaOH with the mixed bases LiOH + NaOH. (Na,Me_4N)-C also formed from mixtures where $SiO_2 : Al_2O_3 = 10$ at 85 °C and with $NaOH + Me_4NOH$. It was however always co-crystallised with other zeolites, as shown in Figure 7.

The Na-C formed at 170 °C had a hexagonal unit cell with $a = 12{\cdot}7$ and $c = 5{\cdot}31$ Å. Small differences in unit-cell dimensions were observed among different preparations, as found also by Barrer and White.[10] The variations in unit cells may arise from different proportions of intracrystalline H_2O, NaOH, and possibly silicate anions. The compositions were determined of a series of cancrinites made with different proportions of the mixed bases NaOH + LiOH. When the cation composition of the solution was plotted against that of the crystals the isotherm was coincident with that for the equilibrium exchange $Li^+ \rightleftharpoons Na^+$ measured by Barrer and Falconer.[24]

Zeolites Related to K-F.—A number of compounds of structural types closely related to that of K-F [11] have been synthesised in this work [Rb-D, Cs-A, (Na,Li)-F, (K,Li)-F, and (Na,K)-F]. Such zeolites have been grown in the diverse range of crystallisation fields [1,11-13,25-27] illustrated in Table 8. Unit cells or pseudo-cells have been determined for Rb-D (this work) and for K-F, K-F(KCl), K-F(KBr), and K-F(KI).[26,28-30] These are given in Table 9 together with unit cells of several zeolites of the natrolite group. K-F and its related species may well belong to this group, particularly in

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[21] *Cf.*, S. P. Zdhanov, in 'Molecular Sieves,' Soc. Chem. Ind., 1968, p. 70.

[22] W. H. Taylor, *Z. Krist.*, 1930, **74**, 1.

[23] R. M. Barrer and J. F. Cole, *J. Chem. Soc.* (*A*), 1970, 1516.

[24] R. M. Barrer and J. D. Falconer, *Proc. Roy. Soc.*, 1956, *A*, **236**, 227.

[25] R. M. Barrer, L. Hinds, and E. A. D. White, *J. Chem. Soc.*, 1953, 1466.

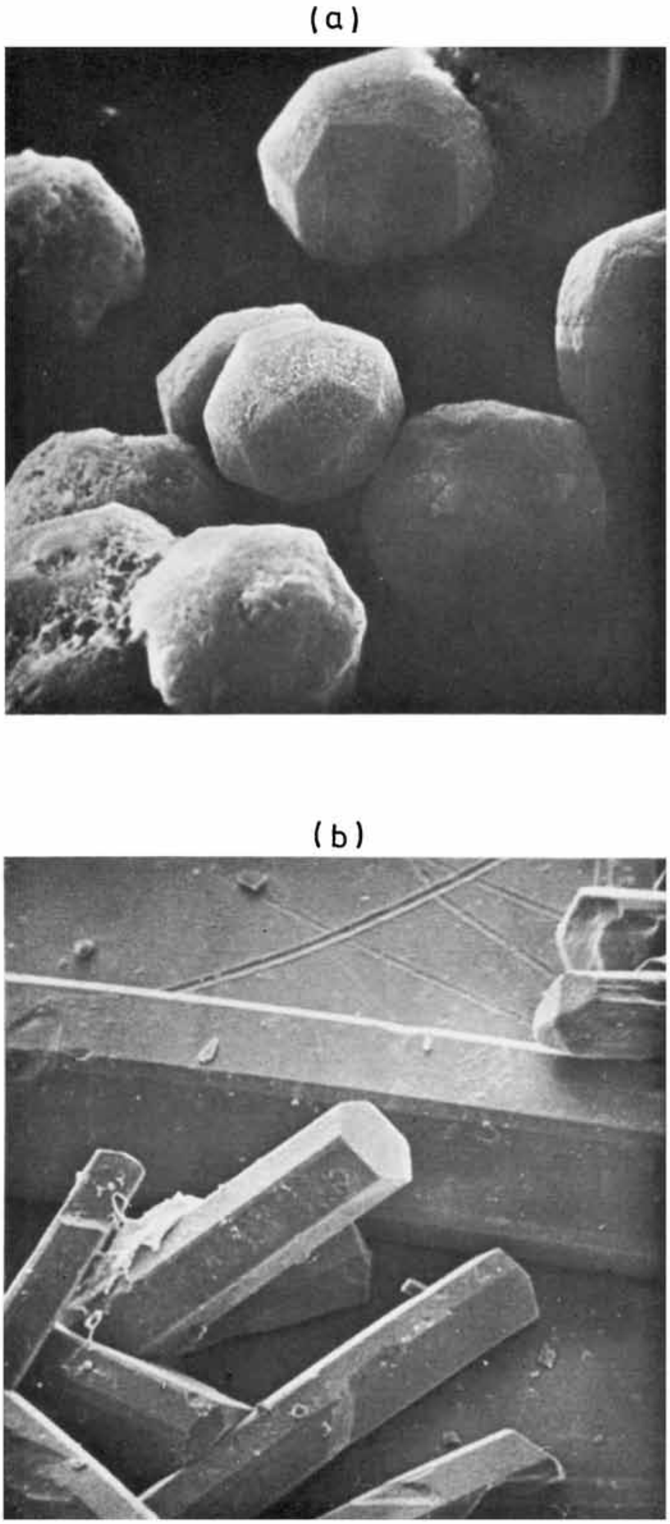
[26] R. M. Barrer and C. Marcilly, *J. Chem. Soc.* (*A*), 1970, 2735.

