

CRYSTAL CHEMISTRY AND SYSTEMATIC
CLASSIFICATION OF HYDRATED
BORATE MINERALS*

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ABSTRACT

A systematic classification is made of hydrated borates of known crystal structures, based upon the structures of the complex boron-oxygen polyions contained in these crystals. From considerations of these known polyanion structures, four rules are deduced governing the nature of such polyanions. The structural formulas of a number of hydrated borates of known composition, but of unknown crystal structure, are predicted from the application of these rules and other reasonable crystal-chemical arguments.

INTRODUCTION

As a result of a number of investigations carried out in this and other laboratories in recent years, our knowledge of the crystal structures of hydrated borates has reached the stage where it is now feasible both to state several rules which seemingly govern the nature of the complex boron-oxygen polyions contained in such crystals, and to attempt a systematic classification of the known hydrated borates. It is the purpose of the present short paper to outline briefly some of the results obtained along these lines; a detailed paper is in preparation and will be published at some future time.

Four rules may be stated (Christ, 1959): (1) boron will link either three oxygens to form a triangle, or four oxygens to form a tetrahedron; (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; (3) in the polyions of hydrated borates, those oxygens not shared by two borons always attach a proton and exist as hydroxyl groups; (4) the insular groups may polymerize in various ways by splitting out water. As a corollary to the second rule it can be stated that the number of possible insular groups seems to be relatively small; as a corollary to the fourth rule, experience has shown that the insular groups can polymerize either to infinite chains, which may in turn be cross-linked, or possibly to dimers, but probably rarely or never to polymers of a degree between these two extremes.

In Table 1 are listed the polyions that have been definitely established by crystal-structure studies, the geometrical descriptions of these polyions, and the names, oxide formulas, and structural formulas of the compounds in which they are found. Illustrations have been omitted from the present paper; the reader is directed to the appropriate drawings in the original papers listed in the references.

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TABLE 1. STRUCTURAL FORMULAS OF HYDRATED BORATES OF KNOWN CRYSTAL STRUCTURES

Name	Oxide Formula	Polyion	Description (Δ = triangle, t = tetrahedron)	Structural Formula	Investigator
Sassolite	$B_2O_3 \cdot 3H_2O$	$B(OH)_3$ (molecule)	Δ	$B(OH)_3$	Zachariasen (1954)
Teepelite Bandykite	$Na_2O \cdot B_2O_3 \cdot 2NaCl \cdot 4H_2O$ $CuO \cdot B_2O_3 \cdot CuCl_2 \cdot 4H_2O$	$[B(OH)_4]^{-1}$	t	$Na_2[B(OH)_4]Cl$ $Cu[B(OH)_4]Cl$	Fornaseri (1949) Collin (1951)
Pinnoite	$MgO \cdot B_2O_3 \cdot 3H_2O$	$[B_3O_3(OH)_6]^{-2}$	$2t$	$Mg[B_3O_3(OH)_6]$	Paton and MacDonald (1957)
Inyoite Synthetic Meyerhofferite	$2CaO \cdot 3B_2O_3 \cdot 13H_2O$ $2CaO \cdot 3B_2O_3 \cdot 9H_2O$ $2CaO \cdot 3B_2O_3 \cdot 7H_2O$	$[B_3O_3(OH)_6]^{-2}$	$2t, 1\Delta$	$Ca[B_3O_3(OH)_6] \cdot 4H_2O$ $Ca[B_3O_3(OH)_6] \cdot 2H_2O$ $Ca[B_3O_3(OH)_6] \cdot H_2O$	Clark (1959) Clark and Christ (1959a) Christ and Clark (1956)
Colemanite	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	$[B_3O_4(OH)_9]_n^{-2n}$	$(2t, 1\Delta)_\infty$ chains	$Ca[B_3O_4(OH)_9] \cdot H_2O$	Christ <i>et al.</i> (1958)
Synthetic	$2CaO \cdot 3B_2O_3 \cdot H_2O$	$[B_3O_5(OH)_n]_n^{-2n}$	$(2t, 1\Delta)_\infty$ sheets	$Ca[B_3O_5(OH)]$	Clark and Christ (to be published)
Monoclinic meta-boric acid	$B_2O_3 \cdot H_2O$	$[B_3O_4(OH)_2]_n^{-n}$	$(1t, 2\Delta)_\infty$ chains	$H[B_3O_4(OH)_2]$	Zachariasen (1952)
Borax	$Ba_2O \cdot 2B_2O_3 \cdot 10H_2O$	$[B_4O_6(OH)_4]^{-2}$	$2t, 2\Delta$	$Na_2[B_4O_6(OH)_4] \cdot 8H_2O$	Morimoto (1956)
"Potassium pentaborate tetrahydrate"	$K_2O \cdot 5B_2O_3 \cdot 8H_2O$	$[B_5O_6(OH)_4]^{-1}$	$1t, 4\Delta$	$K[B_5O_6(OH)_4] \cdot 2H_2O$	Zachariasen (1938)

