Chemistry of Soil Minerals. Part XIV.† Action of Some Basic Solutions on Metakaolinite and Kaolinite

By **Richard M. Barrer,*** (Mme) **Réjane Beaumont,** and **Carmine Collela,** Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

Some reactions have been studied at 80 °C between aqueous alkaline media and metakaolinite with and without added silica. The bases employed were TlOH, $Ba(OH)_2$ + TlOH, $Ba(OH)_2$ + LiOH, and $Ba(OH)_2$ + NaOH. A similar study was made of kaolinite with aqueous $Ba(OH)_2$ + LiOH. Kaolinite was less reactive than metakaolinite and yielded different reaction products. Non-zeolites formed included a barium silicate hydrate, barium aluminate, and a phase similar to cymrite. Three unidentified Tl-bearing species were also formed in minor yields. Zeolites of the following kinds were grown: those of edingtonite type containing $Ba^{2+} + Tl^+$ or $Ba^{2+} + Li^+$; variants of zeolite L, containing $Ba^{2+} + Tl^+$, $Ba^{2+} + Li^+$, or $Ba^{2+} + Na^+$; harmotome- or phillipsite-types containing $Ba^{2+} + Li^+$ or $Ba^{2+} + Na^+$; and zeolites like gismondite with $Ba^{2+} + Na^+$, like gmelinite and containing $Ba^{2+} + Na^+$, and like yugawaralite containing $Ba^{2+} + Li^+$. A lithium-bearing zeolite with no natural counterpart and in which the cations were $Ba^{2+} + Li^+$ was also grown.

Properties of a number of these phases have been examined. From the present and earlier work, it appears that an important factor in promoting growth of chabazite-, edingtonite-, and phillipsite-type zeolites and of zeolite L is the presence of a sufficient amount of at least one of the cations K^+ or Ba^{2+}. On the other hand a sodic environment favours gismondite-, gmelinite-, and faujasite-type zeolites, and Linde A.

SEVERAL recent papers have given an account of the hydrothermal chemistry of kaolinite[1] and of metakaolinite with and without added silica,[2-4] under low-temperature alkaline conditions. The single bases LiOH, NaOH, KOH, RbOH, CsOH, and $Ba(OH)_2$ have been used; and also, in syntheses of salt-bearing sodalites and cancrinites, NaOH with added salts of diverse kinds. In addition reactions with a number of mixed bases have been examined [$Ba(OH)_2$ + KOH; $Ba(OH)_2$ + TMAOH; NaOH + LiOH; NaOH + KOH; KOH + LiOH; NaOH + TMAOH, where TMAOH denotes tetramethylammonium hydroxide]. This work has established conditions for ready production of numerous zeolites and non-zeolites under mild conditions. It has also shown, as with crystallisations of aluminosilicate gels in presence of mixed bases,[5-10] that the resultants of reactions with such mixed bases are not always predictable from the reactions with each base separately. These observations, and the notable variety of the hydrothermal products, have led us to examine further the reactions between kaolinite, metakaolinite, metakaolinite fortified with silica, and alkaline aqueous media. In the present work we have partially explored the behaviour with aqueous TlOH, $Ba(OH)_2$ + TlOH, $Ba(OH)_2$ + LiOH, and $Ba(OH)_2$ + NaOH.

EXPERIMENTAL

Syntheses were effected at 80 °C in sealed polypropylene bottles containing the reaction mixtures and rotated in a thermostatted oven. The usual time allowed for recrystallisation was 7 days. The mixtures were prepared from weighed amounts of solutions of alkali with appropriate amounts of metakaolinite (MTK) or kaolinite with or without measured additions of amorphous silica. Because of its limited solubility in water at room temperature $Ba(OH)_2,8H_2O$ was added as a solid, with care to avoid contact with atmospheric carbon dioxide. TlOH was prepared by the reaction.

$$Tl_2SO_4 + Ba(OH)_2 \longrightarrow 2TlOH + BaSO_4 \downarrow$$

The weight ratio MTK : H_2O was maintained at 1 : 25, with an equivalent ratio when kaolinite was employed (1 g MTK $\equiv$ 1·16 g kaolinite). Where silica was added these additions were in the proportions 1, 2, or 4 mol SiO_2 per mol MTK ($Al_2O_3,2SiO_2$). Experimental runs were normally arranged on the basis of 1 g of MTK.

Reaction products were separated from mother liquors by centrifugation, washed, and dried overnight at 80 °C. They were then stored over saturated $Ca(NO_3)_2$ at 20 °C (R.H. = 56%) before *X*-ray, chemical, thermal, and microscopic analyses. Guinier *X*-ray powder photographs were subjected to densitometer measurements and cell constants were calculated, where possible, with the aid of a computer program. Chemical analyses were made using standard procedures for Si and Al. Atomic absorption photometry served for analyses of Li and Ba. Tl was determined as chromate. Differential thermal analyses (d.t.a.) and thermogravimetric analyses (t.g.a.) were made with a DuPont 900 thermoanalyser and a Stanton thermobalance respectively. Stereoscan photomicrographs of crystals were made with a Jeol JSM-2 electron microscope.

RESULTS

The main phases produced at 80 °C are given in Table 1. The crystallisation fields with TlOH, $Ba(OH)_2$ + LiOH, and $Ba(OH)_2$ + NaOH as the bases are shown in Figures 1, 2, and 3 respectively. In each figure the products are those obtained by the action of the alkaline solutions on metakaolinite (MTK) with and without added silica. In Figures 2 and 3 the quadrants 1, 2, 3, and 4 refer respectively to aluminosilicate compositions in the molar proportions MTK, MTK + SiO_2, MTK + $2SiO_2$, and MTK + $4SiO_2$.

Experiments with $Ba(OH)_2$ + LiOH as the bases, and

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† Part XIII is ref. 12.

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

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

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

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

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

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

[7] D. W. Breck and N. Acara, U.S.P. 2,950,952/1960.

[8] Union Carbide, B.P. 909,624/1962.

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

[10] Mobil Oil, Dutch Pat. Appln. 6,805,355/1968.

