Hydrothermal Chemistry of Silicates. Part XVIII.† Reactions in the System $CaO-B_2O_3-SiO_2-H_2O$

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An investigation of the system $CaO-B_2O_3-SiO_2-H_2O$ at 250 and 415 °C has shown the ready formation of cristobalite, quartz, five identified silicates, six identified borates, and the borosilicates danburite and datolite. In addition ten unidentified and possibly new borates and a number of phases which could not be classified chemically and which may include silicates and borosilicates, were also prepared. Co-crystallisation of mixtures was as typical of this calcic system as it was of the analogous baric one. The unclassified compounds were characterised by their *X*-ray powder patterns and where possible in other ways. No borosilicate zeolites have so far been identified.

As with baric borosilicates few naturally occurring calcic borosilicates are known. They include datolite[1] $2CaO,B_2O_3,2SiO_2,H_2O$, the structure of which consists of sheets of interlinked SiO_4 and BO_3OH tetrahedra, and the related compounds bakerite[2-4] ($4CaO,2{\cdot}5B_2O_3,3SiO_2,2{\cdot}5H_2O$), garrelsite,[2] and homolite;[2,4] danburite ($CaO,B_2O_3,2SiO_2$) which has a three-dimensional framework of Si_2O_7 and B_2O_7 groups, with boron in tetrahedral co-ordination;[5] and howlite[6] ($4CaO,5B_2O_3,2SiO_2,5H_2O$).

The anhydrous system $CaO-B_2O_3-SiO_2$ has yielded only one ternary compound $5CaO,B_2O_3,SiO_2$.[7-9] On the other hand no hydrothermal study of the system $CaO-B_2O_3-SiO_2-H_2O$ has been found. Accordingly, to supplement a hydrothermal investigation of the analogous system with BaO in place of CaO,[10] and to attempt to prepare calcium borosilicates and eventually borosilicate zeolites, the reactions of the above calcic magmas have been examined at 250 and 415 °C.

EXPERIMENTAL

The solid reagents were pure crystalline calcium hydroxide and boric acid, and amorphous silica low in alkali. They were mixed in appropriate amounts and, with protection from CO_2, ground to fine powder and the mixture then introduced into the stainless steel autoclaves of *ca.* 15 ml capacity.[10] Water was added to give 1 g anhydrous matter per 8 g of mixture (water content 87·5% by weight; *ca.* 50% filling of the autoclaves). The sealed autoclaves were heated usually for 7 days but sometimes for 27 days. After the autoclaves had been quenched the solid products were separated and investigated as previously described.[10] When a crystalline product was sufficiently pure ($\geqslant$70% yield) it was analysed chemically. Calcium was determined by atomic absorption spectroscopy, and boron as described previously.[11]

RESULTS

Before selecting 250 and 415 °C as reaction temperatures runs were made at lower temperatures, but crystallisation then proved too slow for convenient study. The experi-

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† Part XVII is reference 10.

[1] T. Ito and H. Mori, *Acta Cryst.*, 1953, **6**, 24.

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

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

[4] J. Murdoch, *Amer. Min.*, 1962, **47**, 919.

[5] C. Dunbar and F. Machatschki, *Z. Krist.*, 1930, **70**, 133.

[6] J. Murdoch, *Amer. Min.*, 1957, **42**, 521.

[7] E. P. Flint and I. S. Wells, *J. Res. Nat. Bur. Stand.*, 1936, **17** (15), 727.

[8] E. P. Flint and I. S. Wells, *Ceram. Abs.*, 1937, **16** (2), 75.

[9] W. K. Knapp and H. Flood, *Amer. Ceram. Soc. Bull.*, 1957, **40** (8), 262.

[10] Part XVII, R. M. Barrer and E. F. Freund, preceding paper.

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

mental results at 250 and 415 °C are summarised in Tables 1 and 2 respectively. It was usual to find mixtures of crystalline compounds after reaction, which complicated identification and the interpretation of chemical analyses. However the numerous crystalline products were identified in a number of cases, as summarised in Table 3, which also gives the naming code of many of the phases in Tables 1 and 2.

