Hydrothermal Chemistry of Silicates. Part XVI.† Replacement of Aluminium by Boron during Zeolite Growth

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The possibility of isomorphous replacement of Al by B during crystallisation of some zeolites has been investigated in the system $Na_2O-Al_2O_3-B_2O_3-SiO_2-H_2O$. Of the zeolites grown the compact analcite structure is essentially free of boron even when the borate concentration is very high. Zeolite A and the gismondite-type zeolite Na-P1 crystallise with significant amounts of boron, which however can readily be washed out again leaving the compounds with only minimal boron content. The faujasite-type zeolite X retains a significant amount of boron after thorough washing, while in sodalite hydrate this boron content is substantial. Various properties have been examined and it is probable that in zeolite X and sodalite hydrate boron is nearly all present as borate in the tetradecahedral sodalite cages which occur in each. Thus substitution of Al by B in the above zeolite frameworks is considered to be insignificant during synthesis in alkaline aqueous media.

ISOMORPHOUS replacement of Al by B in aluminosilicates, and especially in zeolites, has received little attention. Though natural borosilicates are not uncommon,[1,2] boron usually occurs in three-fold co-ordination with oxygen in these compounds and forms structural units which are not part of the silicate network. In a few borosilicates boron does however occur in four-fold co-ordination as part of this network. Such compounds include: datolite[3] and the related species bakerite, herderite, and homilite,[4] and garrelsite[5,6] which have no known counterpart among aluminosilicates; reedmergnerite[7-9] which is a boron-substituted sodium felspar; and danburite[10] which has a three-dimensional framework consisting of Si_2O_7 and B_2O_7 groups. It is also of interest that the borate $Zn_4O(BO_2)_6$ is said to possess the sodalite structure.[11]

The system $Na_2O-B_2O_3-SiO_2-H_2O$ has been partially explored under hydrothermal and pneumatolytic conditions. Reedmergnerite and searlsite were synthesised between 300 and 500 °C under a water pressure of 2000 bar.[12] A new compound of oxide composition $Na_2O,B_2O_3,2SiO_2$, which could be related to danburite, was obtained pneumatolytically at 500 °C from boric acid and a glass of composition $Na_2O,2SiO_2$.[13] A recent study, published during the course of the present work, describes one or more unidentified zeolites synthesised from boric oxide-containing mixtures.[14] However the boron content was very low, generally less than 0·1% B_2O_3, and no evidence was presented to show whether this boron was part of the aluminosilicate framework.

We now report further on typical zeolitisation reactions in the presence of borate. The system $Na_2O-B_2O_3-Al_2O_3-SiO_2-H_2O$ has been chosen, with crystal growth at 80 and 200 °C. Crystalline products have been examined by several methods in order to determine how boron is incorporated into zeolite structures.

EXPERIMENTAL

Silica was introduced as metakaolinite (mkl) of oxide composition $Al_2O_3,2SiO_2$, as sodium metasilicate hydrate, or as colloidal silica ('Syton 2X'). Alumina was introduced as mkl, or as sodium aluminate of oxide composition $1{\cdot}5Na_2O,Al_2O_3,0{\cdot}36H_2O$. Boric oxide was added as disodium tetraborate decahydrate. When mkl was a reactant

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† Part XV, R. M. Barrer and C. Marcilly, *J. Chem. Soc.* (*A*), 1970, 2735.

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

[2] R. M. Adams, 'Boron, Metallic Boron Compounds, and Boranes,' Interscience, New York, 1964.

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[6] C. L. Christ, *Amer. Mineralogy*, 1959, **44**, 176.

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[8] D. E. Appleman and J. R. Clark, *Science*, 1960, **32**, 1837.

[9] D. E. Appleman and J. R. Clark, *Amer. Mineralogy*, 1965, **50**, 1827.

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[11] P. Smith, S. Garcia Blanco, and L. Rivoir, *Z. Krist.*, 1961, **115**, 460.

[12] H. P. Eugster and N. L. McIver, *Bull. Amer. Geol. Soc.*, 1959, **70**, 12 (2), 1598.

[13] G. W. Morey, *J. Soc. Glass Technology*, 1951, **35**, 269.

