Chemistry of Soil Minerals. Part XII. Transformations of Metakaolinite with Solutions Containing Barium Hydroxide

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

Metakaolinite, with or without additions of silica, readily reacts with aqueous solutions of barium hydroxide alone, of barium plus potassium hydroxides, and of barium plus tetramethylammonium hydroxides. In the range 80 to 100° barium hydroxide produced a polymorph of celsian, two unidentified zeolitic phases, Ba-T and Ba-N, and species having a structure resembling that of Linde zeolite L. From $Ba(OH)_2$ + KOH the zeolitic phases formed were of chabazite- and L-type, together with (Ba,K)-T and the non-zeolitic polymorph of celsian. From $Ba(OH)_2$ + $N(CH_3)_4OH$, in addition to this non-zeolite, near-erionites, L-type zeolites, and $[Ba,N(CH_3)_4]$-T were crystallised. The properties of some of the L-type zeolites have been particularly studied. They were prepared with a wide range in Si:Al ratios and in molecule sieving properties. They possessed good thermal stability, as did the H-enriched form of one of the most aluminous preparations.

IN 1962 a novel hexagonal zeolite, Linde L, was reported[1] which was subsequently shown[2] to contain wide channels parallel to the *c*-axis having free diameters of *ca.* 7·5 Å. This wide pore molecular sieve was reported as being silica rich, of oxide composition $(K_2,Na_2)O$, Al_2O_3, $(5—7)SiO_2$, $6H_2O$, the main cation being potassium.[3] In 1964 another zeolite, termed Ba-G[4] was reported, which readily sorbed oxygen gas. As part of an investigation of reactions between aqueous solutions and metakaolinite, with or without added silica, we have been able to provide an improved synthesis of Ba-G, to show that it is structurally similar to zeolite L, and to prepare species of L-type zeolites by new reaction paths. An account follows of these and other syntheses and of some properties of the crystalline phases obtained.

EXPERIMENTAL

The preparation of metakaolinite from kaolinite and the procedures for carrying out subsequent hydrothermal reaction, usually between 80 and 100°, have been outlined elsewhere.[5] The metakaolinite reactant in some cases was fortified by additions of dry powdered silica gel to produce mixtures richer in silica. $Ba(OH)_2$ solutions were prepared from $Ba(OH)_2,8H_2O$, to which in some systems KOH or tetramethylammonium (TMA) hydroxide was added.

The examination of the filtered, washed, air-dried products was made by *X*-ray diffraction, thermogravimetric and differential thermal analysis (t.g.a. and d.t.a.), and by optical and electron microscopy. Some were analysed chemically, ion exchanged, and examined as sorbents.

Reactions with Barium Hydroxide Solutions.—The products obtained with $Ba(OH)_2$ solutions from metakaolinite with or without additions of silica are indicated in Table 1, together with the compositions of particular preparations. According to the ratio $SiO_2:Al_2O_3$ in the parent mixture this ratio could vary substantially in the crystals of Ba-G,*L* (*cf.* Table 5). On the other hand in Ba-P this ratio did not change. The symbol *L* is added to the previous name Ba-G[4] to indicate, as shown later, that this zeolite is related to zeolite L in structure. Figure 1 shows the crystallisation products, normally after 7 days at 80°, in relation to the ratios $SiO_2:Al_2O_3$ and the molality of $Ba(OH)_2$. In this diagram ' Am ' denotes a non-crystalline product.

TABLE 1

Phases crystallised with $Ba(OH)_2$ aq

Crystals	Oxide composition of a particular preparation	Description
Ba-P	$BaO,Al_2O_3,2SiO_2$	Hexagonal polymorph of celsian[4]
Ba-N	$BaO,Al_2O_3,2SiO_2,2\cdot8H_2O$	Zeolite
Ba-T	$BaO,Al_2O_3,2SiO_2,1\cdot2Ba(OH)_2,2H_2O$	Zeolite
Ba-G,*L*	$1\cdot1BaO,Al_2O_3,2\cdot5SiO_2,5\cdot1HO$	Zeolite

Ba-P. This phase, the hexagonal polymorph of celsian, was virtually identical with earlier preparations,[4] and so will not be considered further. The remarkably low temperature of its formation (80°) may be of geological interest.

Ba-N. The zeolite Ba-N crystallised in high yield from metakaolinite at 80° with *ca.* 1·5M-$Ba(OH)_2$. The very sharp *X*-ray pattern gave the *d*-spacings recorded in Table 2, but the compound could not be identified. Crystals of Ba-N having the composition given in Table 1 gave the d.t.a. and t.g.a. traces shown in Figure 2a. The inflexion at *ca.* 200° is followed by a more rapid weight loss, and *X*-ray diffraction in a Lenné–Guinier heating camera

[1] U.S.P. 3,030,181/1962.

[2] R. M. Barrer and H. Villiger, *Z. Krist.*, 1969, **128**, 352.