TABLE 1

Products obtained in the system $CaO–B_2O_3–SiO_2–H_2O$ at 250 °C (crystallisation time 7 days unless otherwise specified). 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
1·0 CaO + 0·25 B_2O_3 + $n SiO_2$	298	0	C(vg) + Ca-α1(l)
	299	0·25	C(g) + Ca-α2(l) + ?(l)
	300	0·5	C(g) + Ca-α2(m) + ?(l)
	301	1	Dat(g) + Ca-α2(m)
	302	2	Gyr(g) + ?(l)
1·0 CaO + 0·5 B_2O_3 + $n SiO_2$	232	0	C(g) + Ca-α3(m) + Ca-α4(l)
	233	0·5	Dat(m) + C(m) + Ca-α5(m) + ?(l)
	234	1	Dat(vg) + ?(l)
	235	2	Dat(g) + Gyr(m)
	236	4	Dat(g) + Gyr(m) + ?(l)
1·0 CaO + 1·0 B_2O_3 + $n SiO_2$	208	0	Ca-α4(g) + Pan(g)
	209	0·5	Dat(g) + Pan(l)
	210	1	Dat(vg) + ?(l)
	211	2	Dat(vg) + ?(l)
	212	4	Dat(vg) + ?(l)
1·0 CaO + 2·0 B_2O_3 + $n SiO_2$	220	0	Pan(g) + Ca-α4(m) + Ca-α6(l)
	221	0·5	Dat(g) + Ca-α6(l) + Ca-α7(l)
	222	1	Dat(vg)
	223	2	Dat(vg)
	224	4	Dat(vg)
1·0 CaO + 2·0 B_2O_3 + $n SiO_2$	244	0	Ca-α8(g) + Ca-α5(m)
	246	0·5	Dat(m) + Ca-α8(m) + ?(m)
Crystallisation time 27 days	247	1	Dat(vg)
	248	2	Dat(vg)
	249	4	Dat(vg)
1·0 CaO + 4·0 B_2O_3 + $n SiO_2$	263	0	Pan(g) + Ca-α6(m) + Ca-α4(l)
	264	0·5	Dat(g) + Ca-α8(g)
	265	1	Dat(g) + Ca-α8(m) + ?(l)
	266	2	Dat(vg)
	267	4	Dat(vg)
1·0 CaO + 8·0 B_2O_3 + $n SiO_2$	275	0	Ca-α8(vg)
	276	0·5	amorphous material + ?(l)
	277	1	Dat(vg)
	278	2	Dat(vg)
	279	4	Dat(vg)

For the compositions $CaO + 2B_2O_3 + nSiO_2 + aq$ (n = 0·25, 0·5, 1·2, 4, and 8) the experiments were repeated with 27 days reaction time, to judge whether or not a final stage—stable or metastable—had been reached after 7 days. At 250 °C Table 1 shows certain differences among the products from low silica magmas but not from those richer in silica. At 415 °C Table 2 also shows differences in the minor phases after 7 and 27 days, but not among those formed in major yield. Thus there is some evolution of metastable species which are slowly replaced by more stable ones.

The species Ca-α1—17 were not identified with any previously reported compounds and were therefore characterised in several ways. The compounds of Table 3 will not be described further with the exception of the datolites and danburites.

Datolite. The rather wide crystallisation fields of the synthetic datolites at 250 and 415 °C are shown in Figures 1 and 2. The compositions of a natural datolite (Table 3), bakerite, and garrelsite are also marked in Figures 1 and 2. They fall near the boundary of the crystallisation field at 250 °C and are outside it at 415 °C. Figures 1 and 2 however give the compositions of the parent magmas yielding datolite, not those of the datolites formed. *X*-Ray powder patterns of reference datolites and of three of our synthetic datolites are compared in Table 4. The datolite obtained at 250 °C (preparation 265) gave rather broad powder lines due to the very small size (<0·1 μm) of crystals composing the large spherulites. At 415 °C datolite grew also as