TABLE 1

The phases formed at 80 °C

Base	Designation of product	Nature	Yield	Reproducibility
TlOH	Tl-A	Unidentified	Minor	
	Tl-B	Unidentified	Minor	Moderate
	Tl-C	Unidentified	Minor	
	Tl-F	Like K-F [a] (edingtonite type)	Major	Good
TlOH + $Ba(OH)_2$	(Ba,Tl)-B	Like Tl-B	Minor	Poor
	(Ba,Tl)-G,*L*	Like zeolite L [b]	Moderate	Moderate
	(Tl,Ba)-F	Like K-F	Moderate	Moderate
$Ba(OH)_2$ + LiOH	(Li,Ba)-A(BW)	Like Li-A(BW) [c]	Minor	Good
	(Ba,Li)-E	Edingtonite	Major	V. Good
	(Ba,Li)-F	Like K-F	Major	V. Good
	(Ba,Li)-G,*L*	Like zeolite L	*ca.* 100%	V. Good
	(Ba,Li)-M	Like K-M [a] (phillipsite type)	Minor	Moderate
	(Ba,Li)-N	Unidentified [d]	Minor	Moderate
	(Ba,Li)-P*	Like cymrite [e,f]	Minor	Moderate
	(Ba,Li)-Q	Like Sr-Q [g] (yugawaralite type)	Minor	Moderate
	(Ba,Li)-T	Like Ba-T [d] (barium silicate hydrate)	Major	Moderate
$Ba(OH)_2$ + NaOH	(Ba,Na)-G,*L*	Like zeolite L	Major	Good
	(Ba,Na)-M	Like K-M	Major	Good
	(Ba,Na)-P	Like Na-P [h] (gismondite type)	Major	Good
	(Ba,Na)-P*	Like cymrite	Minor	Moderate
	(Ba,Na)-S	Like Na-S [h] (gmelinite type)	Minor	Poor
	(Ba,Na)-T	Like Ba-T [d]	Major	Moderate

[a] Ref. 15. [b] Ref. 19. [c] Ref. 11. [d] Ref. 4. [e] Ref. 20. [f] Ref. 21. [g] Ref. 22. [h] Ref. 5.

with kaolinite as the sole source of alumina and silica, are summarised in Table 2. There is a notable difference between the species of Table 2 and those of Figure 2, quadrant 1. When MTK was a component of the reaction mixture the first six (Ba,Li)-aluminosilicates of Table 1 were obtained; with kaolin the last three entirely different (Ba,Li)-aluminosilicates of Table 1 resulted. The nature of the starting materials, even for the same overall oxide composition of the reaction mixture, can thus decisively determine the nature of the products.

The compositions containing metakaolinite were, under the conditions employed (80 °C, *ca.* 1 week), always more reactive than compositions containing kaolinite. The species in Table 2 normally contained some non-crystalline material, and experiments (not recorded in the Table) in which much extra silica was added often yielded only an amorphous product. The addition of extra silica also reduced the reactivity of compositions containing metakaolinite. This is seen in Figures 2 and 3 by the progressively increasing extent of the regions (labelled " Am " in the diagrams) in which there is no crystallisation.

For a large mol fractions BaO/(BaO + Li_2O) and BaO/(BaO + Na_2O) Figures 2 and 3 show that the products are typically baric [the species G,*L* and N for $Ba(OH)_2$ + LiOH and G,*L*, P*, and T for $Ba(OH)_2$ + NaOH], although in the latter case G,*L* can persist as a co-crystallisate with species M down to low mol fractions of BaO. When Li^+ is in excess and when the ratio SiO_2/Al_2O is 2 the lithic zeolite A(BW) [11,12] appears [quadrant 1 of Figure 2 where A(BW) is labelled A for simplicity]. In the other quadrants there are two phases ascribable to the presence of Ba^{2+} but not obtained in an exclusively baric environment. These are (Ba,Li)-E and (Ba,Li)-F. For zeolite S (gmelinite-type) and zeolite P (gismondite-type) a large mol fraction $Na_2O/(BaO + Na_2O)$ appears to be important (Figure 3).

Although not tabulated, experiments in which the mixed bases were $Ba(OH)_2$ + TlOH showed similar behaviour. The mol fraction BaO/(BaO + TlOH) was varied between 0·1 and 0·8 and the total hydroxide molality between 0·1 and 0·878. MTK alone and MTK + $n$$SiO_2$ (n = 1, 2, and 4) were the sources of alumina and silica. The most siliceous compositions did not crystallise at 80 °C and even aluminous compositions did not crystallise well. The main products were the zeolites (Ba,Tl)-G,*L* and (Ba,Tl)-F (Table 1). For mol fractions BaO/(BaO + Tl_2O) above 0·4 G,*L* was dominant while below 0·3 zeolite F and more rarely (Tl,Ba)-B were formed.

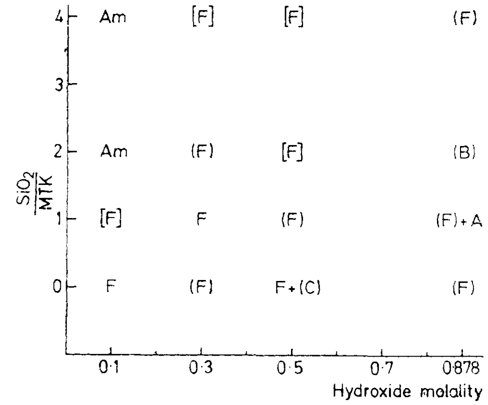

FIGURE 1 Crystallisation field in the system TlOH, MTK, SiO_2, H_2O. SiO_2 : MTK is the ratio silica to metakaolinite in mol. ( ) = Phase present in moderate yield. [ ] = Phase present in very poor yield. Also 'Am' denotes 'amorphous' here and in Figures 2 and 3. A = Tl-A, B = Tl-B, C = Tl-C, and F = Tl-F of Table 2

Among the products of Table 2 the presence of LiOH

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

[12] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 2534.

in the initial mixture may be important only for the synthesis of the yugawaralite-type zeolite (Ba,Li)-Q. The yield of (Ba,Li)-G,*L* increased as the mol fraction BaO/(BaO + Li_2O) increased. With high molality of the solution of mixed bases and especially with large mol fractions of BaO the (Ba,Li)-G,*L* was increasingly replaced by the non-zeolite (Ba,Li)-P*.

