Hydrothermal Chemistry of Silicates. Part 22.[1] Hydrated Barium–Sodium Aluminosilicates

By **Richard M. Barrer** * and **Werner Sieber**, The Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

A partial exploration has been made of crystallisation from tetramethylammonium ' aluminosilicate ' solutions following addition of mixed barium chloride–sodium chloride solutions. Even small quantities of Ba^{2+} influence strongly which structures nucleate and crystallise, and so the system Na_2O–BaO–Al_2O_3–SiO_2–H_2O has also been further explored. Zeolites obtained included variants of offretite, zeolite *A*, zeolite *L*, zeolite M, faujasite, and gismondine. In addition a zeolite U10, probably belonging to the chabazite group, a barium aluminate, and an unidentified phase U11 have been obtained. The properties of U10 have been investigated. The hexagonal unit cell has $a = 13.71 \pm 0.03$ and $c = 15.57 \pm 0.04$ Å.

ALTHOUGH mixtures of univalent cations have been extensively investigated in zeolite synthesis, mixtures of uni- and bi-valent cations have received relatively little attention. The action on metakaolinite of tetramethylammonium and potassium hydroxides in combination with barium hydroxide has been examined.[2] Barrer *et al.*[3] investigated mixtures of metakaolinite with $Ba[OH]_2 + Li[OH]$, $Ba[OH]_2 + Na[OH]$, and $Ba[OH]_2 + Tl[OH]$. The use of tetramethylammonium ' aluminosilicate ' solutions [1] allows the formation of gels in a homogeneous reaction. In view of the limited solubility of $Ba[OH]_2$ it was of interest to apply this technique to barium-containing systems, introducing the Ba^{2+} ion as the chloride. In the course of the present work it was found that even small amounts of barium had a strong influence on the products of the synthesis. The ' system ' Na_2O–BaO–Al_2O_3–SiO_2–H_2O was thus further explored in the absence of tetramethylammonium ions.

EXPERIMENTAL

Tetramethylammonium ' aluminosilicate ' solutions were prepared as described in ref. 1. Sodium and barium ions were added as chloride solutions containing 2 equivalents per litre. Syntheses without tetramethylammonium were carried out in two different ways.

(*a*) Sodium hydroxide and $Ba[OH]_2 \cdot 8H_2O$ were dissolved in water with heating, aluminium isopropoxide was added, and the resulting isopropyl alcohol was boiled off. The solutions were distributed to polypropylene bottles while hot, and mixed with Syton X30 colloidal silica using a high-speed blender.

(*b*) Sodium hydroxide and commercial sodium aluminate (43% Al_2O_3) were dissolved in water by heating, distributed to bottles while hot, and 1 mol dm^{-3} barium chloride solution was added from a pipette. After shaking, Syton X30 was added, and the mixture was mechanically blended. In a series of experiments, tris(2-hydroxyethyl)amine was added to the aluminate solution before blending in the colloidal silica.

The mixtures were kept at 90 °C for various times. The products were identified by Guinier *X*-ray powder patterns. Densities were determined pycnometrically. Further characterisation took place as described in ref. 1.

RESULTS

The crystalline products of the syntheses are summarised in Table 1. Examples of synthesis conditions and products obtained are reported in Tables 2 and 3. $[OH]_T$ is the total analytical hydroxide-ion concentration, t_1 is the time elapsed between preparing the tetramethylammonium aluminosilicate solution and adding the alkali-metal chloride solutions (the aluminosilicate solution was kept at 90 °C during this time), and t_3 is the ripening time of the final mixtures.[1]

TABLE 1

The crystalline products obtained

Reference letter(s)	Structural type	Literature ref. nos.
O	Zeolite, offretite type	2,4
A	Zeolite, type *A*	*a*
X	Zeolite, faujasite type	*b*
M	Zeolite, harmotome–phillipsite type	2,3,9
G,*L*	Zeolite, type *L*	2,3,*c*
P	Zeolite, gismondine type	*d*
U10	Zeolite, new type	
U11	Unidentified	
BNA	Barium sodium aluminate hydrate	6

[a] D. W. Breck, W. G. Eversole, and R. M. Milton, *J. Amer. Chem. Soc.*, 1956, **78**, 2338. [b] R. M. Milton, U.S.P. 3,008,803/1961. [c] A. J. Perrota, *Amer. Mineral*, 1976, **61**, 495. [d] Ch. Baerlocher and W. M. Meier, *Z. Krist.*, 1972, **135**, 339.