[14] P. Onu and V. Ababi, *Anal. Sti.*, *Univ. 'Al I. Cuza' Iasi. Sect. Ic*, 1971, **17**, 95.

it was mixed with the required amounts of sodium hydroxide and disodium tetraborate. Gels were prepared from the other silica sources by slowly adding aluminate solution, eventually mixed with borate, to a silica suspension or solution, with thorough mixing. The mixture was at once brought to the crystallisation temperature, except in the case of zeolite X when the gel was first allowed to mature at room temperature.

Analcite was crystallised at 200 °C in the steel autoclaves and furnace described elsewhere.[15] Other zeolites were grown at 80 °C in polypropylene vessels (30 cm^3). In syntheses of sodalite hydrate the vessels were rotated (100 r.p.m.). After the appropriate heating period the products were centrifuged and the separated crystals suspended in distilled water and centrifuged again. This step was repeated until the pH was less than 10 (the normal washing procedure). Some preparations were given further washings with 100 $cm^3\ g^{-1}$ of water in polypropylene bottles rotated at 20 or 80 °C for 6 h. The crystals were separated by centrifuging and again washed under similar conditions but for 18 h (the extended washing procedure). No loss of crystallinity was observed after such treatment and no further boron was extracted on repeating the treatment.

TABLE 1

Syntheses of sodalite hydrate with borate

Expt. no.	Reactants	Initial oxide composition	Reaction time (days)	Products *
(42)—(46)	$Na_2SiO_3,5H_2O$ Sodium aluminate $Na_2B_4O_7,10H_2O$ NaOH	$5Na_2O,2SiO_2,$ $(1-x)Al_2O_3,xB_2O_3,130H_2O$ (x = 0, 0·1, 0·3, 0·6, and 0·9)	6	(44)—(46): sod. (42) and (43): sod. + ? (traces)
(47)—(51)	$Na_2SiO_3,5H_2O$ Sodium aluminate $Na_2B_4O_7,10H_2O$ NaOH	$5Na_2O,2SiO_2,Al_2O_3,x(Na_2O,B_2O_3),150H_2O$ (x = 0, 0·25, 0·5, 1·0, and 2·0)	5	(47), (48), (50): sod. (49), (51): sod. + ? (traces)
(52)—(55)	mkl † $Na_2B_4O_7,10H_2O$ NaOH	$10Na_2O,2SiO_2,Al_2O_3,x(Na_2O,B_2O_3),180H_2O$ (x = 0, 1, 2, and 4)	4	(54, (55): sod. (52), (53): sod. + ? (traces)
(72)—(79)	$Na_2SiO_3,5H_2O$ Sodium aluminate $Na_2B_4O_7,10H_2O$ NaOH	$8Na_2O,2SiO_2,xAl_2O_3,(1-x)B_2O_3,y$ $(Na_2O,2B_2O_3),180H_2O$ [(72)—(77): $y = 0, x =$ 0, 0·1, 0·6, 0·8, and 0·95; (78) and (79): y = 1 or 4; x = 0·6]	6	sod.

* Sod. = Sodalite hydrate. † mkl = Metakaolinite.

Products were dried at 80 °C and examined by: *X*-ray diffraction with filtered Cu-K_α radiation, using a Guinier camera; optical microscopy with a Leitz polarising, and a Vicker's projection, microscope; by electron microscopy; and by chemical and thermogravimetric analysis (t.g.a.). Boron was determined by extracting it as trimethyl borate with methanol in the presence of anhydrous $CaCl_2$, and by titrating it as boric acid in the presence of mannitol. As Pyrex vessels were used in analysis, a blank test was made which gave 1·0 ± 0·3 mg of B_2O_3, *i.e.* 0·2 ± 0·06% of B_2O_3 for a 500 mg sample of zeolite.

