

431. Hydrothermal Chemistry of Silicates. Part XIII.¹
Synthetic Barium Aluminosilicates.

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The hydrothermal crystallisation of aqueous gels of composition $\text{BaO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ ($1 \leq n \leq 9$) has been studied between 110 and 450°. The products have been studied and characterised by X-ray and electron diffraction, differential thermal analysis, and thermogravimetric analysis, and by their optical and sorptive properties.

The species produced in major and reproducible yield were celsian, hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$, harmotome, and two unidentified zeolites. An unidentified compound with some structural relationship to celsian was also produced. Two unidentified species, which may also be zeolitic, were produced in lower and less reproducible yield. Excess silica crystallised as cristobalite, and excess alumina as boehmite. The crystallisation fields of the species produced are discussed and compared with those of the analogous synthetic aluminosilicates of calcium and strontium.

PREVIOUS work in these laboratories was concerned with the hydrothermal synthesis of aluminosilicates of the alkali cations,²⁻⁵ calcium,⁶ and strontium.¹ The present work reports a study of the crystallisation fields and some properties of synthetic barium aluminosilicates.

In one previous study of the barium aluminosilicates,⁷ synthetic analcite was treated with concentrated solutions of barium salts under hydrothermal conditions. The analcite crystallised at about 200° to a new mineral species $\text{BaO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 0.66\text{BaCl}_2, 2-3\text{H}_2\text{O}$. The occluded barium salt could be removed by hydrothermal extraction, leaving a zeolite with sorptive properties.⁸ If the extraction process was attempted under more vigorous or prolonged treatment the compound would recrystallise to barium feldspar or another unidentified species. Corwin *et al.*⁹ investigated the hydrothermal action of barium hydroxide solution on vitreous silica and showed that an adherent layer of barium silicate is formed which prevents further attack.

Barium aluminosilicates have also been synthesised, and their phase equilibria investigated, in sintering and pyrolytic experiments. Thus, the system barium oxide-alumina-silica was studied by Toropov *et al.*^{10,11} using a quenching technique. No X-ray data were given but two silicates, $2\text{BaO}, 3\text{SiO}_2$ and $\text{BaO}, 2\text{SiO}_2$ were reported in addition to celsian, and also a new aluminosilicate, $3\text{BaO}, 3\text{Al}_2\text{O}_3, 2\text{SiO}_2$.

The monoclinic barium feldspar, celsian, has been synthesised from the oxides¹²⁻¹⁴ by heating them together dry, or with a vanadate flux. A hexagonal polymorph has also been synthesised¹⁵⁻¹⁸ and was produced in good yield as large crystals from kaolin and

¹ Part XII, Barrer and Marshall, *J.*, 1964, 485.

² Barrer and White, *J.*, 1951, 1267.

³ Barrer and White, *J.*, 1952, 1561.

⁴ Barrer and McCallum, *J.*, 1953, 4029.

⁵ Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.

⁶ Barrer and Denny, *J.*, 1961, 983.

⁷ Barrer, *J.*, 1948, 127.

⁸ Barrer and Riley, *J.*, 1948, 133.

⁹ Corwin, Yalman, Edwards, and Owen, *J. Phys. Chem.*, 1957, **61**, 939.

¹⁰ Toropov, Galakhov, and Bondar, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1954, 753.

¹¹ Toropov, Galakhov, and Bondar, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1955, 3.

¹² Fouqué and Michel-Levy, *Bull. Soc. Franc. Min.*, 1880, **3**, 124.

¹³ Dittler, *Min. Petr. Mitt. (Tscherma)*, 1911, **30**, 118.

¹⁴ Eskola, *Amer. J. Sci.*, 1922, **4**, 331.

¹⁵ Weyberg, *Bull. Univ. Varsovie*, 1904, **4**, 1.

¹⁶ Ginzberg, *Min. Abs.*, 1923, **2**, 153.

¹⁷ Dittler and Lasch, *Akad. Wiss. Wien Math.-naturwiss. Kl.*, 1930, **67**, 201.

¹⁸ Thomas, *J. Amer. Ceram. Soc.*, 1950, **33**, 35.

barium carbonate by Yoshiki and Matsumoto.¹⁹ The compound was shown to have a reversible transformation at about 300°, and its structure was determined by Ito²⁰ and Takeuchi.²¹ This polymorph has not been clearly identified in Nature, but the mineral cymrite^{22a} has a very similar *X*-ray pattern.^{22b} A third polymorph, found naturally but not yet synthesised, is paracelsian, which is monoclinic but very close to orthorhombic.²³

EXPERIMENTAL AND RESULTS

The experimental methods and apparatus were identical with those described for the work on the strontium aluminosilicates,¹ using AnalaR barium hydroxide octahydrate as the source of barium.

The species produced are listed in Table 1. A "major" yield indicates a best yield of over 60% as estimated optically and from *X*-ray powder patterns. Since boehmite and cristobalite have often occurred in previous studies of this series^{1,2} they will not be described further here.

Some reaction conditions, and the products obtained from aqueous gels with the dry oxide compositions $\text{BaO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$ ($1 < n < 9$), are shown in Table 2. The crystallisation fields

TABLE 1.
The synthetic barium aluminosilicate phases.

Symbol	Species	Yield	Reproducibility
Ba-A	Unidentified	Major	V. good
Ba-C	Celsian (barium feldspar)	100%	V. good
Ba-E	Boehmite	Major	Good
Ba-G	Barium zeolite	Major	Moderate to poor
Ba-H	α -Cristobalite	Major	Good
Ba-J	Barium zeolite	100%	Moderate
Ba-K	Barium zeolite	100%	Moderate
Ba-M	Harmotome	100%	Moderate to good
Ba-P	Hexagonal polymorph of barium feldspar	100%	Good
Ba-Z	Unidentified	Minor	Poor

are shown in Fig. 1. For various values of n the temperature was varied between 110 and 450°, and the duration of the experiments ranged from a few hours to several weeks. In general, the higher the value of n and the lower the temperature, the longer the time required for crystallisation. The region of the crystallisation field in which no crystallisation was

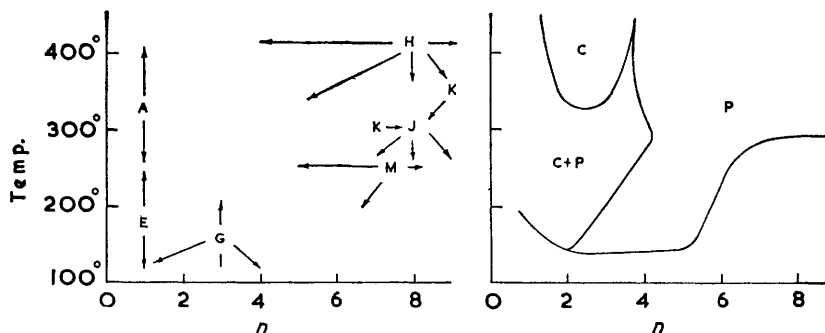


FIG. 1. Crystallisation fields of species produced from aqueous gels of oxide composition $\text{BaO}, \text{Al}_2\text{O}_3, n\text{SiO}_2$. For key see Table 1.

observed was smaller for barium aluminosilicate gels than for those of strontium,¹ which was in turn smaller than for calcium.⁶ This can probably be correlated with the increase in the

¹⁹ Yoshiki and Matsumoto, *J. Amer. Ceram. Soc.*, 1951, **34**, 283.