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

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

[5] R. M. Barrer and D. E. Mainwaring, in preparation.

indicated lattice breakdown in this region. The final recrystallisation product was Ba-P.

Ba-T. Preparation of this zeolitic phase required concentrated solutions of $Ba(OH)_2$ at 80°. Good crystallinity and high yields were obtained when metakaolinite reacted

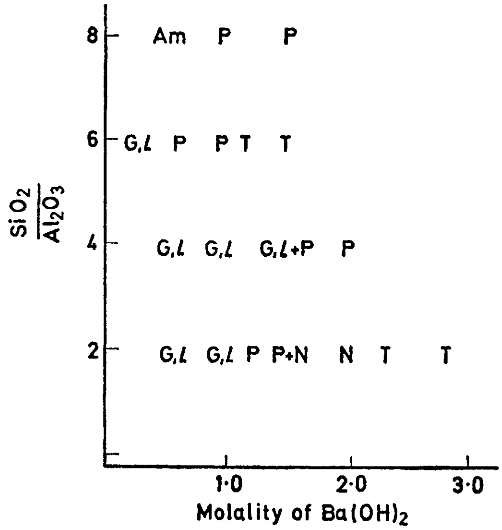

FIGURE 1 Crystallisation field of metakaolinite, with and without added silica, and with barium hydroxide reacting at 80° for 7 days. The starting compositions were in the range 1 metakaolinite + 2·5—28$(BaOH)_2$ + $n SiO_2$ + $275H_2O$ where n = 0, 2, 4, and 6.

TABLE 2

d-Spacings (Å) and intensities of Ba-N, Ba-T, and ignition product of Ba-T

Ba-N		Ba-T				Ignition product of Ba-T	
d	I	d	I	d	I	d	I
7·1	m	7·4	w	2·45	m	5·2	mw
5·6	ms	7·2	w	2·43	ms	4·19	mw
5·2	ms	5·2	ms	2·38	mw	3·96	mw
4·5	w	5·0	w	2·36	mw	3·70	s
4·35	vw	4·3	m	2·35	mw	3·55	m
3·50	m	4·24	mw	2·33	m	3·42	vs
3·40	s	4·20	mw	2·32	vw	3·35	vs
3·15	mw	4·16	m	2·31	vw	3·11	s
2·92	ms	4·00	vw	2·27	w	3·09	m
2·84	w	3·79	s	2·25	mw	3·01	m
2·79	w	3·70	w	2·24	w	2·94	ms
2·69	w	3·68	s	2·22	m	2·91	ms
2·59	w	3·52	m	2·18	m	2·81	s
2·57	ms	3·37	ms	2·15	w	2·75	w
2·44	m	3·30	mw	2·09	w	2·73	w
2·40	w	3·22	s	2·07	w	2·70	m
2·33	w	3·18	s	2·04	w	2·58	w
2·24	m	3·15	w	2·03	m	2·52	w
2·230	w	3·08	w	2·02	m	2·35	ms
2·165	w	3·03	w	2·00	m	2·30	ms
2·078	mw	2·98	m	1·99	mw	2·08	ms
2·051	mw	2·96	m	1·97	mw	2·04	ms
2·020	mw	2·94	vw	1·96	mw		
1·917	w	2·92	w	1·95	w		
1·893	m	2·88	w	1·92	w		
1·845	mw	2·84	w	1·89	w		
1·823	w	2·64	m	1·83	m		
1·762	mw	2·63	w	1·78	m		
1·741	w	2·50	m	1·76	m		

TABLE 3

d-Spacings of Ba-G,*L* and related structures

	Ba-G,*L*				K-L			Ω	
	d_{obs}	d_{calc}	I		d_{calc}	I		d_{calc}	I
100	16·64	16·197	vs	100	15·935	vs	100	15·722	m
110	9·47	9·351	w	110	9·200	vw	110	9·077	vs
200	8·10	8·099	w	200	7·967	vw	200	7·861	m
001	7·587	7·587	mw	001	7·520	mw	101	6·835	m
101	6·868	6·871	vw	101	6·801	vw	210	5·942	s
111	5·885	5·892	m	210	6·023	mw	201	5·460	w
300	5·412	5·399	m	111	5·822	mw	300	5·241	w
400	3·965	4·049	vw	300	5·312	vw	310	4·360	vw
311	3·850	3·865	mw	211	4·701	m	400	3·930	m
002	3·750	3·793	mw	220	4·600	m	002	3·795	vs
102	3·704	3·694	w	310	4·420	w	102	3·689	m
112	3·515	3·515	mw	301	4·339	w	320	3·607	m
202	3·477	3·435	w	400	3·984	vw	401	3·490	s
321	3·319	3·337	m	221	3·924	m	410	3·431	mw
212	3·224	3·225	mw	311	3·810	vw	321	3·258	w
411	3·192	3·204	vw	002	3·760	vw	411	3·126	s
302	3·076	3·104	m	320	3·656	m	302	3·074	m
402	3·052	3·061	mw	401	3·520	m	330	3·026	m
501	2·961	2·979	m	112	3·481	m	420	2·971	mw
510	2·920	2·909	w	202	3·400	vw	222	2·911	s
331	2·872	2·883	mw	321	3·288	mw	510	2·824	w
421	2·823	2·839	mw	212	3·189	m	421	2·767	w
402	2·744	2·768	w	302	3·069	mw	402	2·730	mw
600	2·687	2·699	vw	420	3·011	vw	511	2·646	mw
322	2·631	2·655	m	501	2·934	m	322	2·614	m
601	2·567	2·543	m	222	2·911	m			
003	2·529	2·529	vw	510	2·864	vw			
103	2·498	2·499	w	331	2·840	vw			
521	2·458	2·454	vw	421	2·796	vw			
113	2·441	2·441	vw	402	2·734	vw			
203	2·415	2·414	mw	511	2·675	m			
422	2·389	2·382	m	600	2·656	m			
611	2·365	2·349	vw	430	2·620	vw			
213	2·331	2·337	vw	322	2·621	vw			
512	2·304	2·308	w	502	2·552	vw			

