Hydrothermal Chemistry of Silicates. Part XVII.[1] Reactions in the System $BaO-B_2O_3-SiO_2-H_2O$

By **Richard M. Barrer** and **Edouard F. Freund,*** Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

A partial study of hydrothermal crystallisation at 250 and 415 °C in the system $BaO-B_2O_3-SiO_2-H_2O$ has shown the ready formation of barium silicates, borates, and borosilicates. Of five barium silicates one could not be identified with previously synthesised silicates. Also eleven barium borates and five out of six barium borosilicates could not be identified and may be, or include, novel species. All the compounds have been characterised in various ways. Three of the borosilicates have $BaO/B_2O_3 \sim 1$ and $O/(B + Si) \sim 2$ as with tectosilicates. However one of these at least appears to contain hydroxyl water and all three disobey Lowenstein's rule. Three additional phases could not be classified as silicate, borate, or borosilicate because they were grown only in mixtures of crystalline phases.

An investigation of zeolite formation in the system $Na_2O-Al_2O_3-B_2O_3-SiO_2-H_2O$ has shown that, under the alkaline conditions required, little if any B substituted for Al or Si in the anionic frameworks, although sometimes boron could be trapped as discrete anions in these frameworks.[1] However, it was felt that with less alkaline conditions and at higher temperatures the incorporation of boron into silicate frameworks was possible under hydrothermal conditions. Accordingly a study of the system $BaO-B_2O_3-SiO_2-H_2O$ was undertaken as part of a wider study of hydrothermal formation of borosilicates.

Naturally occurring borosilicates containing barium are rare. Garrelsite,[2] which has been reported as belonging to the datolite group,[3] has the oxide composition $4(Ca,Ba,Mg)O$, $3B_3O_3$, $2SiO_2$, $3H_2O$. However its unit cell parameters [4] are very different from those of datolite. Cappelinite [5] is reported to contain Ba, Y, H, Si, and O but no quantitative analysis was made. The system $BaO-B_2O_3-SiO_2$ has been explored, but only one ternary compound $3BaO,3B_2O_3,2SiO_2$ was observed and this had a narrow field of crystallisation.[6] No previous study of the system $BaO-B_2O_3-SiO_2-H_2O$ was found, although the analogous system $BaO-Al_2O_3-SiO_2-H_2O$ readily yields various zeolites and other aluminosilicates either from gels,[7] or from metakaolinite with or without added silica.[8]

EXPERIMENTAL

The solid reactants were $Ba(OH)_2,8H_2O$; H_3BO_3; and silica gel. They were mixed and introduced into the autoclaves and water was added so as to give 1 g of an-

---

* *Present address:* Institut Français du Pétrole 92502 Rueil-Malmaison, France.

[1] Part XVI, R. M. Barrer and E. F. Freund, *J.C.S. Dalton*, 1974, 1049.

[2] E. L. Muetterties ' The Chemistry of Boron and its Compounds,' Wiley and Sons, New York, 1967.

[3] C. L. Christ, *Amer. Min.*, 1959, **44**, 176.

[4] C. Milton, J. M. Axelrod, and F. S. Grimaldi, *Bull. Geol. Soc. Amer.*, 1955, **66**, 12(2), 1597.

[5] R. M. Adams, ' Boron, metallic Boron Compounds and Boranes,' Interscience Publishers, New York, 1964.

[6] E. M. Levin and G. M. Urgrinic, *J. Res. U.S. Bur. Stand.*, 1953, **51** (1), Research Paper No. 2430, 37.

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

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

hydrous matter per 8 g of mixture. This corresponded with 87·5% by weight of water and gave about 50% filling of the autoclaves, which are described elsewhere.[9]

After being heated for 7 days either at 250 °C or at 415 °C the autoclaves were quenched and the crystals were separated from mother liquor by centrifuging; they were then washed by centrifuging the suspensions twice more in distilled water. The crystals were then dried at 80 °C.

The products were examined by optical, electron, and electron scanning microscopy, by electron diffraction and by X-ray diffraction using Cu-K_α radiation with Guinier cameras. If a given species was present in yields estimated to be $\geqslant 70\%$ the samples were submitted to thermogravimetric (t.g.a.) and chemical analyses. Boron was determined as described earlier[1] and silicon as SiO_2 after elimination of boron. Barium was determined as $BaSO_4$. The samples analysed were often small and precision was therefore sometimes limited. Contaminants were iron oxide from the stainless-steel autoclaves and graphite used to lubricate the seals of the autoclaves.