²⁰ Ito, "X-Ray Studies on Polymorphism," Maruzen, Tokyo, 1950.

²¹ Takeuchi, *Min. J. Japan*, 1958, **2**, 311.

²² (a) Smith, Bannister, and Hey, *Min. Mag.*, 1949, **28**, 676; (b) Runnells, *Amer. Min.*, 1964, **49**, 158.

²³ Smith, *Acta Cryst.*, 1953, **6**, 613.

TABLE 2.

Experimental results (yields: vg = very good; gd = good; m = moderate; f = fair; s = some; tr = trace; x = uncrystallised gel).

BaO,Al ₂ O ₃ ,SiO ₂																
435°	19h	5d	9d	380°	19h	3d	10d	340°	20h	2d	4d	8d				
gd C	gd C	m C		m P	m P	sm P		gd A	gd A	gd A	m A					
gd P	BaCO ₃	gd P		m A	m A	BaCO ₃		BaCO ₃	BaCO ₃	BaCO ₃	BaCO ₃					
(7.5)	(10.5)	(7.0)		BaCO ₂	BaCO ₂	(7.0)		(>10.5)	(>10.5)	(>10.5)	(>10.5)					
				(10.5)	(10.5)											
300°	4d	12d	19d	250°	4d	12d	19d	200°	4d	12d	19d	150°	12d	19d	110°	123d
gd A	vg A	gd A		gd E	vg A	gd A		gd E	gd E	gd E		gd E	gd E		m G	
BaCO ₃	BaCO ₃	BaCO ₃		gd P	BaCO ₃	BaCO ₃		BaCO ₃	gd C	gd C		BaCO ₃	BaCO ₃		(>10.5)	
(>10.5)	(10.5)	(7.5)		gd C	(10.0)	(10.5)		(>10.5)	gd P	gd P		(>10.5)	(>10.5)			
				BaCO ₃				BaCO ₃	BaCO ₃	BaCO ₃						
				(>10.5)				(>10.5)	(>10.5)	(>10.5)						
BaO,2Al ₂ O ₃ ,2SiO ₂																
435°	20h	6d	13d													
gd P	gd P	gd C														
tr C	tr C	(7.0)														
(7.0)	(7.0)															
BaO,Al ₂ O ₃ ,2SiO ₂																
435°	23h	4d	8d	380°	23h	3d	7d	340°	22h	3d	7d	300°	3d	8d	16d	
gd C	gd C	gd C		m C	m C	m C		gd C	gd C	gd C		sm C	gd C	m P		
(7.0)	BaCO ₃	(7.0)		(7.0)	(7.0)	(7.5)		BaCO ₃	(9.0)	tr P		(10.5)	(8.5)	(7.0)		
	(7.5)							(7.5)		(7.5)						
250°	5d	16d		200°	5d	16d		150°	5d	16d		110°	119d			
gd P	gd P			m P	gd P			sm P	m P			m G				
sm C	sm C			tr C	tr C			tr C	tr C			(>10.5)				
(7.5)	(7.0)			BaCO ₂	(10.0)			(9.0)	(>10.5)							
				(7.0)												
BaO,Al ₂ O ₃ ,3SiO ₂																
435°	19h	4d	8d	380°	24h	3d	7d	340°	24h	3d	7d					
m C	m C	gd C		m C	m C	gd C		m C	m C	m C						
(7.0)	(7.0)	(7.0)		(7.0)	(7.0)	(7.0)		(9.0)	sm P	(8.0)						
300°	3d	7d	12d	18d	25d		250°	3d	7d	12d	18d	25d	200°	7d	12d	15d
gd P	gd P	gd P	gd P	gd P	gd P		gd P	gd P	gd P	gd P	gd P	gd P	m G	m G	m G	
m C	m C	m C	m C	m C	sm C		m C	sm C	gd C	gd C	gd C	gd C	(7.5)	m P	sm C	
(8.0)	(7.5)	(8.5)	(—)	(8.5)			(8.5)	(9.0)	(9.0)	(7.0)	(9.0)	(9.0)		(8.5)	(9.0)	
200°	18d	21d	25d	29d		150°	10d	15d	18d	21d	25d	29d	110°	118d		
m G	m G	m G	m G	m P		m G	sm G	m G	m G	gd G	gd G	gd G		m G		
(9.0)	(8.5)	(9.5)		(8.5)		(9.0)	(8.5)	(9.0)	(9.0)	(9.0)	(9.0)	(8.5)		(9.0)		
BaO,Al ₂ O ₃ ,4SiO ₂																
435°	23h	2d	7d	380°	23h	3d	7d	340°	21h	3d	7d	300°	2d	7d	14d	
gd P	gd P	gd P		gd P	gd P	vg P		gd P	gd P	gd P		m P	gd P	gd P		
(7.0)	tr H	sm H		(7.0)	(7.0)	(7.0)		(7.5)	tr H	tr C		(7.0)	(7.0)	gd C		
	(7.0)	(7.0)							(8.5)	(7.5)				(7.5)		
250°	7d	17d		200°	2d	7d	14d	150°	7d	17d		110°	116d			
m P	m P			tr P	tr P	gd P		tr P	tr P			m G				
(7.0)	(9.0)			(7.5)	(7.0)	(7.0)		(7.0)	(9.0)			(9.0)				
BaO,Al ₂ O ₃ ,5SiO ₂																
435°	18h	4d	8d	380°	24h	3d	7d	340°	17h	3d	7d	300°	5d	14d	21d	
gd P	gd P	gd P		gd P	gd P	vg P		gd P	gd P	gd P		m P	gd P	gd P		
tr H	sm H	m H		(8.0)	tr H	sm H		(7.0)	(9.0)	(7.0)		(8.5)	(7.0)	(9.0)		
(7.0)	(7.5)	(7.5)			(7.5)	(7.0)										
250°	5d	14d	21d	200°	5d	14d	21d	150°	14d	21d						
sm P	sm P	sm P		x	tr P	tr P		tr P	tr P							
(9.0)	(8.0)	(9.0)		(9.0)	BaCO ₃	BaCO ₃		BaCO ₃	BaCO ₃							
					(8.5)	(9.5)		(9.5)	(9.0)							
BaO,Al ₂ O ₃ ,6SiO ₂																
435°	19h	5d	9d	380°	24h	3d	7d	340°	2d	6d	9d	300°	5d	13d	22d	
gd P	gd P	gd P		gd P	gd P	gd P		gd P	gd P	gd P		m P	m P	sm P		
sm H	gd H	gd H		(7.0)	sm H	gd H		(7.5)	sm H	sm H		(7.5)	(8.0)	(7.0)		
(7.0)	(7.0)	(7.0)			(7.0)	(7.5)			(7.0)	(7.0)						
250°	5d	13d	22d	200°	5d	13d	22d	150°	13d	22d						
tr P	tr M	x		x	x	x		x	x							
(8.0)	(8.5)	(7.0)		(9.0)	(9.5)	(7.0)		(9.5)	(7.0)							

