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A Crystal-Chemical Classification of Borate Structures with Emphasis on Hydrated Borates

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Abstract. The rules governing formation of hydrated borate polyanions that were proposed by C.L. Christ in 1960 are critically reviewed and new rules added on the basis of recent crystal structure determinations. Principles and classifications previously published by others are also critically reviewed briefly. The fundamental building blocks from which borate polyanions can be constructed are defined on the basis of the number *n* of boron atoms, and the fully hydrated polyanions are illustrated. Known structures are grouped accordingly, and a shorthand notation using *n* and symbols $\Delta =$ triangle, T = tetrahedron is introduced so that the polyanions can be easily characterized. For example, $3{:}\Delta + 2\mathrm{T}$ describes $[B_3O_3(OH)_5]^{2-}$. Correct structural formulas are assigned borates with known structures whereas borates of unknown structure are grouped separately.

Introduction

Some time ago, one of us (Christ, 1960) proposed four rules that seemed to govern the formation of polyanions in hydrated borate minerals. Since then a large number of structure determinations for such minerals have been reported. In this review we shall use the structural information to determine how useful these rules have been, in what ways they require modification or extension, and how the known polyanions can be grouped and classified in terms of specific fundamental building blocks. We shall also consider to a limited extent some anhydrous borates, silicoborates, and other borates. Structural principles and classifications proposed previously by others will be reviewed briefly in the light of current information. Throughout this review we will consider only structures for which there have been determinations by single-crystal, X-ray and (or) neutron diffraction methods. Experience has amply demonstrated that other experimental methods cannot be relied upon to determine *a priori* the exact nature of these complex polyanions.

The 1960 Rules, Modified and Extended

The rules are repeated below as originally given (Christ, 1960), with some further explanations and with revisions and additions that have been developed through study of various structure determinations reported after 1960.

1. Boron Will Link either 3 Oxygens to Form a Triangle, or 4 Oxygens to Form a Tetrahedron. No violations of this rule are known.

2. Polynuclear Anions Are Formed by Corner Sharing only of Boron-Oxygen Triangles and Tetrahedra in Such a Manner that a Compact Insular Group of Low to Medium Negative Charge Results. In most respects this rule is valid. The phrase "low to medium negative charge" was used in the 1960 paper in reaction to some of the more speculative excesses in the early literature on borate crystal chemistry. The phrase should now be dropped. The facts are that most polyanions have a charge of -3 or less, some have a charge of -4, and one has been reported that has a charge of -6 (in borcarite, Table 5).

3. In the Polyions of Hydrated Borates, those Oxygens not Shared by 2 Borons Always Attach a Proton and Exist as Hydroxyl Groups. This statement requires revision for two reasons. First, we now know (Clark, 1964) that an oxygen may be shared by 2 or 3 boron atoms.[1] Second, in the earlier paper, Christ (1960) considered only "fully hydrated" borates, that is, those in which there are sufficient protons present to bond with all of the oxygens not shared by 2 or more borons. Unfortunately, that point was not made explicit at that time but has generally been understood by succeeding crystal structure investigators. Since 1960 a number of new crystal structure determinations have been made of borates that are not fully hydrated. Examination of these structures shows that the proton distribution follows a pattern that can be described in terms of a conjugate acid-base system analogous to that observed in aqueous solution. In the crystals the bases oxide ion, O^{2-}, hydroxyl ion, OH^{1-}, and polyborate ion must be considered. The polyborate anion may be represented in a generalized way by $[\phi(BO_n)_y]^{z-}$, where ϕ stands for that part of the polyanion not subject to protonation, and $n=1$ or 2, where 1 or 2 oxygens are subject to protonation, corresponding to triangular or tetrahedral boron, respectively. The order of protonation of (BO_n) groups in the same $[\phi(BO_n)_y]^{z-}$ polyion can be predicted. Boron has a formal charge of $+3$; in tetrahedral coordination each bonded oxygen will receive a bond strength $+3/4$, and since the oxygen has a formal charge of -2, the bonded oxygen subject to protonation will have a formal charge of -1.25. For triangularly coordinated boron the formal charge on the bonded oxygen subject to protonation is -1. Hence, an oxygen of a tetrahedral group is a stronger base than an oxygen of a triangular group. The proton distribution actually found in all the hydrated borates, of both fully hydrated and partially hydrated forms, can be accounted for by the relative

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[1] The structure of cubic boracite, α-$Mg_3ClB_7O_{13}$, has one oxygen atom at a corner common to four borate tetrahedra (Sueno et al., 1973)

strength scale[2]: $O^{2-} > [\phi(BO_2)_y]^{z-} > [\phi(BO)_y]^{z-} > OH$. The base strength scale is easy to use to make proton assignments: if a crystal structure is known except for proton distribution, then one assigns sufficient protons to those oxygens not in a boron-oxygen configuration to convert what would have been oxide ions to hydroxyl ions, any additional protons are assigned stepwise to protonatable tetrahedral oxygens in borate ions, next protons are assigned to protonatable triangular oxygens in borate ions, and finally protons are assigned to unattached hydroxyl ions to form water molecules. Thus, rule 3 of the 1960 paper is seen to be a special case of the present more general analysis.

4. The Insular Groups May Polymerize in Various Ways by Splitting out Water. This rule is valid, but should be discussed further and extended in several ways. As in the case of rule 3, this rule was written with the fully hydrated borates in mind, and thinking in terms of polymerization by the splitting-out of water among fully protonated polyanions was, and is, a convenient predictive device. Moreover, polymerization may in fact take place through this process in some mineral systems (Christ et al., 1967). When polymerization takes place with loss of water, it involves the breaking of one boron-hydroxyl bond and one hydrogen-oxygen bond (between successive polyanions) and the formation of a water molecule. We now know of one case (transformation of borax to kernite) where in addition a boron-oxygen bond within the polyanion framework is broken, so that the resulting chain polymer is not composed merely of linked units of the original polyanion. This is illustrated in Figure 1. Rule 4 should be extended to include this new feature.

Another principle that has become evident in recent years is that side chains may attach themselves to more complex borate polyanions. This is a principle related to, but different from, rule 4, and so is stated separately:

5. Complex Borate Polyanions May Be Modified by Attachment of an Individual Side Group, such as (but not limited to) an Extra Borate Tetrahedron, an Extra Borate Triangle, 2 Linked Triangles, an Arsenate Tetrahedron, and so on. Another development of recent borate crystal chemistry is the discovery of isolated $B(OH)_3$ molecules in the presence of larger polyanions in several mineral phases. Allowing for the possibility of polymers of $B(OH)_3$ itself we write:

6. Isolated $B(OH)_3$ Groups (or Polymers of these) May Exist in the Presence of Other Anions.

The 1977 Rules Summarized

1. Boron will link either three oxygens to form a triangle or four oxygens to form a tetrahedron.

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[2] Apparent exceptions to this scale are furnished by the isomorphous pair $K_3[B_3O_4(OH)_4] \cdot 2H_2O$ (Zviedre et al., 1974) and $Rb_3[B_3O_4(OH)_4] \cdot 2H_2O$ (Zviedre and Ievins, 1974b). However, this assignment of protons is not the only possible one, as we will discuss elsewhere

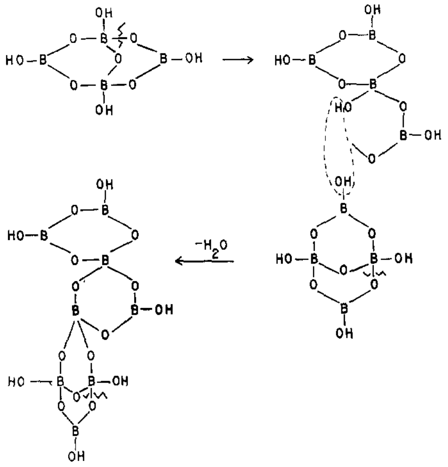

Fig. 1. Schematic drawing showing how isolated 4-1:2Δ+2T polymerize to form chains; note the breaking of B-O bonds (Christ, 1972)

2. Polynuclear anions are formed by corner sharing only of boron-oxygen triangles and tetrahedra in such a manner that a compact insular group results.

