Hydrothermal Chemistry of Silicates. Part XIX.[1] A Partial Study of the System $CaO–B_2O_3–GeO_2–H_2O$

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The hydrothermal reactions of the system $CaO–B_2O_3–GeO_2–H_2O$ at 415 °C show considerable resemblances to reactions in the analogous system with GeO_2 replaced by SiO_2. In each case many crystalline phases were formed, prominent among which were borates. Five of the borates were common to each system. The germanium-containing system also yielded germanates and borogermanates, including the germanium analogue of datolite. The compounds formed have been characterised by their *X*-ray powder patterns and where possible in other ways.

THE two elements which most readily replace aluminium and silicon in aluminosilicates are gallium and germanium. Gallosilicates, aluminogermanates, and gallogermanates have been prepared which are isostructural with various aluminosilicates, both in zeolites [2–4] and in layer compounds such as mica [5,6] and smectites.[7] This isomorphous replacement has so far been only very partially explored, and no study of replacement in borosilicates has been found. In connection with our previous examination [1,8] of hydrothermal reactions in the systems $CaO–B_2O_3–SiO_2–H_2O$ and $BaO–B_2O_3–SiO_2–H_2O$ it was therefore of interest to examine a system in which SiO_2 was replaced by GeO_2 to establish similarities and differences and to see whether borogermanates isostructural with borosilicates can be synthesised. For this purpose the system $CaO–B_2O_3–GeO_2–H_2O$ has been studied at 415 °C.

EXPERIMENTAL

Pure germanium oxide was the source of germanium. The other solid reactants, the relative amounts of dry solids and water, and the experimental procedure were as described earlier.[1,8] In the chemical analysis of the germanium compounds formed after hydrothermal reaction at 415 °C the germanium was determined by atomic absorption spectroscopy, according to a method developed by Johnson *et al* [9] (absorption peak measurement at 265·1 μm; carbon tube atomiser; sample size 1 μl). The germanium was extracted with CCl_4 from the aqueous solution in 8N-HCl. This solution, still containing the boron was then partially neutralised and the boron determined as described previously.[10]

RESULTS

The reaction conditions and the products obtained are summarised in Table 1. Of these the compounds identified with compounds previously obtained are given in Table 2. Phase D and the four other calcium borates Ca-α9, Ca-α13, Ca-α16, and Ca-α17 were among those prepared from the system $CaO–B_2O_3–SiO_2–H_2O$,[1] so that the present system and that of ref. 1 both tend to behave as though they were the same sub-system $CaO–B_2O_3–H_2O$. However some new calcium borates appear, notably CB2 and Ca-α18 which is referred to below. The cristobalite and quartz appearing in siliceous compositions of ref. 1 are replaced by a crystalline germania in the germanium-rich compositions of this work (Table 1). Co-crystallisation of more than one product was as much a feature of the parent compositions containing germania as it was of the compositions $CaO–B_2O_3–SiO_2–H_2O$ [1] and $BaO–B_2O_3–SiO_2–H_2O$.[8]

In addition to the phases referred to above a considerable number of other compounds appeared, which are the Ca-β*j* (*j* = 1 to 10) of Table 1. The *d*-spacings derived from the *X*-ray powder patterns are given in a supplementary publication (SUP No. 21099, 7 pp.).‡ Other aspects of some of the Ca-β*j* are referred to below.

Ca-α18 was obtained only in low yield, in preparation 493, from CaO + $0{\cdot}5B_2O_3$ + aq. It is thus a borate. It crystallised as flexible rods ~25 × 0·5 μm. Electron diffraction showed disorder in the stacking of layers in the crystal and it was not possible to determine the interlayer spacing. The other two axes of the unit cell were *a* (along the fibre axis) = $3{\cdot}4_2$ Å and *b* (normal to this axis) = 4·9 Å.

Ca-β1 was obtained free of other species from CaO + 0·5 or $1{\cdot}0B_2O_3$ + $0{\cdot}5GeO_2$ + aq (preparations 495 and 489 of Table 1). It appeared mixed with other phases over most of the field explored as shown in Figure 1. The crystals grew either in rounded form, mainly 2 to 4 μm in diameter but with a few up to *ca.* 20 μm; or as pyramidal, probably spherulitic, crystals of edge *ca.* 15 μm. The *d*-spacings indexed to the tetragonal unit cell with *a* = 7·21 Å and *c* = 4·79 Å. Thermogravimetric analysis (t.g.a.) shows a single region of weight loss of *ca.* 1·05% above 700 °C (Figure 2) which may arise from volatilisation of B_2O_3. Ca-β1 had the oxide composition CaO, $0{\cdot}81B_2O_3$,$1{\cdot}12GeO_2$. It is thus a borogermanate.