TABLE 2. (Continued.)

BaO,Al ₂ O ₃ ,7SiO ₂														
435°	21h	3d	7d	380°	17h	3d	5d	7d	340°	17h	3d	5d		
	gd P	gd P	gd P		gd P	gd P	gd P		gd P	gd P	gd P			
	gd H	gd H	gd H		(7.0)	(7.0)	(7.0)		(7.0)	(7.0)	(7.0)			
300°	5d	8d	18d	250°	5d	12d	15d	200°	5d	12d	18d	20d(2)		
	m P	m P	m P		sm M	gd M	m M		sm M	m M	gd M	x		
	tr K	gd K	sm K		(7.0)	gd J	m J		(>10.5)	(>10.5)	(>10.5)	(7.5)		
	(7.0)	(7.0)	(7.0)			(7.0)	(8.0)							
200°	33d(2)	5d		150°	3d	15d	18d	110°	102d					
	x	gd M			m M	x	m M		x					
	(8.0)	(7.5)			(10.5)	(7.0)	(10.0)		BaCO ₃					
									(9.5)					
BaO,Al ₂ O ₃ ,7.5SiO ₂														
	250°	12d	13d(2)	19d	19d	19d	220°	13d	19d	30d	33d			
		gd M	gd M	tr J	sm J	gd M		x	sm M	gd M	vg M			
		(9.0)	(9.0)	(9.0)	(9.0)	(9.0)		(9.0)	(9.0)	(9.0)	(8.5)			
BaO,Al ₂ O ₃ ,8SiO ₂														
430°	21h	3d	7d	380°	3d	7d	340°	2d	4d	7d(2)	9d(2)	13d		
	gd P	vg P	vg P		gd P	gd P		x	m P	gd P	m P	gd P		
	tr H	gd H	gd H		gd H	gd H		(8.0)	m Z	gd H	m H	gd H		
	(7.0)	(7.0)	(7.0)		(8.5)	(8.0)			(9.0)	m Z	tr Z	tr Z		
										(8.5)	(8.5)	(8.0)		
300°	3d	4d	6d	6d	6d	6d(2)	6d	9d	9d	13d	15d	15d		
	sm K	tr J	gd K	gd J	sm J	m K	m J	gd K	gd J	gd J	gd K	sm J		
	(9.0)	(8.5)	(8.5)	(8.0)	(8.0)	(8.0)	(8.0)	(8.5)	(8.0)	(9.0)	(8.0)	tr P		
												(8.5)		
300°	16d	20d	20d	26d	30d	30d	250°	6d	10d	13d	15d(2)			
	gd K	gd K	m K	m P	m P	sm P		x	m M	gd M	x			
	tr P	sm J	sm J	sm K	tr J	sm K		(9.0)	(9.5)	(9.5)	(8.5)			
	(8.5)	(9.0)	(8.5)	(8.5)	(8.5)	(8.5)								
250°	15d(2)	15d	16d	17d	17d	18d(2)	19d	19d	20d	23d(3)	30d			
	tr M	m M	gd M	sm J	gd M	m K	sm J	m K	x	m M	gd M			
	(8.5)	(8.5)	(8.5)	(9.0)	(8.5)	(9.0)	(8.5)	(8.5)	(9.5)	m J	(9.0)			
										(9.0)				
200°	6d	13d	19d	20d	25d		150°	6d	13d	20d	110°	125d		
	x	x	x	x	x			x	x	x	x			
	BaCO ₃	BaCO ₃	BaCO ₃	BaCO ₃	BaCO ₃			BaCO ₃	BaCO ₃	BaCO ₃	BaCO ₃			
	(9.5)	(9.5)	(10.0)	(8.5)	(9.0)			(9.5)	(9.5)	(8.5)	(10.0)			
BaO,Al ₂ O ₃ ,9SiO ₂														
430°	19h	3d	7d	380°	3d	7d	340°	15h	3d	6d	300°	3d	9d	14d
	gd P	gd P	gd P		gd P	gd P		x	vg K	gd K		gd P	vg P	vg P
	gd H	gd H	gd H		gd H	gd H		(7.0)	(7.0)	(7.0)		sm Z	sm H	sm H
	(7.0)	(7.0)	(7.0)		(7.0)	(8.5)						(7.5)	(7.0)	(7.5)
250°	3d	9d	14d	200°	3d	9d	14d	150°	3d	9d	14d	110°	110d	125d
	x	x	sm J		x	x	x		x	x	x		x	x
	(8.0)	(8.5)	(8.5)		(9.5)	(9.0)	(8.5)		(10.0)	(9.5)	(10.5)		(10.0)	(10.0)

solubility and basicity of the hydroxides along the series calcium < strontium < barium. In the crystallisation fields of the barium aluminosilicate gels there was not the frequent occurrence of irreproducible syntheses of zeolitic species which characterised the strontium aluminosilicate field.

Barium Zeolites.—Four zeolites were produced, only one of which (Ba-M) was analogous to a known natural zeolite.

Harmotome (Ba-M). This zeolite was formed in good yield at 200–250° from aqueous gels in which the silica:alumina ratio was between 7:1 and 8:1. Small amounts were also produced at 250° when this ratio was as low as 5:1, and in a subsequent series of experiments moderate yields of harmotome also occurred, mixed with Ba-G, at 170° from aqueous gels with the oxide composition BaO,Al₂O₃,3SiO₂. The best yields were obtained from aqueous gels of oxide composition BaO,Al₂O₃,7.5SiO₂ held at 220 or 250° for about 3 weeks. The species crystallised well and often displayed cruciform twinning, which is also characteristic of the naturally occurring mineral (Plate a).