It is a reasonable extrapolation to extend these known structural formulas to those compounds of the same stoichiometric composition. This has been done in Table 2. Thus, it might be expected that inderite, $2\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$, would contain the same $[\text{B}_3\text{O}_3(\text{OH})_6]^{-2}$ rings found in inyoite, or, less likely, the chains of composition $[\text{B}_3\text{O}_4(\text{OH})_3]_n^{-2n}$ found in colemanite. The structural formula assigned to a compound by extrapolation in this way will depend upon the degree of polymerization assumed. In every case the polymerization involves the splitting out of water molecules between two or more insular groups. Any specific case can be understood in terms of the example afforded by the schematic relationship between meyerhofferite and colemanite which may be written:

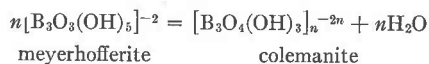


Table 2 lists the probable structural formulas for a number of compounds whose crystal structures are unknown at present. Where there is no evidence to the contrary it is assumed that the polyions are monomeric; if there are data leading to a definite polymer, this polymer is the one listed. Space group and unit-cell volume data are important in limiting the possible polymers, and these have been taken into account in the preparation of Table 2 but are not considered explicitly there.

In the first part of Table 2 are given the structural formulas directly derivable from well-known polyion types. Thus, the formula of frolopite may be derived from that of teepleite or that of pinnoite (Table 1). Inderite, kurnakovite, inderborite, and hydroboracite all have a 2:3:x oxide ratio and are presumed to be related to the known inyoite-colemanite series. Tincalconite probably contains the same polyions as borax, while kernite probably contains infinite chains resulting from the polymerization of these polyions (Christ and Garrels, 1959). A synthetic compound of composition $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Table 1), prepared by Brian J. Skinner, U. S. Geological Survey, by heating inyoite with water at 400°C . and 2000 bars for several days, has been shown to contain sheets consisting of cross-linked colemanite-type chains and has the structural formula $\text{CaB}_3\text{O}_5(\text{OH})$ (Clark and Christ, to be published). For hilgardite (Hurlbut and Taylor, 1937) and parahilgardite (Hurlbut, 1938) the analyses of Gonyer lead to the composition $2\text{CaCl}_2 \cdot 6\text{CaO} \cdot 9\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. This composition is explained (Table 2) if we assume that these two minerals contain the same kind of sheets found in the synthetic compound $\text{CaB}_3\text{O}_5(\text{OH})$.*

* Braitsch (1959a), as a result of new analyses, proposes the formula $\text{Ca}_2\text{B}_3\text{O}_8(\text{OH})_2\text{Cl}$ for parahilgardite and hilgardite, and $(\text{Ca}, \text{Sr})_2\text{B}_3\text{O}_8(\text{OH})_2\text{Cl}$ for a new strontian hilgardite found by him. This work still needs assessment.