RESULTS

Sodalite Hydrate.—Sodalite hydrate was obtained pure or nearly pure under the conditions summarised in Table 1. The crystals were first washed at room temperature by the extended procedure (see Experimental section). On one sample this was followed by 24 h washing at 80 °C, but washings from this final stage contained no detectable boron so that any remaining boron was firmly trapped. The boron content was then determined for all the washed sodalite hydrates of Table 1. Even at low-borate contents of the starting mixture considerable boron was present in the crystals and reached 6·6% B_2O_3 based on the water-free weight of zeolite. The B_2O_3 content is shown in Figure 1 as a function of the concentration of B_2O_3 in the parent mixture. The curves have the form of inclusion isotherms found when salts such as $NaClO_4$ or $NaClO_3$ are encapsulated in sodalite during its growth.[16] The maximum uptake of boron was *ca.* 93% of that expected for a limit of one boron atom per sodalite cage. Indeed the shape of the isotherms of Figure 1 suggests that one boron atom per sodalite cage is the physical limit of uptake. Various salts in sodalite also give limits of one salt ' molecule ' per cage (*e.g.* NaCl, Na_2SO_4, $NaClO_4$, and $NaClO_3$) and this suggests that boron is also probably present as a sodium borate [*e.g.* $NaBO_2$ or $NaB(OH)_4$]. Such borate, like the other salts, competes for the cavities with water or NaOH.

Further evidence as to the location of boron was sought by measuring the unit-cell parameter, *a*, of cubic cells of sodalites of the two series (42)—(46) and (47)—(51) of Table 1.

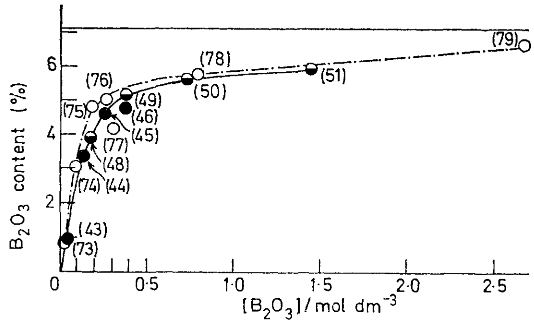

FIGURE 1 Isotherms for uptake of boron during crystallisation of sodalite hydrate (numbers refer to experiments listed in Table 1): (——), % B_2O_3 corresponding to one B atom per sodalite cage

In Figure 2 this parameter is plotted as a function of B_2O_3 content of the zeolite. The parameter increased in a somewhat irregular way with B_2O_3 content and for a given content of B_2O_3 was not the same for the two series of experiments. This behaviour is due, in part, to inaccuracy in measuring *a* because of diffuse diffraction lines associated

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[15] R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 1961, 983.

[16] R. M. Barrer and J. F. Cole, *J. Chem. Soc.* (*A*), 1970, 1516.

with small crystal size, and it may also be due to variations in the contents of the sodalite cages other than those of borate (*e.g.* H_2O, NaOH, or Na_2CO_3). The increase in cell parameter with B_2O_3 content is evidence that at least a large part of the boron is present as guest species in the sodalite cages rather than as part of the aluminosilicate framework, because salt inclusion by sodalite hydrate usually increases *a* [17] whereas substitution of the small boron atom for that of aluminium would be expected to cause framework shrinkage. This is illustrated in Table 2 in the cases of albite [18] and boron-substituted felspar (reedmergnerite [9]), and of phlogopite [19] and boron-substituted phlogopite mica.[20]

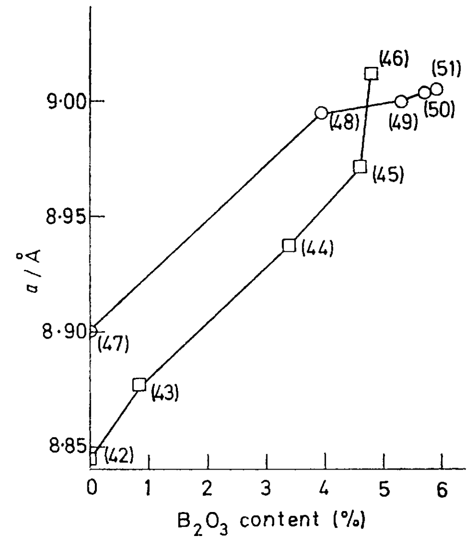

FIGURE 2 Unit-cell parameters, *a*, of some sodalite hydrates as functions of borate content (numbers as in Table 1)

TABLE 2

Cell parameters (*a*, *b*, and *c* in Å) of normal and boron-substituted triclinic felspars and of phlogopite micas