3. In the hydrated borates, protonatable oxygen atoms will be protonated in the following sequence: available protons are first assigned to free O^{2-} ions to convert these to free OH^- ions, additional protons are assigned to tetrahedral oxygens in the borate ion, protons are next assigned to triangular oxygens in the borate ion, and finally any remaining protons are assigned to free OH^- ions to form H_2O molecules.

4. The hydrated insular groups may polymerize in various ways by splitting out water; this process may be accompanied by the breaking of boron-oxygen bonds within the polyanion framework.

5. Complex borate polyanions may be modified by attachment of an individual side group, such as (but not limited to) an extra borate tetrahedron, an extra borate triangle, 2 linked triangles, an arsenate tetrahedron, and so on.

6. Isolated $B(OH)_3$ groups, or polymers of these, may exist in the presence of other anions.

Proposed Principles and Classifications for Borates

To summarize and review all the papers that have been written proposing principles governing formation of borate polyions or developing schemes of classification would require more space than is available. However, a few of these papers should be mentioned. Those not mentioned we consider unworthy of critical comment, being either obsolete due to age or so confused as to be of little value.

First, the scheme we use here of organizing the structures on the basis of the number of boron atoms in a fundamental building block is also used in a comprehensive compilation by Heller (1970) for $n=1$ to 5. He does not consider $n=6$ to be a unique type. He examines borates first according to

Table 1. Examples of Structures Containing FBB 1:Δ, 2:Δ

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
1:Δ, isolated	sassolite (orthoboric acid), $B(OH)_3$	Zachariasen (1954)	kotoite, $Mg_3(BO_3)_2$	Sadanaga (1948)
			jimboite, $Mn_3(BO_3)_2$	Sadanaga et al. (1965)
	pinakiolite, $Mg_2Mn^{3+}O_2(BO_3)$	Takéuchi et al. (1950); Moore, Araki (1974b)	warwickite, $Mg(Mg_{0.5}Ti_{0.5})O(BO_3)$	Takéuchi et al. (1950); Moore, Araki (1974b)
1:$\infty\Delta$, chains	synthetic, $Ca(BO_2)_2(I)$	Zachariasen, Ziegler (1932); Marezio et al. (1963b)		
2:Δ isolated	szaibelyite (ascharite), $Mg_2(OH)[B_2O_4(OH)]$	Peng et al. (1963); Takéuchi, Kudoh (1975)	sussexite, $Mn_2(OH)[B_2O_4(OH)]$	Takéuchi, Kudoh (1975)
	suanite, monoclinic MgB_2O_5	Takéuchi (1952)	synthetic, CoB_2O_5	Berger (1949)
	synthetics, monoclinic MgB_2O_5	Berger (1949)		
	triclinic MgB_2O_5	Block et al. (1959)		

1:Δ isolated groups are found in many other structures. There are no known examples of structures containing either isolated, partially hydrated triangular groups or the fully hydrated 2:Δ pair i.e. the dimer of $B(OH)_3$ (see text)

the kind of cation, then develops and illustrates schematically the various possible polyanions, and finally lists a few "known" structures according to the *n* value and the linkage (isolated, chain, sheet, or three-dimensional network). He also devotes considerable discussion to organoborates. As short as the final list of "known" structures is, it includes many speculative formulas (marked with queries) and most of these have since been shown to be wrong.[3] The principles proposed by Edwards and Ross (1960) are reproduced by Heller without critical comment. However, read with caution, Heller's compilation is useful.

The principles proposed by Edwards and Ross (1960) were repeated in a slightly revised form by Ross and Edwards (1967). Although these postulates are often quoted, they are outdated in the light of recent structural studies. The postulate 1b (Ross and Edwards, 1967), "The ratio of tetrahedral boron to total boron is equivalent to the ratio of cation charge to total boron",

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[3] Howlite is incorrectly classified under $n=5$. A pentaborate polyion of 5:Δ+4T type illustrated as $[B_5O_9(OH)]_n^{4n-}$ by Heller (1970, Fig. 9) is not present in howlite. The correct structural formula for howlite (Finney et al., 1970) is $Ca_2[B_3O_4(OH)_2 \cdot OSiB_2O_4(OH)_3]$

Table 2. Examples of Structures Containing FBB 1:T, 2:T

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
1:T, isolated	synthetics: α-$CsB(OH)_4 \cdot 2H_2O$	Zviedre, Ievins (1974a)	synthetics: $LiB(OH)_4$	Höhne (1965)
	$NaB(OH)_4 \cdot 2H_2O$	Block, Perloff (1963)	monoclinic, α-$Ca[B(OH)_4]_2$	Ozols et al. (1965); Zeigan, Kutschabsky (1966)
	$Ca[B(OH)_4]_2 \cdot 2H_2O$	Sedlacek, Dornberger-Schiff (1971); Wang (1971a, b)	orthorhombic, α'-$Ca[B(OH)_4]_2$ monoclinic, $Sr[B(OH)_4]_2$	Zeigan (1967) Kravchenko (1966)
	$Ba[B(OH)_4]_2 \cdot H_2O$	Ozols et al. (1969); Kutschabsky (1968, 1969)	triclinic, $Sr[B(OH)_4]_2$	Ozols et al. (1962)
	$Ba[B(OH)_4]_2$	Kravchenko (1964)	frolovite, triclinic, β-$Ca[B(OH)_4]_2$	Egorov-Tismenko et al. (1972)
	teepleite, $Na_2Cl[B(OH)_4]$	Fornaseri (1949, 1951)	bandylite, $CuCl[B(OH)_4]$	Fornaseri (1950, 1951); Collin (1951)
	seamanite, $Mn_3(OH)_2(PO_4)[B(OH)_4]$	Moore, Ghose (1971)	cahnite, $Ca_2(AsO_4)[B(OH)_4]$	Prewitt, Buerger (1961)
	sulfoborite, $Mg_3(OH)_2(SO_4)[B(OH)_4]_2$	Iorysh et al. (1976)	sinhalite, $MgAlBO_4$	Fang, Newnham (1965)
1:∞T, chains	vimsite, $Ca[BO(OH)_2]_2$	Shashkin et al. (1969)		
1:∞_3T, network	metaborite (γ-metaboric acid HBO_2-I), cubic HBO_2	Zachariasen (1963b)		
2:T, isolated	pentahydroborite, $Ca[B_2O(OH)_6] \cdot 2H_2O$	Egorov-Tismenko et al. (1973a)	pinnoite, $Mg[B_2O(OH)_6]$	Paton, MacDonald (1957); Krogh-Moe (1967)

was a valid but obscure way of saying that each $B(OH)_4^-$ tetrahedron brings one negative charge as it enters into a polyanion. Unfortunately, the postulate fails for all hexaborate polyanions and for the partially hydrated polyanions, such as the $[B_4O_7(OH)_2]^{4-}$ ion found in roweite (Moore and Araki, 1974a). The structural classification by Ross and Edwards (1967) confuses the concepts of the unit and its linkages and makes no distinction between the different kinds of units within one designation; therefore, it cannot readily be extended to include structures determined since its publication.

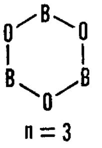
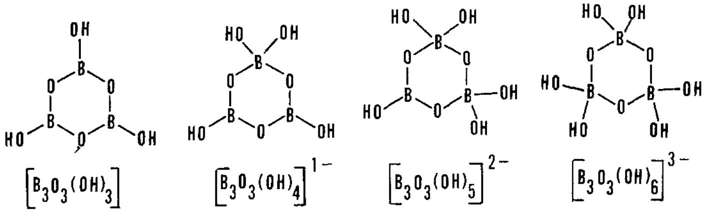


Fig. 2. Triborate FBB



$[B_3O_3(OH)_3]$ (a) 3 : 3Δ

$[B_3O_3(OH)_4]^{1-}$ (b) 3 : 2Δ+T

$[B_3O_3(OH)_5]^{2-}$ (c) 3 : Δ+2T

$[B_3O_3(OH)_6]^{3-}$ (d) 3 : 3T

Fig. 3a–d. The ways in which the triborate FBB can be completed

Tennyson (1963) presented a crystal-chemical classification of borates based on analogy to silicates, using the terms nesoborate (our $n=1$), soroborate (our $2 \leq n \leq 9$, isolated only), inoborate (chains), phylloborate (sheets), and tektoborate (three-dimensional network). We see no objection to use of these terms; they can be applied within our scheme and do have the advantage of being universal in all languages. However, soroborate includes so many different units that it loses significance. If the term is used, it should be followed by n to designate the polyanion. For example, inyoite is a soroborate with $n=3$, and borax is a soroborate with $n=4$-1. For its publication date, Tennyson's classification is good and it is particularly well illustrated. Unfortunately, speculations about structures are included without any notation to warn the reader.