The results of differential thermal analysis (d.t.a.) and thermogravimetric analysis are shown in Figs. 2 and 3. The sample showed a total weight loss of 11.5%, mostly below 450°, and the d.t.a. trace showed three endothermic peaks below 450°, similar to those found with synthetic calcium harmotome.⁶ The water loss may be compared with that of 13.9–15.0%

recorded for natural samples, indicating that the yield was a maximum of 80%, if the remainder can be considered as anhydrous. Like a naturally occurring harmotome,²⁴ Ba-M did not sorb significant amounts of oxygen at 90°K.

The X-ray powder pattern is extremely close to that of natural monoclinic barium harmotome (Table 3). Previous workers in these laboratories reported the synthesis of various members of the phillipsite-harmotome family,^{5,6,24-26} with sodium, potassium, calcium, or dimethylammonium as the cation, but these have been cubic, tetragonal, or orthorhombic forms not identical with the natural monoclinic phase. A possible explanation was suggested by Sadanaga *et al.*,²⁷ who show that the space occupied by the barium cation in harmotome is too large to be satisfactorily filled by a calcium ion, and that no simple adjustment of the co-ordination polyhedron is possible. This implies the slight but definite differences between the structures of harmotome and phillipsite later confirmed by Steinfink.²⁸

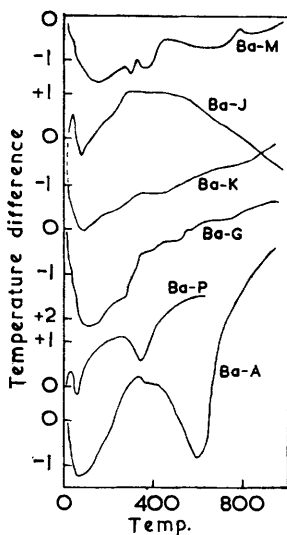


FIG. 2. Differential thermal analysis curves at 10°/min.

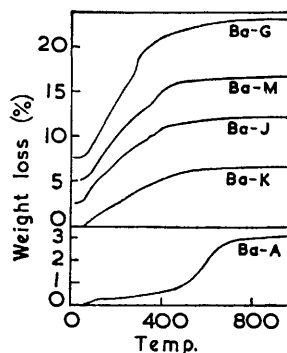


FIG. 3. Thermogravimetric curves at 10°/min.

In the top part of the diagram the scale of ordinates for the four curves is the same, but the numbers refer to the Ba-A curve only. For clarity the top three curves have been displaced by equal amounts. Each is to be considered as starting at zero weight loss.

Zeolite Ba-J. This zeolite occurred in a restricted area of the crystallisation field, and grew from the aqueous gels having silica : alumina ratios between 7 : 1 and 9 : 1 at 250 and 300°. It was very often mixed with other species, particularly harmotome and Ba-K. The best yields were obtained from aqueous gels of oxide composition $\text{BaO}, \text{Al}_2\text{O}_3, 8\text{SiO}_2$ heated for 6—20 days at 300°, but it could not be predicted with certainty whether a particular gel would crystallise to Ba-J, Ba-K, or a mixture of both. The crystals had an irregular fibrous habit (Plate b).

Thermogravimetric analysis showed a weight loss of 8.9% up to 450° and a further loss of 1% between 450 and 1000° (Fig. 3). This behaviour indicates that Ba-J is a zeolite, although the total loss is a little low, possibly owing to the presence of some anhydrous by-product in the sample. The d.t.a. trace showed a single endothermic peak below 300° (Fig. 2). The sample became amorphous on ignition, and this breakdown may explain the steep slope of the curve above 600°. At 90°K outgassed Ba-J sorbed 59 c.c. of oxygen at s.t.p. per gram of hydrated sample. The X-ray pattern of this species (Table 3) could not be matched with that of any known zeolite.

Zeolite Ba-K. This zeolite occurred in much the same region of the crystallisation field

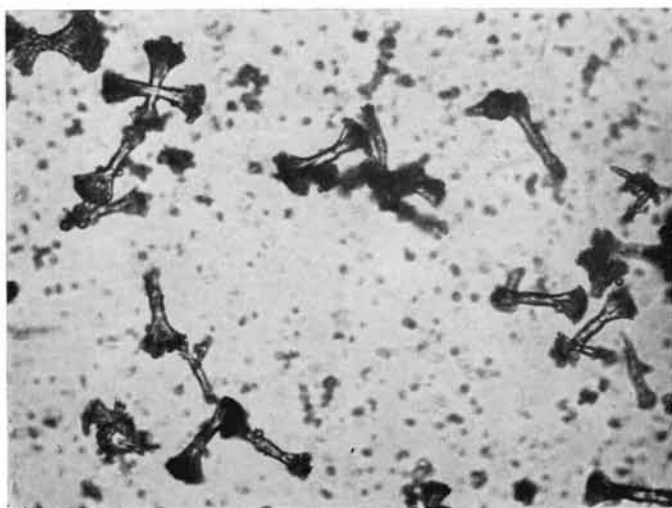
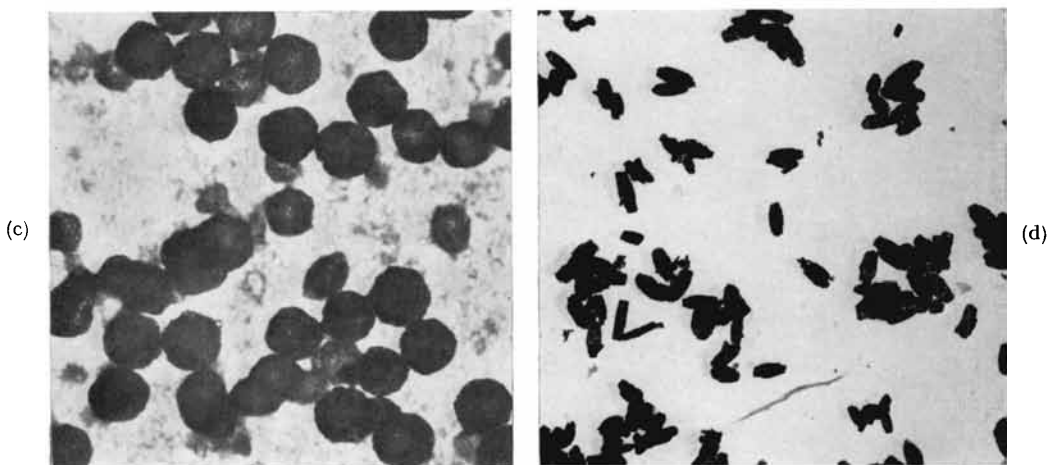
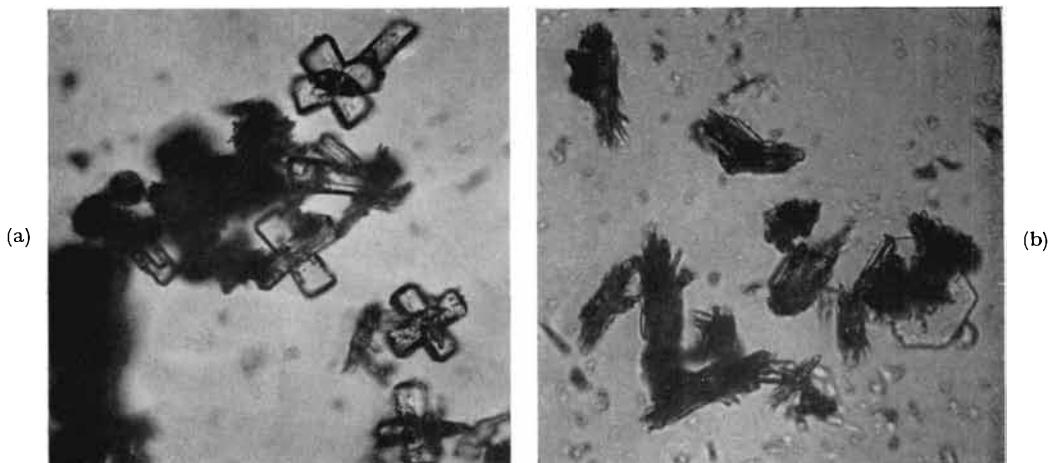
²⁴ Barrer, Bultitude, and Kerr, *J.*, 1959, 1521.