Cell parameter	Low albite ($NaAlSi_3O_8$) [a]	Reedmergnerite ($NaBSi_3O_9$) [b]
a	8·138	7·833 ± 0·001
b	12·789	12·360 ± 0·002
c	7·156	6·803 ± 0·001
α	94°20′	93°18·5′ ± 0·5′
β	116°34′	116°21·1′ ± 0·5′
γ	87°39′	92°0·33′ ± 0·8′
	Phlogopite [c]	Boron phlogopite [d]
a	5·314	5·320 ± 0·01
b	9·204 ± 0·02	9·165 ± 0·02
c	10·314 ± 0·005	10·29 ± 0·01
β	99°54′ ± 5′	100°10′ ± 10′

[a] Ref. 18. [b] Ref. 9. [c] Ref. 19. [d] Ref. 20.

The water content is plotted in Figure 3 as a function of B_2O_3 content. The crystals were first dried at 30 °C and then, after 30 days over a saturated solution of $Ca(NO_3)_2$,$4H_2O$, were subjected to t.g.a. The water content decreased on the whole with B_2O_3 content, but only from *ca.* 13·7 to 9·5%. In a previous study [16] it was shown that the normal saturation content of a sodalite cavity is $4H_2O$, 2NaOH, or one salt ' molecule.' If the boron is present as anhydrous borate, *ca.* 93% of the cages should contain a borate ion such as BO_2^- when the B_2O_3 content of the crystals reaches 6·6% (Figures 1 and 3). The water content of the crystals would however then be very low, contrary to observation (Figure 3). To account for 9·5% water one possibility is that only a third of the cages contain borate ($NaBO_2$) and that the rest of the boron substitutes for aluminium in the framework. In view of results already described and of later observations this does not seem likely. If 93% of the cages each contained $H_2O + NaB(OH)_4$, the water content of the crystals would be *ca.* 10·2%. If this content were $NaOH + NaB(OH)_4$, there would be *ca.* 8·3% weight loss, while if it were $NaB(OH)_4$ alone the loss would be *ca.* 7·3%.

In a further series of experiments the yield of sodalite was determined as a function of the mol fraction $B_2O_3/(B_2O_3 + Al_2O_3)$ in the parent gel. Large, weighed, amounts of parent gels were introduced into the reaction vessels and, after reaction, the crystals were separated and dried at 30 °C. The highly alkaline mother liquors retained any excess of silica in solution. The yield is shown in Figure 4. The theoretical yield, based on the ideal sodalite hydrate composition $3NaAlSiO_4,4H_2O$, is 8·5%, in close agreement with experiment (72). The yields declined in direct proportion to the mol fraction of B_2O_3 as defined above, or increased in direct proportion to the mol fraction of Al_2O_3. This implies that the framework during growth consumes alumina but not B_2O_3, and so indicates that little if any boron is present in the framework. Thus the B_2O_3 content of Figure 1 must represent borate as guest species in the sodalite cages. In Figure 4 the point of zero yield, where no alumina is present in the parent gel, is also shown. For this and other alumina-free compositions (with $Na_2O : SiO_2 \geqslant 0·4 : 1$, $Na_2O : B_2O_3 \geqslant 0·5 : 1$, and a water content $\geqslant$70%)

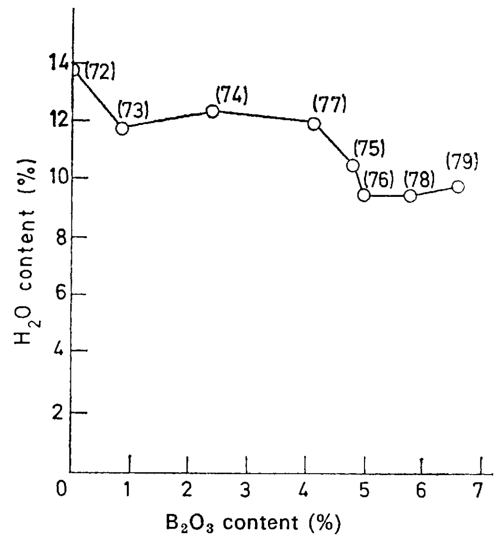

FIGURE 3 Water content of sodalite hydrates in relation to their boron content (numbers as in Table 1)

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[17] See, for example, R. M. Barrer, J. F. Cole, and H. Sticher, *J. Chem. Soc.* (*A*), 1968, 2475, Table 9.