TABLE 2

Crystallisation from tetramethylammonium aluminosilicate and barium chloride–sodium chloride solutions. $[OH]_T = [NMe_4] = 1.25$ mol dm^{-3}

Si : Al	$[OH]_T$: Al	(2Ba + Na) : Al	2Ba : (2Ba + Na)	t_1 (h)	t_3 (h)	Product (*X*-ray)
2.5	2.5	0.7	0.1	0	139	A + tr.X, small yield
2.5	2.5	2.0	0.1	0	139	O, weak
2.5	2.5	0.7	0.4	0	1 440	Amorphous
2.5	2.5	1.3	0.4	0	139	O, strong, sharp
2.5	2.5	2.0	0.1	72	67	O, strong, diffuse
3.5	4.0	2.0	0.1	0	94	O, good yield *
3.5	4.0	2.0	0.4	0	94	O, good yield
3.5	4.0	2.0	1.0	0	94	O, v. weak, much gel
3.5	4.0	2.0	0.4	51	91	O, good yield
3.5	4.0	2.0	1.0	51	91	O, weak, much gel

* Yield, based on aluminium, *ca.* 100%. For analysis of product see text.

---

[1] Part 21, R. M. Barrer and W. Sieber, *J.C.S. Dalton*, 1977, 1020.

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

[3] R. M. Barrer, R. Beaumont, and C. Collela, *J.C.S. Dalton*, 1974, 934.

Experiments using Tetramethylammonium Aluminosilicate. From the results it can be seen that, as soon as the ratio 2Ba : Al is increased to 0.2 : 1 or higher, the offretite-type zeolite O becomes the only crystalline product, albeit in varying yield and crystallinity. It was also obtained in the absence of sodium ions, although the optimum equivalent fraction of barium seems to lie between 0.1 and 0.4. A sample of zeolite O (*cf.* footnote of Table 2) had a density of 2.091 g cm^{-3}, the hexagonal lattice parameters being $a = 13.357 \pm 0.004$ and $c = 7.548 \pm 0.003$ Å (calculated from 42 reflections, with $Pb[NO_3]_2$ as internal standard). Chemical analysis gave unit-cell contents of $(NMe_4)_{1.98}$-$Na_{3.23}Ba_{0.54}Al_{5.4}Si_{11.9}O_{34.6}\cdot 11.6H_2O$. In spite of the excess of silica and the large proportion of $[NMe_4]^+$ ions present in the batch, this offretite was more aluminous than the (K,Na)-O of Aiello and Barrer,[4] yet it showed the same thermostability (stable up to 820 °C). The differential thermal analysis (d.t.a.) trace showed two exotherms at 380 and 440 °C. Whereas some of the $[NMe_4]^+$ ions could be exchanged by 1 mol dm^{-3} NaCl solution, the barium was non-exchangeable.

TABLE 3

Experiments in the system Na_2O–BaO–Al_2O_3–SiO_2–H_2O

Si : Al	$[OH]_T$: Al	$[OH]_T$	2Ba : (2Ba + Na)	t_3/h	Product
0	3.0	5.22	0.048	89	BNA, 67% [a]
0	3.0	2.73	0.286	89	BNA, 84%
0.8	2.5	1.2	0	48	*A*
0.8	2.0	1.0	0.02	45	U10 [b]
0.8	2.5	1.2	0.02	48	U10
0.8	2.5	1.2	0.08	48	G,*L* + U10 + P
0.8	2.5	1.5	0.08	48	G,*L* + U10
0.8	3.0	1.0	0.013	45	U10 + some P
1.0	3.0	1.2	0.1	17	G,*L* + tr.P + tr. U10
1.2	2.5	1.2	0.05	47	U10 + P
1.5	3.0	1.2	0.05	16	M + U10
1.6	2.5	1.2	0	46	*A* + X
2.0	3.0	1.2	0.10	17	M + G,*L*
2.5	3.0	1.2	0.05	44	M
2.5	3.0	1.2	0.10	17	M + G,*L*, weak
3.5	4.0	1.0	0.05	43	M [c]
3.5	4.0	1.0	0.20	22	M [c]
5.0	4.0	1.0	0.20	22	M
2.0 [d]	2.0	1.7	0.005	41	P
2.0 [d]	2.0	1.7	0.024	41	P + U11
2.0 [d]	3.0	3.7	0.016	41	X + tr.P
3.5 [d]	3.0	2.7	0.016	114	X + U11
3.5 [d]	3.0	2.7	0.032	114	U11 + tr. P

[a] Based on total barium available. [b] Some weak lines corresponding to phase P were present in most samples of U10. [c] Gradual transition from phillipsite to harmotome pattern with increasing barium content. [d] Carried out according to method (*b*) (see Experimental section); all the other experiments were according to method (*a*).