TABLE 2. POSTULATED STRUCTURAL FORMULAS OF HYDRATED BORATES OF UNKNOWN CRYSTAL STRUCTURES

Name	Oxide Formula	Polyion	Description <i>t</i> = tetrahedron <i>l</i> = triangle	Structural Formula	References* and Remarks
Frolovite	CaO · BaO ₃ · 4(?)H ₂ O	[B ₇ (OH) ₄] ⁻¹ or [BaO(OH) ₄] ⁻²	<i>l</i> or 2 <i>l</i>	Ca[B ₇ (OH) ₄] ₂ or Ca[BaO(OH) ₄] ₂ · H ₂ O	Petrova (1957) (Petrova gives 3½H ₂ O in oxide formula)
Inderite	2MgO · 3B ₂ O ₃ · 15H ₂ O	[B ₄ O ₆ (OH) ₄] ⁻²	2 <i>l</i> , 1Δ	Mg ₂ [B ₄ O ₆ (OH) ₄] ₃ · 5H ₂ O	Vol. 2, p. 360
Kurnakovite	2MgO · 3B ₂ O ₃ · 15H ₂ O**	[B ₄ O ₆ (OH) ₄] ⁻²	2 <i>l</i> , 1Δ	Mg ₂ [B ₄ O ₆ (OH) ₄] ₃ · 5H ₂ O	Vol. 2, p. 360
Inderborite	MgO · CaO · 3B ₂ O ₃ · 11H ₂ O	[B ₄ O ₆ (OH) ₄] ⁻²	(2 <i>l</i> , 1Δ) _∞ chains	MgCa[B ₄ O ₆ (OH) ₄] ₂ · 6H ₂ O	Vol. 2, p. 355
Hydroboracite	MgO · CaO · 3B ₂ O ₃ · 6H ₂ O	[B ₄ O ₆ (OH) ₄] _n ⁻²ⁿ	(2 <i>l</i> , 1Δ) _∞ chains	MgCa[B ₄ O ₆ (OH) ₄] ₂ · 3H ₂ O	Vol. 2, p. 353
Tinacronite	Na ₂ O · 2B ₂ O ₃ · 5H ₂ O	[B ₄ O ₆ (OH) ₄] ⁻²	2 <i>l</i> , 2Δ	Na ₂ [B ₄ O ₆ (OH) ₄] ₂ · 3H ₂ O	Vol. 2, p. 337 Christ and Garrels (1959)
Kernite	Na ₂ O · 2B ₂ O ₃ · 4H ₂ O	[B ₄ O ₆ (OH) ₄] _n ⁻²ⁿ	(2 <i>l</i> , 2Δ) _∞ chains	Na ₂ [B ₄ O ₆ (OH) ₄] ₂ · 3H ₂ O	Vol. 2, p. 335 Christ and Garrels (1959)
Hilgardite or parahilgardite	2CaCl ₂ · 6CaO · 9B ₂ O ₃ · 4H ₂ O	[B ₄ O ₆ (OH) ₄] _n ⁻²ⁿ	(2 <i>l</i> , 1Δ) ₂₈ sheets	Ca ₉ [B ₄ O ₆ (OH) ₄] ₁₆ Cl ₄ · H ₂ O	Vol. 2, pp. 382-383
Gowerite	CaO · 3B ₂ O ₃ · 5H ₂ O	[B ₄ O ₆ (OH) ₄] ⁻¹	1 <i>l</i> , 2Δ	Ca[B ₄ O ₆ (OH) ₄] ₂ · H ₂ O	Erd <i>et al.</i> (1959) Christ and Clark (1960)