Ca-β3. This compound was formed from a number of compositions rich in germania (Table 1), in which also $CaO/B_2O_3 > 1$. Co-crystallised with GeO_2 and a little Ca-β5 it was the main product in preparation 491. It crystallised in a remarkable way as flexible fibres some more

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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).

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

than 100 µm long but only 0·3 to 1 µm thick. The asbestos-like nature is shown in the Plate (a). At high magnification each fibre appears as a bundle of much thinner fibres of *ca.* 0·07 µm diameter [Plate (b)]. Ca-β3 is thought to be either a germanate or a borogermanate.

TABLE 1

Products obtained in the system CaO–B_2O_3–GeO_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
1·0CaO + 0·25B_2O_3 + *n*GeO_2	499	0	Ca-α9(vg)
	500	0·25	CB2(g) + Ca-β1(g) + GeO_2(l) + Ca-β2(l)
	501	0·5	Ca-β1(g) + Ca-β2(m) + $Ca_3(BO_3)_2$(l) + GeO_2(l)
	502	1	Ca-β1(m) + CG1(g) + Ca-β3(l) + ?(l)
	503	2	Ca-β3(m) + CG1(m) + CG2(m) + ?(l)
	504	4	GeO_2(vg) + CG2(m) + Ca-β3(l) + ?(l)
1·0CaO + 0·5B_2O_3 + *n*GeO_2	493	0	Ca-α13(vg) + (Ca-α18(l)) *
	494	0·25	Ca-β1(g) + Ca-α13(m)
	495	0·5	Ca-β1(vg)
	496	1	Ca-β1(g) + Ca-β3(g) + Ca-β4(m)
	497	2	GeO_2(g) + Ca-β3(m) + CG2(m) + Ca-β5(m) + ?(l)
	498	4	GeO_2(vg) + Ca-β3(l) + CG2(l) + ?(l)
1·0CaO + 1·0B_2O_3 + *n*GeO_2	487	0	D(g) + Ca-α16(g)
	488	0·25	D(m) + Ca-α16(m) + Ca-β1(m)
	489	0·5	Ca-β1(vg)
	490	1	Ca-β1(g) + Ca-β4(g) + GeO_2
	491	2	Ca-β3(g) + GeO_2(m) + Ca-β5(l)
	492	4	GeO_2(g) + Ca-β6(m) + CG2(l) + ?(l)
1·0CaO + 2·0B_2O_3 + *n*GeO_2	461	0	D(vg) + Ca-β4(l) + Ca-α17(l)
	462	0·5	Ca-β(7) + Ca-β4(m) + Ca-β1(l) + Ca-α17(l)
	463	1	Ca-β4(m) + Ca-β1(m) + Ca-α17(m) + GeO_2(l)
	464	2	GeO_2(m) + Ca-β7(m) + Ca-β4(l) + Ca-β1(l) + Ca-α17(l)
	465	4	GeO_2(g) + Ca-β6(g) + ?(l)
	466	8	GeO_2(g) + Ca-β6(g)
1·0CaO + 4·0B_2O_3 + *n*GeO_2	475	0	D(vg) + Ca-α16(l)
	476	0·5	D(g) + Ca-β1(l) + (Ca-β8 + Ca-β9)(l) + GeO_2(l)
	477	1	(Ca-β8 + Ca-β9)(g) + GeO_2(m) + Ca-β1(l)
	478	2	Ca-β5(g) + GeO_2(g) + Ca-β10(l)
	479	4	GeO_2(g) + Ca-β5(m) + Ca-α17(m) + Ca-β10(l)
	480	8	GeO_2(g) + Ca-β6(g)
1·0CaO + 8·0B_2O_3 + *n*GeO_2	481	0	D(vg) + Ca-α16(l)
	482	0·5	D(m) + Ca-β4(m) + Ca-β1(m)
	483	1	Ca-β1(vg) + Ca-β4(l) + D(l)
	484	2	Ca-β5(g) + Ca-β3(m) + Ca-β10(l)
	485	4	GeO_2(g) + Ca-β5(g) + Ca-β10(l)
	486	8	GeO_2(vg) + Ca-β6(l)

* Detected only by electron diffraction.

Ca-β4. Ca-β4 crystallised in low yield from a composition free of GeO_2 (preparation 461, Table 1). It is therefore a calcium borate. It also grew from various compositions containing GeO_2, the best yield being that of preparation 490 from CaO + B_2O_3 + GeO_2 + aq. Ca-β4 grew as rods *ca.* 30 µm long and 1 µm thick.