²⁵ Barrer and Baynham, *J.*, 1956, 2882.

²⁶ Barrer and Denny, *J.*, 1961, 971.

²⁷ Sadanaga, Marumo, and Takeuchi, *Acta Cryst.*, 1961, 14, 1153.

²⁸ Steinfink, *Acta Cryst.*, 1962, 15, 644.



(a) Ba-M, 320 \times . (b) Ba-J, 550 \times . (c) Ba-Z, 245 \times . (d) Ba-C, 6000 \times .
(e) Ba-K, 250 \times .

TABLE 3.
X-Ray patterns for zeolitic species (d in Å).

Ba-M		Natural harmotome *		Ba-M		Natural harmotome *		Ba-M		Natural harmotome *		Ba-M		Natural harmotome *	
d	Int	d	Int	d	Int	d	Int	d	Int	d	Int	d	Int	d	Int
8.24	vs	8.09	s	3.57	vw	—	—	2.525	w	2.517	m	2.008	vw	—	—
7.56	vw	7.86	vw	3.52	w	—	—	2.058	w	—	—	1.996	vw	1.998	mw
7.18	s	7.14	s	3.46	mw	3.46	vw	2.464	m	2.460	w	1.964	w	—	—
7.03	w	6.99	w	3.23	s	3.24	m	—	—	2.406	vw	1.947	m	1.948	m
6.39	vs	6.37	s	3.19	mw	3.19	m	2.368	m	2.368	w	1.921	w	1.919	vw
6.11	vw	6.26	w	3.16	ms	3.16	m	2.315	ms	2.320	mw	1.894	mw	1.897	vw
—	—	5.60	m	3.12	vs	3.11	ms	2.295	m	2.294	mw	1.840	vw	1.837	w
5.02	ms	5.01	m	3.07	m	3.07	w	2.256	w	2.258	vw	1.818	mw	1.822	w
—	—	4.72	vw	—	—	3.00	w	2.236	m	2.235	mw	1.802	w	1.799	w
4.29	ms	4.27	m	2.91	ms	2.91	mw	2.213	w	2.205	w	1.776	m(b)	1.770	vw
4.10	s	4.08	s	2.838	w	2.803	mw	2.147	m	2.145	m	1.771	ms(b)	1.709	m
4.06	s	—	—	2.745	w	—	—	2.119	w	—	—	1.670	m	1.675	w
4.03	s	4.03	ms	2.724	s	2.725	m	2.084	vw	2.088	vw	1.639	w	1.638	w
3.89	m	3.93	mw	2.674	s	2.693	mw	2.062	m	2.065	w	1.530	m	1.530	w
—	—	3.88	mw	2.668	s	2.669	m	2.052	m	2.049	mw	1.473	w	1.478	w
—	—	3.76	vw	2.624	w	2.628	w	2.021	mw	2.020	w	—	—	1.469	vw
3.66	w	3.67	vw	2.557	w	2.560	vw	—	—	—	—	—	—	—	—

* Strontian Argyll.

Ba-K				Ba-J											
d	Int	d	Int	d	Int	d	Int								
10.59	ms	3.53	ms	2.648	w	1.846	m	11.39	s	4.08	w	2.88	m	2.189	vw
7.39	mw	3.49	m	2.613	mw	1.801	w	10.53	vw	4.02	ms	2.82	w	2.169	vw
6.87	w	3.45	w	2.553	w	1.760	w	10.22	w	3.97	m	2.797	w	2.125	vw
6.07	ms	3.34	vw	2.493	m	1.730	w	7.39	m	3.91	ms	2.709	m	2.107	vw
5.58	ms	3.29	mw	2.469	w	1.694	vw	7.04	w	3.81	m	2.664	m	2.028	vw
5.29	w	3.16	s	2.433	w	1.650	vw	6.23	m	3.70	w	2.636	vw	1.987	vw
5.08	w	3.06	w	2.336	w	1.559	vw	6.08	vw	3.66	ms	2.605	w	1.953	vw
4.72	m	3.03	ms	2.301	m	1.539	w	5.84	m	3.61	s	2.455	ms	1.847	ms
4.59	ms	2.94	m	2.234	vw	1.525	vw	5.73	mw	3.45	s	2.419	ms	1.819	w
4.30	ms	2.88	vw	2.206	w	1.509	vw	5.63	vw	3.28	w	2.370	ms	1.794	w
4.21	ms	2.79	mw	2.117	w	1.286	w	4.79	m	3.20	w	2.334	w	1.775	vw
3.89	w	2.72	m	1.965	w	1.271	vw	4.58	s	3.16	w	2.307	vw	1.708	m
3.67	vw	—	—	1.919	w	—	—	4.52	s	3.12	vs	2.287	vw	1.670	mw
—	—	—	—	—	—	—	—	4.30	vw	2.98	m	2.262	m	1.632	w
—	—	—	—	—	—	—	—	4.19	w	2.82	w	2.213	vw	1.596	w