Bokij and Kravchenko (1966) wrote a lengthy review, discussing earlier reviews and classifications critically, and presenting a scheme to cover all compounds containing boron. Their scheme is cumbersome as there is no shorthand notation and they use old-fashioned chemical terminology. Nevertheless, the authors clearly recognized and understood the nature of borates and their review is thorough. The usual caveat is in order, as their list of examples includes speculations together with proven structures, but it is an extensive, well-organized list.

Definition of the Fundamental Building Blocks and Resultant Polyanions

Obviously, the units from which any polyanion must be developed are borate triangles and tetrahedra. Each such unit may occur isolated in a structure. Defining n as the number of boron atoms characteristic of a fundamental building block (FBB), $n=1$ for these simple units. By using a convenient shorthand notation, we can distinguish the cases of isolated triangles, 1:Δ, and isolated

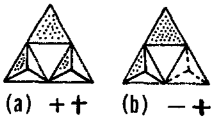


Fig. 4a and b. The two steric forms of 3:Δ+2T (Rumanova, 1972). **a** 3:Δ+2T (+ +); **b** 3:Δ+2T (− +)

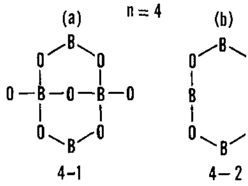


Fig. 5a and b. Tetraborate FBB

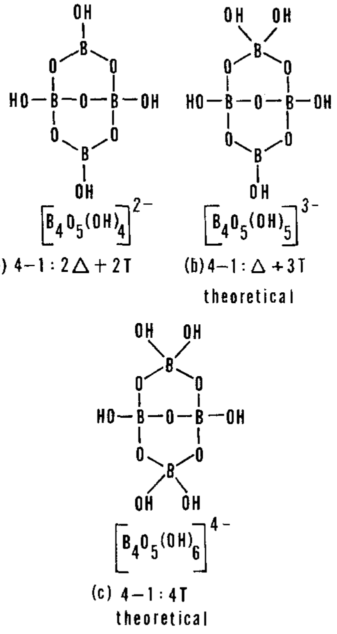
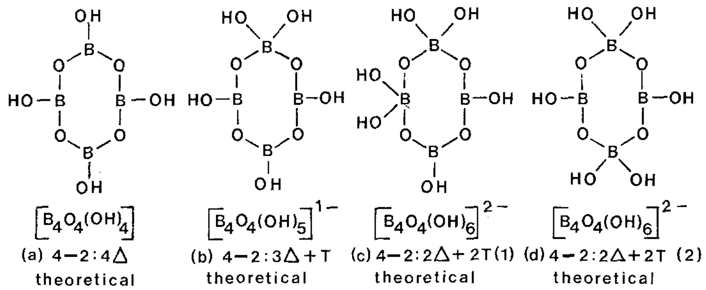


Fig. 6a–c. The ways in which tetraborate FBB 4-1 can be completed

tetrahedra, 1:T. Each unit may combine with others of its kind to form pairs (dimers), chains, sheets, or three-dimensional network (T only). The shorthand notation is 2:Δ or 2:T for isolated pairs. 1: $\infty\Delta$ or 1:∞T is used to indicate chains, 1:$\infty_2\Delta$ or 1:∞_2T, sheets, and 1:∞_3T, a network structure. In Tables 1 and 2 we list some representative structures having borate units with $n=1$ or 2. In the hydrated borates triangles and tetrahedra do not occur together, either in isolated form or as mixed dimers. However, there are examples of triangles and tetrahedra together in anhydrous borates such as calciborite (Table 4).

The true polyanions, in which both triangles and tetrahedra may (but do not always) exist together in the hydrated borates, begin with $n=3$. The triborate

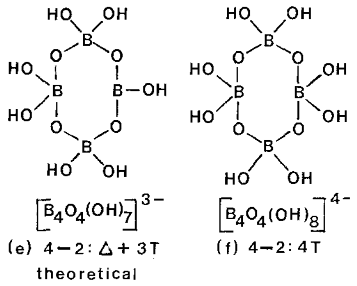


$[B_4O_4(OH)_4]$ (a) 4–2:4Δ theoretical

$[B_4O_4(OH)_5]^{1-}$ (b) 4–2:3Δ+T theoretical

$[B_4O_4(OH)_6]^{2-}$ (c) 4–2:2Δ+2T(1) theoretical

$[B_4O_4(OH)_6]^{2-}$ (d) 4–2:2Δ+2T (2) theoretical



$[B_4O_4(OH)_7]^{3-}$ (e) 4–2:Δ+3T theoretical

$[B_4O_4(OH)_8]^{4-}$ (f) 4–2:4T

Fig. 7a—f. The ways in which tetraborate FBB 4-2 can be completed

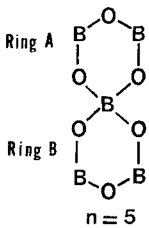


Fig. 8. Pentaborate FBB

FBB is illustrated in Figure 2. It can be completed with triangles and (or) tetrahedra in four ways, illustrated in Figure 3 for the fully hydrated forms, and each form can be referred to by the shorthand notation 3:3Δ, 3:2Δ+T, 3:Δ+2T, 3:3T. Rumanova (1972) pointed out that the form 3:Δ+2T could occur in structures with two different steric arrangements as shown in Figure 4. The shorthand notation can be extended to cover this distinction by using 3:Δ+2T(+ +) for the case illustrated in Figure 4a and 3:Δ+2T(− +) for the case illustrated in Figure 4b[4]. In this review we shall not consider further such steric distinctions, although they can be applied also to 3:3T and to some higher-order *n* cases where there is more than one tetrahedron.

For *n*=4, we have the unique case of 2 distinct tetraborate FBB's, both illustrated in Figure 5. The 2 kinds can be referred to as 4-1 and 4-2, respectively; 4-2 is the tetraborate analogue of the triborate FBB. Completion of 4-1 and

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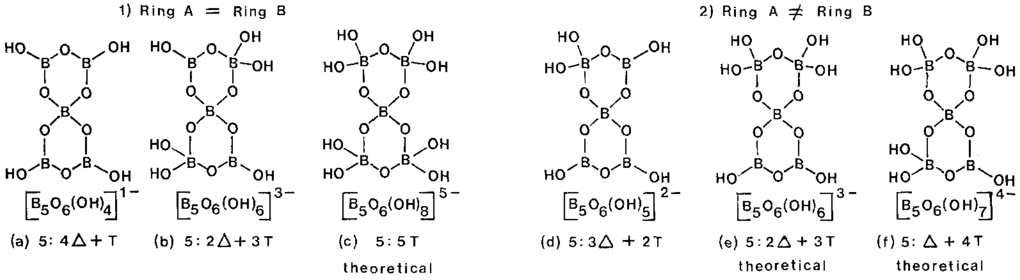
[4] The equivalent notations (− − and (+ −) are available if, for example, several structures are being compared



(a) 5: 4Δ + T (b) 5: 2Δ + 3T (c) 5: 5T theoretical (d) 5: 3Δ + 2T (e) 5: 2Δ + 3T theoretical (f) 5: Δ + 4T theoretical