at this temperature with 2·5 to 3·0M-Ba(OH)$_2$. *X*-Ray diffraction in the heating camera showed that the product with the oxide composition given in Table 1 became amorphous above *ca.* 225°. Gradual recrystallisation occurred between 500 and 800°. The *d*-spacings of Ba-T and of its recrystallisation product are recorded in Table 2.

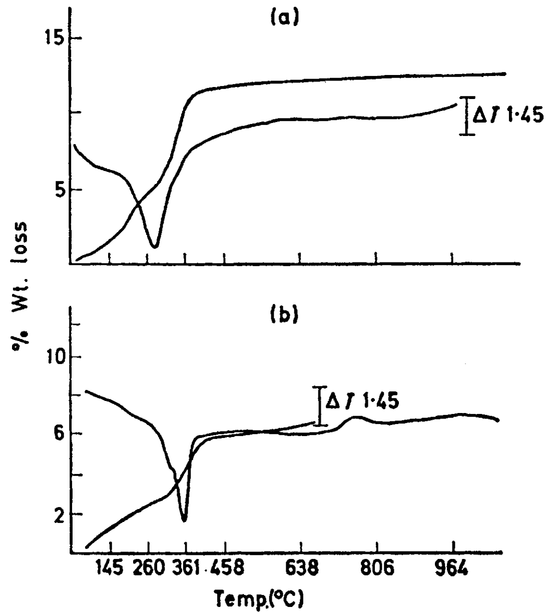

FIGURE 2 The d.t.a. and t.g.a. curves of products (a) Ba-N and (b) Ba-T equilibrated at 56% R.H. For d.t.a. the heating rate was 16°/min and for t.g.a. the heating rate was 10°/min. In both cases heating was in air

The d.t.a. and t.g.a. curves shown in Figure 2b indicate an endothermal water loss of *ca.* 6%. An outgassed sample failed to sorb oxygen at 78 K.

*Ba-G,*L. Best yields of this zeolite were obtained at 100° with 1M-Ba(OH)$_2$ and a reaction time of *ca.* 10 days. Even better crystallisations were achieved, as indicated later, with solutions of mixed bases. The *X*-ray diffraction pattern gave the *d*-spacings in Table 3, which were indexed to a hexagonal unit cell that replaces the tetragonal one proposed earlier.[4] The unit cell dimensions are compared below with those of zeolites L [2] and Ω: [6]

Ba-G,*L*	$a = 18{\cdot}70$ Å	$c = 7{\cdot}59$ Å
Zeolite L	$a = 18{\cdot}40$ Å	$c = 7{\cdot}52$ Å
Zeolite Ω	$a = 18{\cdot}15$ Å	$c = 7{\cdot}59$ Å

Detailed comparisons of the powder patterns of these three zeolites supported the view that Ba-G,*L* was based upon the framework structure of L rather than that of Ω. Ba-G,*L* is thus thought to be an aluminous barium zeolite related to zeolite L. The slight excess of BaO over Al$_2$O$_3$ (Table 1) may arise if there is a little barium (*e.g.* as hydroxide or silicate) intercalated within the structure. The sorption properties of Ba-G,*L* are considered later.

Reactions with Mixed Ba(OH)$_2$ + KOH.—Crystalline products obtained when metakaolinite, with or without additions of silica, reacted with solutions of Ba(OH)$_2$ + KOH, are indicated in Table 4. The symbol *Cha* is used to indicate that a zeolite has a chabazite-like structure. The crystallisations of these species from the compositions 1 metakaolinite + (1·5—10)[mBa(OH)$_2$ + 2(1 − m)KOH] + 275H$_2$O (where $0 \leq m \leq 1$) after 4 days at 85° are shown in Figure 3a, and crystallisations when 2SiO$_2$ and 4SiO$_2$ were added to the above compositions held at 85° for 4 days are shown in Figures 3b and c respectively. Finally with 4SiO$_2$ added and the mixture kept for 8 days at 85°, the crystallisations are those shown in Figure 3d.