Ba-G				Ba-Z									
d	Int	hkl	d	Int	hkl	d	Int	d	Int	d	Int	d	Int
16.15	s	100	3.75	vw	005	2.690	s	1.800	w	10.56	w	2.91	m
9.35	vw	111	3.49	m	323	2.635	mw	1.790	w	8.90	m	2.84	w
8.10	vw	102	3.32	m	421	2.502	w	1.745	vw	6.90	mw	2.421	ms
7.53	m	200	3.23	m	403	2.447	mw	1.714	w	5.07	w	2.373	w
6.83	mw	210	3.19	m	422	2.390	vw	1.593	vw	4.60	s	1.988	vw
5.85	vw	103	3.08	s	225	2.294	vw	1.553	vw	3.45	vs	1.785	vw
5.38	w	220	2.92	s	206	2.224	m	1.539	w	3.29	w	1.765	vw
4.85	w	203	2.874	vw	216	2.203	m	1.441	vw	3.17	m	1.592	mw
4.72	w	004	2.817	vw	325	2.187	w	1.430	vw	—	—	—	—
3.95	vs	204	2.753	vw	424	1.874	m	1.345	vw	—	—	—	—
3.84	w	322	—	—	—	—	—	—	—	—	—	—	—

as Ba-J. It formed from aqueous gels with silica : alumina ratios of 7 : 1 and 8 : 1 at 300° and of 9 : 1 at 340°. At 300° it was often mixed with Ba-J or Ba-P. It crystallised in a distinctive variation of the spherulitic habit (Plate e), but even the best samples may have contained some amorphous silica.

The results of d.t.a. and thermogravimetric analysis show a weight loss of 7% on ignition to 950°, most of which had taken place by 500° (Fig. 3), and this, together with the d.t.a. curve (Fig. 2) suggested that the species might be zeolitic. This was confirmed by the observation that an outgassed sample sorbed 46 c.c. of oxygen at s.t.p. per gram of hydrated sample at 90°K.

The X-ray powder pattern of Ba-K is given in Table 3, but it was not possible to identify this species with any known zeolite.

Zeolite Ba-G. This zeolite crystallised from aqueous gels of oxide composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ held at 150—200° for at least 3—4 weeks. Ba-G was produced in moderate to good yield, but was always mixed with unreacted gel and often also with barium carbonate. It was difficult to purify by treatment with dilute acid. Also, in later attempts to produce larger quantities of Ba-G, it could not be obtained free from harmotome. Some Ba-G was also formed from gels with silica : alumina ratios between 1 : 1 and 4 : 1, treated at 110° for about 4 months.

D.t.a. and thermogravimetric analysis curves were obtained from one of the higher-yield samples of Ba-G (Figs. 2 and 3). There is a total weight loss of 15%, and the shapes of the

curves are typically zeolitic. A qualitative ion-exchange experiment on a small sample showed that the barium could be readily replaced by sodium, with little change in the X-ray powder pattern (Table 3). The pattern could not be identified with that of any known zeolite, but the first 21 lines were indexed on the tetragonal system to give a unit cell with $a = 18.89$ and $c = 15.16$ Å. A sample containing about 60% of Ba-G sorbed 50 c.c. (at s.t.p.) of oxygen at 90°K.

Felspars.—Two polymorphs of the felspar composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were produced in this work: Ba-C, which is synthetic celsian, closely similar to the natural monoclinic mineral, and Ba-P, its hexagonal polymorph. There was some evidence to show that Ba-P was a metastable form, and that gels which produced it would yield Ba-C under more vigorous or prolonged treatments. This is in agreement with the results of Sorrel²⁹ who investigated the two modifications by pyrolytic methods.

Celsian (Ba-C). This species was formed from 150° upwards from aqueous gels of oxide composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, although below 300° the yield was poor and the celsian was mixed with Ba-P. The optimum yields were obtained from gels of the above composition treated for 1–2 days at 400–450°. It would also form, often mixed with other species, from

TABLE 4.
X-Ray patterns for felspar species (d in Å).

Natural celsian *		Ba-C		Ba-A		Ba-A (ignited)		Ba-C		Ba-A		Ba-A (ignited)	
d	Int	d	Int	d	Int	d	Int	d	Int	d	Int	d	Int
6.53	s	6.51	s	6.54	m	6.52	ms	2.110	w	2.132	s	2.126	s
5.88	m	5.85	w	5.88	vw	5.18	w	2.093	w	—	—	2.023	w
4.63	ms	4.62	mw	4.82	vw	4.64	w	2.061	w	—	—	—	—
—	—	—	—	4.56	vs	4.54	vs	2.014	vw	—	—	—	—
—	—	—	—	—	—	3.95	w	1.995	vw	—	—	—	—
3.90	mw	3.90	w	3.92	w	3.91	w	1.950	mw	1.957	w	1.956	w
3.81	ms	3.80	m	3.81	mw	3.80	m	1.910	w	1.914	vw	1.914	w
3.63	w	3.63	w	3.64	w	3.63	w	—	—	1.813	m	1.811	ms
3.56	ms	3.56	mw	3.56	mw	3.56	m	1.797	mw	1.789	m	1.774	w
3.50	s	3.47	s	3.48	m	3.48	ms	—	—	1.752	m	1.740	m
3.35	s	3.35	s	3.36	ms	3.35	s	1.672	w	1.694	m	1.690	m
3.29	w	3.28	mw	3.30	ms	3.28	s	1.649	w	1.645	m	1.637	m
3.27	w	—	—	—	—	—	—	1.627	w	1.614	vw	—	—
3.25	w	3.25	mw	—	—	—	—	—	—	1.607	m	1.604	m
3.03	m	3.02	m	3.02	m	3.02	m	1.577	w	1.568	mw	1.567	m
—	—	—	—	—	—	2.97	w	1.533	w	1.538	w	1.540	vw
2.92	mw	2.91	mw	2.92	w	2.92	mw	1.522	w	1.524	vw	1.526	vw
2.778	m	2.77	m	2.797	s	2.796	s	—	—	1.514	w	—	—
—	—	—	—	2.768	s	2.751	s	—	—	1.504	w	1.608	mw
2.613	w	2.608	w	—	—	—	—	1.502	mw	1.441	mw	1.442	w
2.590	m	2.583	ms	2.587	s	2.580	s	1.450	vw	1.398	ms	1.396	m
2.430	vw	2.425	w	—	—	—	—	—	—	1.319	w	1.319	w
2.337	vw	2.326	mw	2.334	vw	2.336	m	—	—	1.310	vw	1.304	w
2.275	vw	—	—	—	—	—	—	—	—	1.273	vw	1.287	w
2.258	vw	2.260	w	2.278	w	2.277	mw	—	—	—	—	1.262	w
—	—	—	—	2.248	w	—	—	—	—	1.246	w	1.244	w
2.221	vw	2.218	w	2.218	vw	2.225	mw	—	—	1.211	w	—	—
2.178	w	2.173	m	2.172	w	2.176	w	—	—	—	—	—	—

* From Jakobsberg, Sweden.