[27] R. M. Barrer, C. Colella, and (Mme) R. Beaumont, unpublished work.

[28] Ch. Baerlocher, personal communication.

[29] See W. M. Meier and D. H. Olson, in 'Molecular Sieve Zeolites,' Advances in Chemistry Series, No. 101, Amer. Chem. Soc., 1971, p. 155.

[30] W. H. Taylor, *Mineralog Mag.*, 1935, **24**, 208.



PLATE

view of the 6·6 Å unit or multiple of this unit characteristic of the *c* axes. The particular ' fibrous ' zeolite to which K-F is most closely related is evidently still to be found and is the subject of further investigation.

The *X*-ray powder patterns of preparations of (Na,K)-F showed that the unit-cell size changed with the cation fraction of Na^+. For certain values of this fraction two diffraction patterns with slightly different *d*-spacings were present indicating two very similar co-existing phases. Exchange isotherms for Na $\rightleftharpoons$ K and Na $\rightleftharpoons$ Li have both indicated immiscibility gaps.[31]

TABLE 8

Some syntheses of zeolites related to the K-F structure

Designations of variants	Oxide composition	Synthesis conditions
K-F	$K_2O,Al_2O_3,2SiO_2,3H_2O$	<150 °C, K-aluminosilicate gels [11]
	$K_2O,Al_2O_3,2SiO_2,3H_2O$	80 °C, KOH(aq) + kaolinite [12]
	$K_2O,Al_2O_3,2{\cdot}1SiO_2,3H_2O$	80 °C, KOH(aq) + metakaolinite [16]
Rb-D	$Rb_2O,Al_2O_3,2SiO_2,H_2O$	165 °C, Rb-aluminosilicate gels [1]
	$Rb_2O,Al_2O_3,2SiO_2,2{\cdot}6H_2O$	80 °C, RbOH(aq) + kaolinite [12]
	$Rb_2O,Al_2O_3,2SiO_2,2{\cdot}5H_2O$	80 °C, RbOH(aq) + metakaolinite
Cs-D	$Cs_2O,Al_2O_3,2SiO_2,2{\cdot}4H_2O$	80 °C, CsOH(aq) + kaolinite [1]
		80 °C, CsOH(aq) + metakaolinite
Na,Li-F	$0{\cdot}8Li_2O,0{\cdot}2Na_2O,Al_2O_3,2SiO_2,3H_2O$	80 °C, NaOH, LiOH(aq) + metakaolinite
Na,Li-F	$0{\cdot}75Li_2O,0{\cdot}25Na_2O,Al_2O_3,2SiO_2,3{\cdot}2H_2O$	100 °C, (Na,Li)-aluminosilicate gels [13]
(Na,K)-F	$(NaK)_2O,Al_2O_3,xSiO_2,yH_2O$ *	80 °C, NaOH, KOH(aq) + metakaolinite
(K,Li)-F	$(Li,K)_2O,Al_2O_3,xSiO_2,yH_2O$ *	80 °C, KOH, LiOH(aq) + metakaolinite
Species N	$K_2O,Al_2O_3,4SiO_2,yKCl$ *	200—450 °C, analcite + excess of KCl [25]
K-F(KCl)	$K_2O,Al_2O_3,2{\cdot}54SiO_2,0{\cdot}8KCl,0{\cdot}5H_2O$	100 °C, K-aluminosilicate gels + excess of KCl [26]
K-F(KCl)	$K_2O,Al_2O_3,2SiO_2,0{\cdot}3KCl,2{\cdot}5H_2O$	80 °C, KOH(aq), KCl (excess) + kaolinite [26]
Species O	$K_2O,Al_2O_3,4SiO_2,yKBr$ *	200—450 °C, analcite + excess of KBr [25]
K-F(KBr)	$K_2O,Al_2O_3,2{\cdot}53SiO_2,0{\cdot}72KBr,0{\cdot}4H_2O$	200 °C, K-aluminosilicate gels + excess of KBr [26]
K-F(KBr)	$K_2O,Al_2O_3,2SiO_2,0{\cdot}2KBr,2{\cdot}5H_2O$	80 °C, KOH(aq), KBr (excess) + kaolinite [26]
K-F(KI)	$K_2O,Al_2O_3,2{\cdot}52SiO_2,0{\cdot}45KI,0{\cdot}5H_2O$	200 °C, K-aluminosilicate gels + excess of KI [26]
(Ba,Li)-F	$(Ba,Li_2)O,Al_2O_3,xSiO_2,yH_2O$	80 °C, $Ba(OH)_2$, LiOH(aq) + metakaolinite [27]

* Values of *x* and *y* not determined.