TABLE 4

Crystallisation from Ba(OH)$_2$ + KOH

Crystals	Description
(K,Ba)-*Cha*	Chabazite-type zeolites
(Ba,K)-G,*L*	L-type zeolites
Ba-P	Hexagonal polymorph of celsian
(Ba,K)-T	Analogue of zeolite Ba-T

Figure 3 relates the products to the mol fractions BaO/(BaO + K$_2$O) and to the total alkali concentration. These two variables, for a given temperature and time, dominate the behaviour. Thus Ba-P requires a high mol fraction of BaO which becomes smaller only at the highest concentrations of total bases. (Ba,K)-T Requires lower mol fractions of BaO, but always at higher concentrations of base which must be larger the smaller the mol fraction of BaO. (Ba,K)-G,*L* appears all the way from high to low mol fractions of BaO and over a considerable range of total base concentrations. Just as with (Ba,K)-T, the greater the total base concentration the smaller the mol fraction of BaO at which (Ba,K)-G,*L* appeared. The chabazite-type zeolites (K,Ba)-*Cha* on the other hand appeared when the

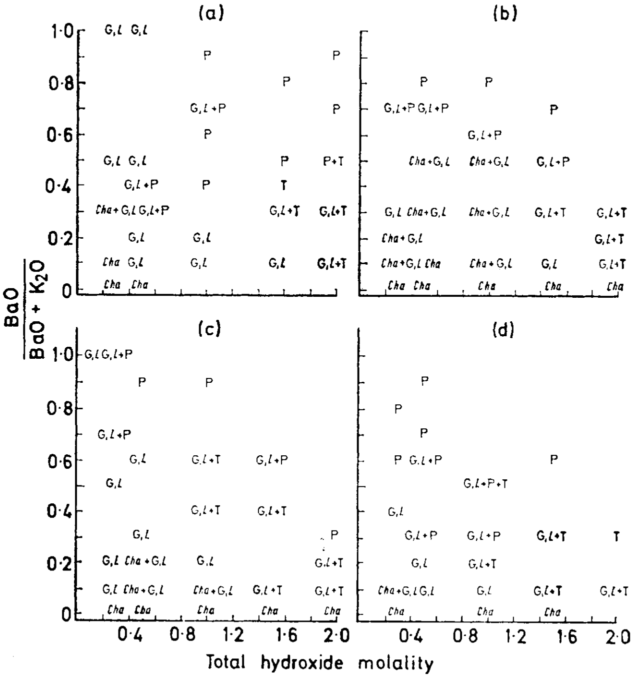

FIGURE 3 Crystallisation field of metakaolinite with and without added silica, and barium + potassium hydroxides reacting at 80° for 4 days (a, b, and c) and for 8 days (d). The starting compositions were in the following ranges: (a) 1 metakaolinite + 1·5—10[mBa(OH)$_2$ + 2(1 − m)KOH] + 275H$_2$O; (b) 1 metakaolinite + 1·5—10[mBa(OH)$_2$ + 2(1 − m)KOH] + 2SiO$_2$ + 275H$_2$O; (c) 1 metakaolinite + 1·5—10[mBa(OH)$_2$ + 2(1 − m)KOH] + 4SiO$_2$ + 275H$_2$O; (d) 1 metakaolinite + 1·5—10[mBa(OH)$_2$ + 2(1 − m)KOH] + 6SiO$_2$ + 275H$_2$O

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[6] R. M. Barrer and H. Villiger, *Chem. Comm.*, 1969, p. 659.

mol fraction of BaO lay between about 0·5 and 0 over the full range of concentrations of total bases. However the greater this mol fraction the smaller the base concentration required for chabazite-type zeolites to appear. These zeolites were similar to the near-chabazites termed K-G prepared by Barrer and Baynham.[7]

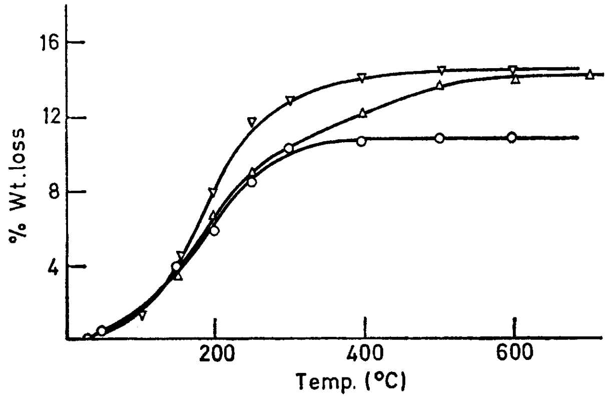

FIGURE 4 Dehydration of various cationic forms of (Ba,K)-G,*L* equilibrated at 56%. Heating rate 10°/min in air. ○ (K,Ba)-form = 10·8%, △ NH_4-form = 14·2%, ▽ H-form = 14·5%