Properties of some Crystalline Phases.—Most of the phases of Table 1 were characterised as described in the Experimental section. Some of the results are given below.

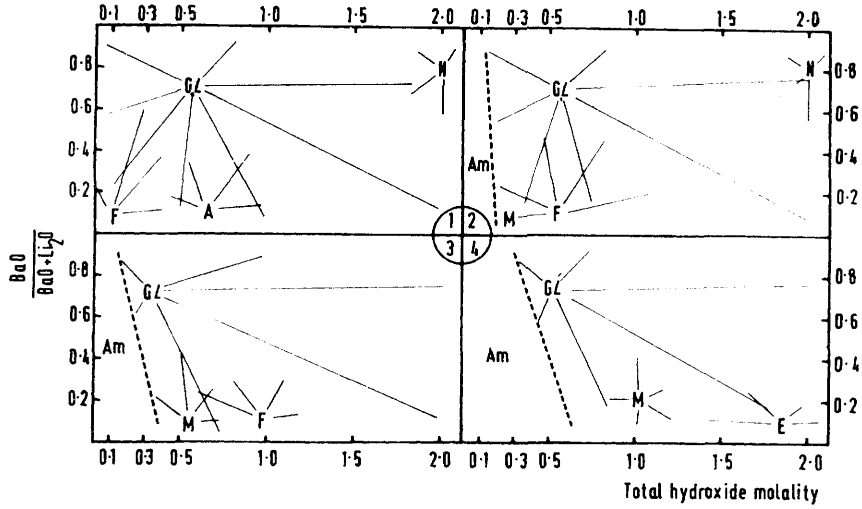

FIGURE 2 Crystallisation field in the system $Ba(OH)_2$, LiOH, MTK, SiO_2, H_2O; quadrant 1: MTK with no added SiO_2; quadrant 2: SiO_2/MTK = 1 (molar ratio); quadrant 3: SiO_2/MTK = 2; quadrant 4: SiO_2/MTK = 4

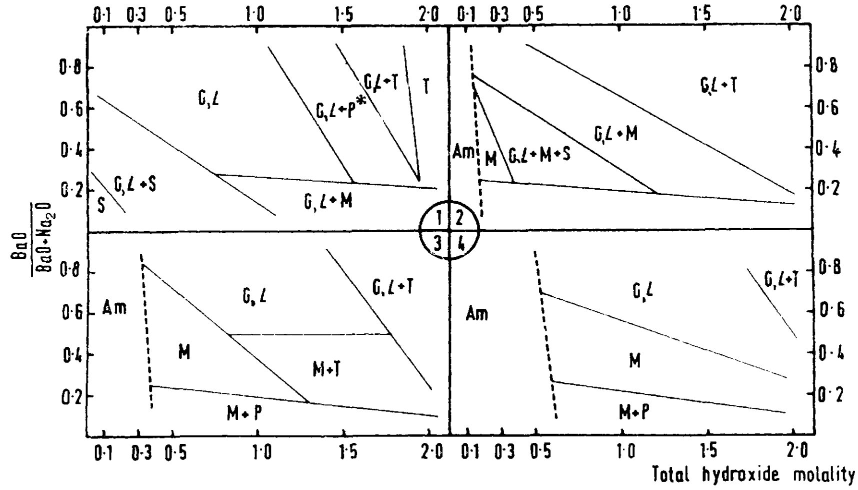

FIGURE 3 Crystallisation field in the field $Ba(OH)_2$, NaOH, MTK, SiO_2, H_2O; quadrant 1: MTK with no added SiO_2; quadrant 2: SiO_2/MTK = 1 (molar ratio); quadrant 3: SiO_2/MTK = 2; quadrant 4: SiO_2/MTK = 4

TABLE 2

Results in the system kaolinite + $Ba(OH)_2$ + LiOH + H_2O

$\frac{BaO}{BaO + Li_2O}$	Total hydroxide molality			
	0·1	0·3	0·5	1·0
0·1	Mod[a] (Ba,Li)-Q	Mod (Ba,Li)-Q Poor (Ba, Li)-G,*L*	Poor (Ba, Li)-Q Poor (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L* Poor (Ba,Li)-P*
0·2	Mod (Ba,Li)-Q Poor (Ba,Li)-G,*L*	Poor (Ba,Li)-Q Poor (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L* Poor (Ba,Li)-P*
0·4	Mod (Ba,Li)-Q Poor (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L*	Mod (Ba,Li)-P*
0·6	Poor (Ba,Li)-Q Poor (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L* Mod (Ba,Li)-P*	Mod (Ba,Li)-P*
0·8	Poor (Ba,Li)-Q Poor (Ba,Li)-G,*L*	Mod (Ba,Li)-G,*L*	Mod (Ba,Li)-P*	Mod (Ba,Li)-P*

[a] Mod = moderate yield.

Tl-A, Tl-B, (Tl,Ba)-B, Tl-C. Because none of these phases was obtained free of non-crystalline material meaningful chemical analyses were not possible. *d*-Spacings are however recorded in Table **3**.

TABLE 3

d-Spacings **in Å** of the products Tl-A, Tl-B**, and Tl-C**

Tl-A		Tl-B		Tl-C	
d	Int	*d*	Int	*d*	**Int**
11·90	vvw (br)	7·40	mw	6·15	w
8·22	w (br)	6·15	mw	4·62	vs
5·58	w	4·70	w (v **br**)	4·09	m
5·05	mw (br)	4·33	mw	3·23	ms
4·69	vs	3·68	w	3·08	vs
4·34	w	3·43	mw	2·93	mw
3·76	vw	3·17	m	2·90	w
3·71	vw	3·11	ms	2·83	mw
3·66	vw	3·05	m	2·68	ms
3·62	vw	3·00	ms	2·24	mw
3·56	vw	2·97	mw	2·15	w
3·42	w	2·87	m	2·07	w
3·18	w (br)	2·80	mw	2·05	mw
3·15	w (br)	2·75	vvw	2·02	w
3·14	w (br)	2·65	w	1·97	mw
2·92	s	2·59	m (br)	1·87	mw
2·88	w	2·54	m	1·81	vw
2·79	w	2·45	vvw	1·76	vw
2·67	w	2·36	w	1·68	w
2·60	s	2·27	vw	1·66	w
2·31	w (br)	2·21	vvw	1·63	w
2·05	ms	2·10	m	1·61	w