Veatchite	SrO · 3B ₂ O ₃ · 2(?)H ₂ O	[B ₆ O ₇ (OH) ₆] ⁻²	(1 <i>l</i> , 2Δ) ₂ dimers	Sr[B ₆ O ₇ (OH) ₆] ₂	Clark <i>et al.</i> (1959, 1960) This formulation requires at least 3H ₂ O in oxide formula.
<i>p</i> -Veatchite	SrO · 3B ₂ O ₃ · 2(?)H ₂ O	[B ₆ O ₇ (OH) ₆] ⁻²	(1 <i>l</i> , 2Δ) ₂ dimers	Sr[B ₆ O ₇ (OH) ₆] ₂	Braitseh (1959b) Remarks above apply here also.
Ammonioborite	(NH ₄) ₂ O · 5B ₂ O ₃ · 5½H ₂ O	[B ₆ O ₆ (OH) ₄] ⁻¹	1 <i>l</i> , 4Δ	NH ₄ [B ₆ O ₆ (OH) ₄] ₂ · 3H ₂ O	Clark and Christ (1959b)
Lardereite	(NH ₄) ₂ O · 5B ₂ O ₃ · 5(?)H ₂ O	[B ₆ O ₆ (OH) ₄] ⁻¹	1 <i>l</i> , 4Δ	NH ₄ [B ₆ O ₆ (OH) ₄] ₂ · 3(?)H ₂ O	Clark and Christ (1959b)
Sborgite	Na ₂ O · 3B ₂ O ₃ · 10H ₂ O	[B ₆ O ₆ (OH) ₆] ⁻²	2 <i>l</i> , 3Δ	Na[B ₆ O ₆ (OH) ₆] ₂ · 5H ₂ O	Cipriani (1957)
Escurrite	2Na ₂ O · 5B ₂ O ₃ · 7H ₂ O	[B ₆ O ₆ (OH) ₆] ⁻²	2 <i>l</i> , 3Δ	Na ₂ [B ₆ O ₆ (OH) ₆] ₂ · H ₂ O	Muessing and Allen (1957)
Ulexite	Na ₂ O · 2CaO · 5B ₂ O ₃ · 16H ₂ O	[B ₆ O ₆ (OH) ₆] ⁻²	3 <i>l</i> , 2Δ	NaCa[B ₆ O ₆ (OH) ₆] ₂ · 5H ₂ O	Vol. 2, p. 345
Probertite	Na ₂ O · 2CaO · 5B ₂ O ₃ · 10H ₂ O	[B ₆ O ₆ (OH) ₆] ⁻²	3 <i>l</i> , 2Δ	NaCa[B ₆ O ₆ (OH) ₆] ₂ · 2H ₂ O	Clark and Christ (1959c) Vol. 2, p. 343
Preobrazhenskite	3MgO · 5B ₂ O ₃ · 4½H ₂ O	[B ₆ O ₇ (OH) ₆] _n ⁻²ⁿ	(3 <i>l</i> , 2Δ) _∞ chains	Mg ₃ [B ₆ O ₇ (OH) ₆] ₂ · 4H ₂ O	Clark and Christ (1959c) Clark and Christ (1959c)
Tersschite	4CaO · 5B ₂ O ₃ · 20H ₂ O	[B ₆ O ₆ (OH) ₆] ⁻¹	4 <i>l</i> , 1Δ	Ca ₄ [B ₆ O ₆ (OH) ₆] ₂ · 6½H ₂ O	Varzhemskii (1956)
Kaliborite	K ₂ O · 4MgO · 11B ₂ O ₃ · 18H ₂ O	[B ₆ O ₆ (OH) ₄] ⁻¹ and [B ₆ O ₆ (OH) ₄] ⁻²	1 <i>l</i> , 4Δ and 2 <i>l</i> , 1Δ	KMg ₄ [B ₆ O ₆ (OH) ₄] ₂ [B ₆ O ₆ (OH) ₆] ₂ · 2H ₂ O	Meixner (1953) Vol. 2, p. 367