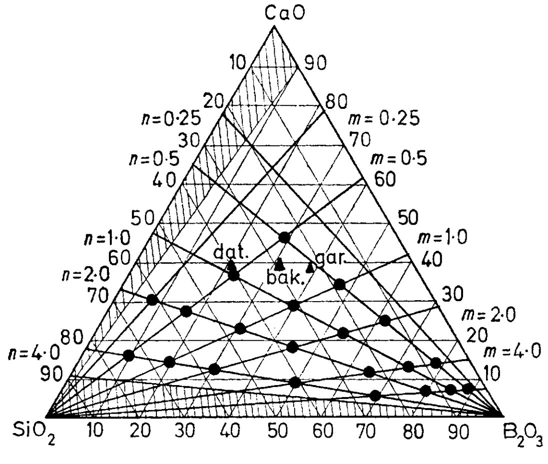

FIGURE 1 The compositions of parent magmas yielding datolites at 250 °C, (●). Also shown are the compositions of a natural datolite, bakerite, and garrelsite, (▲). In Figures 1 and 2 cross-hatched areas are those in which no compositions were studied and the scales along each edge are in weight %. Moles of B_2O_3 (m) and of SiO_2 (n) per mole of CaO are also given

spherulites [Plate (a)] with larger individual crystallites of 0·5—0·74 μm in preparation 260.

Preparation 192 of Table 2 was analysed and had the composition in Table 5, which is compared with those of datolite and related species in the same Table. The B/Si ratio can evidently vary among datolite-type compounds much as the Al/Si ratio varies in certain aluminosilicates, so that there may be a range of compositions among the datolites of Tables 1 and 2.

TABLE 2

Products obtained in the system $CaO–B_2O_3–SiO_2–H_2O$ at 415 °C (crystallisation time 7 days unless otherwise specified). 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
1·0 CaO + 0·25 B_2O_3 + $n$$SiO_2$	237	0	Ca-α9(vg) + ?(l)
	238	0·25	Ca-α9(g) + Ca-α10(m) + Wol(l) + Ca-α11(l) + ?(l)
	239	0·5	Ca-α10(g) + Wol(m) + Ca-α11(m) + ?(l)
	240	1	Wol(g) + Ca-α11(m) + ?(l)
	241	2	Ca-α12(g) + Wol(g) + ?(l)
	242	4	α-C(g) + Wol(m) + Ca-α12(l) + Tru(l) + ?(l)
	243	8	α-C(vg) + Wol(l) + Tru(l) + Ca-α12(l) + ?(l)
1·0 CaO + 0·5 B_2O_3 + $n$$SiO_2$	213	0	Ca-α13(vg)
	214	0·25	Ca-α13(g) + Ca-α14(m)
	215	0·5	Ca-α14(g) + Ca-α13(m) + α-C(l) + ?(l)
	216	1	Ca-α10(g) + Dat(m) + α-C(m) + Ca-α15(l)
	217	2	α-C(g) + Ca-α10(m) + Ca-α15(l)
	218	4	α-C(g) + Ca-10(m) + Ca-α15(l)
	219	8	α-C(vg) + Ca-α10(l) + ?(l)
1·0 CaO + 1·0 B_2O_3 + $n$$SiO_2$	189	0	D(g) + Ca-α13(m) + Ca-α16(l)
	190	0·25	Wol(g) + Fro(l) + ?(m)
	191	0·5	Gin(m) + CB1(m) + Wol(m)
	192	1	Dat(vg) + ?(l)
	193	2	Dat(g) + α-C(g)
	194	4	α-C(g) + α-Q(m) + Dat(l) + CS1(l) + Xon(l)
	195	8	α-C(g) + Xon(m) + Tru(l)
1·0 CaO + 2·0 B_2O_3 + $n$$SiO_2$	201	0	D(g) + Ca-α16(g)
	202	0·25	D(m) + Dat(m) + Ca-α16(m)
	203	0·5	D(m) + Dat(m) + Ca-α16(m)
	204	1	Dat(g) + Ca-α16(m) + D(l) + ?(l)
	205	2	Dat(g) + Dan(g) + ?(l)
	206	4	α-C(g) + Dat(m) + Dan(l) + CS1(l) + ?(l)
	207	8	α-C(vg) + Dan(l) + Tru(l) + CS1(l) + ?(l)
1·0 CaO + 2·0 B_2O_3 + $n$$SiO_2$ Crystallisation time 27 days	249	0	D(g) + Ca-α16(m) + ?(l)
	250	0·25	D(m) + Ca-α16(m) + Dat(l) + ?(l)
	251	0·5	D(g) + Dat(m) + ?(l)
	252	1	Dat(vg) + ?(l)
	253	2	Dat(g) + Dan(g) + ?(l)
	254	4	Dat(m) + Dan(m) + α-C(m) + ?(l)
	255	8	Dat(m) + Dan(m) + α-C(m) + ?(l)
1·0 CaO + 4·0 B_2O_3 + $n$$SiO_2$	256	0	D(g) + Ca-α17(m)
	257	0·25	Leak
	258	0·5	D(g) + Dat(g) + Ca-α17(l)
	259	1	Dat(vg) + D(l)
	260	2	Dat(g) + Dan(g)
	261	4	Dan(g) + α-C(g)
	262	8	α-C(g) + Dan(m)
1·0 CaO + 8·0 B_2O_3 + $n$$SiO_2$	268	0	D(vg) + Ca-α16(l)
	269	0·25	D(g) + Ca-α16(m) + Dat(l)
	270	0·5	D(g) + Dat(m) + Ca-α16(l) + ?(l)
	271	1	Dat(g) + Dan(l) + D(l)
	272	2	Dan(g) + α-C(g) + ?(l)
	273	4	Dan(g) + α-C(g) + ?(l)
	274	8	Dan(g) + Dat(g)