TABLE 4

Indexing of (Ba,Li)-E

I	*d*/Å (obs.)	*d*/Å (calc.)	*hkl*
vvw	6·770	6·767	110
ms	6·541	6·540	001
ms	5·406	5·400	101
ms	4·794	4·785	200
ms	4·712	4·703	111
w	4·271	4·280	210
vvw	3·859	3·862	201
s	3·585	3·581	211
w	3·387	3·384	220
w	3·271	3·270	002
w	3·094	3·094	102
m	3·027	3·026	310
w	3·006	3·005	221
mw	2·945	2·944	112
vvw	2·865	2·867	301
s	2·745	2·747	311
vvw	2·695	2·700	202
vw	2·653	2·654	320
ms	2·599	2·598	212
vw	2·460	2·460	321
vvw	2·391	2·393	400
vvw	2·354	2·351	222
vvw	2·325	2·321	410
m	2·283	2·284	302
m (br)	2·256	2·256	330
		2·247	401
vvw	2·220	2·221	312
m (br)	2·186	2·187	411
		2·180	003
		2·140	420
mw (v br)	2·133	2·132	331
		2·126	103
w	2·075	2·075	113
w	2·061	2·061	322

(Ba,Li)-E. This zeolite gave an *X*-ray powder pattern very close to that of a natural edingtonite. As with natural edingtonite, among the *h*00 reflections only those with $h = 2n$ appeared (Table 4). The zeolite was formed only by treatment of 1MTK + $4SiO_2$ with mol fractions $BaO/(BaO + Li_2O)$ between 0·1 and 0·2 and with total hydroxide molality between 1·5 and 2·0 (Figure 2, quadrant 4). The *d*-spacings in Table 4 refer to the crystals obtained with **total** molality 1·5. Tetragonal unit cells of both preparations are given in Table 5. The slight differences in the cell parameters (*a* decreases and *c* increases with **total** hydroxide molality) may arise from small differences in chemical composition. The unit cell volumes of 599 ± 0·5 and 595 ± 0·5 Å^3 decrease with increasing molality of the contact solution.

TABLE 5

Tetragonal unit cells of (Ba,Li)-E, Tl-F, and (Ba,Li)-F

Zeolite	*a*/Å	*c*/Å
(Ba,Li)-E [from 1·5 m $Ba(OH)_2 + LiOH$]	9·571 ± 0·002	6·540 ± 0·002
(Ba,Li)-E [from 2·0 m $Ba(OH)_2 + LiOH$]	9·520 ± 0·002	6·570 ± 0·003
Tl-F	$9{\cdot}95_8$	$6{\cdot}60_2$
(Ba,Li)-F	9·870 ± 0·002	6·560 ± 0·004
Edingtonite[a] (orthorhombic)	$a = 9{\cdot}54$ $b = 9{\cdot}65$	$c = 6{\cdot}50$

[a] Ref. 13.

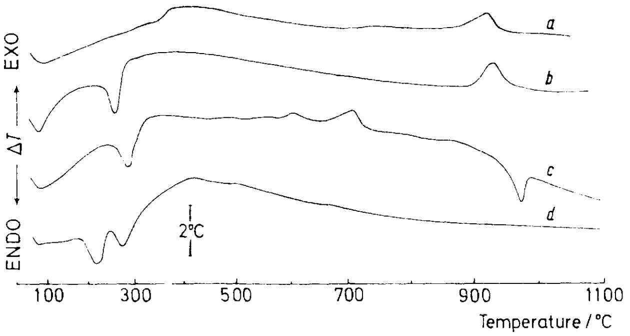

FIGURE 4 DTA diagrams, heating rate 15 °C min^{-1}, weight of sample 20 mg, atmosphere : air; a, (Ba,Li)-E; b, **(Ba,Li)-F;** c, (Ba,Li)-M; d, (Ba,Na)-M

An initial chemical analysis of part of a sample of (Ba,Li)-E suggested the presence of a certain amount of amorphous silica and a considerable excess of LiOH. After washing another part at 80 °C the rinse water contained some silica and LiOH, both of which were determined and used to correct the original analysis. The corrected oxide composition was 0·45 BaO, 0·52 Li_2O, Al_2O_3, 3·21 SiO_2, 3·8 H_2O compared with BaO, Al_2O_3, 3 SiO_2, 4 H_2O for an ideal † edingtonite.[13] The ratio Li^+/Ba^{2+} is 2·3 in the zeolite as compared with 18·0 in the parent mixture so that the crystals are strongly selective for Ba^{2+}.

The t.g.a. curve of the crystals washed as above, dried, and conditioned at R.H. = 56% showed an endothermic water loss of 15·1%. After dehydration at temperatures rising to 600 °C the sample was amorphous. In the t.g.a. curve of Figure 4a the asymmetrical exothermal peak *ca.* 930 °C is associated with the appearance of a phase like (Ba,Li)-P* or Ba-P [14] and of a phase similar to the ignition

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† The water content cited in ref. 13 is high. Edingtonites rich in Ba usually contain *ca.* 14% by weight of H_2O referred to the hydrated crystals.

[13] W. M. Meier in ' Moecular Sieves,' *Soc. Chem. Ind.*, London, 196, p. 10.

[14] R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1964, 2296.

product of Ba-A.[14] These relations are indicated by the *d*-spacings given in Table 6, and for (Ba,Li)-P* and Ba-P in Table 9.

Tl-F, (Tl,Ba)-F, (Ba,Li)-F. As indicated in Table 1 all these zeolites are similar to K-F[15] which has been shown to have an edingtonite type of aluminosilicate framework.[16] Edingtonite-type zeolites have now been prepared with a variety of cations, for example with $(K^+ + Li^+)$,[12] $(K^+ + Na^+)$,[12] Rb^+,[12] and Cs^+[17] in addition to the preparations reported in this paper with Tl^+, $Tl^+ + Ba^{2+}$, and $Ba^{2+} + Li^+$. A common feature is the presence of at least one sufficiently large uni- or di-valent cation [K^+, Ba^{2+} (radius 1·33 Å); Rb^+, Tl^+ (1·48 Å); Cs^+ (1·69 Å)].