Fig. 9a–f. The ways in which the pentaborate FBB can be completed

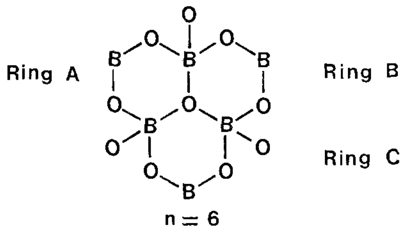
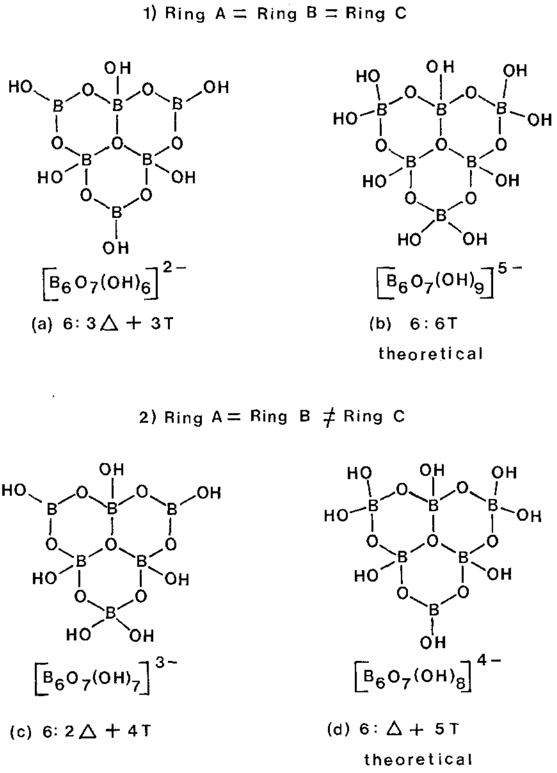


Fig. 10. Hexaborate FBB



(a) 6: 3Δ + 3T (b) 6: 6T theoretical (c) 6: 2Δ + 4T (d) 6: Δ + 5T theoretical

Fig. 11a–d. The ways in which the hexaborate FBB can be completed

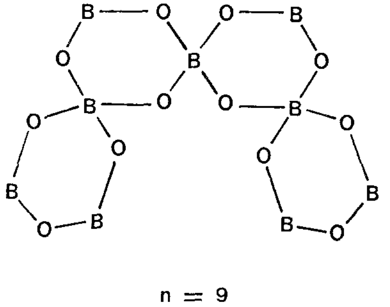


Fig. 12. Nonaborate FBB

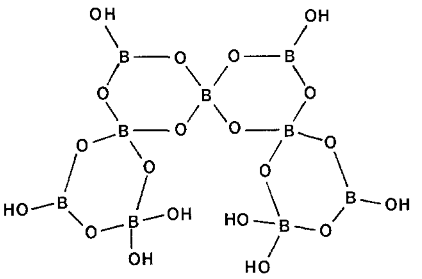
4-2 in the various possible ways gives 3 forms of 4-1, and 4 forms of 4-2, shown as fully hydrated forms in Figures 6 and 7, respectively.

The pentaborate FBB is shown in Figure 8, and its six possible fully hydrated forms are illustrated in Figure 9. It is convenient to divide these forms into 2 groups in terms of the two six-membered rings which can be labeled *A* and *B*. The FBB can be completed in 3 different ways so that $A=B$ and in 3 other ways so that $A \neq B$. The shorthand notation $5{:}2\Delta+3\mathrm{T}$ is identical for 2 cases, one having $A=\mathrm{B}$ and one, $A \neq B$. We suggest distinguishing by putting $(A \neq B)$ following the latter. There are no known examples of isolated polyanions in the $A \neq B$ group.

The hexaborate FBB, shown in Figure 10, can be completed in four different ways (Fig. 11). As in the pentaborate forms, it is convenient to separate the possibilities according to whether the rings *A*, *B*, and *C* are all completed in the same way $(A=B=C)$ or differently $(A=B \neq C)$. Having all 3 rings completed differently $(A \neq B \neq C)$ is not possible. The shorthand notation for the 2 forms having $A=B=C$ is $6{:}3\Delta+3\mathrm{T}$ and $6{:}6\mathrm{T}$. For the 2 forms having $A=B \neq C$, it is $6{:}2\Delta+4\mathrm{T}$ and $6{:}\Delta+5\mathrm{T}$.

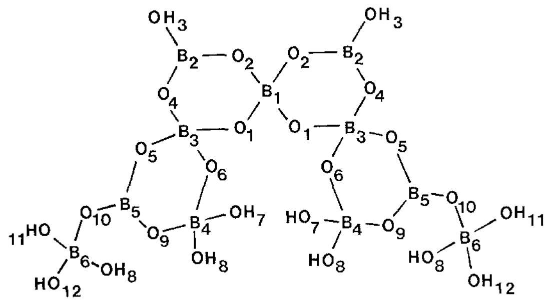
To date, there is only one example of a true FBB with $n>6$. This FBB has $n=9$ and is found modified, in sheet form, in the structure of preobrazhenskite, $\mathrm{HMg_3\{B_9O_{12}(OH)_4 \cdot [O_2B(OH)_2]_2\}}$ (Rumanova et al., 1972). This FBB is shown in Figure 12, a fully hydrated form $9{:}4\Delta+5\mathrm{T}$ is illustrated in Figure 13a, and Figure 13b shows a fully hydrated modified form, $9{:}(4\Delta+5\mathrm{T})+2\mathrm{T}$, from which the sheets in preobrazhenskite are developed. The FBB (Fig. 12) could be completed as $9{:}9\mathrm{T}$ with all rings equivalent, or, as before, one or more rings might be completed differently, giving forms such as $9{:}3\Delta+6\mathrm{T}$ (not illustrated).

For all these cases, our illustrations are for fully hydrated, isolated polyanions, and the chemical formula given is for that form. The state of hydration may be varied from full through partial to anhydrous, and the polyanions may be combined into pairs or triplets (dimers or trimers), linked into chains, sheets, or frameworks, or modified according to rule 5. The chemical formulas will then change accordingly. We emphasize that such changes in hydration, combinations, linkages, or modifications do *not* produce a "new" polyanion. The adjective "new" should be reserved for the appearance of a distinctive FBB that is different from those already defined. For example, if a pentaborate



$[B_9O_{12}(OH)_8]^{5-}$

(a) 9: 4Δ + 5T



$\{B_9O_{12}(OH)_6 \cdot [OB(OH)_3]_2\}^{7-}$

(b) 9: (4Δ + 5T) + 2T

Fig. 13a and b. Two forms of the nonaborate FBB **a** 9:4Δ+5T; **b** 9:(4Δ+5T)+2T. Numbers are for preobrazhenskite as given by Rumanova et al. (1972); sheets form by connecting related OH(8) atoms which become O(8)

analogue of the triborate were found, it would be truly new. Finally, in each illustration of a completed form, we have noted "theoretical" if it has not yet been found in some state of hydration, linkage, or modification in a structure.

Discussion of FBB in Structures

Triborate FBB. Completed entirely with triangles, the FBB 3:3Δ (Fig. 3a) is electrically neutral when fully hydrated and is found in the orthorhombic (α) form of metaboric acid (Tazaki, 1940; Peters and Milberg, 1964), for which the structural formula is $B_3O_3(OH)_3$. In anhydrous form it appears in the structures of the synthetic sodium and potassium borates, $Na_3B_3O_6$ (Fang, 1938, Marezio et al., 1963a) and $K_3B_3O_6$ (Zachariasen, 1937a; Schneider and Carpenter, 1970).

The triborate unit 3:2Δ+T (Fig. 3b) was recently found in fully hydrated isolated form in the structure of ameghinite, $Na[B_3O_3(OH)_4]$ (Dal Negro et al., 1975). It occurs in the chains found by Zachariasen (1963a) in the monoclinic

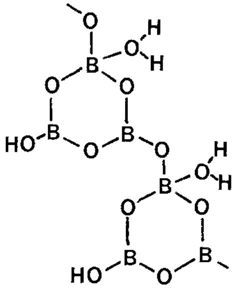


Fig. 14. Schematic drawing of the chain in monoclinic metaboric acid, β-HBO_2(II), as described by Zachariasen (1963a)

(β) form of metaboric acid, for which the structural formula is $B_3O_4(OH)(OH_2)$. This chain is illustrated in Figure 14 to show which oxygen atoms attach 1 or 2 protons, as this is an example of a water molecule being part of the polyanionic chain. This same unit $3:2\Delta+T$ appears in partially hydrated form, isolated, in the structure of a synthetic sodium borate, $Na_3B_3O_5(OH)_2$ (Corazza et al., 1975a). In accordance with rule 3 of the present study the available protons are attached to the tetrahedral oxygens of the polyanion. Anhydrous, linked into sheets, the unit was first reported by Krogh-Moe (1960) in synthetic CsB_3O_5 (refinement by Krogh-Moe, 1974).