TABLE 1

Products obtained in the system BaO–B_2O_3–SiO_2–H_2O at 250 °C (crystallisation time 7 days)

l = low yield; m = medium yield; g = good yield; vg = very good yield

Starting molar composition (of solid matter)	Expt. no.	n	Result as determined by X-ray diffraction
$1{\cdot}0BaO + 0{\cdot}25B_2O_3 + nSiO_2$	400	0	Ba-α1(g) + Ba-α2(m)
	401	1	BaS1(g) + Ba-α3(m) + BaS2(l)
	402	2	BaS3(g) + Ba-α4(m) + ?(l)
	403	4	BaS4(m) + αC(g) + Ba-α4(l) + ?(l)
	404	8	Ba-α5
$1{\cdot}0BaO + 0{\cdot}5B_2O_3 + nSiO_2$	388	0	Ba-α6(g) + Ba-α2(g) + Ba-α1(l)
	389	1	BaS1(g) + BaS2(l) + Ba-α3(m)
	390	2	Ba-α4(vg)
	391	4	Ba-α7(vg)
	392	8	Ba-α7(vg)
$1{\cdot}0BaO + 1{\cdot}0B_2O_3 + nSiO_2$	383	0	Ba-α6(g) + Ba-α2(g)
	384	1	Ba-α8(vg)
	385	2	Ba-α4(g) + Ba-α7(l)
	386	4	Ba-α7(g) + Ba-α4(l)
	387	16	Ba-α4(m) + Ba-α7(m) + amorphous SiO_2
$1{\cdot}0BaO + 2{\cdot}0B_2O_3 + nSiO_2$	323	0	Ba-α2(g) + Ba-α6(l) + Ba-α9(l)
	324	1	Ba-α10(m) + ?(l)
	325	2	Ba-α10(vg)
	326	4	Ba-α10(g) + ?(l)
	327	8	Ba-α10(g) + ?(l)
$1{\cdot}0BaO + 4{\cdot}0B_2O_3 + nSiO_2$	340	0	Ba-α6(g) + ?(l)
	341	1	Ba-α8(vg)
	342	2	Ba-α8(g) + ?(m)
	343	8	Ba-α7(g) + ?(l)
	344	16	Ba-α7(g) + ?(l)
$1{\cdot}0BaO + 8{\cdot}0B_2O_3 + nSiO_2$	352	0	Ba-α11(g) + Ba-α6(l)
	353	1	Ba-α11(vg)
	354	4	Ba-α8(g) + ?(l)
	355	8	Ba-α8(g) + ?(l)
	356	16	?(l) + amorphous SiO_2

RESULTS

It was soon apparent that a notable range of crystalline species could be made under hydrothermal conditions at both 250 and 415 °C. At 250 °C single phases or simple mixtures were obtained; at 415 °C there was a trend towards more complex mixtures. The crystalline products, yields, and initial compositions are summarised in Tables 1 and 2. The products include α-cristobalite, silicates, borates, and borosilicates. Four of the five silicates were identified as phases already known (Table 3) and are therefore not characterised further. There were in addition twenty species given the general designation Ba-αi (i = 1—20), and a known barium borosilicate, Ba-BS[6] (Table 2). These were characterised as described below.

Ba-α5 (*Silicate*).—Ba-α5 was obtained only at 250 °C (Table 1, preparation 404; reactant composition $BaO + 0{\cdot}25B_2O_3 + 8SiO_2$ + aq). The crystals were rounded (~3 μm in diameter) and formed in clusters. The t.g.a. curve (Figure 1) showed a two-stage weight loss, ~1·5% between 200 and 500 °C which could be due to molecular water, and ~1·4% between 600 and 800 °C which could be hydroxyl water, or volatilisation of B_2O_3. On the former basis the chemical analysis approximated to BaO, $8SiO_2$, $2H_2O$ and on the latter to BaO, $8SiO_2$, H_2O (with $0{\cdot}19B_2O_3$ and $0{\cdot}28SiO_2$ as impurities).

Barium Borates.—The ten compounds Ba-αi (i = 1, 2, 6, 9, 11, 12, 13, 17, 18, and 20) were formed from mixtures containing no silica and are therefore borates. In addition *Ba-α3*, which was observed at 250 °C in low yield in preparations 401 (reactant composition $BaO + 0{\cdot}25B_2O_3 + SiO_2$ + aq) and 389 (from $BaO + 0{\cdot}5B_2O_3 + SiO_2$ + aq), is most probably a borate because it was co-crystallised in both preparations with two barium silicates. Because *Ba-α1* and *Ba-α2* appeared only in mixtures their compositions are not known. It is likely that Ba-α2 has $BaO/B_2O_3 > 1$ because in preparation 383 of Table 1 it co-crystallised with Ba-α6 which has $BaO/B_2O_3 = 0{\cdot}4$ while in the parent magma $BaO/B_2O_3 = 1$.

---

[9] *E.g.* D. J. Marshall, 'The Hydrothermal Synthesis of Aluminosilicates,' Ph.D. Thesis, London University, 1962.

The *d*-spacings of the borates are deposited as a Supplementary publication (SUP No. 21098, 12 pp) * and some other properties are summarised in Table 4. Thermogravimetric analyses are given in Figures 1—3. They tend to show stepwise weight losses in which, however, the steps are sometimes ill-defined. The temperatures at which weight losses occur show that crystal water is not zeolitic in character and may at least in part be present as hydroxyl. Weight loss in the vicinity of 1000 °C could be associated with volatilisation of boric oxide. This high-temperature loss is pronounced with Ba-α20 and occurs to a limited extent with Ba-α18, Ba-α13, and Ba-α12. All these borates were prepared at 415 °C. Ba-α11 and Ba-α6, made at 250 °C, did not show this high-temperature weight loss. Additional information on several of the borates is given below.