An offretite-type phase has been obtained [2] from the reaction of $[NMe_4][OH]$ and $Ba[OH]_2$ with metakaolinite, although only in admixture with other phases. The binary combination of Na^+ and $[NMe_4]^+$ ions yields no offretite, but *A*-type phases.[5]

The Binary (Na,Ba) *System.*—The novel compound U10 crystallised from a considerable range of batch compositions. Its field of formation is limited mainly by the appearance of competing species. U10 was obtained in its purest form at low ratios of Si : Al and Ba : Al, but equivalent fractions of Ba^{2+} below *ca.* 1% yielded mostly the sodium zeolites *A*, P, and X. Increasing barium contents lead to the formation of the barium zeolites G,*L* (at low Si : Al) and M (at higher Si : Al). The zeolite M showed some variation in its powder pattern: depending on the equivalent fraction of Ba^{2+} in the reaction mixture, a transition from a phillipsite-like to a typical harmotome pattern was observed (*cf.* ref. 3, p. 939). The barium aluminate BNA was never observed in the presence of any amount of silica in the reaction mixture, even though it readily crystallised from a mixture of sodium aluminate and barium chloride. This represents evidence against the presence of free aluminate ions in zeolite synthesis mixtures. Analysis of a sample of BNA obtained from a mixture with 2Ba : (2Ba + Na) = 0.29 gave the following composition in wt. %: BaO, 62.4; Al_2O_3, 20.5; Na_2O, 0.25; H_2O, 16.9; total, 100.05. This agrees with the formula $Ba_2Al_2O_5\cdot 4.67H_2O$, with only 1 mol % of the barium replaced by sodium. A high selectivity for barium is thus apparent in this phase. The powder pattern of BNA corresponds with that given by Carlson and Wells.[6]

Since the powder lines of compound U10, as obtained from the mixtures described in Table 3, were invariably rather broad and diffuse, experiments were made to obtain larger crystals by incorporation of tris(2-hydroxyethyl)-amine in the aqueous synthesis mixtures.[7] Crystals of U10 showing the sharpest lines were obtained from a batch of the following composition (in mol per kg of mixture): $[OH]_T = 1.18$, $[Si] = [Al] = 0.79$, $[Na] = 1.18$, $[Ba] = 0.04$, and $[N(C_2H_4OH)_3] = 2.68$. The chemical compositions of two samples of U10 are shown in Table 4. Powder patterns of products from batches with and without $N(C_2H_4OH)_3$ are compared in Table 5, which also includes the poorly crystalline species U11.

TABLE 4

The composition of species U10

	Oxides	wt. %	Atom ratio (Al = 1) in crystal	Atom ratio (Al = 1) in batch	No. of atoms per unit per cell
a	SiO_2	32.79 ± 0.05	1.01	0.8	17.87 Si
	Al_2O_3	27.55 ± 0.06			17.66 Al
	BaO	2.17 ± 0.04	0.026	0.02	0.46 Ba
	Na_2O	16.5 ± 0.2	0.98	1.96	17.40 Na
	H_2O	20.35 ± 0.2	2.09	73.5	36.90 H_2O
b	SiO_2	32.97 ± 0.1	1.10	0.91	18.81 Si
	Al_2O_3	25.50 ± 0.2			17.11 Al
	BaO	4.97 ± 0.06	0.065	0.05	1.11 Ba
	K_2O	20.94 ± 0.1	0.89	1.50 [c]	15.22 K
	H_2O	15.95	1.77	22.7	30.33 H_2O

[a] Sample no. G1, prepared without $N(C_2H_4OH)_3$; unit-cell contents calculated from observed density and cell volume. [b] Prepared in the presence of 40 wt. % $N(C_2H_4OH)_3$, and exchanged twice with 1 mol dm^{-3} KCl (48 h + 10 d, 16-fold molar excess, room temperature). Unit-cell contents calculated for 72 oxygen atoms. [c] Na^+.