TABLE 9

Unit cells for zeolites related to K-F and for some natrolite-group zeolites

Phase	Unit-cell type	Cell dimensions/Å
K-F	Orthorhombic	$a = 14{\cdot}02$, $b = 13{\cdot}92$, $c = 13{\cdot}14$ [28]
Rb-D	Tetragonal, body centred	$a = 9{\cdot}98$, $c = 13{\cdot}23$
K-F(KCl)	Tetragonal, body centred	$a = 9{\cdot}83$, $c = 13{\cdot}12$ [26]
K-F(KBr)	Tetragonal, primitive	$a = 9{\cdot}79$, $c = 6{\cdot}54$ [26]
K-F(KI)	Tetragonal, primitive	$a = 9{\cdot}81$, $c = 6{\cdot}59$ [26]
Thomsonite	Orthorhombic	$a = 13{\cdot}07$, $b = 13{\cdot}08$, $c = 13{\cdot}18$ [29]
Natrolite	Orthorhombic	$a = 18{\cdot}30$, $b = 18{\cdot}63$, $c = 6{\cdot}60$ [29]
Edingtonite	Orthorhombic, primitive	$a = 9{\cdot}54$, $b = 9{\cdot}65$, $c = 6{\cdot}50$ [29]
K-edingtonite	Orthorhombic	$a = 19{\cdot}46$, $b = 20{\cdot}04$, $c = 13{\cdot}36$ [30]

In contrast, (Li,K)-F shows no immiscibility gap. Various preparations were analysed and the Li^+ cation fraction in solution was plotted against this fraction in the crystals. Over the experimental range where the cation fraction was between 0·2 and 0·65 the continuous isotherm was similar in position to, though somewhat smaller in slope than, the equilibrium exchange isotherm determined by Barrer and Munday,[31] which also showed no immiscibility gap.

Crystallisation fields of zeolites are often such that two or more products co-crystallise over considerable ranges of composition of the parent magma. However, the boundary between (Li,K)-F and (Li,K)-A was relatively sharp and crystallisation across the boundary region served to measure the change in yields of each. These yields were determined by intensity measurements relative to an internal standard (ZnO) of the 2·95 Å line of K-F and the 3·01 Å line of Li-A. Figure 8 shows that the yield of (Li,K)-A increased smoothly to 100% while that of (Li,K)-F showed a plateau region before declining toward zero.

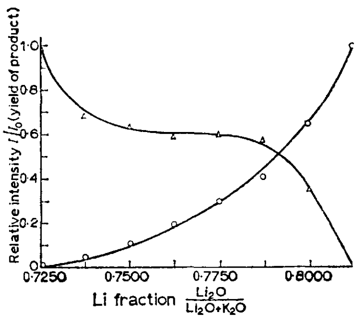


FIGURE 8 Yields of (Li,K)-A and of (Li,K)-F as functions of the cation fraction of Li; ○, A, 2·95 Å; △, F, 3·01 Å

The Chabazite-like Zeolite (K,Na)-G.—This zeolite was the analogue of the near-chabazite, K-G, described elsewhere.[11,16] In the K-rich part of the crystallisation field the *X*-ray powder pattern showed both sharp and diffuse lines; as the crystallising mixture became richer

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[31] R. M. Barrer and B. Munday, *J. Chem. Soc.* (*A*), 1971, 2914.

in Na all lines became sharp. For a particular aluminous preparation which had the oxide composition $0·4K_2O,0·6Na_2O,Al_2O_3,2SiO_2,3H_2O$ the hexagonal unit cell had $a = 13·710 \pm 0·001$ and $c = 15·713 \pm 0·003$ Å. The unit cells of the K- and Na-exchanged forms of this preparation had respectively $a = 13·737 \pm 0·002$, $c = 15·772 \pm 0·005$; and $a = 13·682 \pm 0·006$, $c = 15·650 \pm 0·001$ Å. The unit-cell dimensions thus change appreciably with cation fractions of K^+ and Na^+.

Zeolites Related to K-M.—The phases Rb-M, (Na,K)-M, and (Li,K)-M were all similar to the zeolite K-M [11] which resembles phillipsite. Rb-M formed from compositions where $SiO_2 : Al_2O_3$ was 4 and 6, and (Na,K)-M and (Li,K)-M, from compositions where this ratio was 6, 8, and 10. An analysed sample of (Na,K)-M had the oxide composition $0·7K_2O,0·3Na_2O,Al_2O_3,5·9SiO_2,4H_2O$ and so was a siliceous form of the zeolite. In the natural phillipsite studied by Steinfink [32] the ratio $SiO_2 : Al_2O_3$ was 4·4, and in the synthetic near-phillipsites (ZK19) reported by Kuhl [33] $3·26 \leqslant (SiO_2 : Al_2O_3) \leqslant 6·22$. The *X*-ray diffraction pattern of our sample was very sharp and indexed to an orthorhombic unit cell with $a = 9·957 \pm 0·003$, $b = 14·248 \pm 0·004$, and $c = 14·246 \pm 0·010$ Å. These figures may be compared with $a = 9·96_5$, $b = 14·25_2$, and $c = 14·25_2$ Å for the phillipsite examined by Steinfink.[32] D.t.a. and t.g.a. traces of the K-exchanged forms of (K,Na)-M and of phillipsite were compared with each other and with these traces for the parent (K,Na)-M and for Rb-M. All showed two endothermal stages of water loss below *ca.* 300 °C. (K,Na)-M outgassed at 350 °C, like K-M, would not sorb O_2 at 78 K or n-butane at 273 K. However at high pressures and temperatures K-M and phillipsite each sorb substantial amounts of gases like Kr and Ar.[34]