TABLE 2

Compounds identified after reaction at 415 °C in the system CaO–B_2O_3–GeO_2–H_2O

Code	Compound and oxide formula	Ref.
CB2	Borate, 3CaO,B_2O_3	ASTM No. 3-1089
D	Phase D, CaO,B_2O_3	Ref. 11
Ca-α9	Borate, 3CaO, B_2O_3,0·5H_2O	Ref. 1
Ca-α13	Borate, 2CaO,B_2O_3	Ref. 1
Ca-α16	Borate	Ref. 1
Ca-α17	Borate	Ref. 1
GeO_2	Phase 6-T, GeO_2	ASTM No. 9-379
CG1	Germanate, 2CaO,3GeO_2	ASTM No. 12-343
CG2	Germanate, CaO,2GeO_2	ASTM No. 12-357

Ca-β5. Ca-β5 co-crystallised with some Ca-β3 and a little Ca-β10 in preparation 484, from CaO + 8B_2O_3 + 2GeO_2 + aq. The mixture of resultants had the oxide composition CaO, 0·81B_2O_3, 1·18GeO_2, 0·79H_2O. Ca-β5 is thus most probably a borogermanate. The crystals were very small (*ca.* 0·1 µm in diameter) and the *X*-ray diffraction lines were consequently somewhat broadened. The crystallisation field is shown in Figure 1.

Ca-β6. This species crystallised admixed with GeO_2 from compositions rich in GeO_2 (Table 1 and Figure 1), the crystals being less than 0·5 µm in diameter. The field of formation suggests that Ca-β6 is also a borogermanate.

Ca-β7. This compound formed in preparations 462 and 464 (Table 1 and Figure 1), but was always accompanied by other species. The t.g.a. curve of preparation 462 (Figure 2) resembles that of datolite and has two steps. There is 0·5% loss between 350 and 420 °C and an additional 3·6% loss between 550 and 750 °C. The oxide composition of preparation 462, which contained some Ca-β4 (borate) and a little Ca-β1 (borogermanate) and Ca-α17 (borate), was CaO, 0·95B_2O_3, 1·24GeO_2, 0·60H_2O. The *X*-ray powder data agreed very well with those of datolite (Table 3), showing only some intensity differences. Ca-β7 is thus the boro-

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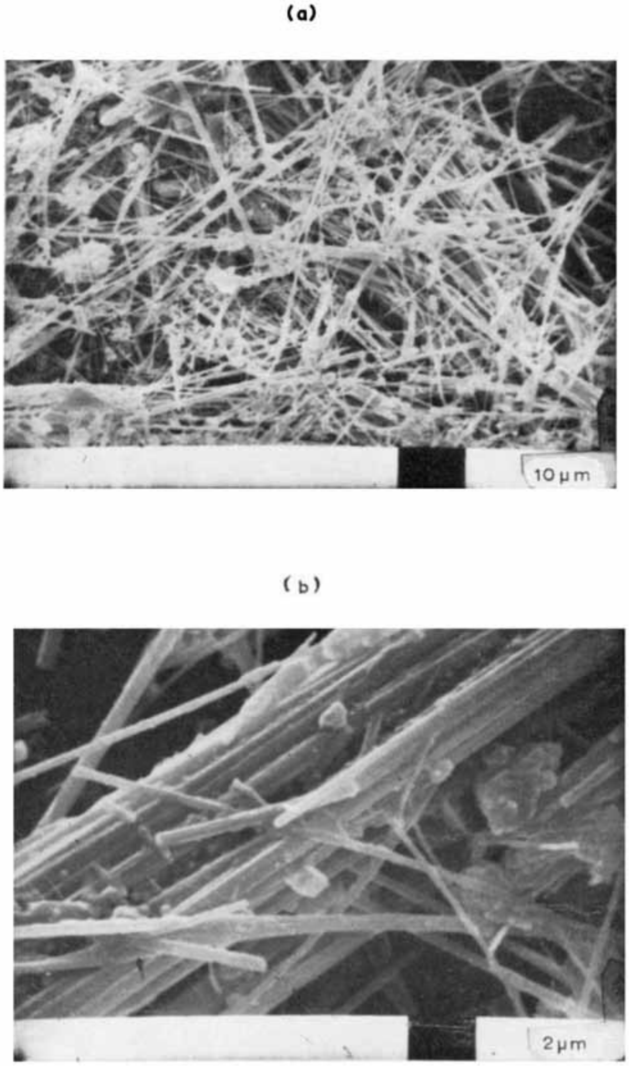

Plate (a) Fibrous crystals of Ca-β3. (b) The bundle-like character of a single fibre of Ca-β3 germanate analogue of datolite. It indexed to a monoclinic unit cell with a = 9·60 Å, b = 7·60 Å, c = 4·82 Å and β = 90° 12′.