Ca-*Danburite*. Danburite formed only at 415 °C, usually with datolite or α-cristobalite or both. Its crystallisation field is shown in Figure 2, on which is marked the composition of a natural danburite. It grew as bundles of fibres (each fibre *ca.* 20 μm long and 0·3 μm in diameter in preparation 262) and also as well-developed crystals (6—10 μm by 2 μm in preparation 260). In the latter preparation it was co-crystallised with datolite [Plate (b)]. Because danburite could not be separated from other phases no chemical analyses were made. However the *X*-ray powder patterns in Table 6 show close agreement between the *d*-spacings of the reference danburite and those of several of the preparations of this work.

The Phases Ca-α1. The *d*-spacings of Ca-α1—17 are deposited as a Supplementary Publication (SUP No. 21097, 7 pp).* Except for Ca-α8 and Ca-α9 all these compounds were obtained in mixtures and their characterisation has been by means of their *X*-ray powder patterns. However their classification as borates, borosilicates, or silicates has been attempted where additional chemical evidence is available.

Borates.—The compounds Ca-α1, Ca-α3, Ca-α4, Ca-α5, Ca-α6, Ca-α8, Ca-α9, Ca-α13, Ca-α16, Ca-α17 (and also Ca-α18 [12]) were all obtained from the system $CaO–B_2O_3–H_2O$ in absence of silica, and therefore are all borates. Many of

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[12] Part XIX, R. M. Barrer and E. F. Freund, *J.C.S. Dalton*, in the press .