(Ba,K)-G,L. One analysed specimen of this zeolite prepared from metakaolinite without added SiO_2 had the oxide composition $0{\cdot}85BaO,0{\cdot}15K_2O,Al_2O_3,2{\cdot}14SiO_2,2{\cdot}6H_2O$. The *d*-spacings are very similar to those of Ba-G,*L*, and were indexed * to the hexagonal unit cell with $a = 18{\cdot}701 \pm 0{\cdot}002$ Å and $c = 7{\cdot}501 \pm 0{\cdot}001$ Å [8] and cell content $Ba_{7\cdot4}K_{2\cdot6}[Al_{17\cdot4}Si_{18\cdot6}O_{72}]22{\cdot}6H_2O$. Like Ba-G,*L* the analysed sample of (Ba,K)-G,*L* is aluminous, but is based upon the framework of zeolite L. T.g.a. curves of the parent (Ba,K)-G,*L*, of a partly ion-exchanged NH_4-form and of the H-form obtained by heating the NH_4-form to *ca.* 700° are shown in Figure 4. The H-form was stable to at least this temperature while the (Ba,K)-G,*L* heated in the Lenné–Guinier camera was stable to at least 800°. The NH_4-enriched crystals had the oxide formula $0{\cdot}41(NH_4)_2O, 0{\cdot}64(K_2,Ba)O, Al_2O_3, 2{\cdot}16SiO_2, 2{\cdot}8H_2O$, so that as observed also with zeolite L [2,9] only a fraction of the original cations are exchangeable under mild conditions. The thermal stability of (Ba,K)-G,*L* and of its partial H-form are notable properties of so aluminous a zeolite. The difficultly exchangeable metal ions, assumed (by analogy with zeolite L) to be in the smaller cavities of the zeolite, may confer this stability by supporting the framework. The d.t.a. curves in Figure 5 indicate endothermal water loss, followed in the NH_4-enriched crystals by the exothermal oxidation of the NH_4^+ ions to yield the H-form. Near 1000° both NH_4-enriched and parent (Ba,K)-G,*L* show small exothermal peaks near 1000°, probably associ-

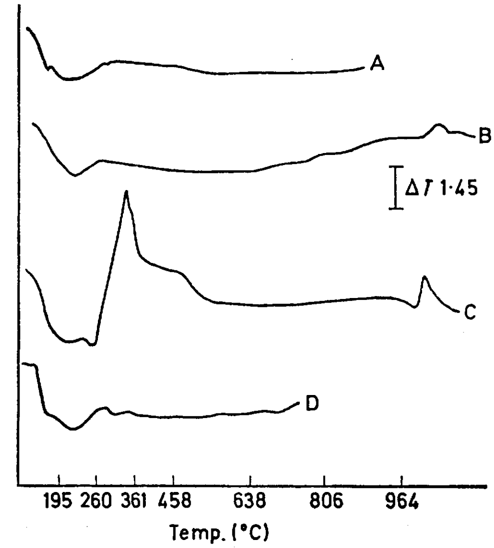

FIGURE 5 The d.t.a. curves of (Ba,K)-G,*L* enriched by ion exchange in various cations and equilibrated at 56% R.H. Heating rate 16°/min in air. A = Original (Ba,K)-G,*L*, B = (Ba,K)-G,*L* heated to 600 °C and rehydrated, C = hydrated NH_4-form, D = hydrated H-form