The triborate unit that has been reported most frequently to date is $3:\Delta+2T$ (Figure 3c). It has been found in isolated form, as chains, and as sheets, as well as in the silicoborate framework structure of howlite, $Ca_2[B_3O_4(OH)_2\cdot OSiB_2O_4(OH)_3]$ (Finney et al., 1970); examples are listed in Table 3. It occurs isolated and partially hydrated (rule 3) in the structures of $KBO_2\cdot 4/3H_2O = K_3[B_3O_4(OH)_4]\cdot 2H_2O$ (Zviedre et al., 1974) and $RbBO_2\cdot 4/3H_2O = Rb_3[B_3O_4(OH)_4]\cdot 2H_2O$ (Zviedre and Ievins, 1974b). It is also found fully hydrated and modified by attachment of a side tetrahedron (rule 5) in the structure of hydrochlorborite, $Ca_2[B_3O_3(OH)_4\cdot OB(OH)_3]Cl\cdot 7H_2O$ (Brown and Clark, 1977).[5]

The triborate unit $3:3T$ (Fig. 3d) is found in fully hydrated, isolated form in nifontovite, $Ca_3[B_3O_3(OH)_6]_2\cdot 2H_2O$ (Egorov-Tismenko et al., 1973b). It is also modified (rule 5) by attachment of a side tetrahedron in the structure of uralborite (Shashkin et al., 1970a), for which the structural formula should be written $Ca_2[B_3O_3(OH)_5\cdot OB(OH)_3]$. Again, the formula written $Ca_2[B_4O_4(OH)_8]$, as Shashkin et al. did, should be avoided because it implies the presence of a tetraborate unit. The dimorph of uralborite is vimsite, and in that structure (Shashkin et al., 1969) the borate unit is a pyroxene-like chain of tetrahedra (Table 2). Thus, vimsite has the structural formula $Ca[BO(OH)_2]_2$. A summary of the group of calcium borates $CaB_2O_4\cdot xH_2O$, $x\leq 6$, is given in Table 4 to show the variety of structures existing within this group. Finally, in Table 3 we list the known structures with triborate units.

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[5] Modification by attachment of a side triangle was reported by Abdullaev and Mamedov (1969) in the structure of a synthetic magnesium borate, for which the structural formula should be written $Mg[B_3O_3(OH)_4\cdot OB(OH)_2]\cdot 6H_2O$. Although the borate arrangement is plausible, the structure as reported contains some impossibly short O–O and B–B contacts (S. Ghose, U. of Washington, Seattle, unpubl. data, 1977), so it is not included in Table 3

Table 3. Structures Containing Triborate Units

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
$3:3\Delta$, isolated	α-metaboric acid (HBO_2-III), $B_3O_3(OH)_3$, orthorhombic	Tazaki (1940); Peters, Milberg (1964)	synthetics: $Na_3B_3O_6$	Fang (1938); Marezio et al. (1963a)
			$K_3B_3O_6$	Zachariasen (1937a); Schneider, Carpenter (1970)
$3:2\Delta+T$, isolated	ameghinite, $Na[B_3O_3(OH)_4]$	Dal Negro et al. (1975)	synthetics: $Na_3[B_3O_5(OH)_2]$	Corazza et al. (1975a)
$3:2\Delta+T$, chains	β-metaboric acid (HBO_2-II), $B_3O_4(OH)(OH_2)$, monoclinic	Zachariasen (1963a)	CsB_3O_5	Krogh-Moe (1960, 1974)
$3:\Delta+2T$, isolated	inderborite, $CaMg[B_3O_3(OH)_5]_2\cdot 6H_2O$	Kurkutova et al. (1966)	kurnakovite, triclinic $Mg[B_3O_3(OH)_5]\cdot 5H_2O$	Da-Nean (1965); Razmanova et al. (1970); Corazza (1974)
	inderite, monoclinic $Mg[B_3O_3(OH)_5]\cdot 5H_2O$	Ashirov et al. (1962a); Rumanova, Ashirov (1964a); Corazza (1976)	inyoite, $Ca[B_3O_3(OH)_5]\cdot 4H_2O$	Clark (1959); Clark et al. (1964)
	synthetics: $Ca[B_3O_3(OH)_5]\cdot 2H_2O$	Clark, Christ (1959); Clark et al. (1964)	meyerhofferite, $Ca[B_3O_3(OH)_5]\cdot H_2O$	Clark et al. (1964); Christ, Clark (1960)
	$Zn[B_3O_3(OH)_5]\cdot H_2O$	Ozols et al. (1973)	solongoite, $Ca_2Cl[B_3O_4(OH)_4]$	Yamnova et al. (1974)
	$K_3[B_3O_4(OH)_4]\cdot 2H_2O$	Zviedre et al. (1974)		
	$Rb_3[B_3O_4(OH)_4]\cdot 2H_2O$	Zviedre, Ievins (1974b)		
$3:(\Delta+2T)+T$, isolated, modified	hydrochlorborite, $Ca_2[B_3O_3(OH)_4\cdot OB(OH)_3]Cl\cdot 7H_2O$	Brown, Clark (1977)		
$3:\Delta+2T$, chains	hydroboracite, $CaMg[B_3O_4(OH)_3]_2\cdot 3H_2O$	Ashirov et al. (1962b); Rumanova, Ashirov (1964b)	colemanite, $Ca[B_3O_4(OH)_3]\cdot H_2O$	Christ et al. (1958); Clark et al. (1964); Hainsworth, Petch (1966)

Table 3 (continued)

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
3:Δ+2T, sheets	fabianite, monoclinic $Ca[B_3O_5(OH)]$	Konnert et al. (1970b)	synthetic, orthorhombic $Ca[B_3O_5(OH)]$	Clark et al. (1962, 1964); Konnert et al. (1970b)
3:3T, isolated	nifontovite, $Ca_3[B_3O_3(OH)_6]_2\cdot 2H_2O$	Egorov-Tismenko et al. (1973b)		
3:(3T)+T, isolated, modified	uralborite, $Ca_2[B_3O_3(OH)_5\cdot OB(OH)_3]$	Shashkin et al. (1970a)		

Tetraborate FBB. The tetraborate unit 4-1:2Δ+2T (Fig. 6a) was first found in the structure of borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ (Morimoto, 1956). Since then it has been found, again in fully hydrated, isolated form, in the structures of tincalconite, $Na_2[B_4O_5(OH)_4]\cdot 3H_2O$ (Giacovazzo et al., 1973), hungchaoite, $Mg[B_4O_5(OH)_4]\cdot 7H_2O$ (Wan and Ghose, 1977)[6] and a synthetic manganese borate, $Mn[B_4O_5(OH)_4]\cdot 7H_2O$ (Berzina et al., 1975). It occurs partially hydrated, but still isolated, in the structure of roweite $Ca_2Mn_2(OH)_4[B_4O_7(OH)_2]$ (Moore and Araki, 1974a). In the tetraborate unit of this structure the tetrahedral oxygens are protonated, and the triangular oxygens are not; in addition, the structure contains OH^- groups as distinct entities, and no water molecules. Thus, roweite furnishes a particularly good example of the usefulness of the entire relative base strength method for proton assignment given in modified rule 3.

This same 4-1 unit polymerizes as described by Christ (1972), not just by polymerization as in the triborate cases, but also by breaking a B-O bond in each polyanion entering the chain (Fig. 1). The structure of kernite, $Na_2[B_4O_6(OH)_2]\cdot 3H_2O$ (Giese, 1966; Cialdi et al., 1967; Cooper et al., 1973) contains these chains. The large activation energy needed to form the chains from the isolated polyanions is considered responsible for the difficulty in transforming borax to kernite (Christ and Garrels, 1959; Christ et al., 1967; Christ, 1972). Although it is possible, theoretically, to complete the 4-1 FBB in 2 other ways (Fig. 5b, c), there are no examples of such forms known at present.