TABLE 6

d Spacings in Å of ignition products of (Ba,Li)-E and of (Ba,Li)-F

(Ba,Li)-E (Ignited)		Ba-A[a] (Ignited)		(Ba,Li)-F (Ignited)	
d	Int	*d*	Int	*d*	Int
7·80	s			5·40	w
6·50	vvw	6·52	vs	4·52	w
5·80	vw	5·81	w	4·42	vw
4·60	ms	4·64	w	3·48	s
		4·54	vs	3·42	ms
3·95	vs	3·95	w	2·87	mw
3·90	m	3·91	w	2·68	w
		3·80	m	2·54	m
		3·63	w	2·47	vw
3·52	vw	3·56	m	2·37	vw
3·47	vs	3·48	ms	2·20	m
3·34	vw	3·35	s	1·88	m
3·26	vw	3·28	s	1·86	mw
		3·02	m		
2·97	s	2·97	w		
		2·92	mw		
		2·796	s		
		2·751	s		
2·67	s				
2·59	vvw	2·580	s		
2·32	m	2·336	m		
2·24	w	2·277	mw		
2·21	ms	2·225	mw		
		2·176	w		
2·11	vw	2·126	s		
		2·023	w		
1·98	w				

[a] Ref. 14.

The best yield of Tl-F at 80 °C was obtained from the initial composition 0·555 TlOH + 1·0 MTK + 308·5 H_2O. *d*-Spacings are given in Table 7. (Ba,Li)-F was obtained at low Ba/Li ratios in the contact solution and only two preparations were free of co-crystallisate. Its crystallisation field (Figure 2) shifted towards higher alkalinity of contact solution as the ratio SiO_2/Al_2O_3 in the initial mixture increased. Two compositions which yielded (Ba,Li)-F free of co-crystallisate were: 0·028 $Ba(OH)_2$ + 0·50 LiOH + 1·0 MTK + 308·5 H_2O; and 0·14 $Ba(OH)_2$ + 2·50 LiOH + 1·0 MTK + 1 SiO_2 + 308·5 H_2O.

The *d*-spacings of the first of these two preparations are also given in Table 7. Both Tl-F and (Ba,Li)-F were indexed to the tetragonal unit cells given in Table 5. The cell dimensions for (Ba,Li)-F in particular are close to those of K-F(Cl), K-F(Br), and K-F(I)[18] which are forms of K-F containing amounts of included KCl, KBr, and KI respectively. Despite good agreement of calculated and observed spacings all the tetragonal unit

TABLE 7

Indexing of Tl-F and (Ba,Li)-F

Tl-F

I	*d*/Å (obs.)	*d*/Å (calc.)	*hkl*
w	7·030	7·041	110
vvw	6·604	6·602	001
w	4·974	4·979	200
m	4·818	4·816	111
s	3·981	3·975	201
s	3·516	3·521	220
w	3·321	3·319	300
w	3·301	3·301	002
w	3·151	3·149	310
w	3·127	3·133	102
ms	3·105	3·104	221
s	2·987	2·989	112
vw	2·964	2·966	301
s	2·839	2·842	311
vw	2·750	2·751	202
vw	2·650	2·652	212
vw	2·552	2·548	321
vvw	2·487	2·489	400
vw	2·406	2·408	222
mw	2·347	2·347	330
mw	2·279	2·278	312
w	2·267	2·268	411
vvw	2·226	2·227	420
vvw	2·210	2·211	331
vw	2·202	2·201	003
w	2·116	2·118	322
w	2·110	2·110	421
w	2·103	2·101	113
vvw	2·009	2·013	203
vw	1·991	1·992	430, 500
w	1·987	1·988	402
vvw	1·971	1·973	213
w	1·953	1·953	510
vw	1·946	1·949	412
w	1·913	1·913	332
vw	1·906	1·907	431, 501
vw	1·872	1·873	511
w	1·868	1·866	223
w	1·847	1·849	520
vvw	1·844	1·846	422
vvw	1·834	1·834	303
w	1·805	1·804	313
mw	1·761	1·760	440
w	1·709	1·708	530
w	1·707	1·705	432, 502
vw	1·701	1·701	441
vvw	1·683	1·681	512
vw	1·658	1·659	600
w	1·653	1·653	531

(Ba,Li)-F

I	*d*/Å (obs.)	*d*/Å (calc.)	*hkl*
s	7·01	6·98	110
m	6·59	6·56	001
vvw	5·48	5·46	101
vvw	4·96	4·94	200
m	4·782	4·780	111
w	3·946	3·944	201
vw	3·664	3·662	211
vw	3·491	3·490	220
w	3·279	3·280	002
w	3·126	3·121	310
s	3·081	3·081	221
m	2·971	2·968	112
s	2·818	2·818	311
vvw (br)	2·733	2·737	320
vvw	2·525	2·526	321
mw	2·467	2·468	400
vvw	2·333	2·327	330
vvw	2·305	2·309	401
vvw	2·252	2·249	411

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

[16] C. Baerlocher and R. M. Barrer, *Zeit. Krist.*, in the press.

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

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

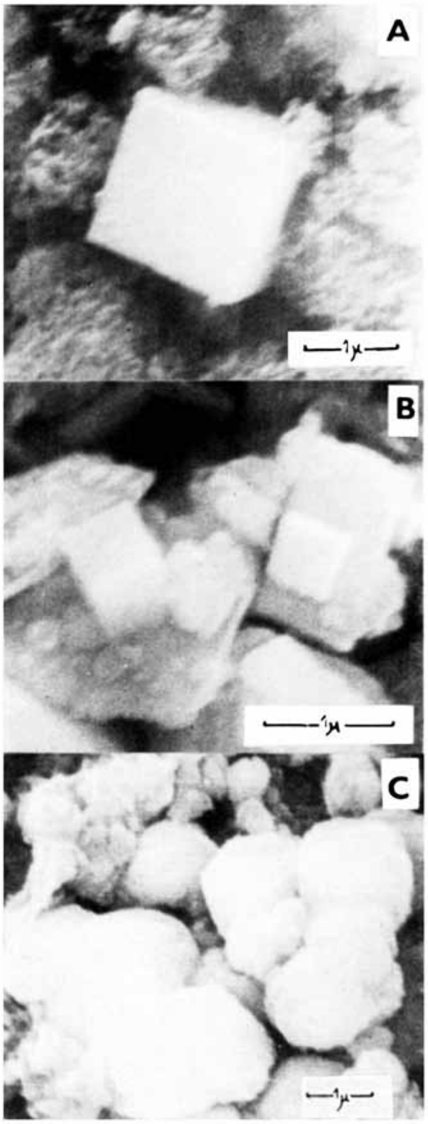

PLATE Scanning electron micrographs for: A, (Ba,Li)-E zeolite; B, (Ba,Li)-F zeolite; C, (Ba,Li)-M zeolite