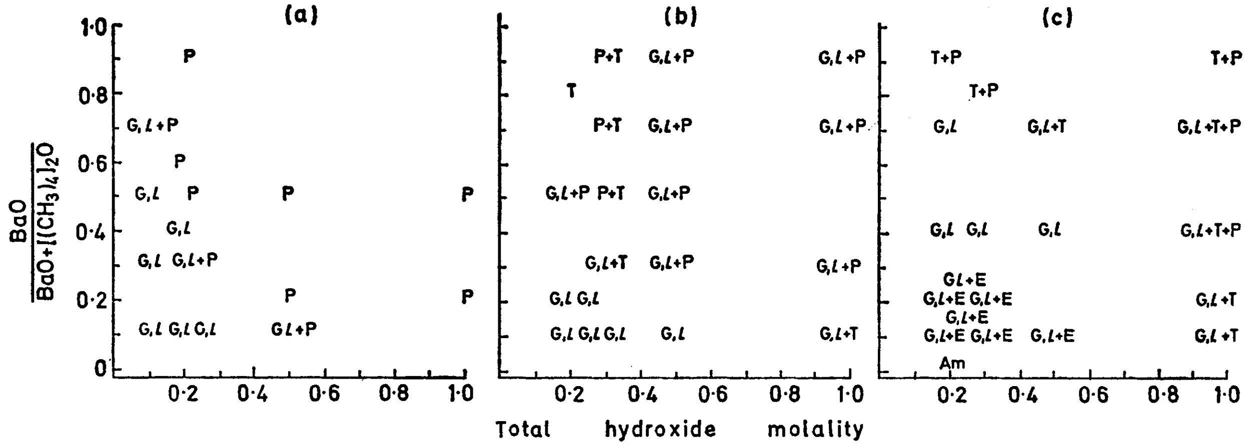

FIGURE 6 Crystallisation fields of metakaolinite with and without added silica, and barium + tetramethylammonium hydroxides reacting at 80° for 7 days. The starting compositions were in the following ranges: (a) 1 metakaolinite + 1—5[mBa(OH)$_2$ + 2(1 − m)(CH$_3$)$_4$NOH] + 275H$_2$O; (b) 1 metakaolinite + 1 − 5[mBa(OH)$_2$ + 2(1 − m)(CH$_3$)$_4$NOH] + 4SiO$_2$ + 275H$_2$O; (c) 1 metakaolinite + 1—5[mBa(OH)$_2$ + 2(1 − m)(CH$_3$)$_4$NOH] + 6SiO$_2$ + 275H$_2$O

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* The detailed structure of this phase has now been determined and will be described elsewhere.[8]

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

[8] Ch. Baerlocher and R. M. Barrer, in preparation.

[9] R. M. Barrer and I. Galabova, in preparation.

ated with recrystallisation of the zeolites or of their amorphous breakdown products.

TABLE 5

A comparison of the *d*-spacings of species E, synthetic sodium tetramethylammonium offretite [11] and natural offretite [12]

$(CH_3)_4N$,Ba-E		$(CH_3)_4N$,Na-E		Natural erionite	
11·50	ms	11·58	vw	11·41	100
9·20	w	9·21	vs	9·07	11
7·65	w	7·64	w	7·51	7
6·63	m	6·66	vs	6·61	73
6·40	m	6·38	mw	6·28	5
5·80	mw			5·72	16
5·45	mw	5·39	mw	5·34	14
4·60	m	4·60	m	4·595	8
				4·551	12
				4·322	67
		4·19	ms	4·156	24
3·82	ms	3·83	m	3·813	37
3·75	s	3·78	s	3·746	65
3·65	m	3·62	ms	3·570	24
				3·402	4
3·35	mw	3·32	mw	3·303	39
				3·276	25
3·24	m			3·271	25
		3·182	w		
3·125	w	3·120	vw	3·106	12
3·050	w	3·042	vw	—	5
2·940	m	2·942	mw	2·923	10
				2·910	10
2·865	m	2·864	m	2·869	60
				2·839	50
2·825	m	2·825	ms	2·812	52

Crystallisations with mixed $Ba(OH)_2 + (TMA)OH$.—To increase still further the size of the second cation tetramethylammonium hydroxide was introduced. This base was first shown to function as mineraliser and reactant in zeolite synthesis in 1961.[10] The reaction mixtures in molar proportions were 1 metakaolinite + (2—10)[mBaO + $(1 - m)(TMA)_2O$] + $x SiO_2 + 275H_2O$, where $0 \leqslant m \leqslant 1$ and $x = 0$, 4, or 6. They were heated to 85° for 7 days. The crystalline phases obtained were:

Ba-P	(hexagonal polymorph of celsian)
(Ba,TMA)-T	(analogues of Ba-T)
(Ba,TMA)-E	(analogues of zeolite erionite)
(Ba,TMA)-G,*L*	(analogues of Ba-G,*L*).

The crystallisations from the mixtures are related to the mol fractions of BaO and the total base concentrations in Figure 6. Without additions of silica only Ba-P and (Ba,TMA)-G,*L* were obtained (Figure 6a); from mixtures rich in silica zeolite (Ba,TMA)-T also appeared usually in admixture with (Ba,TMA)-G,*L* or with Ba-P (Figures 6b and c), while the most siliceous reaction mixtures also yielded (Ba,TMA)-E with (Ba,TMA)-G,*L* (Figure 6c). The *X*-ray powder pattern of (Ba,TMA)-E gave *d*-spacings which are compared in Table 5 with those of a synthetic (Na,TMA)-erionite [11] and a natural erionite.[12] The similarity of the three phases is apparent, the unit cells of the synthetic crystals being a little larger than that of the naturally occurring specimen. The powder patterns of (Ba,TMA)-G,*L* emphasised their close structural relation to zeolite L.

*Sorption by Zeolites Ba-G,*L*, (Ba,K)-G,*L*, and (Ba,TMA)-G,*L*.—The wide-pore structure of zeolite L can admit large guest molecules provided the channels parallel to *c* are not blocked by large ions or immobile adventitious guest species. An examination was therefore made of the sorption of O_2, n-C_4H_{10}, iso-C_4H_{10}, neo-C_5H_{12}, and cyclohexane. At 78 K oxygen was freely sorbed in outgassed Ba-G,*L* and in its Ca- and Na-enriched forms prepared by ion exchange (Figure 7a). However, unlike zeolite L,[13] the zeolite did not sorb neo-C_5H_{12} at 273 K. Intracrystalline barium hydroxide or silicate, suggested by the analysis (Table 1), may prevent penetration by larger molecules.