The tetraborate unit 4-2:4T has been reported, isolated and partially hydrated, in the structure of borcarite, $Ca_4Mg[B_4O_6(OH)_6][CO_3]_2$ (Solov'yeva and Bakakin, 1968; Yamnova et al., 1976). So far, this is the only example of a 4-2 unit. The known structures containing tetraborate units are summarized in Table 5.

Pentaborate FBB. All the known structures based on pentaborate units are listed in Table 6. The pentaborate unit 5:4Δ+T (Fig. 9a, 1) was found many

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[6] Wan and Ghose (1977) write the formula as $[Mg(H_2O)_5B_4O_5(OH)_4]\cdot 2H_2O$ to show the existence of a molecular complex in the structure

Table 4. Calcium Borates, $CaB_2O_4 \cdot xH_2O(CaO \cdot B_2O_3 \cdot xH_2O)$, $6 \geqq x \leqq 0$

x	Compound	n, FBB	Structural formula	Reference
6	hexahydroborite synthetic	1:T	$Ca[B(OH)_4]_2 \cdot 2H_2O$	Simonov et al. (1976); Sedlacek, Dornberger-Schiff (1971); Wang (1971a, b)
5	pentahydroborite	2:T	$Ca[B_2O(OH)_6] \cdot 2H_2O$	Egorov-Tismenko et al. (1973a)
4, β	frolovite, triclinic	1:T	$Ca[B(OH)_4]_2$	Egorov-Tismenko et al. (1972)
4, α	synthetic, monoclinic	1:T	$Ca[B(OH)_4]_2$	Ozols et al. (1965); Zeigan, Kutschabsky (1966)
4, α'	synthetic, orthorhombic	1:T	$Ca[B(OH)_4]_2$	Zeigan (1967)
2–2/3	nifontovite	3:3T	$Ca_3[B_3O_3(OH)_6]_2 \cdot 2H_2O$	Egorov-Tismenko et al. (1973b)
2	uralborite, $P2_1/n$	3:3T+T	$Ca[B_3O_3(OH)_5 \cdot OB(OH)_3]$	Shashkin et al. (1970a)
2	vimsite, $C2/c$	$1{:}\infty T$	$Ca[BO(OH)_2]_2$	Shashkin et al. (1969)
0 (I)	synthetic, *Pnca*	$1{:}\infty\Delta$	$Ca[BO_2]_2$	Zachariasen, Ziegler (1932); Marezio et al. (1963b)
0 (II)	calciborite, *Pccn*	$2{:}\infty(\Delta+T)$	$Ca[B_2O_4]$	Zachariasen (1967); Shashkin et al. (1970b)
0 (III)	synthetic, $Pna2_1$	$3{:}\infty_3[3T+(2\Delta, T)]$	$Ca_3[B_6O_{12}]$	Marezio et al. (1969a)
0 (IV)	synthetic, cubic	$3{:}\infty_3(3T)$	$Ca_3[B_3O_6]_2$	Marezio et al. (1969b)

Other members of this series, for which structures have not yet been determined, are: korzhinskite ($x=1$); sibirskite ($x=0.5$?); see Table 8

years ago in isolated, fully hydrated form, in the structure of the synthetic potassium borate, $K[B_5O_6(OH)_4] \cdot 2H_2O$ (Zachariasen, 1937b). Its correct structural formula was not recognized until later (Smith and Richards, 1952; Silvidi and McGrath, 1959; Christ, 1960; Zachariasen and Plettinger, 1963; Ashmore and Petch, 1970). The corresponding mineral, santite, described by Merlino and Sartori (1970), has the same structure, as does the synthetic ammonium analogue. The sodium mineral, sborgite, $Na[B_5O_6(OH)_4] \cdot 3H_2O$ (Merlino and Sartori, 1972) has the same isolated polyanions. Merlino and Sartori (1971) found the only known example of isolated, trimer units, $5{:}(4\Delta+T)_3$,

Table 5. Structures Containing Tetraborate Units

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
4–1: $2\Delta+2T$, isolated	borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	Morimoto (1956)	synthetic, $Rb_2Sr[B_4O_5(OH)_4]_2\cdot 8H_2O$	Ivchenko, Kurkutova (1975)
	hungchaoite, $Mg[B_4O_5(OH)_4]\cdot 7H_2O$	Wan, Ghose (1977)	tincalconite, $Na[B_4O_5(OH)_4]\cdot 3H_2O$	Giacovazzo et al. (1973)
	synthetic, $Mn[B_4O_5(OH)_4]\cdot 7H_2O$	Berzina et al. (1975)		
	synthetic, $K_2[B_4O_5(OH)_4]\cdot 2H_2O$	Marezio et al. (1963c)	roweite, $Ca_2Mn_2(OH)_4[B_4O_7(OH)_2]$	Moore, Araki (1974a)
chains	kernite, $Na_2[B_4O_6(OH)_2]\cdot 3H_2O$	Giese (1966); Cialdi et al. (1967); Cooper et al. (1973)		
4-2: 4T, isolated	borcarite, $Ca_4Mg(CO_3)_2[B_4O_6(OH)_6]$	Solov'yeva, Bakakin (1968); Yamnova et al. (1975)		

in the structure of ammonioborite. The structural formula should be written $(NH_4)_3[B_5O_6(OH)_3\cdot OB_5O_6(OH)_2\cdot OB_5O_6(OH)_3]\cdot 4H_2O$, rather than $(NH_4)_3[B_{15}O_{20}(OH)_8]\cdot 4H_2O$, so that the trimer character is correctly indicated. The single unit also forms chains, $5{:}\infty(4\Delta+T)$, by polymerization; these occur in the structure of larderellite, $(NH_4)[B_5O_7(OH)_2]\cdot H_2O$ (Merlino and Sartori, 1969).

The unit $5{:}2\Delta+3T$, $\Delta=B$ (Fig. 9b, 1) is found isolated and fully hydrated in the structure of ulexite, $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$ (Clark and Appleman, 1964: Ghose et al., 1977). It forms chains $5{:}\infty(2\Delta+3T)$ in probertite $NaCa[B_5O_7(OH)_4]\cdot 3H_2O$ (Kurbanov et al., 1963; Rumanova et al., 1966). The corresponding sheets $5{:}\infty_2(2\Delta+3T)$ are found in heidornite, $Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]$ (Burzlaff, 1967). The unit is also found in the framework structure of the silicoborate mineral garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose et al., 1976). The first example of a modification was found in the chains of kaliborite (Corazza and Sabelli, 1966). These chains, $5{:}\infty[(2\Delta+3T)+\Delta]$, are similar to those in probertite but are modified by attachment of a $BO(OH)_2$ triangle *via* a tetrahedral oxygen atom of the chain. The structural formula of kaliborite should therefore be written $HKMg_2[B_5O_7(OH)_3\cdot OB(OH)_2]_2\cdot 4H_2O$, so that its modified pentaborate character is evident. Writing the formula so it shows B_6 or B_{12} masks the true nature of the polyanion.