The void volume of U10 per cm^3 of crystal, based on the water contents, is 43.8%. As shown in Table 5, the powder pattern of U10 can be indexed according to a hexagonal unit cell with the parameters $a = 13.71 \pm 0.03$ and $c = 15.57 \pm 0.04$ Å. Electron micrographs (scanning and carbon replicas, total magnification up to 2×10^5) failed to show

---

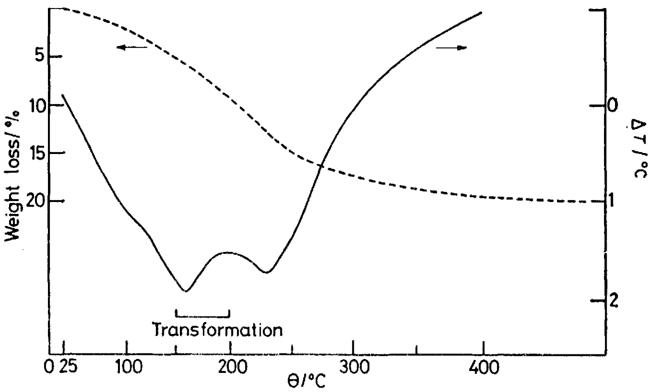
[4] R. Aiello and R. M. Barrer, *J. Chem. Soc.* (*A*), 1970, 1470.

[5] G. T. Kerr, *Inorg. Chem.*, 1966, **5**, 1537.

[6] E. T. Carlson and L. S. Wells, *Bur. Stand. J. Res.*, 1948, **41**, 103.

[7] J. F. Charnell, *J. Crystal Growth*, 1971, **8**, 291.

recognisable crystal shapes. Electron-diffraction patterns could not be obtained. The product appears to consist of conglomerates, the primary crystallites showing faces of *ca.* 0.03 µm in diameter, in agreement with the broadened lines of the *X*-ray pattern. Thermogravimetric analysis (t.g.a.) and d.t.a. curves of U10 are shown in the Figure.



Thermogravimetric (— — —, 4 °C min^{-1}) and differential thermal analyses (——, 20 °C min^{-1}) of zeolite U10

The water loss is gradual, even if the heating is carried out in a step-wise manner, awaiting constant weight at various intermediate temperatures. Powder patterns taken at the end of each step indicate that U10 undergoes an irreversible transformation between 150 and 200 °C. This corresponds to an exothermic peak in the d.t.a., which is superimposed on the endotherm caused by the dehydration. The powder lines of the resulting product are included in Table 5. The lines are more diffuse than those of the original U10. The calcium ion-exchanged form showed a similar transformation over the same temperature range. At 200 °C it had lost 50% of its water-sorption capacity. Potassium ion-exchange (1 mol dm^{-3} KCl, 2 × 48 h, room temperature or 90 °C) led to considerable changes in the powder pattern of U10, approaching that of zeolite K-G1.[8] These changes were however reversed by re-exchange with sodium ions. An original sample of K-G1, on the other hand, did *not* produce a pattern resembling U10 on sodium exchange. The barium ions contained in U10 remained non-exchangeable by either Na$^+$ or K$^+$ (*cf.* Table 4). On heating, K^{ex}-U10 suffered some loss of crystallinity between 200 and 260 °C, but some diffuse lines remained up to 950 °C.

TABLE 5

Powder patterns of U10 and its modifications

No. G1[a]		No. TB15[b]			No. TB15h[c]		Species U11	
d/Å	*I*	*hkl*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
12	mw	100	12.1	m			12	s (br.)
9.4	vs	101	9.41	vs				
		002	7.60	vw				
6.90	w	110	6.87	w			6.9	s
		102	6.50	vw	6.4	s		
5.4	w(br)	201	5.54	w				
5.15	m	112	5.12	m				
		103 202	4.74	vw				
4.30	m	211	4.32	ms			4.5— 4.1	w (band)
4.09	ms	113	4.12	m				
3.97	mw	300	4.02	m				
3.87	w	212 004	3.88	w	3.85	vw		
		301	3.825	vw				
3.70	w	104	3.708	mw	3.68	m		
		302	3.488	vw				
		220 213	3.428	w			3.42	ms
		204	3.260	w				
3.22	w	311	3 220	m	3.20	vw		
		312	3.039	w				
		105	3.019	m				
2.98	m	400	2.946	m	2.96	vw	2.96— 2.82	m (band)
2.90	s	214	2.918	s				
2.84	w	223	2.890	vw				
					2.86	vw		
		304 205	2.763	vw				
2.70	w				2.60	vw		

[a] Prepared without N(C$_2$H$_4$OH)$_3$. [b] Prepared with added N(C$_2$H$_4$OH)$_3$. [c] No. TB15 after heating to 330 °C in air.