TABLE 7 (*Continued*)

(Ba, Li)-F

I	*d*/Å (obs.)	*d*/Å (calc.)	*hkl*
w	2·192	2·193	331
vw	1·973	1·972	402
mw	1·852	1·853	223
w	1·829	1·831	422
mw	1·743	1·745	440
w	1·691	1·691	502
mw	1·665	1·667	512
vw	1·638	1·639	531
vw	1·593	1·593	333
w	1·517	1·518	621
vw	1·504	1·504	532
w (br)	1·450	1·449	513
w (br)	1·410	1·410	700
w (br)	1·365	1·365	711

cells of Table 5 may be pseudo-cells only. The cells of Tl-F and of (Ba,Li)-F are considerably larger than those of (Ba,Li)-E. This suggests that they may be more aluminous and therefore richer in cations than (Ba,Li)-E, which was formed from a much more siliceous medium.

The water losses observed in t.g.a. were 4·2% for Tl-F and 12·1% for (Ba,Li)-F. The d.t.a. curves showed endothermic effects of maximum intensity *ca.* 100 °C for Tl-F and *ca.* 90 and *ca.* 260 °C for (Ba,Li)-F (Figure 4b). Tl-F also gave a small exothermic peak at 1013 °C, the product being amorphous, while (Ba,Li)-F recrystallised exothermally *ca.* 930 °C to a product different from that obtained by ignition of (Ba,Li)-E (Table 6). The similar crystal form of (Ba,Li)-F and of (Ba,Li)-E is shown in the stereoscan electron micrographs of Plates B and A respectively.

(Ba,Tl)-G,*L*, (Ba,Li)-G,*L*, *and* (Ba,Na)-G,*L*. These zeolites were all based upon the framework of zeolite L.[19] Zeolite L was originally synthesised using KOH + NaOH as mixed bases but novel variants additional to those above have also been made with $Ba(OH)_2$ alone and with $Ba(OH)_2$ + KOH.[4] The cations which favour the growth of G,*L* therefore appear to be K^+ and Ba^{2+}. The baric forms of the zeolite had very different SiO_2/Al_2O_3 ratios from those usually formed with KOH + NaOH and they showed excellent sorbent properties and were thermally very stable.[4] Samples of (Ba,Li)-G,*L* and (Ba,Na)-G,*L* derived respectively from parent oxide compositions

$$0{\cdot}663\ BaO,\ 0{\cdot}166\ Li_2O,\ Al_2O_3,\ 4\ SiO_2,\ 308\ H_2O$$

and

$$0{\cdot}663\ BaO,\ 0{\cdot}166\ Na_2O,\ Al_2O_3,\ 2\ SiO_2,\ 308\ H_2O$$

gave the hexagonal unit cells

$$a = 18{\cdot}54_8\ \text{Å};\ c = 7{\cdot}46_1\ \text{Å}\ [(\text{Ba,Li})\text{-G},L]$$
$$a = 18{\cdot}63_4\ \text{Å};\ c = 7{\cdot}50_4\ \text{Å}\ [(\text{Ba,Na})\text{-G},L]$$

The crystals were not analysed because they contained some non-crystallised material.

(Ba,Li)-M *and* (Ba,Na)-M. These two zeolites each appear to be based upon a harmotome- or phillipsite-type framework. The *d*-spacings are given in Table 8 together with those of Ba-M[14] and of a natural harmotome.[14] As with zeolites F and G,*L* the formation of M-type zeolites is favoured by the presence of larger cations in the reaction mixture (for M these include K^+,[15] Rb^+,[12] and Ba^{2+} [14]). Also, as with (Ba,Li)-F, the crystallisation field of (Ba,Li)-M shifted towards higher alkalinity as the initial ratio SiO_2/Al_2O_3 increased (Figure 2). The d.t.a. curve of (Ba,Li)-M (Figure 4c) shows endothermal minima due to water loss *ca.* 100 and *ca.* 280 °C. There are at higher temperatures two exothermal recrystallisation processes and an endothermal process, the sample finally melting. The stereoscan electron micrograph of Plate C shows that the crystals are often formed as aggregates. The d.t.a. curve of (Ba,Na)-M in Figure 4d shows two very clear endothermal minima *ca.* 220 and 274 °C associated with water loss. The water content determined by t.g.a. was 14·0%, close to that of natural harmotome. When heated for several hours at 1100 °C the ignition product was similar to that obtained by heating Ba-A.[14]

TABLE 8

X-Ray patterns for harmotome–phillipsite-type zeolites [a] (*d* in Å)