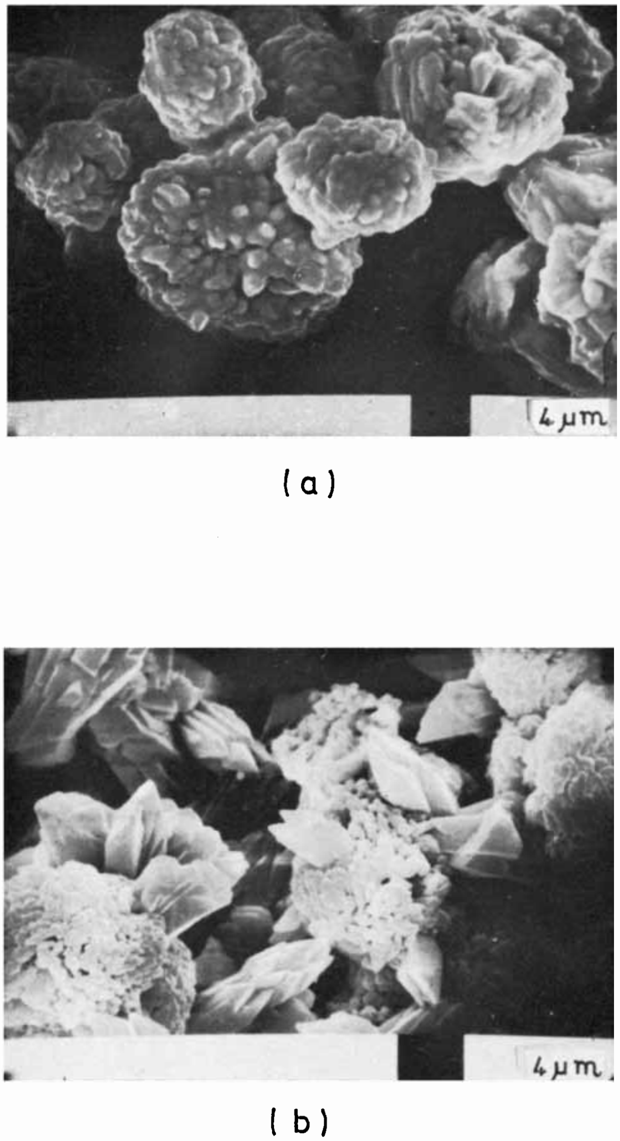

Plate (a) Spherulites of datolite. (b) Danburite co-crystallised with datolite

TABLE 3

Compounds of Tables 1 and 2 which were identified

Code	Temp. (t/°C)	Chemical nature and oxide formula	Reference
(a) Silica and silicates			
α-C	415	α-cristobalite, SiO_2	ASTM No. 11-695
α-Q	415	α-quartz, SiO_2	ASTM No. 5-490
Tru	415	Truscottite, CaO,-$2SiO_2,0{\cdot}5H_2O$	ASTM No. 7-302
Wol	415	Wollastonite, CaO,-SiO_2	ASTM No. 10-483
Xon	415	Xonotolite, 6CaO,-$6SiO_2,H_2O$	ASTM Nos. 10-488 and 15-595
CS1	415	Calcium silicate, 6CaO,-$4SiO_2,3H_2O$	ASTM No. 3-560
Gyr	250	Gyrolite,4CaO,-$6SiO_2,4H_2O$	ASTM No. 9-452
(b) Borates			
C	250	Calcium borate, $2CaO,B_2O_3,H_2O$	ASTM No. 15-544
CB1	415	Calcium borate	ASTM No. 15-532
D	415	Phase D, CaO,B_2O_3	Reference 13
Fro	415	Folovite, CaO,B_2O_3,-$2{\cdot}5H_2O$	ASTM No. 13-453
Gin	415	Ginorite, 2CaO,-$7B_2O_3,8H_2O$	ASTM No. 8-116
Pan	250	Pandermite,* 4CaO,-$5B_2O_3,7H_2O$	ASTM No. 10-463
(c) Borosilicates			
Dan	415	Danburite, CaO,-$B_2O_3,2SiO_2$	ASTM No. 13-308
Dat	250 and 415	Datolite, 2CaO,-B_2O_3,S_2iO_2,H_2O	ASTM No. 11-70

* The X-ray spectrum is very close to that of priceite (ASTM No. 9-147).

them also formed, along with other phases, when silica was present. Ca-α1 formed in low yield at 250 °C from $4CaO + B_2O_3 + aq$, along with phase C which has the composition $2CaO,B_2O_3,H_2O$. Therefore Ca-α1 may have a high ratio CaO/B_2O_3. Similarly because, among other preparations given in Table 1, *Ca*-α8 grew from the initial mix $CaO + 8B_2O_3 + aq$ (preparation 275) it may be a borate with a low ratio CaO/B_2O_3. *Ca*-α6 formed at 250 °C in low to medium yield only (Table 1). *Ca*-α9 formed rods of maximum length ~85 μm and diameter ~30 μm.

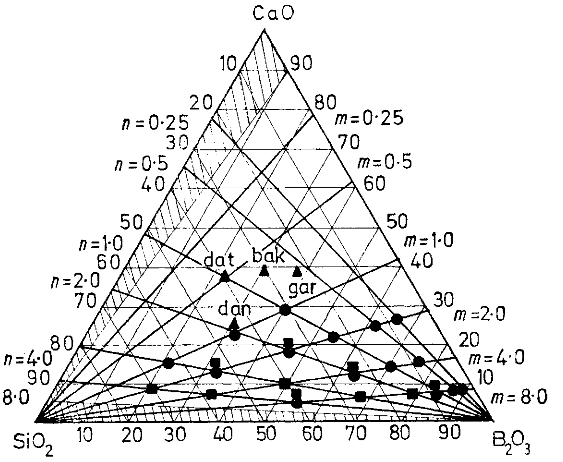

FIGURE 2 The composition of parent magmas yielding datolites (●) and danburites (■) at 415 °C. The compositions of a natural datolite, bakerite, garrelsite, and danburate are also shown (▲)

TABLE 4

d-Spacings of datolite (*d*-spacings in this and other tables are in Å)