Oxygen isotherms at 78 K in four preparations of (Ba,K)-G,*L* are compared in Figure 7b. All sorb oxygen very freely but in amounts which differ, possibly according to the % yield of the zeolite. Aluminous (Ba,K)-G,*L* behaved differently in sorbing hydrocarbons from the aluminous Ba-G,*L*. In the (Ba,K)-G,*L* having $SiO_2/Al_2O_3 = 2{\cdot}08$ n-C_4H_{10}, iso-C_4H_{10}, and neo-C_5H_{12} were sorbed rapidly and reversibly (Figure 8a). Figure 8b shows the reversible uptake of iso-C_4H_{10} in three Li-exchanged preparations of (Ba,K)-G,*L* having ratios SiO_2/Al_2O_3 = 2·08, 4·00, and 5·40 respectively. The different saturation capacities again may reflect different % yields of the original crystals. A comparison of saturation capacities of some preparations of zeolite G,*L* is presented in Table 6. The oxygen capacity in the first preparation is not matched by that of n- and iso-C_4H_{10} probably because of the partial channel blocking of the hydrocarbons referred to in the previous paragraph. Also Ba- and (Ba,K)-G,*L* are denser than (K,Na)-L because of their greater Al content and heavier cations. Accordingly 1 g of zeolite G,*L* contains fewer unit cells than 1 g of (K,Na)-L.

Three samples, 1, 2, and 3, of (Ba,TMA)-G,*L* were also examined, after being heated in air to 540, 590, and 700° respectively to remove TMA. The samples so treated and then equilibrated with the atmosphere were subsequently thoroughly outgassed at temperatures rising to 300° when

TABLE 6

Approximate saturation capacities of different zeolites having the L-type framework

	SiO_2/Al_2O_3		Capacities in cm³ at s.t.p. per g				
Cations present	During synthesis	In the product	O_2 at 78 K	n-C_4H_{10} at 273 K	iso-C_4H_{10} at 273 K	neo-C_5H_{12} at 273 K	Lattice stable at °C
Ba	2	2·50	87	12·2	9·7	nil	
Ba,K	2	2·08	82	23·5	19·4	13·0	>800
Ba	5	4·80	72	9·5			
Ba,K	6	5·40	74	11·0	10·9		>800
(K,Na)	15—28 [a]	6·4		25 [b]	20 [b]	10 [b]	

[a] Ref. 1. From isotherms of Barrer and Lee.[13]

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[10] R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 1961, 971.

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

[12] R. A. Sheppard and A. J. Gude, *Amer. Mineral.*, 1969, **54**, 875.

[13] R. M. Barrer and J. A. Lee, *Surface Sci.*, 1968, **12**, 341.

they lost water in amounts respectively equal to 15·3, 16·1, and 21·7% of their dry weights. The first and third of the heat-treated samples were analysed and from the BaO/Al_2O_3 ratios the amounts of $(TMA)_2O$ in the parent crystals were inferred. The water-free oxide compositions were then:

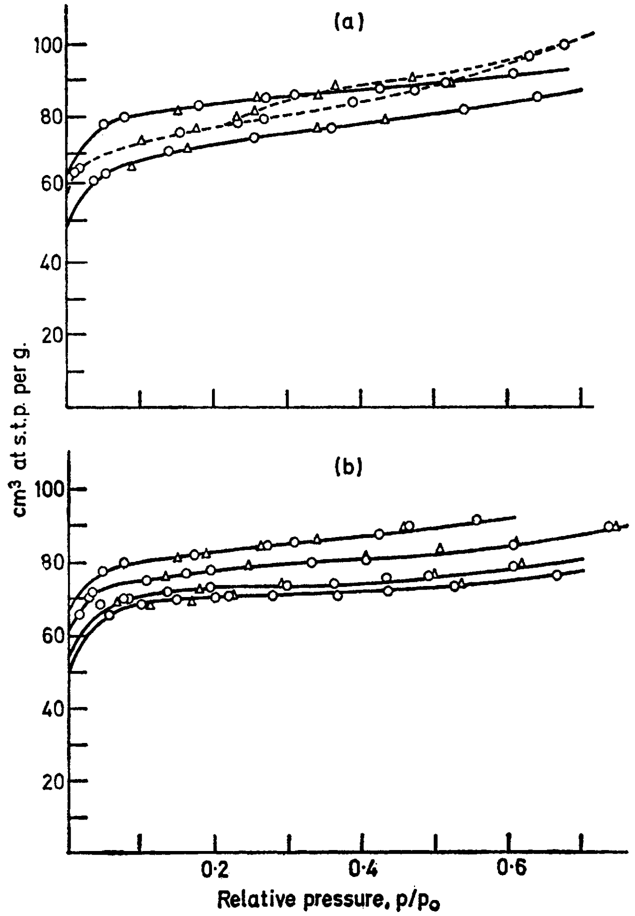

FIGURE 7 Sorption of oxygen at 78 K on various ion exchanged forms of (a) Ba-G,*L* and (b) (Ba,K)-G,*L*. ○ = Sorption and △ = desorption