TABLE 2

Products obtained in the system $BaO–B_2O_3–SiO_2–H_2O$ at 415 °C (crystallisation time 7 days)

l = low yield; m = medium yield; g = good yield; vg = very good yield

Starting molar composition (of solid matter)	Expt. no.	*n*	Result as determined by *X*-ray diffraction
$1{\cdot}0BaO + 0{\cdot}25B_2O_3 + nSiO_2$	393	0	Ba-α12(vg)
	394	0·5	BaS2(g) + Ba-α13(m) + Ba-BS(l)
	395	1	Ba-BS(g) + BaS1(g) + ?(l)
	396	2	Ba-α14(vg)
	397	4	Ba-α15(g) + αC(m) + Ba-α14(l)
	398	8	Ba-α15(g) + αC(g) + Ba-α14(l)
	399	16	αC(g) + Ba-α15(m) + Ba-α14(l)
$1{\cdot}0BaO + 0{\cdot}5B_2O_3 + nSiO_2$	376	0	Ba-α13(g) + ?(m)
	377	0·5	BaS2(g) + Ba-α13(m) + ?(l)
	378	1	BaS1(g) + Ba-BS(m) + ?(l)
	379	2	Ba-α14(vg) + ?(l)
	380	4	Ba-α14(g) + Ba-α15(m) + αC(l) + ?(l)
	381	8	Ba-α14(g) + αC(g) + Ba-α15(l)
	382	16	αC(g) + Ba-α14(g) + Ba-α15(l)
$1{\cdot}0BaO + 1{\cdot}0B_2O_3 + nSiO_2$	357	0	Ba-α13(vg)
	358	0·5	Ba-BS(g) + Ba-α13(m) + ?(l)
	359	1	Ba-BS(g) + ?(m)
	360	2	Ba-α10(m) + Ba-α14(m) + ?(m)
	361	4	αC(g) + Ba-α15(m) + Ba-α16(m) + Ba-α10(l)
	362	8	αC(vg) + Ba-α15(m) + ?(l)
	363	16	αC(vg) + Ba-α15(m)
$1{\cdot}0BaO + 2{\cdot}0B_2O_3 + nSiO_2$	316	0	Ba-α17(vg) + Ba–α18(l)
	317	0·5	Ba-BS(g) + Ba-α17(m) + ?(l)
	318	1	Ba-BS(g) + Ba-α10(m) + ?(l)
	319	2	Ba-α10(vg) + αC(l)
	320	4	Ba-α10(g) + Ba-BS(m)
	321	8	αC(g) + Ba-α10(m) + Ba-α16(l) + Ba-α19(l)
	322	16	αC(g) + Ba-α15(m) + Ba-α10(l)
$1{\cdot}0BaO + 4{\cdot}0B_2O_3 + nSiO_2$	303	0	Ba-α18(vg)
	304	0·5	Ba-BS(g) + Ba-α10(l) + Ba-α18(l)
	305	1	Ba-BS(g) + Ba-α10(l) + ?(l)
	306	2	Ba-α10(g) + Ba-BS(l)
	307	4	Ba-α10(g) + αC(l) + ?(l)
	308	8	αC(g) + Ba-α10(g)
	309	16	αC(vg) + Ba-α10(m)
$1{\cdot}9BaO + 8{\cdot}0B_2O_3 + nSiO_2$	345	0	Ba-α20(g) + Ba-α18(l)
	346	0·5	Ba-BS(g) + Ba-α10(m) + ?(l)
	347	1	Ba-α10(g) + Ba-α20(l) + ?(l)
	348	2	Ba-α10(vg)
	349	4	Ba-α10(vg) + αC(l)
	350	8	Ba-α10(g) + αC(g)
	351	16	αC(g) + Ba-α10(g)

TABLE 3

Silicates from the system $BaO–B_2O_3–SiO_2–H_2O$

Code	Oxide formula	Reference
BaS1	$2BaO,3SiO_2$	ASTM No. 12-694
BaS2	α-BaO,SiO_2	ASTM No. 21-84
BaS3	$BaO,2SiO_2$	ASTM No. 11-170
BaS4	β-$BaO,2SiO_2$	ASTM No. 10-46
α-C	α-Cristobalite, SiO_2	ASTM No. 11-695

The *d*-spacings of Ba-α5 are given in the Supplementary publication along with those of other species Ba-α*i*.

Ba-α6. Ba-α6 crystallised at 250 °C from a wide range of compositions $BaO + nB_2O_3 + aq$ (n = 0·5, 1, 2, 4, and 8). It was the main phase and appeared as cylinder-shaped crystals up to 50 μm long (preparation 340, n = 4).

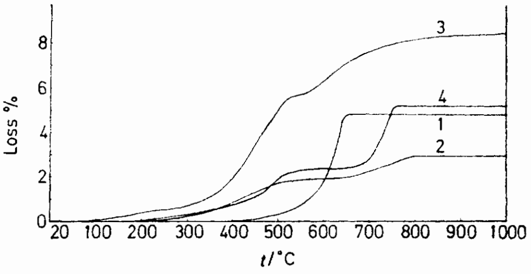

FIGURE 1 Thermogravimetric analyses for: curve 1, Ba-α4; curve 2, Ba-α5; curve 3, Ba-α6; and curve 4, Ba-α7

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

Thermogravimetric analysis (Figure 1) indicates a first stage weight loss of 5·7% ending at ~530 °C (molecular water) and a second stage (2·7%) above this temperature which could be hydroxyl water. On this assumption the compound, which melted below 1000 °C, has the oxide composition given in Table 4.