TABLE 10

d-Spacings/Å of Rb-M and K-M

Rb-M		K-M	
d	*I*	*d*	*I*
—	—	10·22	mw
8·37	ms	$8·35_2$	m
7·16	ms	$7·14_9$	m
5·40	m	$5·38_4$	m
5·07	sd *	$5·06_7$	ms
4·48	ms	$4·47_8$	m
4·32	sd	4·307	m
—	—	4·115	mw
3·67	mw	3·664	m
—	—	3·530	w
—	—	3·245	s
3·192	vsd	3·185	sd
3·172	w	3·169	m
2·975	ms	2·973	s
—	—	2·786	m
2·741	sd	2·736	mw
—	—	2·678	mw
2·562	ms	2·555	mw
2·429	mw	2·426	m
—	—	2·378	mw
2·194	mw	2·185	mw
2·170	w	2·169	mw
2·147	mw	2·150	vw

* d Denotes diffuse.

Rb-M has not previously been synthesised. Accordingly *d*-spacings and intensities are compared in Table 10 with those of K-M. The water loss after equilibration at 56% R.H. was 12·6% and for the K-exchanged form was 14·4%. Rb-M was notable in that even after being heated to 1000 °C in t.g.a. it retained its structure.

The Near-Gismondites Na-P.—The phases Na-P1 (pseudo-cubic), Na-P2 (pseudo-tetragonal), and Na-P3 (pseudo-orthorhombic) were observed over a range of compositions and temperatures (Figure 2). Na-P3 was not often observed, nor was there any apparent correlation between the initial composition or the temperature and the appearance of Na-P1 and Na-P2. However these zeolites did not form from metakaolinite unless SiO_2 was added. Analyses of some preparations [35–37] of Na-P have given the oxide compositions of Table 11. That given by Taylor and Roy [37] seems unusual in the $Na_2O : Al_2O_3$ ratio, and is also less siliceous than the other samples of Na-P2. The pseudo-orthorhombic phase, Na-P3, was not analysed because it was always co-crystallised with other species [Figure 2(c)].

TABLE 11

Compositions of some Na-P zeolites

Phase	$SiO_2 : Al_2O_3$ in initial mixture	Oxide formula
Na-P1	4·0	$0·99Na_2O,1·0Al_2O_3,3·40SiO_2,4·0H_2O$
Na-P1 [35]		$1·00Na_2O,1·0Al_2O_3,(3·03—3·65)SiO_2$ $(4·10—4·40)H_2O$
Na-P1 [36]		$1·00Na_2O,1·0Al_2O_3,3·80SiO_2,4·60H_2O$
Na-P2	6·0	$1·00Na_2O,1·0Al_2O_3,4·10SiO_2,4·5H_2O$
Na-P2 [35]		$1·00Na_2O,1·0Al_2O_3,4·40SiO_2,4·6H_2O$
Na-P2 [37]		$0·89Na_2O,1·0Al_2O_3,3·18SiO_2,4·62H_2O$

The pseudo-cell dimensions of one of each of the near-gismondite phases Na-P1 and Na-P2 were respectively $a = 9·99$; and $a = 10·11$ $c = 9·80$ Å. Pseudo-tetragonal unit cells [37] of the K-form of a sample of Na-P2 ($a = 9·93$, $c = 9·67$ Å) and of the Ca-form ($a = 9·88$, $c = 10·30$ Å) may be compared with that of the Na-P2. Various cationic forms of a zeolite Na-P2

TABLE 12

Water contents of cationic forms of Na-P1 and Na-P2

	Na-P1 [38]	Na-P2
Cation	wt % water losses on heating	
Li^+	17·4	17·7
Na^+	15·8	15·2
K^+	10·3	10·5
Rb^+	8·4	8·4
Cs^+	8·6	7·5
Ca^{2+}	19·2	19·3
Sr^{2+}	17·1	17·0
Ba^{2+}	14·8	14·9

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[32] H. Steinfink, *Acta Cryst.*, 1962, **15**, 644.

[33] G. H. Kuhl, in 'Molecular Sieves,' Soc. Chem. Ind., 1968, p. 85.

[34] R. M. Barrer and D. E. W. Vaughan, *Trans. Faraday Soc.*, 1971, **67**, 2129.

[35] H. Borer, Ph.D. Thesis, E.T.H., Zurich, 1969.