Bakerite ASTM No. 14–686 Monoclinic, group $P21/c$ $a = 9{\cdot}60$ Å $b = 7{\cdot}60$ Å $c = 4{\cdot}82$ Å $\beta = 90°\ 12'$								Datolite ASTM No. 11–70 Monoclinic $a = 9{\cdot}62$ Å $b = 7{\cdot}60$ Å $c = 4{\cdot}84$ Å $\beta = 90°\ 09'$								Preparation no.					
																193 (415 °C)		260 (415 °C)		265 (250 °C)	
d	I				h	k	l	d	I				h	k	l	d	I	d	I	d	I
5·98	5				1	1	0	5·98	7				1	1	0	6·00	vw	6·00	w	5·98+	vw
4·82	20	2	0	0,	0	0	1	4·83	16	2	0	0,	0	0	1	4·83	vw	4·85	wm	4·83	wm
3·74	50	1	1	1,	$\bar{1}$	1	1	3·763	45	1	1	1,	$\bar{1}$	1	1	3·76	ms	3·76	m	3·74	s
3·40	30	2	0	1,	$\bar{2}$	0	1	3·404	30	2	0	1,	$\bar{2}$	1	1	3·41	m	3·41	w	3·38	ms
3·11	100	2	1	1,	$\bar{2}$	1	1	3·114	100	2	1	1,	$\bar{2}$	1	1	3·12	vs	3·11	vs	3·09	s-vs
2·99	40	3	1	0,	2	2	0	2·986	35	2	2	0,	0	2	1	2·98	s	2·99	m	2·975	ms
2·85	60	1	2	1,	$\bar{1}$	2	1	2·855	65	1	2	1,	$\bar{1}$	2	1	2·86	vs	2·86	ms	2·84	vs
2·51	60	3	1	1,	$\bar{3}$	1	1	2·524	30	3	1	1,	$\bar{3}$	1	1	2·52	ms	2·52	m	2·50	m-ms
2·45	5	3	2	0,	1	3	0									2·48	w	2·47	w		
2·395	10				4	0	0	2·407	9				4	0	0	2·41	vw	2·41	w	2·39	vw
2·29	5	4	1	0,	0	1	2	2·297	9	4	1	0,	0	1	2	2·29	vw	2·295	w	2·28	vw
2·236	60	2	3	0,	0	3	1	2·243	35	$\bar{1}$	1	2,	2	3	0	2·24	s	2·24	ms	2·23	s
2·18	50	1	3	1,	$\bar{1}$	3	1	2·189	68	3	2	1,	$\bar{3}$	2	1	2·18	s	2·19	ms	2·17	m-ms
2·153	5	2	0	2,	$\bar{2}$	0	2	2·158	13	4	0	1,	$\bar{4}$	0	1	2·16	w				
2·074	10	2	1	2,	$\bar{2}$	1	2	2·075	9	4	1	1,	$\bar{4}$	1	1	2·075	vw	2·08	w	2·06	w
2·03	5	4	2	0,	2	3	1	2·039	7	4	2	0,	$\bar{2}$	3	1	2·03	vw	2·04	vw	2·03	w
1·987	40	3	3	0,	1	2	2	1·997	35				$\bar{1}$	2	2	1·99	m	1·995	m	1·980	m
								1·995	35				1	2	2	2 lines		2 lines			
1·907	5				0	4	0											1·904	w		
1·86	40	5	1	0,	3	1	2	1·875	40	$\bar{4}$	2	1,	2	1	3	1·87	m	1·872	m	1·858	m
1·764	10	2	4	0,	0	4	1	1·770	11				1	4	1	1·77	wm	1·771	m	1·760	m
								1·747	7	$\bar{5}$	1	1,	4	3	0						
1·710	20	5	2	0,	1	3	2	1·718	13				5	2	0	1·715	wm	1·710	w	1·700	w
								1·708	9							2 lines					
1·657	20	2	4	1,	4	1	2	1·662	7							1·66	w	1·655	ms		
1·639	40	2	3	2,	$\bar{2}$	3	2	1·644	40							1·643	m			1·633	ms
								1·620	5												
1·610	5	0	0	3,	5	2	1	1·612	5												
								1·606	5												
1·560	5																				
								1·526	20							1·524	vw				

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[13] P. B. Hart and C. S. Brown, *J. Inorg. and Nuclear Chem.*, 1962, **24**, 1057.