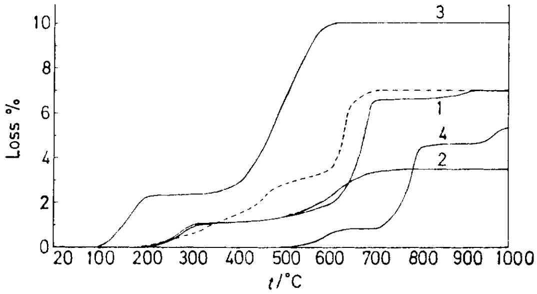

FIGURE 2 Thermogravimetic analyses for: curve 1, Ba-α8; curve 2, Ba-α10; curve 3, Ba-α11; and curve 4, Ba-α12. The dashed curve is for datolite

Ba-α11. This compound crystallised at 250 °C (Table 1). Preparation 353 on heating lost weight in two steps (Figure 2), 2·3% between 100 and 200 °C (molecular water); and 7·7% more between ~350 and 600 °C (dehydroxylation). The chemical analysis (Table 4) gives $B_2O_3/BaO = 3$, the highest observed among all the borates.

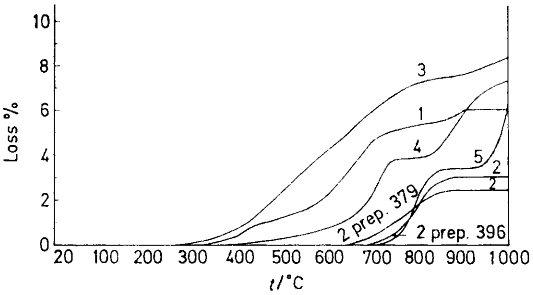

FIGURE 3 Thermogravimetric analyses for: curve 1, Ba-α13; curves 2, Ba-α14 (two different preparations); curve 3, Ba-α17; curve 4, Ba-α18; and curve 5, Ba-α20

Ba-α12. Ba-α12 was obtained pure except for a little iron oxide contaminant. The t.g.a. curve (Figure 2) showed a three-stage weight loss [0·8% between 500 and 680 °C (dehydroxylation); 3·8% between 700 and 800 °C; and a small loss above 900 °C]. The second and third losses may be due to volatilisation of B_2O_3 in which case the borate is nearly anhydrous (Table 4).

TABLE 4

Some properties of species Ba-α*i*

Code	Temp. of cryst. (*t* °C)	Crystal habit	Chemical nature	Composition	Unit cell
Ba-α1	250	Small crystals 1 μm	Barium borate	—	
Ba-α2	250	Rod like 1 μm × 7 μm	Barium borate	$BaO/B_2O_3 > 1$?	
Ba-α3	250	—	Barium borate ?	—	
Ba-α5	250	Round 3 μm	Barium silicate	$BaO, 8SiO_2, 2H_2O$	
Ba-α6	250	Cylindrical 50 μm long	Barium borate	$2BaO, 5B_2O_3, 3{\cdot}3H_2O$	
Ba-α9	250		Barium borate	—	
Ba-α11	250	Small crystals <1 μm	Barium borate	$BaO, 3B_2O_3, 2{\cdot}2H_2O$	
Ba-α12	415	Small crystals ~0·8 μm	Barium borate	$5BaO, 2B_2O_3$	
Ba-α13	415	Needles 20—30 μm × 2 μm = bunches of fibres	Barium borate	$BaO, B_2O_3, 0{\cdot}78(?)H_2O$	
Ba-α17	415	Large irregular crystals 1—2 mm	Barium borate	BaO, B_2O_3, H_2O	Space group *P21/C* $a = 6{\cdot}61 \pm 0{\cdot}005$ Å $b = 8{\cdot}63 \pm 0{\cdot}01$ Å $c = 14{\cdot}640 \pm 0{\cdot}005$ Å $\alpha = 93° 45' \pm 6'$
Ba-α18	415	Flat crystals 150 μm × 150 μm × 1 μm	Barium borate	$BaO, 2B_2O_3, 1{\cdot}26H_2O$	
Ba-α20	415	Round 200 μm	Barium borate	$BaO, 2B_2O_3$	
Ba-α4	250	Spherulites 20 μm composed of crystallites 0·2 μm	Barium borosilicate	$2BaO, B_2O_3, 4SiO_2, 1{\cdot}74H_2O$	Tetragonal $a = 12{\cdot}05_4$ Å $c = 8{\cdot}91_6$ Å
Ba-α7	250	Spherulites 15 μm composed of crystallites 0·1 μm	Barium borosilicate	$2BaO, B_2O_3, 6{\cdot}5SiO_2, 2{\cdot}3H_2O$	
Ba-α8	250	Spherulites 15 μm composed of crystallites 0·5 μm	Barium borosilicate	$BaO, 1{\cdot}09B_2O_3, 0{\cdot}77SiO_2, 1{\cdot}06H_2O$	
Ba-α10	250 and 415	250 °C: Spherulites 50 μm composed of crystallites 0·1 μm 415 °C: Spherulites + single crystals (bipyramids)	Barium borosilicate	$BaO, 1{\cdot}02B_2O_3, 1{\cdot}68SiO_2, 0{\cdot}65H_2O$ (250 °C) $BaO, 1{\cdot}12B_2O_3, 1{\cdot}82SiO_2$ $0{\cdot}21H_2O$ (415 °C)	
Ba-α14	415	Long crystals 100 μm × 30 μm	Barium borosilicate	$BaO, B_2O_3, 3{\cdot}6$—$4{\cdot}4SiO_2$	
Ba-α15	415	Cubes 5—8 μm	Unknown	—	
Ba-α16	415	Rod-like 7—12 μm × 0·4—0·8 μm	Unknown	—	Orthorhombic $a = 4{\cdot}17 \pm 0{\cdot}06$ Å $b = 11{\cdot}72 \pm 0{\cdot}07$ Å $c = 31{\cdot}4 \pm 0{\cdot}8$ Å
Ba-α19	415	Rod-like 4 μm × 0·4 μm	Unknown		Orthorhombic $a = 7{\cdot}51$ Å $b = 4{\cdot}61$ Å $c = 26{\cdot}3$ Å