[36] A. Dyer and A. Molyneux, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2831.

[37] A. M. Taylor and R. Roy, *Amer. Mineralogist.*, 1964, **49**, 656.

were prepared and the water contents were determined, with the results in Table 12. These are compared with water contents obtained by Barrer and Munday[38] for the same forms derived from Na-P1. The similarity supports the view[38] that Na-P1 and Na-P2 are easily interconvertible without bond-breaking. The d.t.a. traces of the cation exchange forms of Na-P2 show low-temperature endotherms of considerable diversity (Figure 9). The water loss involved more than one stage, and may be influenced by simultaneous lattice changes.

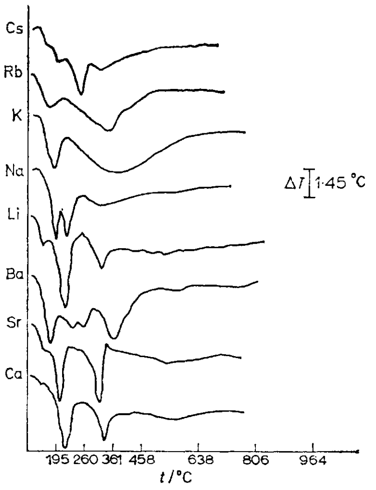

FIGURE 9 D.t.a. traces of cation exchanged forms derived from Na-P2; heating rate 14 K min^{-1} in air

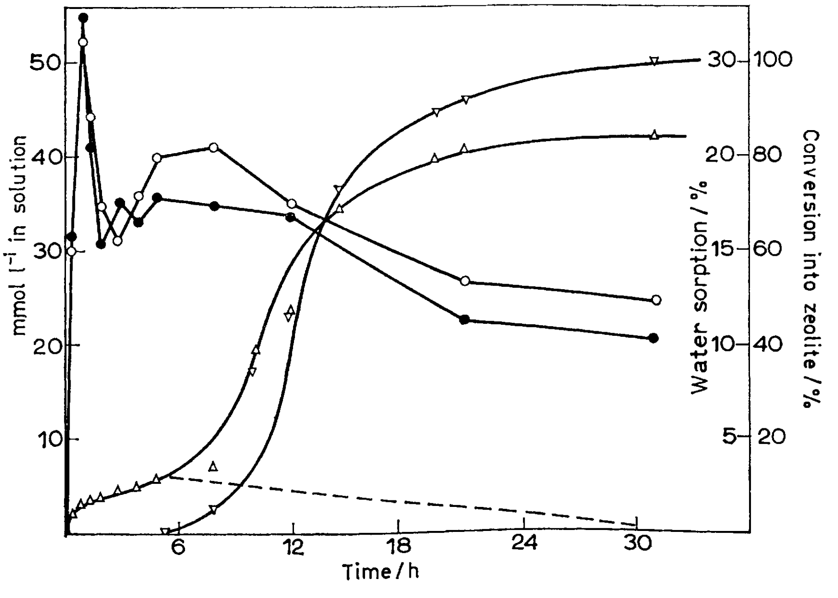

FIGURE 10 Kinetics of formation of Na-Q at 80 °C in 1N-NaOH, using the method of Ciric (ref. 39); ○, Al concn.; ● Si concn.; △ water sorption; ▽ conversion into zeolite

(Na,Li)-P2 generally appeared at higher cation fractions of Li and more frequently than (Na,Li)-P1. One or both were readily formed from MTK + nSiO$_2$ where $n = 4$, 6, and 8 (Figure 5).

The Zeolites related to Linde A: Na-Q, (Na,Li)-Q, *and* (Na,Me$_4$N)-Q.—The zeolite Na-Q formed from metakaolinite at temperatures up to 110 °C. 80—100 °C was adequate for rapid crystallisation in near 100% yields, for concentrations of NaOH between 0·5 and 3N. Under more highly alkaline conditions ready re-crystallisation to hydroxysodalite (Na-T) took place. At 80 °C and with low alkalinity excellent crystals were obtained which were stable in the mother liquor for at least 14 days. The cubic pseudo-cell had $a = 12{\cdot}30$ Å.

The rate of formation of Na-Q, measured at 80 °C in 1N-NaOH, is shown in Figure 10, the water content being used in the way suggested by Ciric[39] to determine the yield of zeolite. Hydration of metakaolinite accounts for the first 'knee' on the curve. The formation of crystals follows the sigmoid contour observed in earlier studies of zeolite growth.[40] The amounts of dissolved Si and Al show high maxima after a short time followed by a rapid and then a more gradual decline. The curves for Si and Al follow each other closely so that Si : Al in solution is always nearly unity. This ratio is unity in the parent metakaolinite, and probably in all the samples of Na-Q. One of these, obtained by use of 2M-NaOH, was analysed and gave the oxide composition Na$_2$O,Al$_2$O$_3$,2SiO$_2$,4·5H$_2$O.