TABLE 5

Compositions of datolite and related phases

Compound	Oxide formula	Ratio B/Si
Datolite	$CaO,0{\cdot}5B_2O_3,1{\cdot}0SiO_2,0{\cdot}5H_2O$	1·00
Bakerite	$CaO,0{\cdot}63B_2O_3,0{\cdot}75SiO_2,0{\cdot}63H_2O$	1·82
Ca-Garrelsite	$CaO,0{\cdot}75B_2O_3,0{\cdot}50SiO_2,0{\cdot}75H_2O$	3·00
Preparation 192	$CaO,0{\cdot}73B_2O_3,0{\cdot}91SiO_2,0{\cdot}40H_2O$	1·61

TABLE 6

d-Spacings of danburite. Orthorhombic unit cell $a = 8{\cdot}048$ Å, $b = 8{\cdot}763$ Å, $c = 7{\cdot}731$ Å

Danburite ASTM 13–308			Preparation no. 205		Preparation no. 260		Preparation no. 272	
d	*I*	*h k*	*d*	*I*	*d*	*I*	*d*	*I*
5·80	2	0 1 1	5·80	vw	5·80	w	5·80	w
4·38	2	0 2 0			4·39	w		
4·02	8	2 0 0			4·05	w	4·05	w
3·86	45	0 0 2	3·87	m	3·88	vs	3·85	s
3·65	10	2 1 0	3·68	vw	3·68	wm	3·65	w
3·57	100	2 0 1	3·58	ms-s	3·58	vs	3·57	s
3·44	70	1 2 1	3·45	ms	3·44	vs	3·42	s
3·30	35	2 1 1	3·32	w	3·31	m	3·295	m
3·23	60	1 1 2	3·24	ms	3·24	vs	3·22	s
2·96	100	2 2 0	2·97	ms-s	2·95	vs	2·95	s
2·90	25	0 2 2	2·89	w	2·895	ms	2·88	m
2·738	80	1 3 0, 0 3 1	2·73	ms (broad)	2·74	vs	2·73	s
2·654	60	2 1 2	2·66	ms	2·66	vs	2·645	ms
2·561	16	3 1 0	2·57	vw	2·575	wm	2·56	w
2·471	10	0 1 3	2·47	vw	2·47	m	2·46	m
2·431	25	3 1 1	2·440	vw	2·44	ms	2·43	m
2·351	20	2 2 2	2·355	w	2·36	ms	2·345	ms
2·283	2	3 2 0			2·295	w	2·28	w
2·190	10	0 4 0, 3 2 1			2·19	ms	2·18	w
2·168	16	2 0 3	2·170	m	2·175	m	2·16	m
2·138	45	1 2 3	2·140	m-ms	2·14	s	2·13	s
2·110	6	1 4 0	2·105	vw	2·11	w	2·10	w
2·034	2	1 4 1	2·040	w	2·04	w	2·03	vw
2·013	30	4 0 0, 2 3 2	2·015	m	2·015	ms	2·01	ms
1·969	20	3 3 0, 3 2 2	1·972	w	1·973	m	1·968	m
1·943	30	4 0 1, 2 2 3	1·943	m	1·945	ms	1·938	ms
1·932	20	0 0 4, 0 3 3	1·926	m	1·930	ms	1·922	ms

The *d*-spacings obtained are close to those of the reference compound $Ca_3(BO_3)_2$ but there are also noticeable differences. The thermogravimetric analysis (t.g.a.) curve shows a two-stage weight loss (Figure 3), 1·2% between 500 and 600 °C and 1·9% between 640 and 850 °C. Both could be due to loss of hydroxyl water.* Analysis gave the composition $3CaO,B_2O_3,0{\cdot}5H_2O$. *Ca-α*13 was obtained at 415 °C nearly free of other species from CaO + $0{\cdot}5B_2O_3$ + aq. It crystallised as sharp-ended needles, sometimes in bundles, and up to 50 μm long. The t.g.a. curve (Figure 3) shows only one region of weight loss, starting at *ca.* 700 °C, which might arise from volatilisation of B_2O_3. The anhydrous material had the composition $2CaO,B_2O_3$. *Ca-α*16 was formed in several preparations at 415 °C, the best yield being from CaO + B_2O_3 + aq. It grew as thin rods *ca.* 100 by *ca.* 1·2 μm. It co-crystallised with phase D (Table 3) of composition CaO,B_2O_3, so that since $CaO/B_2O_3 = 1$ in the parent composition and in phase D it could also have this value in Ca-α16. *Ca-α*17 also co-crystallised with phase D from CaO + $4B_2O_3$ + aq, so that its ratio CaO/B_2O_3 is probably low. *Ca-α*18 is described in ref. 13 since it was not observed in the experiments in Tables 1 and 2.