Ba-α13. The compound crystallised at 415 °C free from other phases (preparation 357, from $BaO + B_2O_3 + aq$). The needle-like crystals [Plate (a)], 20—30 µm long and 2 µm broad, were remarkably flexible. The reason for this could be that each needle was found to be a bundle of fibrous crystals with diameters less than 0·2 µm.

Ba-α17. This phase grew at 415 °C with a yield estimated as $\geqslant 80\%$, along with Ba-α18, in preparation 316 (Table 2) (initial composition $BaO + 2B_2O_3 + aq$). The crystals grew to 1 or 2 mm and a 0·4 mm crystal was selected to determine the space group and unit-cell parameters given in the Supplementary publication. The powder pattern was indexed for *d*-spacings down to 2·245 Å. The t.g.a. curve (Figure 3) showed a more continuous weight loss than those of other borates. The slight break in the curve around 750 °C may denote the onset of volatilisation of some B_2O_3. The density of the crystals was $3{\cdot}64 \pm 0{\cdot}05$ g cm^{-3} at 25 °C as determined in a micro density bottle, using a high purity sample. Since optical examination showed some inclusions (mother liquor or air bubbles) this density is a lower limit. The unit-cell volume is 837 Å^3. For the oxide composition BaO, B_2O_3, H_2O (Table 4) and a density 3·835 there are eight formula weights per unit cell. For crystallographic reasons (symmetry of the unit cell) the number of formula weights per unit cell must be an even integer, and so the above composition and density are strongly supported. The actual analysis gave BaO, $1{\cdot}29B_2O_3$, $1{\cdot}06H_2O$. However, as noted above Ba-α17 was formed with a little Ba-α18 which is richer in B_2O_3 (Table 4).

Ba-α18. Ba-α18 was obtained free of other crystalline species at 415 °C in preparation 303 from the composition $BaO + 4B_2O_3 + aq$. The thin flat crystal (Plate b) had a larger dimension up to 150 µm. The t.g.a. curve showed 3·8% weight loss between 450 and 750 °C (dehydroxylation) and 3·5% loss above 820 °C (possibly volatilisation of B_2O_3). The compound, of the composition given in Table 4, fused below 1000 °C.

Ba-α20. This phase, together with a little Ba-α18, grew at 415 °C (preparation 345 of Table 2, from $BaO + 8B_2O_3 + aq$). The rounded crystals had diameters up to 200 µm. The t.g.a. curve (Figure 3) showed 3·4% weight loss between 700 and 900 °C and 2·7% above 950 °C. Both steps could result from volatilisation of B_2O_3 so that in Table 4 the composition given is that for an anhydrous phase. The sample analysed contained a little Ba-α18 but since for this compound $B_2O_3/BaO = 2$ and is the same as for the overall analysis of the mixture no correction is required in finding $B_2O_3/BaO = 2$ for Ba-α20.

Barium Borosilicates.—Table 4 includes five species which appear to be new barium borosilicates. In addition the known[6] synthetic barium borosilicate, Ba-BS, was formed. The *d*-spacings of these five compounds are included in the Supplementary publication and the crystalisation fields at 250 and 415 °C are given in Figures 4 and 5 respectively. These are not necessarily fields of thermodynamic stability since metastable phases are common in hydrothermal systems. Some other aspects of these compounds are recorded below.

Ba-BS. Ba-BS had previously been synthesised in the absence of water over a narrow field of formation.[6] In the hydrothermal systems at 415 °C, on the other hand, it crystallised over a rather extended field although always as a co-crystallisate (Figure 5). The rounded crystals had diameters in the range 10—20 µm. The *d*-spacings (see Supplementory publication) agree with the ASTM reference, but no chemical analysis was made because the samples were not pure. The composition of the reference material[6] is 3BaO, $3B_2O_3$, $2SiO_2$.

Ba-α4. At 250 °C spherulites of diameters up to 20 µm formed, which were composed of much smaller crystallites of ~0·2 µm. Preparation 390 (from $BaO + 0{\cdot}5B_2O_3 + 2SiO_2 + aq$; Table 1) yielded Ba-α4 free of other crystalline compounds. The *X*-ray powder lines were indexed to the tetragonal unit cell given in Table 4 and the Supplementary publication and Table 4 also gives the composition. The t.g.a. curve (Figure 1) shows a single stage weight loss of 4·85% between 400 and 650 °C (dehydroxylation).