Zeolite (Na,Li)-Q formed from metakaolinite at total alkali concentration 1N when the cation fraction of Li lay between 0·5 and 0. For 0·5 and 2M-alkali this cation fraction was respectively 0·1—0 and 0·3—0

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[38] R. M. Barrer and B. Munday, *J. Chem. Soc.* (*A*), 1971, 2909.
[39] J. Ciric, *J. Colloid Interface Sci.*, 1968, **28**, 315.
[40] *E.g.*, D. Dominé and J. Quobex, in 'Molecular Sieves,' Soc. Chem. Ind., 1968, p. 78.

(Figure 5). (Na,Me_4N)-Q formed at high or low cation fractions of Me_4N^+ for total alkali concentrations between 1 and 2 molal, but also appeared when this concentration was as high as 4M (Figure 7). At 85 °C and for 4 days' reaction time it was always mixed with other phases.

The Faujasite-type Zeolites Na-R, (Na,Li)-R, *and* (Na,Me_4N)-R.—The synthetic analogue of faujasite, Na-R, was not often crystallised. When it did form it was from reaction mixtures more siliceous than those which yielded Na-Q. At 80 °C the best yield of Na-R (*ca.* 70%) appeared after *ca.* 3 days. After this period there was a gradual conversion into Na-P2. The *X*-ray powder pattern was very similar to that of Linde X. (Na,Li)-R appeared together with (Na,Li)-P2 from compositions with $SiO_2 : Al_2O_3 = 8$, alkali concentrations 1 and 2 molal, and cation fractions of Na of 1·0 or 0·9. Thus, its synthesis does not extend appreciably into Li-rich systems.

(Na,Me_4N)-R occurred more frequently than either Na-R or (Na,Li)-R, from the compositions in which the ratio $SiO_2 : Al_2O_3 = 2$, 6, and 10, alkali concentrations from 0·5 to 3 molal, and for both large and small cation fractions of Me_4N^+.

The Zeolites Related to Gmelinite: Na-S, (Na,K)-S, (K,Li)-S, *and* (Na,Li)-S.—The zeolite Na-S gave an *X*-ray powder pattern which exhibited both sharp and diffuse lines. The latter may represent disordering in some planes owing, for example, to stacking faults. Only minimal changes in this pattern were observed among all the samples made. Na-S formed from mixtures with $SiO_2 : Al_2O_3 = 6$ and 10 in regions of low alkalinity (Figure 2). The oxide composition of one analysed preparation was $0{\cdot}99Na_2O,Al_2O_3,4{\cdot}03SiO_2,6{\cdot}0H_2O$.

(Na,K)-S and (Na,Li)-S also formed from silica-rich mixtures at low alkalinity, but only with high cation fractions of Na (Figures 4 and 5). Silica-rich mixtures also yielded (K,Li)-S, with Li cation fractions between 0·1 and 0·5, in this system under more alkaline conditions (Figure 6). These zeolites of gmelinite type were however not seen when NaOH and Me_4NOH were the mixed bases (Figure 7).

Li-, Ca-, NH_4-, and H-forms were prepared from Na-S, and oxygen isotherms at 78 K were measured on some of these [Figure 11(a)]. With the probable exception of NH_4-S the crystals were permeable to oxygen. Intracrystalline sorption was followed at higher relative pressures p/p_0 by surface condensation associated with hysteresis loops closing at p/p_0 between 0·22 and 0·26. Approximate saturation capacities were (in cm^3 at s.t.p. per g of outgassed crystals): Li-S, 160; Ca-S, 142; Na-S, 102; H-S, 58; and NH_4-S, 18. The *X*-ray powder pattern of H-S indicated lattice damage following its preparation by heating the NH_4-form and thus accounts for its low capacity. The Li- and Ca-forms were excellent sorbents of high capacity. Moreover the Li-forms of two different preparations were able to sorb n-butane [Figure 11(b)]. That showing the smaller capacity had been synthesised (by Dr J. F. Cole in these laboratories) in presence of gelatine in an attempt to eliminate stacking faults. Although this sample was subsequently heated in oxygen to remove entrained organic matter it was less satisfactory than its counterpart made without addition of gelatine.