* Vol. 2 in this column stands for Palache, Berman, and Frondel (1951).

** Oxide formula with 15 H₂O is correct. (Schaller and Mrose, private communication.)

Zachariasen (1952) has shown that crystalline monoclinic metaboric acid, HBO_2 , contains chains of composition $[\text{B}_3\text{O}_4(\text{OH})_2]_n^{-n}$. The corresponding insular ring, consisting of two triangles and a tetrahedron, would have the formula $[\text{B}_3\text{O}_3(\text{OH})_4]^{-1}$. Either the chains or the rings (or intermediate polymers) would explain minerals of the type $\text{MO} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, such as gowerite (Erd *et al.*, 1959; Christ and Clark, 1960), veatchite (Clark *et al.*, 1959; Clark and Mrose, 1960), or *p*-veatchite (Braitsch 1959b), as shown in Table 2. For veatchite, $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 2(?)\text{H}_2\text{O}$, preliminary crystal structure studies (Clark and Christ, to be published) indicate the presence of dimers of composition $[\text{B}_6\text{O}_7(\text{OH})_6]^{-2}$. This assumption leads to the structural formula $\text{SrB}_6\text{O}_7(\text{OH})_6$, and the corresponding oxide formula $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Presumably *p*-veatchite also contains these dimers.

The remaining polynuclear ion to be considered is the pentaborate ion discovered by Zachariasen (1938) in "potassium pentaborate tetrahydrate," $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. Zachariasen formulated this pentaborate ion as $[\text{B}_5\text{O}_8(\text{OH})_2]^{-3}$, assumed that the crystal contained hydronium ions, and wrote the formula of the compound as $\text{KH}_2(\text{H}_3\text{O})_2\text{B}_5\text{O}_{10}$. However, since aqueous solutions of all of the known borates are weakly to strongly alkaline (except for the weak acid orthoboric acid) it seems very unlikely that in this or any other hydrated borate crystal will the polyion act as a proton donor. The formation of hydronium ions in crystals appears to take place only in the hydrates of strong acids, as for example in $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (Luzzati, 1953). This conclusion is in agreement with the results of proton magnetic resonance studies of Silvidi and McGrath (1959) and Smith and Richards (1952). With these considerations in mind and invoking Rule 3, we accept the main results of Zachariasen and conclude that potassium pentaborate tetrahydrate contains polyions of composition $[\text{B}_5\text{O}_6(\text{OH})_4]^{-1}$, consisting of one tetrahedron and four triangles linked at corners and assign to the compound the structural formula $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$.* The structural formulas for the minerals larderelite and ammonioborite (Table 2) follow immediately from these considerations.

On purely stereochemical grounds one might expect to be able to replace each of the $\text{O}_2\text{B}(\text{OH})$ triangles of the pentaborate ring successively by $\text{O}_2\text{B}(\text{OH})_2$ tetrahedra. Such a procedure will lead from the 1:5:*x* ratio of potassium pentaborate tetrahydrate to the successive ratios

* The results of Silvidi and McGrath (1959) also indicate to them that the pentaborate ring contains an *intra* hydrogen bond (Fig. 4, their paper). The fact that such a bond would place the proton at about 1 Å from the highly electropositive boron renders this postulate completely untenable. The stoichiometry of the compound indicated by their Fig. 4 is also puzzling.

2:5: x , 3:5: x , 4:5: x , and 5:5: x . This has been done in postulating structural formulas in Table 2 for ezcurrite, 2:5:7, ulexite, 3:5:16, probertite, 3:5:10, preobrazhenskite, 3:5:4 $\frac{1}{2}$, and tertschite, 4:5:20. Presumably, minerals of ratio 5:5: x , containing pentaborate ions consisting of five linked tetrahedra would be unstable toward minerals of the pinnoite structure which contains polyions of two linked tetrahedra (Table 1).

Finally, in Table 2 we list kaliborite which probably represents the unusual case of a mineral containing two distinct kinds of polyions.

A large number of synthetic hydrated borates have been reported in the literature and are summarized in Kemp (1956). In the interests of brevity these have not been considered here, but will be taken up in the more detailed paper.

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