Ba-P		Ba-P (ignited)		α -Hexagonal ²¹ $\text{BaAl}_2\text{Si}_2\text{O}_8$		β -Hexagonal ²¹ $\text{BaAl}_2\text{Si}_2\text{O}_8$ (at 450°)		Ba-P		Ba-P (ignited)	
d	Int	d	Int	d	Int	d	Int	d	Int	d	Int
7.74	m	7.77	m	7.79	100	7.79	112	1.702	m	1.690	m
3.96	s	3.95	vs	3.949	43	3.963	47	1.592	m	1.582	m
—	—	—	—	3.899	18	3.901	20	1.561	mw	1.565	mw
2.97	s	2.96	s	2.968	49	2.977	59	1.540	w	1.526	w
2.67	ms	2.65	ms	2.647	13	2.659	15	1.464	w	1.469	w
—	—	—	—	2.597	20	2.603	22	1.445	vw	1.440	vw
2.31	mw	2.29	w	2.292	4	2.300	5	1.331	w	1.322	w
2.250	m	2.254	m	2.259	18	2.266	15	1.319	vw	—	—
2.215	m	2.196	ms	2.195	11	2.206	11	1.282	w	1.288	mw
1.982	vw	1.971	vw	—	—	—	—	1.262	vw	1.253	vw
1.933	w	1.942	w	1.947	65	1.951	60	—	—	—	—
1.854	m	1.850	m	1.853	7	1.860	6	—	—	—	—

gels with silica : alumina ratios of 1 : 1 or 3 : 1 (Table 2). The crystals were very small, even in the best syntheses (Plate d).

Samples of celsian could be heated to at least 1100° without any change in the X-ray powder pattern. This pattern was extremely close to that of natural celsian (Table 4).

²⁹ Sorrel, *Amer. Min.*, 1962, **47**, 291.

Hexagonal polymorph Ba-P. This species has been prepared by pyrolytic methods and is known by various names in the literature.^{16,17,19-21} It will here be referred to as hexagonal BaAl₂Si₂O₈. It occurred very widely over the whole range of compositions studied, but was in most cases accompanied by other species. The best yields were obtained from aqueous gels of oxide composition BaO,Al₂O₃,4SiO₂, above 300°. The crystals were always extremely small and had no clear habit.

A typical example of the reproducible d.t.a. curve given by Ba-P is shown in Fig. 2. The first peak is due to the loss of surface-held moisture, probably mostly from the amorphous material present. The thermobalance shows that there is no loss of weight associated with the second endothermic peak which falls at $348 \pm 7^\circ$. This indicates that the peak is caused by a phase transformation, probably of the $\alpha \rightleftharpoons \beta$ type, in agreement with the work of Yoshiki and Matsumoto.¹⁹ From dilatometric studies they found that the plot of expansion against temperature had a distinct step at about 300° which was reversible on cooling. There was also a sharp discontinuity in the specific heat at 300°, which they explained as being due to an enantiotropic transformation, similar to the $\alpha \rightleftharpoons \beta$ transformation in quartz. This result was confirmed by Takeuchi²¹ who gave the transition point as $295 \pm 5^\circ$, which is about 50° lower than that observed for Ba-P by the d.t.a. method. This suggests that the $\alpha \rightleftharpoons \beta$ transition is sluggish in the samples prepared by the hydrothermal method. In addition, the d.t.a. cooling curve did not show the exothermic peak which would be expected from a reversible transition, and the X-ray pattern of samples heated to 450° and then cooled showed slight but significant differences from that of the fresh samples. Thus, in the case of Ba-P, the high-temperature form persists metastably on relatively rapid cooling.

The X-ray data agreed well with those previously published (Table 4), and were indexed to a hexagonal unit cell, although Takeuchi showed that the low-temperature form is only pseudo-hexagonal. The unit-cell parameters obtained by various workers are given in Table 5.

TABLE 5.

Modification	Unit cells found for hexagonal BaAl ₂ Si ₂ O ₈ .				
	α	α	α	β at 450°	β at 20°
<i>a</i> (Å)	5.25	5.293	5.33	5.313	5.29
<i>c</i> (Å)	7.84	7.790	7.72	7.805	7.76
Authors	Ito ²⁰	Takeuchi ²¹	Present work	Takeuchi ²¹	Present work

Unidentified Species.—Two other species were produced which could not be identified with any recognised group of minerals.

Species Ba-A. This species formed from aqueous gels of oxide composition BaO,Al₂O₃,SiO₂ at 250—380°. The best yields were obtained at 300 and 340°, and were well crystallised, although mixed with barium carbonate which could be readily removed with dilute acid. The crystals were extremely small.

The results of d.t.a. and thermogravimetric analysis are in Figs. 2 and 3. The total weight loss at 1000° was 3.2%, and there was a steady loss of 2.0% at 500—700°, associated with an endothermic peak at 600° on the d.t.a. trace. This behaviour could be explained if there were hydroxyl groups in the structure which are driven off by 750°. However, an infrared spectrum of Ba-A did not show any peak at 2.75 μ which should appear if OH is present.

The X-ray powder pattern was very similar to that of the celsian (Ba-C). There were a few additional lines and a number of small shifts and intensity changes. On ignition, the powder pattern showed a few further slight differences but did not become identical with that of Ba-C (Table 4). The infrared spectrum of Ba-A was also very similar to that of celsian but had an additional peak at 11.4 μ , which shifted to 11.1 μ after ignition.

The structure of Ba-A is therefore very similar to that of celsian, slightly altered to accommodate a volatile group. The sharp and reproducible nature of the X-ray pattern indicates that this product is not a mixture and it therefore seems to be a new species.