The unit $5{:}3\Delta+2T$ (Fig. 9d, 2) has not been found in isolated fully hydrated form; however, chains $5{:}\infty(3\Delta+2T)$ made up of units of this kind are found in the structure of ezcurrite, $Na_2[B_5O_7(OH)_3]\cdot 2H_2O$ (Cannillo et al., 1973), and sheets $5{:}\infty_2(3\Delta+2T)$ composed of these units have been found in a number

Table 6. Structures Containing Pentaborate Units

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
$5:4\Delta+\mathrm{T}$, isolated	sborgite, $\mathrm{Na[B_5O_6(OH)_4]\cdot 3H_2O}$	Merlino, Sartori (1972)	synthetic, $\mathrm{K[B_5O_6(OH)_4]\cdot 2H_2O}$	Zachariasen (1937b); Zachariasen, Plettinger (1963); Ashmore, Petch (1970)
	santite, $\mathrm{K[B_5O_6(OH)_4]\cdot 2H_2O}$	Merlino, Sartori (1970)		
			synthetic, $\beta\text{-}\mathrm{NH_4[B_5O_6(OH)_4]\cdot 2H_2O}$	Merlino (1969)
$5:(4\Delta+\mathrm{T})_3$, isolated trimer	ammonioborite, $\mathrm{(NH_4)_3[B_5O_6(OH)_3\cdot OB_5(OH)_2\cdot OB_5O_6(OH)_3]\cdot 4H_2O}$	Merlino, Sartori (1971)		
$5:4\Delta+\mathrm{T}$, chains	larderellite, $\mathrm{(NH_4)[B_5O_7(OH)_2]\cdot H_2O}$	Merlino, Sartori (1969)		
$5:3\Delta+2\mathrm{T}$, chains	ezcurrite, $\mathrm{Na_2[B_5O_7(OH)_3]\cdot 2H_2O}$	Cannillo et al. (1973)		
$5:3\Delta+2\mathrm{T}$, sheets	nasinite, $\mathrm{Na_2[B_5O_8(OH)]\cdot 2H_2O}$	Corazza et al. (1975b)	synthetic, $\mathrm{K_2[B_5O_8(OH)]\cdot 2H_2O}$	Marezio (1969)
	biringuccite, $\mathrm{Na_4[B_5O_8(OH)\cdot OB_5O_7(OH)]\cdot 2H_2O}$	Corazza et al. (1974)		
$5:3\Delta+2\mathrm{T}$, sheets, + isolated $\mathrm{B(OH)_3}$	gowerite, $\mathrm{Ca[B_5O_8(OH)\cdot B(OH)_3]\cdot 3H_2O}$	Konnert et al. (1972)	veatchite, *Aa* $\mathrm{Sr_2[B_5O_8(OH)]_2\cdot B(OH)_3\cdot H_2O}$	Clark, Christ (1971)
	p-veatchite, $P2_1$ $\mathrm{Sr_2[B_5O_8(OH)]_2\cdot B(OH)_3\cdot H_2O}$	Rumanova, Gandymov (1971); Rumanova et al. (1971)		
$5:2\Delta+3\mathrm{T}$, $A=B$ isolated	ulexite, $\mathrm{NaCa[B_5O_6(OH)_6]\cdot 5H_2O}$	Clark, Appleman (1964); Ghose et al. (1977)		
$5:2\Delta+3\mathrm{T}$, $A=B$ chains	probertite $\mathrm{NaCa[B_5O_7(OH)_4]\cdot 3H_2O}$	Kurbanov et al. (1963); Rumanova et al. (1966)		
$5:2\Delta+3\mathrm{T}$, $A=B$ chains, modified	kaliborite, $\mathrm{HKMg_2[B_5O_7(OH)_3\cdot OB(OH)_2]_2\cdot 4H_2O}$	Corazza, Sabelli (1966)		
$5:2\Delta+3\mathrm{T}$, $A=B$ sheets	heidornite, $\mathrm{Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]}$	Burzlaff (1967)		

Table 7. Structures Containing Hexaborate Units

FBB, linkage	Name, structural formula	Reference	Name, structural formula	Reference
$6{:}3\Delta+3T$, isolated	rivadavite, $Na_6Mg[B_6O_7(OH)_6]_4 \cdot 10H_2O$	Dal Negro, Ungaretti (1973)	macallisterite, $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$	Dal Negro et al. (1969)
	synthetics,			
	$Co[B_6O_7(OH)_6] \cdot 7H_2O$	Silins et al. (1974)	synthetics,	
	$K_2Co[B_6O_7(OH)_6]_2 \cdot 4H_2O$	Silins et al. (1973)	$Ni[B_6O_7(OH)_6] \cdot 7H_2O$	Silins et al. (1974)
	$Mg[B_6O_7(OH)_6] \cdot 3H_2O$	Genkina et al. (1976)	$Ni[B_6O_7(OH)_6] \cdot 5H_2O$	Silins, Ievins (1975)
			aksaite, $Mg[B_6O_7(OH)_6] \cdot 2H_2O$	Dal Negro et al. (1971); Hanic et al. (1971)
$6{:}3\Delta+3T$, chains	aristarainite, $Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4H_2O$	Ghose, Wan (1976)		
$6{:}3\Delta+3T$, sheets	nobleite, $Ca[B_6O_9(OH)_2] \cdot 3H_2O$	Clark (1964)	tunellite, $Sr[B_6O_9(OH)_2] \cdot 3H_2O$	Clark (1964)
$6{:}3\Delta+3T$, sheets modified	strontioginorite, $SrCa[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB_2O(OH)_3] \cdot 5H_2O$	Konnert et al. (1970a)	strontioborite, $Sr[B_6O_9(OH) \cdot OB_2O(OH)_3]$	Brovkin et al. (1975)
$6{:}2\Delta+4T$, isolated modified	teruggite, $Ca_4Mg[B_6O_7(OH)_6 \cdot OAsO_3]_2 \cdot 14H_2O$	Dal Negro et al. (1973)		

of structures (Table 6). In three of these structures the sheets occur in the presence of isolated $B(OH)_3$ groups (rule 6), confirming the suggestion by Petersen et al. (1959) that some hexaborates might be "pentaborates plus boric acid". These sheets contain spaces within which cations of various sizes can be fitted, and the sheets themselves can be stacked into a structure in various ways. Furthermore, a sheet can be composed of one or more crystallographically distinct polyanions and there may be one or more crystallographically distinct sheets. All these possibilities combine to give considerable structural flexibility, so it is not surprising to find a variety of structures having these sheets.

Hexaborate FBB. A list of the structures containing the hexaborate unit is given in Table 7. The first example of the unit $6{:}3\Delta+3T$ (Fig. 11a, 1) was found with the units linked into sheets $6{:}\infty_2(3\Delta+3T)$ in the structure of tunellite, $Sr[B_6O_9(OH)_2] \cdot 3H_2O$ (Clark, 1964). Later the polyanions were found isolated, fully hydrated in the structures of mcallisterite[7], $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$ (Dal

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[7] Mcallisterite = macallisterite, the former spelling now being preferred (Fleischer, 1972)

Negro et al., 1969) and aksaite, $Mg[B_6O_7(OH)_6]\cdot 2H_2O$ (Dal Negro et al., 1971). These 2 structural determinations, particularly the one for mcallisterite where the polyanion has exact trigonal symmetry with the central oxygen atom located on a triad axis, clearly demonstrate the unique character of this hexaborate polyanion and dispose of arguments that it might be considered as merely a group of triborate units (Heller, 1970). Chains formed by linking hexaborate polyanions are found in the structure of aristarainite, $Na_2Mg[B_6O_8(OH)_4]_2\cdot 4H_2O$ (Ghose and Wan, 1976). In the structure of strontioginorite (Konnert et al., 1970a) two crystallographically distinct hexaborate polyanions link into sheets. However, the sheet is modified by attachment of a side chain composed of two linked triangles forming the dimer $[-OB(OH)OB(OH)_2]^{1-}$. Writing the structural formula to indicate all this becomes lengthy: $SrCa[B_6O_9(OH)_2\cdot OB_6O_8(OH)\cdot OB_2O(OH)_3]\cdot 5H_2O$. For consistency, however, it should be so written, even though it is tempting to shorten it to $SrCa[B_{14}O_{20}(OH)_6]\cdot 5H_2O$, as Konnert et al. did. The shorthand notation for the modified polyanion is $6:\infty_2[(3\Delta+3T)+2\Delta]$. Strontioborite has a similar structural formula $Sr[B_6O_9(OH)\cdot OB_2O(OH)_3]$ (Brovkin et al., 1975). Again, this formula should not be written as $SrB_8O_{11}(OH)_4$.

The unit $6:6T$ (Fig. 11b, 1) is found in anhydrous form, linked by triangles, in the three-dimensional network of the orthorhombic form of boracite, $Mg_3Cl[B_6O_{10}\cdot OBO_2]$ (Dowty and Clark, 1973).

The unit $6:2\Delta+4T$, $A=B\neq C$ (Fig. 11c, 2) occurs isolated with modification in the structure of teruggite, $Ca_4Mg[B_6O_7(OH)_6\cdot OAsO_3]_2\cdot 14H_2O$ (Dal Negro et al., 1973). As the structural formula shows, the unit attaches an arsenate tetrahedron. So far this is the only known example of this unit; in shorthand notation it is $6:(2\Delta+4T)+AsO_4$.