(Ba,Na)-M		Ba-M [b]		Natural [b] harmotome		(Ba,Li)-M	
d	Int	*d*	Int	*d*	Int	*d*	Int
8·16	ms	8·24	vs	8·09	s	8·19	mw
7·85	w	7·86	vw	7·86	vw		
7·14	ms	7·18	s	7·14	s	7·14	mw
		7·03	w	6·99	w		
6·37	ms	6·39	vs	6·37	s	6·38	mw
6·20	vw	6·11	vw	6·26	w		
				5·60	m		
5·03	mw	5·02	ms	5·01	m	5·01	w
				4·72	vw		
4·29	mw	4·29	ms	4·27	m	4·30	w
		4·10	s	4·08	s		
4·07	s	4·06	s			4·08	m
		4·03	s	4·03	s		
3·91	mw	3·89	m	3·93	mw		
				3·88	mw		
				3·76	vw		
3·67	vvw	3·66	w	3·67	vw		
		3·57	vvw				
		3·52	w			3·52	vw
3·46	vw	3·46	mw	3·46	vw		
3·41	vw					3·40	vw
3·24	m	3·23	s	3·24	m	3·24	mw
3·23	w	3·19	mw	3·19	m		
3·17	m	3·16	ms	3·16	m		
3·14	s	3·12	vs	3·11	ms	3·16	m
3·08	w	3·07	m	3·07	w		
				3·00	w		
2·93	m	2·91	ms	2·91	mw	2·93	mw
2·845	vvw	2·838	w	2·803	mw	2·820	w
		2·745	w				
2·732	m	2·724	s	2·725	m	2·733	mw
2·685	m	2·674	s	2·693	mw		
2·674	ms	2·668	s	2·669	m	2·674	m
2·630	w	2·624	w	2·628	w	2·633	w
2·561	w	2·557	w	2·560	vw		
2·538	mw	2·525	w	2·517	m	2·549	vw
2·514	w	2·508	w				
2·477	w	2·464	m	2·460	w		
2·440	w					2·431	vw
				2·406	vw		
2·370	w	2·368	m	2·368	w		
2·358	w					2·354	vw
2·320	mw	2·315	ms	2·320	mw	2·325	w
2·307	w	2·295	m	2·294	mw		
2·260	vw	2·256	w	2·258	vw	2·259	vvw
2·239	vw	2·236	m	2·235	mw		
		2·213	w	2·205	w		
2·153	mw	2·147	m	2·145	m	2·161	w

[a] Lines of samples (Ba,Na)-M and (Ba,Li)-M are usually rather broad. [b] Ref. 14.

(Ba,Li)-P*, (Ba,Na)-P* (*Cymrite-type Crystals*). This phase resembles but is not identical with the polymorph

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[19] D. W. Breck and E. M. Flanigen in 'Molecular Sieves,' *Soc. Chem. Ind.*, London, 1968, p. 47.

of celsian, $BaAl_2Si_2O_8$, previously designated Ba-P,[14] and also it bears no relation to the gismondite-like zeolite Na-P.[5] The *d*-spacings given in Table 9 suggest that (Ba,Li)-P* is nearer to cymrite[20,21] than to Ba-P.[14] Lines at 4·65 and 2·22 Å are among those absent from Ba-P and present in (Ba,Li)-P*. Also the line intensities of (Ba,Li)-P* correspond more closely with those of cymrite than of Ba-P.

TABLE 9

X-Ray spacings of (Ba,Li)-P* and related species (*d* in Å)

(Ba,Li)-P*		Cymrite[a]		α-Hexagonal[b] $BaAl_2Si_2O_8$		Ba-P[c]	
d	Int	*d*	Int	*d*	Int	*d*	Int
7·64	mw (br)	7·71	50	7·79	100	7·74	m
4·65	w	4·62	10				
3·98	vvs	3·96	90	3·95	43	3·96	s
		3·85	10	3·90	18		
2·96	s (br)	2·96	100	2·97	49	2·97	s
2·68	vs	2·67	70	2·65	13	2·67	ms
(covered by kaolinite lines)		2·57	10	2·597	20		
		2·53	10				
2·32	m	2·31	20	2·292	4	2·31	mw
2·24	w (br)	2·24	40	2·259	18	2·25	m
2·22	ms	2·21	40				
2·195	w (br)	2·195	10	2·195	11	2·215	m
1·981	vw	1·982	10			1·982	vw
1·925	w (vbr)	1·925	30	1·947	65	1·933	w
1·852	m(br)	1·850	40	1·853	7	1·854	m
		1·778	5				
1·709	m	1·703	20			1·702	m
1·596	m	1·591	30			1·592	m
1·560	vw	1·560	20			1·561	mw
1·547	m	1·541	20			1·540	w

[a] Ref. 21. [b] Y. Takeuchi, *Mineral. J. Japan*, 1958, **2**, 311. [c] Ref. 14.

The d.t.a. curve of (Ba,Li)-P* showed, besides the endothermal dehydration of unreacted kaolinite, an endothermic process maximal *ca.* 392 °C. The t.g.a. curve showed this to be due to a 6% weight loss of water excluding water loss of the kaolinite content found from t.g.a. (the water loss of pure kaolinite is 14%). The water loss from a pure natural cymrite is 7·17%.[21] Despite the water loss (Ba,Li)-P* remained essentially unchanged when heated to 1100 °C, apart from a small decrease in the *a*-dimension and a small increase in the *c*-dimension. A qualitative chemical test showed little or no Li^+ to be present so that the compound during crystallisation is highly selective for Ba^{2+}. (Ba,Na)-P* is very similar to (Ba,Li)-P* and will not be separately described.

(Ba,Li)-Q. This yugawaralite-type zeolite was obtained only when kaolinite was the source of alumina and silica. It was always associated with some Ba-aluminate, the *d*-spacings of which are shown in Table 10 which also compares the spacings of (Ba,Li)-Q with those of the analogous yugawaralite-type zeolite Sr-Q.[22,23] The d.t.a. curve shows the endotherm due to water loss to be at its maximum *ca.* 135 °C. The water loss, estimated from the t.g.a. curve after allowing for unreacted kaolinite, was about 15·4% of the weight of (Ba,Li)-Q plus Ba-aluminate.

(Ba,Li)-T. This phase was dominant in the crystallisation fields in which the sources of alumina plus silica were in the proportion kaolin (1 mol) + 1, 2, or 4 mol of added SiO_2. Either T was formed or the reactants yielded amorphous products. The amount of amorphous material increased with increasing SiO_2/Al_2O_3 ratios.

The *X*-ray pattern of (Ba,Li)-T was identical with that of the previously reported Ba-T,[4] which was considered to be a zeolitic phase with included $Ba(OH)_2$ having the composition BaO, Al_2O_3, 2 SiO_2, 1·2 $Ba(OH)_2$, 2 H_2O. However the pattern proves to be that of a known barium silicate hydrate, $BaSiO_3,H_2O$,[24] so that the original Ba-T, like (Ba,Li)-T, was not pure and was a silicate not a zeolite.