Other Compounds. Because of co-crystallisation it was not possible to assign compositions or even to give with certainty the class of compound for some species. Thus, *Ca-α*10 formed at 415 °C, the best yield being from 2CaO + BaO_3 + $2SiO_2$ + aq, together with Ca-α15, datolite and α-cristobalite. The crystals were filaments 10—50 μm long and *ca.* 1 μm in diameter. *Ca-α*14 grew as tapering needles, 10—15 μm long and 2—3 μm wide at the broader end, from 4CaO + $2B_2O_3$ + 1 and $2SiO_2$ + aq. Since it co-crystallised with Ca-α13 of composition $2CaO,B_2O_3$ Ca-α14 may be a silicate.

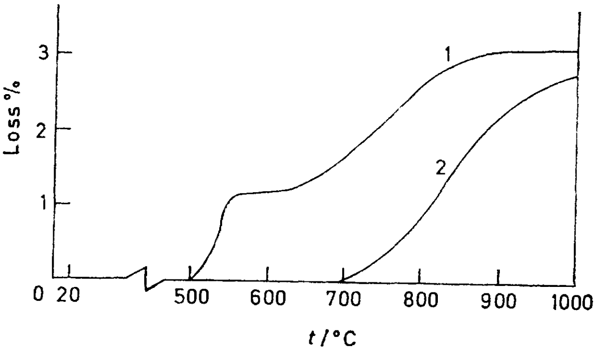

FIGURE 3 Thermogravimetric analyses for: curve 1, Ca-α9 and curve 2, Ca-α13

*Ca-α*2, *Ca-α*7, *Ca-α*11, and *Ca-α*15 all formed only when silica was present and so are probably either borosilicates or silicates. Ca-α2 crystallised at 250 °C with datolite or phase C (borate, Table 3), from compositions 4CaO + B_2O_3 + 1 to $4SiO_2$ + aq. Several of the weaker *d*-spacings of Ca-α2 present in preparation 301 could arise from other phases since they are missing in preparation 300. Ca-α7 formed at 250 °C from CaO + $2B_2O_3$ + $0{\cdot}5SiO_2$ + aq together with datolite and the borate Ca-α6. *Ca-α*12 formed in good yield at 415 °C from 4CaO + B_2O_3 +

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* The analytical and t.g.a. measurements on Ca-α9 were made on a higher yield sample formed in the system $CaO–B_2O_3–GeO_2–H_2O$ described elsewhere.[12]

$2SiO_2$ + aq, together with a medium yield of wollastonite (CaO,SiO_2). Ca-α12 Is thus most likely to be a borosilicate.

DISCUSSION

The diversity of compounds formed under hydrothermal conditions in the system $CaO–B_2O_3–SiO_2–H_2O$ has some parallel in the system $CaO–Al_2O_3–SiO_2–H_2O$.[14] In each case low-temperature crystallisation proceeded slowly, and also it was usual to find co-crystallisation of two or more compounds. In the system containing B_2O_3 borates were particularly numerous (at least six known and nine unidentified) and silicates also occurred frequently (Table 3). Borosilicates danburite and datolite were easily grown and several unidentified phases may also be borosilicates. In the system containing Al_2O_3 [14] several silicates and aluminates were formed but the most numerous phases were tectosilicates including a considerable number of zeolites. In contrast with this it has not so far been possible to demonstrate the existence of borosilicate zeolites, either with CaO or BaO [10] as the bases.

However the mineral danburite is a framework structure and this, considered with certain of the borosilicates reported in the system $BaO–B_2O_3–SiO_3–H_2O$,[10] suggests that framework borosilicates are not uncommon. In danburite as in some of the barium borosilicates Lowenstein's rule [15] does not hold and BO_4 tetrahedra link directly with other BO_4 tetrahedra.

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