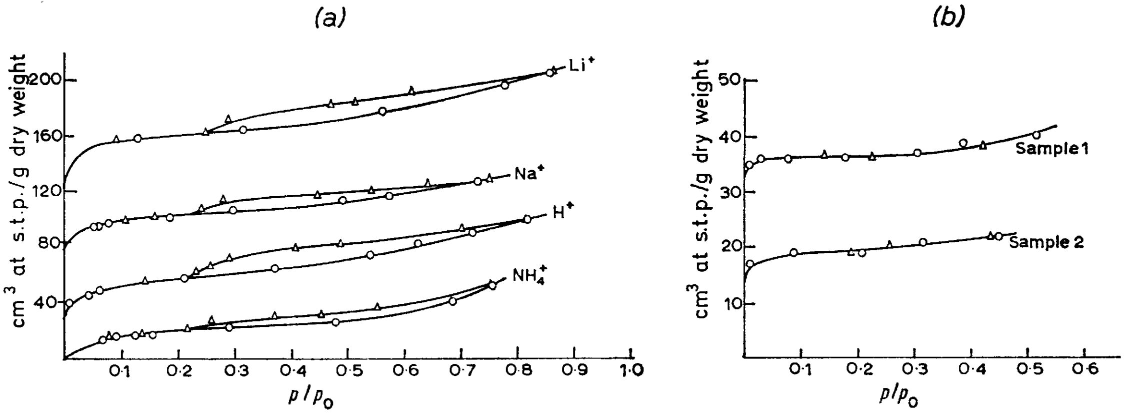

FIGURE 11 Sorption in exchange forms of Na-S; (a) Isotherms of O_2 at 78 K in Li^+-, Na^+-, H^+-, and NH_4^+-exchanged modifications; (b) Isotherms of $n\text{-}C_4H_{10}$ at 273 K in two samples of the Li-exchanged form of Na-S; ○, sorption; △, desorption

The Phases Related to Sodalite: Na-T, (Na,K)-T, (Na,Li)-T, *and* (Na,Me_4N)-T.—These sodalite-type phases were all formed at 80 °C under very alkaline conditions, from metakaolinite alone or from mixtures of metakaolinite and silica. The least alkaline solutions from which the crystals formed were observed when the mixed bases were NaOH + Me_4NOH (Figure 7), although usually they co-crystallised with other phases. The formation of sodalite-type crystals was also possible over a wide range of cation fractions of Me_4N^+, from 0 to 1 in some of these systems. (Na,Li)-T also appeared over a range in cation fractions of Li as high as 0·9 (Figure 5). In silica-rich systems in particular the metasilicate Li-D was a frequent co-crystallisate. (Na,K)-T on the other hand formed only with sodium-rich mixtures of NaOH + KOH.

Na-T appeared over a large area of the most alkaline part of the sodium crystallisation field, between 80 and 140 °C. The more siliceous the parent magma the more alkaline the required solutions. A preparation from metakaolinite and 4M-NaOH at 80 °C had the oxide composition $Na_2O,Al_2O_3,2{\cdot}03SiO_2,0{\cdot}58NaOH,1{\cdot}25H_2O$. The *d*-spacings of sodalite hydrates prepared from metakaolinite and aqueous sodium hydroxide were related to the alkali concentration. Unit cells of different dimensions were also observed when the basic sodalites were made from aluminosilicate gels.[10] In some syntheses the *X*-ray powder patterns appeared to indicate a mixture of two sodalites having different unit cells in the same crystallisate. With 4M-NaOH this did not happen, the cell edge being in a particular preparation $8{\cdot}90_5$ Å, but with 6M-NaOH the cell edges of the two phases were 8·94, and $8{\cdot}91_0$ Å while with 10M-NaOH these edges were $8{\cdot}95_7$ and $8{\cdot}86_3$ Å.

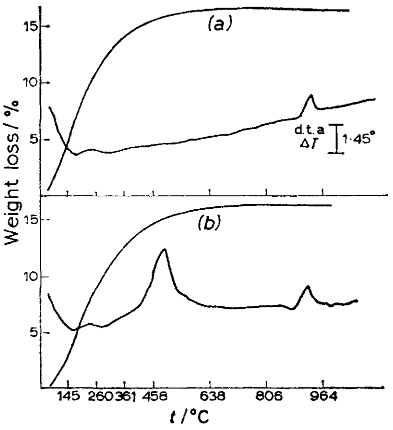

FIGURE 12 The d.t.a. and t.g.a traces of (Na,Me_4N)-V (a) after being heated to 500 °C in air and (b) as prepared

(Na,Me_4N)-V. This zeolite appeared at 80 °C only in the presence of both NaOH + Me_4NOH, from compositions in which $SiO_2 : Al_2O_3 = 2$, 6, or 8 (Figure 7). The richer in silica the parent composition the more concentrated were the mixed bases required to yield the zeolite, which usually crystallised along with other species. The compound gave an intense *X*-ray diffraction pattern with broader diffraction lines than those observed in well crystallised zeolites such as analcite (Na-B). Line-broadening appeared to be due to the small size of the crystallites in the spheroidal aggregates observed under the microscope. The new zeolite was similar to the zeolite termed Linde N.[19] A sample was analysed to give the oxide composition $0{\cdot}88Na_2O,0{\cdot}1(Me_4N)_2O,Al_2O_3,2SiO_2,3H_2O$. Like Linde N it was therefore an aluminous phase. The d.t.a. and t.g.a. traces of the parent crystals and of the same crystals heated at 500 °C in air and rehydrated at room temperature and 56% R.H. are shown in Figure 12(a) and (b). In each case the crystals lost *ca.* 16·5% by weight. The d.t.a. trace of the parent crystals showed an exothermal peak near 500 °C attributable to oxidation of the Me_4N^+ cations, and both samples showed a second exotherm a little above 900 °C.