Sample 1: $0{\cdot}78BaO,0{\cdot}22\,(TMA)_2O,Al_2O_3,2{\cdot}35SiO_2$
Sample 3: $0{\cdot}84BaO,0{\cdot}16\,(TMA)_2O,Al_2O_3,2{\cdot}23SiO_2$

At 78 K the nitrogen saturation capacities of samples 2 and 3 (heat treated as noted above) were *ca.* 74 and *ca.* 83 cm^3 at s.t.p. per g of outgassed zeolite. All three of the heat-treated samples were thermally stable wide pore sorbents which freely sorbed cyclohexane at 22°. Uptakes were largest on sample 3 (heated in air to 700°) which at 1·5 cmHg vapour pressure of sorbate, took up 12·3% of cyclohexane and 7·2% of n-hexane. Under the same conditions sample 1 absorbed 7·7$_5$ and 6·25%, respectively.

DISCUSSION

When $Ba(OH)_2$ is a component in the aqueous solution zeolites having structures similar to that of zeolite L[1] occur all the way from silica-poor to silica-rich reaction mixtures. These crystals also vary from silica-poor to silica-rich (with ratios SiO_2/Al_2O_3 from 2·0 up to at least 5·4). Since zeolite L is reported as having these ratios between 5 and 7,[3] the zeolites G,*L* include many phases with framework compositions and charges very different from zeolite L, and formed with different charge-compensating ions which mineralise growth and participate in it. Thus the new zeolites Ba- and (Ba,K)-G,*L* can differ in composition and some properties from zeolite L more widely than zeolite Na-X differs from Na-Y.[3] The permissible ratios SiO_2/Al_2O_3 have now been shown in L-type zeolites to cover the range 2 to at least 7. The range is thus comparable with that found among synthetic and natural chabazite-type zeolites,[5,6,14] (2·13 to 7·76). When such wide composition ranges are found the chemical and physical properties also alter greatly between the extremes. As in some mineralogical situations, the extremes could be considered as different species (e.g.s. heulandite and clinoptilolite; or sodalite and nosean) which may form a range of solid solutions based upon a common type of framework.

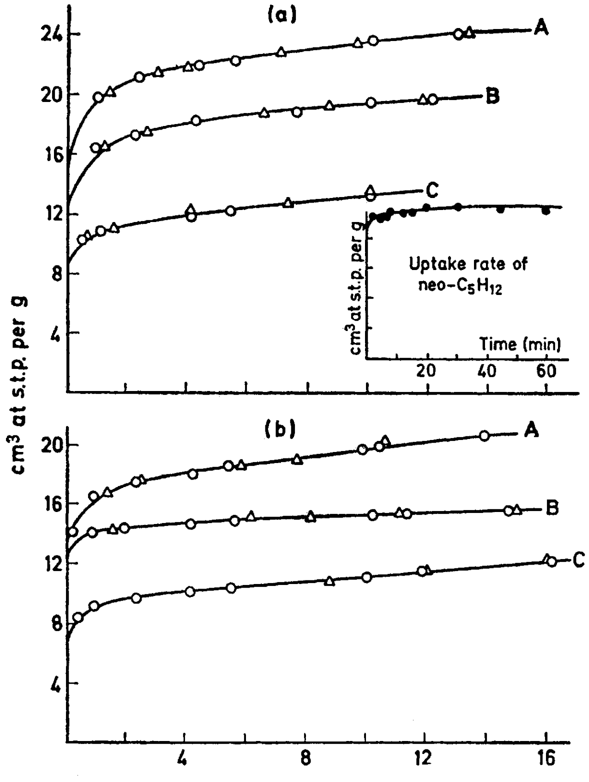

FIGURE 8 (a) Sorption of hydrocarbons on (Ba,K)-G,*L* at 273 K. A = n-C_4A_{10}, B = iso-C_4H_{10}, C = neo-C_5H_{12}; (b) Sorption of isobutane on Li-exchanged forms of (Ba,K)-G,*L* with silica : alumina ratios of 2·08, 4·00, and 5·40. A = G,*L* (2·08), B = G,*L* (4·00), C = G,*L* (5·40). O = Sorption, △ = desorption

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[14] A. J. Gude and R. A. Sheppard, *Amer. Mineral.*, 1966, **51**, 909.

Further variations in properties even among the end members can be attributed to variable intercalation from the crystallising magma of guest species other than water. This can particularly influence the molecule sieving properties as demonstrated in this paper for the preparation of Ba-G,*L* with $SiO_2/Al_2O_3 = 2{\cdot}5$.

One of us (D. E. M.) thanks English Clays Ltd. for the award of a research scholarship which enabled him to take part in this programme. We also thank Dr I. S. Kerr for assistance with electron microscopy and Mr Ch. Baerlocher for the determination of the unit cell of (Ba,K)-G,*L*.

[2/113 *Received, 19th January,* 1972]