[18] R. B. Ferguson, R. J. Traill, and W. H. Taylor, *Acta Cryst.*, 1958, **11**, 331.

[19] H. S. Yoder and H. P. Eugster, *Geochim. Cosmochim. Acta*, 1954, **6** (4), 157.

[20] H. P. Eugster and T. L. Wright, U.S. Geol. Survey, Prof. Paper 400, 1960, No. 202, **B**.441.

limpid solutions were obtained over periods extending to 3 months.

For sodalites of the series (72)—(79) of Table 1 the ratios Si : Al and Si : (Al + B) were next determined (Table 3). Sample (72) was prepared in absence of borate and samples (73)—(79) in the presence of increasing amounts of borate. The ratios Si : Al in the well-washed crystals were all close to unity, being slightly greater for high Si : Al ratios in the parent mixture and slightly, but not significantly, lower when these ratios in the parent mixture were 1·0 and 1·11 : 1. In general, therefore, in sodalites the value of Si : Al remains close to one whatever the values of Si : Al and of Si : (Al + B) in the parent mixtures. Accordingly if O, Si, and Al are the only framework constituents and Lowenstein's rule is obeyed, Si and Al atoms must alternate on (Si,Al) sites. The ratios Si : (Al + B) on the other hand are all well below unity so that if Si, Al, and B are framework constituents Lowenstein's principle cannot be followed. The consistency of the results in column 3 of Table 3 and the low values of Si : (Al + B) in column 5 further support the view that boron is present primarily as borate encapsulated in sodalite cages.

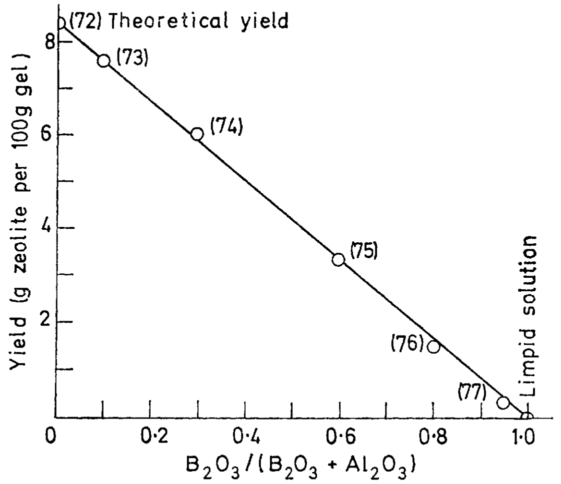

FIGURE 4 Yield of sodalite hydrate in relation to the mol fraction $B_2O_3/(B_2O_3 + Al_2O_3)$ (numbers as in Table 1)

TABLE 3

Ratios Si : Al and Si : (Al + B) in well washed sodalite hydrates

	Si:Al		Si:(Al + B)	
Sample	In starting material	In sodalite	In starting material	In zeolite
(72)	1·0	0·970, 0·988	1·0 (no boron present)	
(73)	1·11	0·940	1·0	0·908
(74)	1·43	0·990	1·0	0·873
(75)	2·5	1·026	1·0	0·842
(76)	5·0	1·048	1·0	0·852
(77)	20·0	1·110, 1·097	1·0	0·924
(78)	5·0	1·054	0·33	0·830
(79)	5·0	1·098, 1·097	0·11	0·831

Zeolite A.—Zeolite A was synthesised at 80 °C, without stirring, from gel compositions $4Na_2O,Al_2O_3,2SiO_2,250H_2O + n(0{\cdot}75Na_2O + B_2O_3)$ where $n = 0$, 0·5, 1, 2, 4, and 8 [series (95)—(100)]. These compositions were prepared from sodium hydroxide, sodium aluminate, sodium silicate pentahydrate, and disodium tetraborate decahydrate. *X*-Ray examination showed zeolite A as the only detectable reaction product for all the above values of *n*. These correspond to concentrations of B_2O_3 between 0 and 1·76 mol dm^{-3} in the parent mixtures.