TABLE 13

d-Spacings/Å of (Na,Me_4N)-V and the products obtained from it by heating

	(Na,Me_4N)-V			First alteration product		Second alteration product	
Indices	d_{obs}	d_{calc}	Intensity	*d*	*I*	*d*	*I*
001	21·54	21·56	m	4·25	s	8·7	mw
100	$13{\cdot}09_4$	13·082	ms	3·60	s	5·0	m
101	$11{\cdot}19_2$	11·185	ms	2·22	vw	4·35	s
110	$9{\cdot}27_6$	9·250	m	2·13	m	4·20	s
003	$7{\cdot}10_1$	7·188	w	1·84	mw	3·85	s
200	$6{\cdot}54_1$	6·541	vs	1·69	s	3·35	s
210	$5{\cdot}84_6$	5·850	w	1·50	vs	3·11	ms
211	$5{\cdot}64_4$	5·646	w	1·415	m	3·08	s
004	$5{\cdot}33_7$	5·391	mw	1·300	m	2·88	m
212	$5{\cdot}15_3$	5·142	w	1·260	m	2·58	s
203	$4{\cdot}79_9$	4·838	mw	1·163	mw	2·50	s
221	$4{\cdot}51_4$	4·522	w			2·40	m
300	$4{\cdot}34_9$	4·361	w			2·35	s
301	$4{\cdot}26_7$	4·274	mw			2·31	s
310	$4{\cdot}12_8$	4·136	w			2·17	mw
302	$4{\cdot}04_6$	4·042	s			2·13	m
214	$3{\cdot}94_5$	3·965	w			2·10	ms
303	$3{\cdot}76_5$	3·728	ms			2·08	ms
320	$3{\cdot}70_9$	3·628	s			1·99	w
321	$3{\cdot}56_7$	3·578	w			1·93	m
224	$3{\cdot}51_9$	3·510	w			1·88	m
322	$3{\cdot}43_3$	3·438	w				
116	$3{\cdot}36_7$	3·350	w				
401	$3{\cdot}22_7$	3·233	m				
225	$3{\cdot}16_3$	3·154	w				
402	$3{\cdot}13_1$	3·129	m				
412	$3{\cdot}04_5$	3·044	w				
315	2·993	2·986	ms				
420	2·917	2·925	w				
421	2·884	2·898	w				
422	2·828	2·823	mw				
325	2·761	2·776	m				
414	2·725	2·734	w				
423	2·700	2·709	mw				
334	2·664	2·677	m				
500	2·610	2·616	w				
424	2·590	2·571	w				
511	2·548	2·548	m				
415	2·517	2·556	w				
503	2·450	2·458	m				
416	2·382	2·379	w				

The crystals were also examined in a Lenné–Guinier *X*-ray heating camera. They were stable up to about 650 °C whereupon they re-crystallised to the first of two high-temperature phases. This phase was stable only over an interval of 50 °C after which a second product began to form. The *d*-spacings of each are given in Table 13. The original zeolite did not sorb oxygen at 78 K either before or after removal of Me_4N^+ cations.

An attempt was made to index the lines of (Na,Me_4N)-V and to determine the unit cell. Agreement was found with a tetragonal unit cell having $a = 13{\cdot}08 \pm 0{\cdot}01$ and $b = 21{\cdot}56 \pm 0{\cdot}04$ Å. This may be an alternative to the cubic unit cell with $a = 37{\cdot}21_9$ Å ascribed to the analogous Linde zeolite N.[19] Table 13 gives the indexed lines (for the tetragonal cell) and their intensities. Despite this agreement with the tetragonal unit cell the number of absences for this cell is considerably greater than for the large cubic cell.*

Conclusion.—Mixtures of two or more bases yield many of the phases obtained with each single base although often under altered conditions of alkalinity, temperature, or ratios of SiO_2 to Al_2O_3. Co-crystallisation therefore is more common with mixed bases than when single bases are employed. In addition, however, new phases may result with mixtures of bases. Examples are the formation of zeolite ZSM-3[41] with mixtures of LiOH + NaOH; of zeolite Ω,[5] and, in the present work, of (Na,Me_4N)-V with NaOH + Me_4NOH; and of offretite[5] with KOH + Me_4NOH or NaOH + KOH + Me_4NOH. Since there is a considerable range of possible mixtures of bases only very partially examined or not examined new opportunities may exist for additions to the presently known zeolites, or for better syntheses of known ones. When mixtures of bases are used it has been suggested[5] that one cation may stabilise one kind of structural unit in solution and the second cation another such unit. Then by condensation–polymerisation crystal structures form from these units which can differ from those obtained with a single cation.

It is emphasised that the crystallisation fields of Figures 1—7, though reproducible under our conditions, do not necessarily indicate thermodynamic stability relationships of the phases obtained. It has been well demonstrated in other researches in this series and elsewhere that kinetic considerations and the history and nature of the starting materials can decisively influence the course of crystallisation, especially at low temperatures.[42]

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* We are indebted to Dr. I. S. Kerr of this Department for this observation.

[41] G. T. Kokotailo and J. Ciric, in 'Molecular Sieve Zeolites,' Advances in Chemistry Series No. 101, Amer. Chem. Soc., 1971, p. 109.

[42] R. M. Barrer, *Chem. in Britain*, 1966, p. 180.