DISCUSSION

The present work has shown that small equivalent fractions of barium ions can exert a strong influence on the products obtained from otherwise well known zeolite-synthesis mixtures. In the presence of tetramethylammonium and sodium ions, barium leads to replacement of zeolite Na-*A* by an offretite-type zeolite. If Ba^{2+} is added to a mixture which otherwise would form pure Na-*A* the new species U10 is obtained. When the amount of Ba^{2+} is increased U10 is superseded by the zeolite Na,Ba-G,*L*. At higher Si : Al ratios Na-P gives way to the phillipsite–harmotome-type zeolite M.[9]

The species U10, even though its crystallisation depends on the presence of Ba^{2+}, only contains 2.6% of this ion with respect to its total cationic contents. This is not sufficient to account for one Ba^{2+} per unit cell. The same observation applies to zeolite O (0.54 Ba^{2+} per unit cell). Some unit cells therefore only contain sodium (*viz.* [NMe$_4$]$^+$) ions. Two possible explanations of this fact can be considered. (*a*) Barium ions are exchanged by sodium in the course of crystallisation, as soon as the U10 (or offretite) framework is formed. The barium ions thus liberated give rise to further crystallisation of the same species. (*b*) Barium ions cause nuclei to be formed, on which Na-U10 (or Na,NMe$_4$-O) grows sufficiently fast to exclude nucleation and/or significant growth of other sodium zeolites.

The barium ions contained in zeolites U10 and O were shown to be non-exchangeable. Mechanism (*a*) therefore appears unlikely. This is the first instance, to our knowledge, that evidence has been provided for a structure-determining effect of a cation *operating specifically at the nucleation stage* of zeolite crystallisation. The exceedingly small size of the U10 crystallites suggests high supersaturation in the starting mixture, and formation of a large number of nuclei. The barium aluminosilicate thus appears to be much less soluble than the zeolite Na-*A* formed in the absence of Ba^{2+}. It is well known that Na-*A* is metastable under synthesis

---

[8] R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882; R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 1254.

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

conditions, transforming eventually to Na-P or sodalite hydrate. It is conceivable that the lowering of solubility brought about by the barium ions causes the 'jumping' of the metastable phase by the system. Na-P, unlike Na-*A*, is often found as an admixture in samples of U10. The high selectivity of aluminate anions for Ba^{2+} over Na^+ is illustrated by the crystallisation of virtually pure $Ba_2Al_2O_5\cdot5H_2O$ from a solution containing an excess of sodium ions. It is not unreasonable to think that this selectivity extends to aluminosilicate anions. The 'catalytic' influence of small amounts of foreign ions could help to explain certain cases of poor reproducibility encountered in zeolite synthesis.

Evidence for the zeolitic nature of species U10 is provided by its chemical composition and its dehydration behaviour, as well as by the powder-diffraction pattern. The ratio of non-framework cations to aluminium is exactly 1 : 1. The ratio Si : Al is $\geqslant 1:1$ in the crystal even when it is lower in the synthesis mixture. On heating the water is removed gradually with increasing temperature, and partial rehydration is possible. The transformation at the comparatively low temperatures of 150—200 °C is rather unusual for a zeolite. Breck [10] however mentions that the structure of phillipsite degrades at 200 °C, the structure of stilbite changes at 120 °C, and that of mesolite at 300 °C. The lattice constants of U10 are similar to those of chabazite.[11] The relative intensities of the powder lines are quite different. Several of the lines observed with U10 are extinguished under the space group ($R\bar{3}m$, see ref. 12) of chabazite. This indicates lower symmetry in the case of U10. The chabazite framework can be represented as an AABBCC stacking of 'six-rings.' [13] Several other stackings with a repeat period of six 'layers' can be constructed, giving rise to similar lattice constants. All these are of lower symmetry than the chabazite framework. The number of (Si + Al) atoms found per unit cell of U10 is very close to 36, as required by a structure of this group. The present powder data do not allow a conclusive choice between the possible structures. If U10 is assigned a particular sequence of layers the powder pattern of species U11 could be interpreted as arising from a phase partly disordered in the *z* direction, with mostly *hk*0 reflections remaining.

We thank W. R. Grace Corp. for support, which allowed one of us (W. S.) to take part in this work.

[7/1534 *Received*, 25*th August*, 1977]

---

[10] D. W. Breck, 'Zeolite Molecular Sieves,' Wiley, New York, London, Toronto, 1974.

[11] E. Passaglia, *Amer. Mineral*,. 1970, **55**, 1278.

[12] W. M. Meier and D. H. Olson, *Adv. Chem. Ser.*, *Amer. Chem. Soc.*, 1971, **101**, 155.

[13] W. M. Meier, 'Molecular Sieves,' Soc. Chem. Industry, London, 1968, p.10.