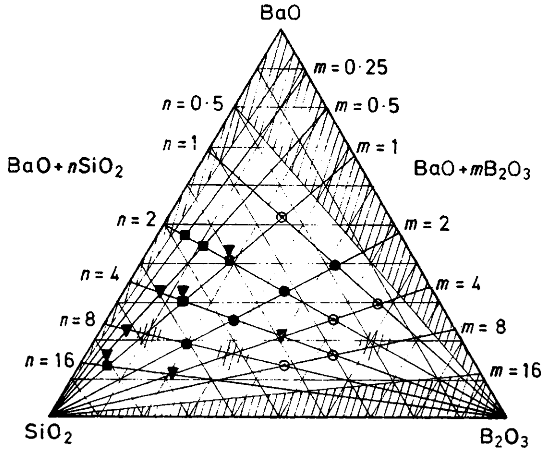

FIGURE 4 Crystallisation fields at 250 °C of Ba-α4 (■), Ba-α7 (▼), Ba-α8 (○), and Ba-α10 (●)

In Figures 4 and 5 the cross-hatched areas are those in which no compositions were studied. The scales (unmarked) along the sides of the triangular diagrams are weight %. Numbers of moles of SiO_2 and of B_2O_3 per mole of BaO are also given.

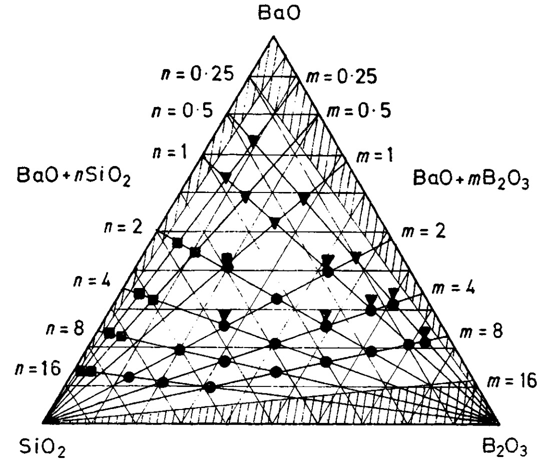

FIGURE 5 Crystallisation fields at 415 °C of Ba-α10 (●), Ba-α14 (■), and Ba-BS (▼)

Ba-α7. Ba-α7 grew at 250 °C from a considerable field of parent silica-rich compositions (Figure 4). It was obtained free of other species in preparations 391 and 322 from $BaO + 0{\cdot}5B_2O_3 + nSiO_2 + aq$ where $n = 4$ and 8 respectively (Table 1). Optical examination showed smooth-looking spherulites of ~15 µm diameter but stereo-