The crystals, washed according to the normal procedure (see Experimental section), had boron contents (Table 4) which increased irregularly with the boron content of the starting mixture, reaching 3·3% B_2O_3 for concentrations of B_2O_3 of 1·76 mol dm^{-3} in the parent mixture. However, rewashing at room temperature for 24 h in distilled water reduced the B_2O_3 content to very low levels (maximum value 0·65%) which did not depend significantly on the concentration of B_2O_3 in the parent mixtures. Further washing of a selected sample did not further reduce the B_2O_3 content. These results indicate that much of the borate initially present is in hexacosahedral cavities from which it is easily removable. The residual boron may be either in sodalite cages (1·98% B_2O_3 represents one $NaBO_2$ per cage) or it may be substituting for aluminium in the framework. Before rewashing the crystals their water contents were somewhat irregular (Table 4), but afterwards the water content was constant at 22·5 ± 0·5%. Unit-cell parameters of samples which had undergone the normal washing procedure showed no measurable variation.

TABLE 4

Boron and water content of zeolites A of series (95)—(100) after 2 weeks over saturated $Ca(NO_3)_2,4H_2O$ solution

		B_2O_3 (%) in X		
Sample	$[B_2O_3]$ in parent gel (mol dm^{-3})	Normal washing	24 h rewashed	Water content of normally washed crystals (%)
(95)	0	0	0	22·0
(96)	0·11	0·68	0·65	19·4
(97)	0·22	0·65	0·58	22·4
(98)	0·45	0·35	0·25	18·6
(99)	0·88	2·0	0·25	14·8
(100)	1·76	3·3	0·35	16·7

Zeolite X.—Zeolite X was synthesised from gel compositions $6Na_2O,Al_2O_3,6SiO_2,250H_2O + n(0{\cdot}5Na_2O + B_2O_3)$ where $n = 0$, 0·5, 1, 2, 4, and 6 [series (109) and (114)]. The reactants were those indicated for zeolite A except that Syton 2X was the source of silica. After 7 days the products were shown by *X*-ray diffraction to be the faujasite-type zeolite X, mixed with very small amounts of zeolite Na–P1 (gismondite type). The maximum content of Na–P1, as judged from relative intensities of *X*-ray diffraction lines, was never more than *ca*. 10%. The B_2O_3 content was determined only on samples which had been rewashed overnight. The relation between this content and the concentration of B_2O_3 in the parent gel is shown in Figure 5. The smoothed isotherm recalls those obtained for salts incorporated during growth in sodalite [16] (*cf*. also Figure 1), but the largest uptake represents only *ca*. 40% of the amount corresponding to one boron atom per sodalite cage. It can be assumed that rewashing has removed borate from the hexacosahedral cages of type (II) which are present in faujasites, and that only sodalite cages will encapsulate borate permanently.

Zeolite Na–P1.—Pure Na–P1 (gismondite type [21]) was not prepared, but some instances when the zeolite was present in reasonable amounts are given in Table 5. The starting compositions were $6Na_2O,Al_2O_3,6SiO_2,250H_2O + n(0{\cdot}5Na_2O + B_2O_3)$ with $n = 0$, 0·5, 1, 2, 4, 6, 8, 10, and 12, the reactants being those already given for zeolite X. The mixtures were crystallised at 80 °C for 9 days with stirring. Although some preparations, given normal washing except that the temperature was 80 °C, initially contained borate, this was extensively removed by rewashing for 24 h at 25 °C. Accordingly only limited, if any, isomorphous replacement of Al by B can have occurred.