TABLE 10

X-Ray spacings of (Ba,Li)-Q and Ba-aluminate (*d* in Å)

(Ba,Li)-Q		Sr-Q[a]	
d	Int	*d*	Int
10·0	m	9·66	w
		7·89	vvw
		6·96	mw
		6·61	vw
		6·30	w
5·88	m	5·88	vs
4·98	w		
4·69	mw	4·76	vs
4·55[c]	vw	4·65	s
4·24	ms	4·31	s
		4·16	ms
		4·06	w
3·97	vw	3·94	ms
		3·76	mw
3·64	w	3·67	vw
		3·54	w
3·41	mw (br)	3·48	w
3·34	vw	3·30	w
3·25	vvw	3·27	s
		3·14	w
3·08	vvw	3·10	ms
3·01	w (br)	3·03	vs
		2·95	w
2·93	vvw	2·93	ms
2·88	vvw	2·89	vvw
2·77	vvw	2·768	mw
2·71	ms	2·738	mw
2·68	w	2·657	m
		2·542	vvw
		2·454	w
2·42	w	2·416	m
		2·374	vw
		2·328	w
2·19[c]	w	2·196	w
2·15	w	2·146	w
2·12	w	2·129	vw
		2·095	w
2·07	w	2·076	vw
		2·032	vw
2·03	mw	2·000	m
1·96	w	1·976	vw
1·95	w	1·954	vw
1·92	w	1·924	vw
1·88	w	1·894	ms
1·84	w	1·828	vw

Synthetic Ba-aluminate		BaO,Al_2O_3[b]	
d	Int	*d*	Int
4·55[c]	vw	4·56	80
		4·06	20
3·17	ms	3·17	100
2·65	m	2·62	80
		2·51	20
		2·46	10
		2·26	20
2·24	w	2·24	70
		2·20	20
2·19[c]	w	2·189	10
2·03	mw	2·012	60
		1·997	30
		1·951	10
		14 further weaker lines	

[a] Ref. 22. [b] *X*-Ray Data File, ASTM Card No. 2–545. [c] These lines are common to both the phases.

DISCUSSION

A number of zeolites have now been made in these laboratories from more than one cationic composition. Some examples, with the cations present in synthesis, are summarised in Table 11. Of the zeolites referred to in the Table there are four which appear to grow well in sodic environments. They are gismondite, gmelinite, faujasite, and Linde Sieve A, or variants of these. One, Li-A(BW),[11,12] definitely needs a lithic environment while four types namely, chabazite, edingtonite, harmotome (or phillipsite), and zeolite L

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[20] W. Campbell Smith, F. A. Bannister, and M. H. Hey, *Min. Mag.*, 1949, **28**, 676.

[21] D. D. Runnells, *Amer. Mineralog.*, 1964, **49**, 158.

[22] R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1964, 485.

[23] R. M. Barrer and D. J. Marshall, *Amer. Mineralog.*, 1965, **50**, 484.

[24] *X*-Ray Data File, ASTM Card No. 18–179.

TABLE 11

Some zeolite syntheses from more than one cation composition [a]

Framework type	Cations present in synthesis [b]	Environment favouring synthesis
Analcime-leucite-pollucite	Na, K, Rb, Cs, Tl, NH_4, (Tl,Na), (Tl,Rb), (Na,Cs), (K,Rb), Ca,Sr	
Chabazite	K, (K,Na), (K,Li), (K,Na,TMA), Sr, Ba, (Ba,K)	Potassic; baric (?)
Edingtonite	K, Rb, Cs, Tl, (K,Li), (Na,Li), (Ba,Tl), (Ba,Li)	Potassic; baric
Faujasite	Na, (Na,Li), (Na,TMA), TMA [c]	Sodic
Gismondite	Na, (Na,K), (Na,Li), (Na,Ba), (Na,TMA)	Sodic
Gmelinite	Na, (Na,K), (Na,Li), (Na,Ba), (Na,TMA), (Ca,TMA), Sr, (Ba,Na)	Sodic
Harmotome-phillipsite	Na, K, Rb, NH_4, (K,Na), (K,Li), Ca, (Ca,TMA), Ba, (Ba,Li), (Ba,Na) $MeNH_3$,[c] Me_2NH_2,[c] Me_3NH,[c] TMA [c]	Potassic; baric; calcic (?)
Zeolite L [d]	K, (K,Na), (K,Na,TMA) Ba, (Ba,K), (Ba,Tl), (Ba,Na), (Ba,Li)	Potassic; baric
Zeolite Li-A(BW) [e]	Li, (Li,Na), (Li,K), (Li,Ba)	Lithic
Linde A	Na, (Na,K), (Na,TMA), TMA [c]	Sodic
Mordenite	Na, Ca, Sr	
Yugawaralite	Sr, (Ba,Li)	

[a] Syntheses are examples from the series of papers 'Hydrothermal Chemistry of the Silicates, Parts I—XV' and the series 'Chemistry of Soil Minerals. Parts I—XIV' respectively, appearing in the *Journal of the Chemical Society* from 1951 (ref. 11) onwards and from 1965 onwards (R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1965, 6616). [b] For ions in parentheses each ion is present in comparable amounts. [c] Traces of ions such as Na^+ or K^+ are also thought to be present. [d] Ref. 19. [e] Refs. 11 and 12.

and variants of these appear to form easily in baric or potassic environments. The analcime type of structure has been formed comparably well in a range of environments, although because of the comparative compactness of the framework crystals of analcime-type containing large cations prove to be non-hydrated felspathoids rather than zeolites. Similar environmental influences have recently been evaluated by Flanigen.[25]

In a successful crystallisation such variables as alkali concentration, SiO_2/Al_2O_3 ratio, the nature of the starting materials and the temperature have all proved to be important. Nevertheless the cationic composition of the magma can be discerned from Table 11 as another major factor. It is interesting that K^+ and Ba^{2+}, despite their difference in valence, tend to play equivalent roles in favouring the appearance of certain zeolites. This may be connected with their nearly equal cationic radii. Continued study of zeolite synthesis should show other regularities and may also demonstrate that certain zeolites can be synthesised from even more diverse cationic compositions than those in Table 11. However, there is undoubtedly considerable specificity about certain cation pairings in directing and favouring the formation of particular zeolites.

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[3/2107 *Received*, 15*th October*, 1973]

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[25] E. M. Flanigen in 'Molecular Sieves,' eds. W. M. Meier and J. B. Uytterhoeven, Adv. in Chem. Series No. 121, Amer. Chem. Soc., 1973, p. 119.