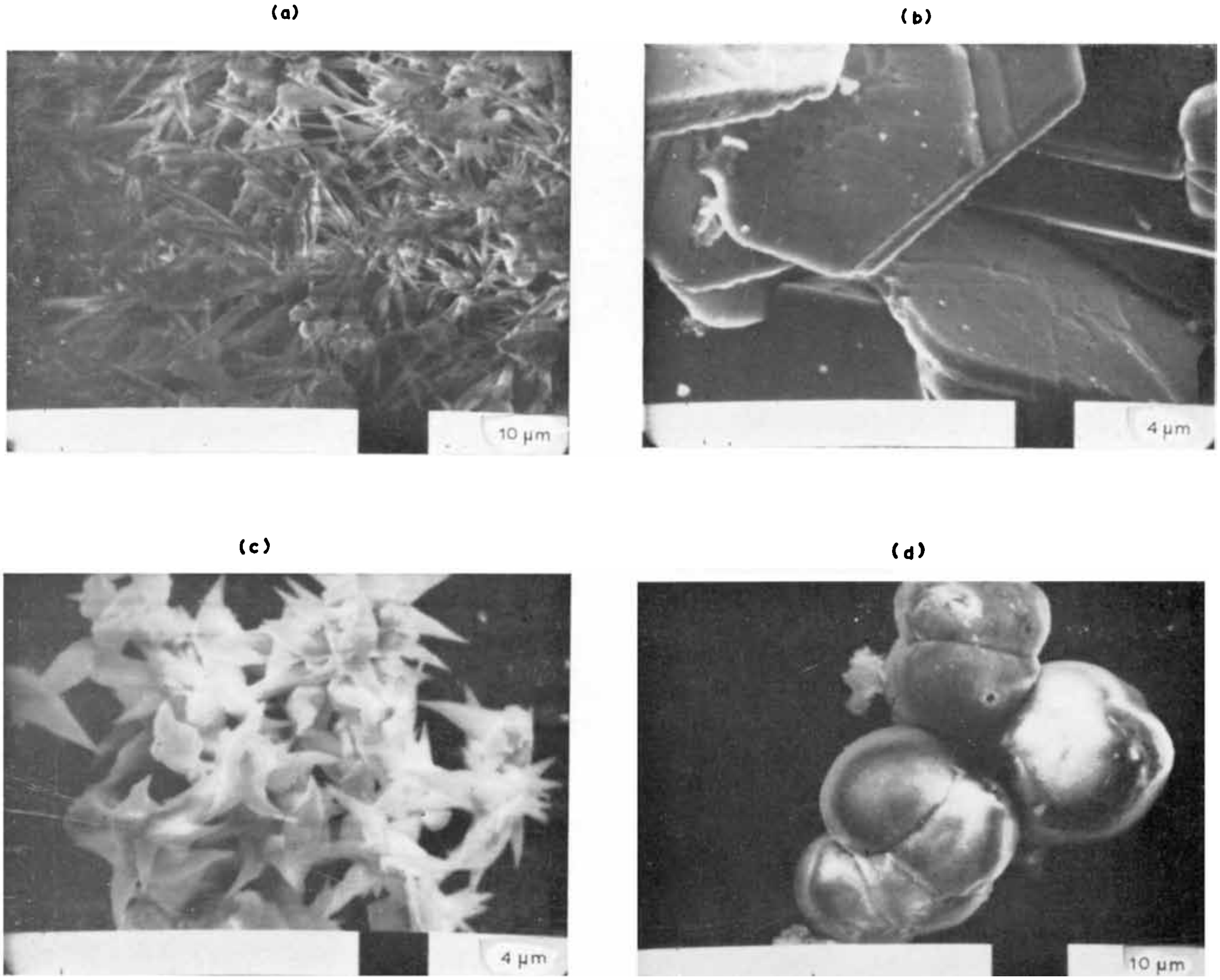

PLATE (a) Ba-α13; (b) Ba-α18; (c) Ba-α10 (grown at 415 °C); (d) Ba-α10 (spherulites grown at 250 °C) scan electron micrographs revealed that the spherulites were composed of crystallites less than 0·1 μm in size. Presumably as a result the *X*-ray powder diffraction lines were somewhat broadened. There is a two-stage weight loss in t.g.a. (Figure 1) of 2·4% between ~200 and 600 °C (molecular water) and an extra 2·8% between 650 and 750 °C, the origin of which is not certain but could be due to hydroxyl water. This assumption, with the analysis, gives the oxide formula in Table 4.

Ba-α8. Ba-α8 appeared at 250 °C from several compositions (Table 1 and Figure 4). Preparations 384 (from BaO + B_2O_3 + SiO_2 + aq) and 341 (from BaO + $4B_2O_3$ + SiO + aq) yielded the compound free of other species, as spherulites of ~15 μm diameter, composed of smaller crystallites of ~0·5 μm. The power patterns of both preparations were identical but rather complex (see Supplementary publication indicating low symmetry of the unit cell). In t.g.a. (Figure 2) a first-stage weight loss of 1·1% occurred below 300 °C (molecular water); and a second of 5·4% took place between 500 and 700 °C (hydroxyl water). A third above 700 °C could be due to volatilisation of B_2O_3. The total water loss on this basis is 6·5% and is used in the chemical formula in Table 4.

Ba-α10. Ba-α10 crystallised at 250 °C, and also at 415 °C where its crystallisation field was large (Figures 4 and 5). At 415 °C it appeared as rectangular bipyramids with the largest dimension up to 50 μm (preparation 319) or as spherulites, some round and some with the curious shape seen in the Plate (c), both forms co-existing. A similar shape has been observed by Morse and Donnay.[10] The *X*-ray powder patterns even of the spherulites all gave sharp lines. At 250 °C Ba-α10 formed as smooth spherulites up to 50 μm in diameter and composed of crystallites less than 0·1 μm [Plate (d)]. The lines in the *X*-ray powder pattern were broader than those obtained for preparations at 415 °C and there were some intensity differences.

Preparations 325 (at 250 °C) and 348 (at 415 °C) were each submitted to t.g.a. and to chemical analysis. The compositions are given in Table 4. In t.g.a., preparation 325 lost ~1·0% between 200 and 250 °C (molecular water) and 2·5% between 400 and 750 °C (hydroxyl water). The weight loss from preparation 348 was only 1·1% up to 1000 °C. Comparison of t.g.a. and of *X*-ray powder data between datolite and Ba-α10 showed little resemblance, although the bipyramid crystals of Ba-α10 recall the striated bipyramids of garrelsite,[3] a mineral of the datolite group.

Ba-α14. The compound was observed in several preparations at 415 °C (Table 2 and Figure 5). Preparation 396 from BaO + $0{\cdot}25B_2O_3$ + $4SiO_2$ + aq yielded Ba-α14 free of other species and preparation 379, from BaO + $0{\cdot}5B_2O_3$ + $2SiO_2$ + aq gave it in major yield. The crystals were large, up to 100 μm in length and 30 μm broad. Both the above preparations were submitted to t.g.a. and chemical analysis. The weight losses in t.g.a. were ~3·0 and 2·4% respectively up to 1000 °C (Figure 3) and began above 700 and 650 °C. They could therefore arise from volatilisation of a little B_2O_3. On this assumption the compositions are those given in Table 4.