FBB with $n>6$. As previously mentioned, the only example is for the nonaborate FBB, $9:\infty_2[4\Delta+5T]$ (Fig. 13b) in preobrazhenskite, $HMg_3\{B_9O_{12}(OH)_4\cdot[O_2B(OH)_2]_2\}$(Rumanova et al., 1972). The formula should not be written with B_{11}. The implication that HO_2 groups comparable to HF_2 are present in the structure, as stated in the text and by the formula $Mg_3[B_{11}O_{14}(OH)_8HO_2]$ given by Rumanova et al. (1972), is wrong.

Anhydrous Borates Having Two or More FBB

A number of these structures have been reported, and we mention here only a few examples. The rare-earth metaborates $Sm(BO_2)_3$, and $Gd(BO_2)_3$ (Abdullaev et al., 1975) contain the same chains as in the mineral calciborite, CaB_2O_4-II, first solved for synthetic crystals by Zachariasen (1967) and described in relation to other CaB_2O_4 polymorphs by Marezio et al. (1969a, b). The structure was confirmed for the mineral by Shashkin et al. (1970b). It would be preferable to write the formulas of these rare-earth metaborates as $Sm_2(B_2O_4)_3$ and $Gd_2(B_2O_4)_3$ to show the relationship. Barium tetraborate, $BaO\cdot 2B_2O_3$, has a three-dimensional network built with $3:\Delta+2T$ groups linked to $5:3\Delta+2T$ groups (Block and Perloff, 1965). $K_2O\cdot 2B_2O_3$ has a three-dimensional network

Table 8. List of Borate Minerals For Which Structures Are Not Yet Established

Mineral	Chemical formula[a]	Reference[b]	Mineral	Chemical formula[a]	Reference[b]
kurgantaite	$(Sr, Ca)B_2O_4 \cdot 0.5H_2O$	Fleischer (1955)	parahilgardite[d]	? $Ca_2B_5O_9Cl \cdot 2H_2O$	Palache et al., p. 382 (1951)
korzhinskite	$CaB_2O_4 \cdot H_2O$	Fleischer (1964)	strontiohilgardite[d]	? $(Sr,Ca)_2B_5O_9Cl \cdot 2H_2O$	Fleischer (1959)
chelkarite	? $CaMgB_2O_4Cl_2 \cdot 7H_2O$	Fleischer (1971, 1975)	volkovskite	$(Sr,Ca)B_6O_{10} \cdot 3H_2O$	Fleischer (1966a)
lüneburgite[c]	$Mg_3B_2O(OH)_4(PO_4)_2 \cdot 6H_2O$	Palache et al., p. 385 (1951)	satimolite	$Na_2KAl_4B_6O_{15}Cl_3 \cdot 13H_2O$	Fleischer (1970)
wiserite	$Mn_4B_2O_5(OH,Cl)_4$	Fleischer (1960)	tyretskite	? $Ca_4B_{10}O_{19} \cdot 3H_2O$	Davies, Machin (1968)
sibirskite	? $Ca_2B_2O_5 \cdot H_2O$	Fleischer (1963)	priceite	? $Ca_4B_{10}O_{19} \cdot 7H_2O$	Palache et al., p. 341–343 (1951)
carboborite	$Ca_2MgB_2O_5(CO_3) \cdot 10H_2O$	Fleischer (1965)	tertschite	$Ca_4B_{10}O_{19} \cdot 20H_2O$	Fleischer (1954)
halurgite	$MgB_4O_7 \cdot 2.5H_2O$	Fleischer (1962)	kurchatovite	$Ca_6Mg_5MnB_{12}O_{30}$	Fleischer (1966b)
olshanskyite	$Ca_3B_4O_9 \cdot 9H_2O$	Fleischer (1969)	wardsmithite	$Ca_5MgB_{24}O_{42} \cdot 6H_2O$	Erd et al. (1970)
			braitschite	? $(Na_2,Ca)_6(RE)_2^{3+}B_{24}O_{45} \cdot 6H_2O$	Raup et al. (1968)

[a] The formula is for the chemical composition and has no structural significance, ? indicates a doubtful formula, and RE = rare-earth elements

[b] In most cases the reference is for a summary where other references are available

[c] As written, the formula implies a $2{:}\Delta$ unit, fully hydrated and therefore electrically neutral

[d] The structure of hilgardite has just been determined (S. Ghose, unpubl. data) and its formula is $Ca_2B_5O_9Cl \cdot H_2O$ instead of $Ca_2B_5O_9Cl \cdot 2H_2O$ as previously proposed (Palache et al., p. 382, 1951)

composed of corner-sharing triangles, 4-1:$2\Delta+2T$ groups, and 3:$\Delta+2T$ groups (Krogh-Moe, 1972a). The high-temperature sodium borate, β-$Na_2O \cdot 3B_2O_3$, has double layers consisting of corner-linked tetrahedra, 3:$\Delta+2T$ groups, and 5:$4\Delta+T$ groups (Krogh-Moe, 1972b).

As we pointed out previously, FBB of different types do not exist together in structures of hydrated borates, so the crystal chemistry of the anhydrous borates is different. How different is well illustrated by comparing the structure of $Ca_2B_6O_{11}$ (Zayakin and Brovkin, 1976) with those of the hydrated members of the series $Ca_2B_6O_{11} \cdot xH_2O$, $1 \leqq x \leqq 15$ (Table 3). The structures of all the hydrated ones contain the triborate polyanion 3:$\Delta+2T$ (Fig. 3c), either isolated or linked to form chains or sheets. However, the anhydrous structure contains pentaborate-type units, 5:$2\Delta+3T$, $\Delta=B$ (Table 6, Fig. 9-1b) linked into a framework via extra tetrahedra. Thus, the anhydrous structure is not only *not* directly related to the hydrated structures but even contains a different FBB.

Hydrated Structures Not Yet Studied by Single-Crystal X-Ray Diffraction Methods

Unknown structures are listed in Table 8 for minerals only. There are undoubtedly numerous synthetic borates that could be added to this list. As Barrer and Freund (1974) discovered, hydrothermal experiments on systems such as CaO-B_2O_3-SiO_2-H_2O invariably produce compounds that cannot be identified. Some hydrothermal research on the system CaO-B_2O_3-H_2O using crystals of meyerhofferite, inyoite, and colemanite as starting materials was carried out at the U.S. Geological Survey in 1960–1962 by B.J. Skinner (now at Yale U., unpubl. data). Calciborite, CaB_2O_4 (II), was produced, as well as orthorhombic $CaB_3O_5(OH)$, the latter being identified by solution of its structure (Clark et al., 1962). Its monoclinic dimorph, fabianite, was discovered in salt deposits near Diepholz, Germany (Gaertner et al., 1962; Kühn et al., 1962), and the fabianite structure was described by Konnert et al. (1970b). Another product of Skinner's experiments was a triclinic phase appearing in excellent prismatic crystals. By analogy of its X-ray diffraction powder pattern to that reported for $3CaO \cdot 9B_2O_3 \cdot H_2O$ by Hart and Brown (1962), it was tentatively identified as that compound, but its structure has never been studied.

Conclusion

By using the 1977 rules and the nomenclature proposed, the structures of hydrated borates can be conveniently and readily classified provided care is taken when identifying the FBB. Furthermore, this nomenclature can easily be extended to cover cases such as $n=7$ or higher should such polyanions be found, as it has already been used for $n=9$. Obviously more experimental information about systems such as MgO-B_2O_3-H_2O, including correlation of the physical chemistry of such systems with crystal-structure determinations, is needed to complete details of the overall picture. Parallels between borate chemistry and carbon chemistry can be recognized and suggest tempting bypaths. We hope this survey and classification of the known structures will provide a basis for further studies.

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Note Added in Proof. The structure of parahilgardite is now known (S. Ghose, unpubl. data); its chemical formula is the same as that given for hilgardite in Table 8 (footnote d). The structure of kurchatovite (Table 8) has been solved; it has isolated 2:Δ borate groups. *Reference:* Yakubovich et al., Dokl. Akad. Nauk SSSR **230**, 837–840 (1976, in Russian); Chem. Abstr. **85**, 200865c (1976).