Species Ba-Z. This species was formed from aqueous gels of oxide composition BaO,Al₂O₃,8SiO₂ at 340° and once from a gel of BaO,Al₂O₃,9SiO₂ at 300°. It was never obtained pure, and was usually present only in small amounts. The best sample crystallised as large spherules (Plate c). The X-ray pattern was not identified with that of any known species (Table 6), but qualitative experiments showed that it could exchange sodium or

potassium for barium from concentrated solutions at room temperature, and so Ba-Z may be a new zeolite or feldspathoid.

DISCUSSION

The work on hydrothermal synthesis in these laboratories has been presented in terms of the crystallisation fields of the species produced. The fields of different species may overlap, and the boundaries are often indistinct and readily altered by changes in the starting materials. However, although the factors controlling the crystallisation field of a species are complex and not readily related to the main thermodynamic variables, it is of interest to compare these crystallisation fields for analogous aluminosilicates of calcium, strontium, and barium.

The Hexagonal Polymorphs of Felspars.—The synthesis of the hexagonal polymorphs of the respective felspars shows some progressive variation along the series from calcium to barium. In each case the crystals grew from aqueous gels having a wide range of silica: alumina ratios, but the crystallisation field moved progressively further into the silica-rich region, going from calcium to barium. The appearance of this phase may thus be catalysed either by the alkaline-earth cations, or more probably by hydroxide ions since it has already been pointed out that the solubility and basicity of the hydroxides increase from calcium to barium. In each case also it was noticed that the hexagonal form appeared frequently from runs of short duration but was replaced by the monoclinic (or, in the case of strontium, orthorhombic) felspar in longer runs. This shows that the hexagonal species is metastable, though the barium form is rather more persistent than the others, confirming the results of Sorrel.²⁹ Accordingly, the crystallisation field of celsian (Ba-C) was much more restricted than those of orthorhombic $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Sr-C) and anorthite (Ca-F). The X-ray powder patterns of the three hexagonal phases are also very similar, and the lines show a steady displacement along the series. The unit cells

TABLE 6.

Unit-cell data for the hydrothermally prepared species.

Cation	Cation radius (Å)	a (Å)	c (Å)	Unit-cell vol. (Å ³)	Calc. density (g./cm. ³)
Ca ²⁺	1.05	5.10	7.44	167.6	2.76
Sr ²⁺	1.18	5.19	7.59	177.1	3.06
Ba ²⁺	1.40	5.33	7.72	189.9	3.29

of the hydrothermally prepared species are shown in Table 6. There is a linear relationship between the unit-cell volume and the cation radius, indicating that the framework expands regularly to accommodate the larger cations.

Other Feldspathic Crystals.—Comparison of the crystallisation fields of the other felspar species produced is more difficult, and is complicated by the fact that Sr-C was the orthorhombic polymorph, whereas anorthite (Ca-F) and celsian (Ba-C) are monoclinic. As the monoclinic strontium felspar is readily formed by dry heating treatments, it is difficult to explain the formation of orthorhombic $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Sr-C), except as an example of Ostwald's step rule. Sr-C was unaffected by heating to 1050° but was slowly changed into the monoclinic polymorph at 1250°.

Analcites.—In previous work in these laboratories many members of the analcite family have been readily synthesised. In the case of calcium⁶ a tetragonal analcite similar to the natural mineral wairakite was produced from a wide range of compositions and temperatures, although never in 100% yield. A cubic form was produced at higher temperatures in rather better yield. Both forms were hydrated. However, strontium analcite was crystallised once only,¹ in a hydrated cubic form, and no barium analcite was produced. It seems that the size of the cation exercises a considerable influence on the growth of analcites. The temperature of formation of the cubic hydrated forms increases as the cation radius increases, whilst that of the anhydrous forms decreases. Accordingly, a hydrated barium analcite would not be expected to form much below 450°, and, although

an anhydrous tetragonal form might be expected from 300° upwards, its formation is probably prevented by the easy prior growth and persistence of hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$.

Micas.—Of the three cations under consideration, only with strontium was a mica readily formed. The only micas previously synthesised in this series (in which the crystallising magmas have been generally rich in alkali) were a paragonite³ and an ammonium mica,²⁶ although micas of the muscovite type have been readily synthesised by the hydrothermal method.³⁰ A synthesis of margarite has been reported³¹ but in general the hydrothermal crystallisation of brittle micas containing bivalent cations has proved more difficult. In this work, the strontium mica crystallised well and reproducibly,¹ but a synthetic calcium margarite was not formed.⁶ There was no reproducible occurrence of a barium mica, and no such mica was fully identified by X-ray diffraction, but on one occasion a gel of composition $\text{BaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ treated at 435° for 5 days yielded a product containing a considerable number of platy hexagonal crystals which gave a hexagonal electron diffraction pattern with a repeat distance of 5.45 Å in the *a* direction. This was an isolated occurrence, and gels with the optimum mica composition, $\text{BaO}, 2\text{Al}_2\text{O}_3, 2\text{SiO}_2$, gave only hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$ and celsian at 435°. Since the growth of layer lattice aluminosilicates is usually favoured by less-alkaline conditions than that of three-dimensional framework aluminosilicates, it could be that the greater basic strength of barium hydroxide, as compared with that of strontium hydroxide, prevented the reproducible crystallisation of a barium mica.

Zeolites.—The zeolites which crystallised containing one of the three cations calcium, strontium, or barium bear surprisingly little resemblance to each other. In the case of barium and calcium a member of the harmotome family was formed, but the calcium form had a tetragonal structure⁶ and the barium harmotome was monoclinic. Both gave very similar d.t.a. curves, but no species with the harmotome structure was formed from strontium aluminosilicate gels.¹ Mordenite was observed on two occasions in the crystallisation field of the strontium aluminosilicates, but its formation was not reproducible, and it occurred only in very minor yield with calcium, and not at all with barium. None of the other zeolites produced was duplicated with other alkaline-earth cations despite frequent zeolite formation. Thus, in addition to the zeolites already mentioned, thomsonite and epistilbite were also formed with calcium;⁶ chabazite, gmelinite, heulandite, Sr-D, and Sr-Q with strontium;¹ and Ba-G, Ba-K, Ba-J, and possibly Ba-Z, with barium. It does not seem possible to predict which structures will be formed with a given cation, but it seems likely that the condition of alkalinity and solubility in the parent gels have a greater effect than cation size. The crystal habits observed suggest that all the zeolites obtained in good yield grew from conditions of high supersaturation. A considerable number of strontium and barium zeolites appeared to be species without natural counterparts, and a number of these possessed rigid and open aluminosilicate frameworks which were porous to oxygen gas and therefore evidently capable of functioning as molecular sieves.

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