Other Compounds.—The species *Ba*-α15, *Ba*-α16, and *Ba*-α19 all formed at 415 °C but only with other species (Table 2). Thus although the *X*-ray powder patterns could be identified (see Supplementary publication) meaningful chemical analyses could not be made and the chemical nature (borate, borosilicate, or silicate) could not be determined. Ba-α15 grew as small cubic crystals (dimension 5—8 μm) from silica-rich compositions with ratios BaO/B_2O_3 between 0·5 and 2, along with α-cristobalite and other phases. Ba-α16 (preparations 361 and 321 of Table 2) grew as rods 7—12 μm long and 0·4—0·8 μm in breadth. Electron diffraction of one of these crystals indicated a *c*-centred orthorhombic unit cell. The dimensions yielding the best fit to the *d*-spacings are given in Table 4, the *c*-value being the least accurate. Ba-α19 also grew in low yield as rods ~4 μm long and 0·4 μm broad. However the electron diffraction pattern of a single crystal indicated an orthorhombic unit cell, the dimensions of which, refined to give the best fit to the *X*-ray powder data, are given in the Supplementary publication and in Table 4.

DISCUSSION

For the barium borates grown at 415 °C, as the ratio B_2O_3/BaO in the parent mixture increases, the same ratio in the products moves towards what appears to be a final value of 2 (Figure 6). The straight line in this Figure is the locus of equal values of B_2O_3/BaO in the parent mixture and in the crystals grown from it. At high ratios B_2O_3/BaO excess boric acid is rejected, while at sufficiently low values (*e.g.* $B_2O_3/BaO = 0{\cdot}25$ in Figure 6) it is excess $Ba(OH)_2$ which is rejected.

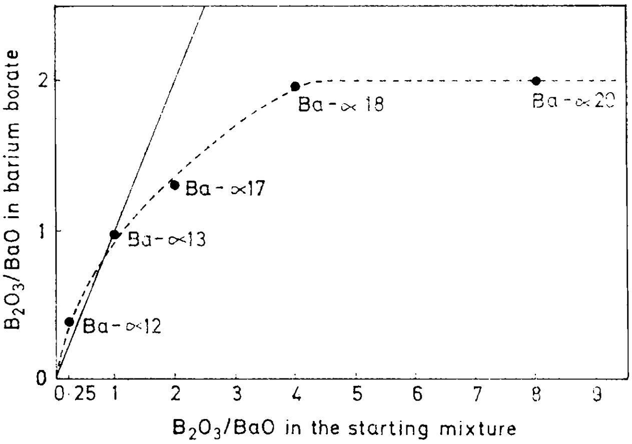

FIGURE 6 B_2O_3/BaO in barium borate as a function of B_2O_3/BaO in the starting mixture for crystallisations at 415 °C. The straight line is the locus corresponding with B_2O_3/BaO in the product = B_2O_3/BaO in the initial mixture

At 250 °C the ratio B_2O_3/BaO in the borates Ba-α6 and Ba-α11 exceeded the maximum of 2 observed at 415 °C. Indeed most of the borate compositions in Table 4 require polymeric borate anions, the boron being in 3-fold co-ordination with oxygen.

The borosilicates all showed a characteristic tendency to spherulitic growth, while weight loss in stages during t.g.a. was typical of most of the borates and borosilicates. In no case could these weight losses reasonably be interpreted as indicating significant zeolitic water and the borosilicates could not be regarded as zeolites. Their tectosilicate character also requires consideration. In the aluminosilicate tectosilicates

---

[10] H. W. Morse and J. D. H. Donnay, *Amer. Min.*, 1936, **21**, 391.

one must have basic oxide/Al_2O_3 = 1 and O/(Al + Si) = 2, and there is no hydroxyl water attached to the framework Al or Si atoms. The first two of these tectosilicate requirements are effectively valid for Ba-BS, Ba-α8, and Ba-α10, but not for Ba-α4, Ba-α7, and Ba-α14, as is seen from Table 5. However, Ba-α8 and Ba-α10 appear to contain some and a little hydroxyl water respectively which suggests some BO_3OH groups in the framework so that full tectosilicate character may be lacking.

TABLE 5

Character of some borosilicates

Compound	BaO/B_2O_3	B/Si	O/(B + Si)	OH present
Ba-BS	1·0	3	2	No
Ba-α4	2·0	0·5	$2{\cdot}1_7$	Yes
Ba-α7	2·0	0·31	$2{\cdot}4_0$	Yes
Ba-α8	$0{\cdot}9_2$	$2{\cdot}8_3$	$1{\cdot}9_7$	Yes
Ba-α10	$0{\cdot}9_3$	$1{\cdot}2_2$	$1{\cdot}9_8$	Little
Ba-α14	2·0	0·5	$2{\cdot}1_7$	No

In tectosilicate aluminosilicates a widely valid rule is that AlO_4 tetrahedra are not linked directly to other AlO_4 tetrahedra in the frameworks.[11] This means that the ratio Al/Si cannot exceed unity. However if Ba-BS, Ba-α8, and Ba-α10 are true tectosilicates they do not obey this rule, as seen from the ratios B/Si in Table 6.

We thank Dr. I. S. Kerr of this Department for help with crystallographic work and electron diffraction. One of us (E. F. F.) thanks the Institut Français du Pétrole for partial financial support and the British Council for the award of a scholarship.

[4/393 *Received, 27th February,* 1974]

---

[11] W. Lowenstein, *Amer. Min.*, 1954, **39**, 92.