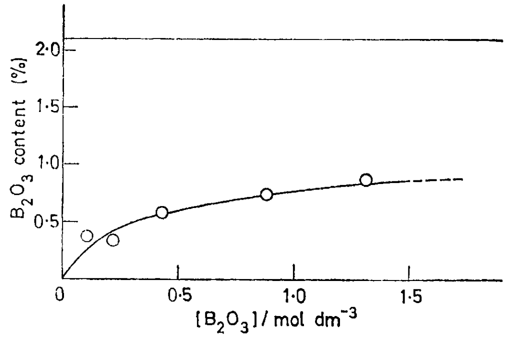

FIGURE 5 Isotherm for uptake of boron during crystallisation of zeolite X: (——), % B_2O_3 corresponding to one B atom per sodalite cage

Analcite.—The framework of analcite, unlike those of sodalite and zeolites A, X, and Na–P1, is so compact that encapsulation of borate during crystal growth is hardly possible. Accordingly the synthesis of this zeolite in the presence of borate should provide a critical test of isomorphous replacement of Al by B during zeolitisation. Analcite was synthesised at 200 °C from gels of compositions $1{\cdot}5Na_2O,Al_2O_3,4SiO_2,240H_2O + n(0{\cdot}5Na_2O + B_2O_3)$ where $n = 0$, 0·2, 0·4, and 2·0. The reactants were the same as those used in preparing zeolite X, and the reaction time allowed was 6 days. Large cubic crystals of *ca.* 50 μm diameter were formed and identified by *X*-ray diffraction as analcites. There was no detectable variation among the unit-cell parameters. After the normal washing procedures the preparations were analysed for boron, but the amounts obtained were not significantly above the blank of the method. The maximum B_2O_3 present was therefore not more than *ca.* 0·06%, corresponding to maximum possible isomorphous replacement of Al by B of less than 0·4%.

TABLE 5

Syntheses in which Na–P1 was a resultant, and B_2O_3 content

			B_2O_3 (in water-free crystals) (%)	
Sample	B_2O_3 in parent gel (mol dm^{-3})	Main phases *	Normal washing, but at 80 °C	After rewashing
(156)	0	X(Na–P1, chab., sod.)		
(157)	0·11	X(Na–P1, chab., sod.)		
(158)	0·22	X(Na–P1)		
(159)	0·45	X(Na–P1)		
(160)	0·88	X(Na–P1)		
(161)	1·32	Na–P1	0·35	<0·10
(162)	1·76	Na–P1 (chab.)	3·80	0·40
(163)	2·20	Na–P1	4·05	<0·10
(164)	2·64	Na–P1 (gel)	2·10	<0·10

* Phases in parentheses are present in minor yield.

DISCUSSION

Where the framework was compact and unable to encapsulate borate (analcite), or where it was open but included borate could be washed out (Na–P1 and Na–A), the results are consistent in indicating only minimal residual boron, so that under the alkaline conditions required for zeolite formation not more than trace amounts of boron can substitute for aluminium. It remains possible that more extensive substitution requires less-alkaline conditions and higher temperatures than are needed for zeolite growth.

In sodalite and zeolite X considerable boron is retained after thorough washing. In view of the observations on analcite, Na–P1, and Na–A, and other observed properties of the sodalites, it is reasonable to locate this boron as borate in the sodalite cages. The ion BO_2^- has a van der Waals dimension critical for penetration of a porous crystal of *ca.* 2·8 Å and that of $B(OH)_4^-$ is *ca.* 4·7 Å if OH and O are assumed to have the same van der Waals radii. Under our mild conditions these ions could not readily enter or leave sodalite cages already formed, which have six-ring windows with free diameters of *ca.* 2·1—2·3 Å. Accordingly they can be incorporated only during crystal growth before the cages are complete. Sodalite cages are also present in zeolite A, and the much smaller borate content of these cages in zeolite A than in X and sodalite hydrate may reflect a different mode of growth. However Kuhl [22] has reported that in presence of phosphate as much as one P atom per sodalite cage may be incorporated in zeolite A during growth.

It may be concluded that zeolite formation from compositions containing borate does not yield crystals in which boron replaces aluminium in the aluminosilicate frameworks in appreciable amounts. On the other hand in suitably open zeolites some borate is incorporated, part or most of which can be washed out. Nearly all the remaining boron can be assumed to be locked into cavities during growth.

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[21] C. H. Baerlocher and W. M. Meier, *Z. Krist.*, 1972, **135**, 339.

[22] G. H. Kuhl in ' Molecular Sieve Zeolites, I,' Advances in Chemistry Series, No. **101**, Amer. Chem. Soc., 1971, p. 75.