Ca-β8 *and* Ca-β9. These compounds were admixed in preparations 476 and 477 (Table 1) and the d-spacings could not be sorted out. Accordingly they are presented together in the Supplementary publication. Their formation from $CaO + B_2O_3 + GeO_2$ mixtures rich in B_2O_3 and the nature of the accompanying phases makes it very probable that one or both of Ca-β8 and Ca-β9 were borates.

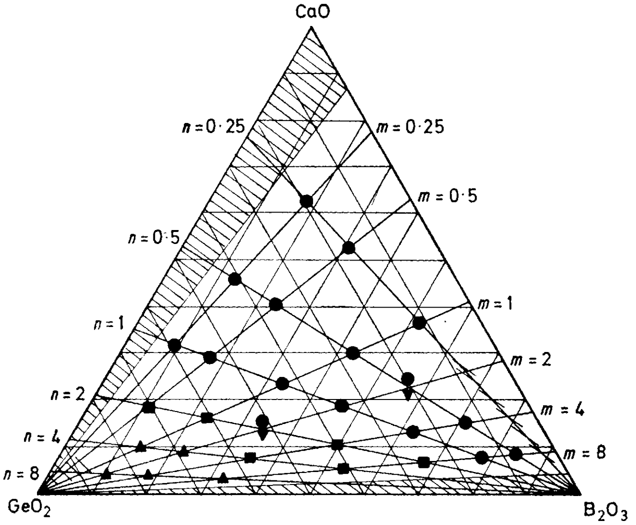

FIGURE 1 Compositions of parent magmas from which the compounds Ca-β1 (●), Ca-β5 (■), Ca-β6 (▲), and Ca-β7 (▼) crystallised. The cross-hatched areas are those in which no experiments were made. The un-numbered scales at the sides of the triangle refer to weight %. Moles of $B_2O_3(m)$ and of $GeO_2(n)$ are also shown per mol of CaO

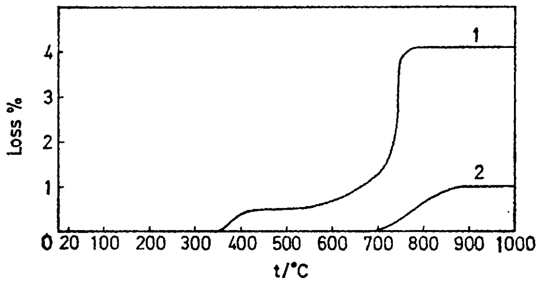

FIGURE 2 Thermogravimetric analyses of curve 2, Ca-β1; and curve 1, Ca-β7

Ca-β10 appeared only in low yield admixed with GeO_2 and other phases in preparations 479, 484, and 485. From the yield and nature of the co-crystallising phases and the compositions of the parent mixtures Ca-β10 could be a borate, although the small yields make its nature uncertain. It formed rods *ca.* 15 μm long and *ca.* 2 μm broad.

DISCUSSION

This work has established that from hydrothermal systems germanium may replace silicon 100% in at least one structure, that of the borosilicate datolite. It also seems that other calcium borogermanates (Ca-β1 and possibly Ca-β5 and Ca-β6) can be prepared without much difficulty. It would be interesting to prepare datolites in presence of both GeO_2 and SiO_2 to establish whether there is complete mutual solid solubility between the silicon and germanium end members. The great variety of compounds formed from $CaO–B_2O_3–GeO_2–H_2O$ has its parallels in syntheses from compositions in which SiO_2 replaces GeO_2 [1] and also BaO replaces CaO.[8] The ready co-crystallisations from all these systems and also from $CaO–Al_2O_3–SiO_2–H_2O$ [12] may reflect relative insolubility of alkaline earth-metal borates, aluminates, silicates, germanates, aluminosilicates, borosilicates, and borogermanates, and also local chemical inhomogeneities in the aqueous magmas from which crystallisations occur. Metastable phases once precipitated may persist for considerable periods in contact with the mother liquor, and are quite stable when removed from this liquor. This has been a most interesting aspect of hydrothermal reactions which so often permit the reproducible formation of metastable phases which may have properties of the greatest interest.

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[4/644 *Received, 29th March*, 1974

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