BORATE MINERALS. II. A HIERARCHY OF STRUCTURES BASED UPON THE BORATE FUNDAMENTAL BUILDING BLOCK

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Abstract

A hierarchical structural classification is developed for borate minerals, based on the linkage of (BO₃) triangles and (BO₄) tetrahedra to form *FBBs* (fundamental building blocks) that polymerize to form the structural unit, a tightly bonded anionic polyhedral array whose excess charge is balanced by the presence of large low-valence interstitial cations. Thirty-one minerals, with nineteen distinct structure-types, contain isolated borate polyhedra. Twenty-seven minerals, with twenty-five distinct structure-types, contain finite clusters of borate polyhedra. Ten minerals, with the distinct structure-types, contain chains of borate polyhedra. Fifteen minerals, with thirteen distinct structure-types, contain frameworks of borate polyhedra. It is only the close-packed structures of the isolated polyhedra class that show significant isotypism.

Keywords: borate minerals, crystal structures, structural hierarchy.

Sommaire

Nous développons ici un schéma de classification structurale des minéraux du groupe des borates, fondé sur l'articulation des triangles (BO₃) et des tétraèdres (BO₄), qui forment des modules structuraux fondamentaux. Ceux-ci, polymérisés, constituent l'unité structurale de la maille, un agencement compact d'anions fait de ces polyèdres dont l'excédent de charge est neutralisé par des cations interstitiels à rayon relativement gros et à valence relativement faible. Trente-et-un minéraux, classifiés en dix-neuf types structuraux, contiennent des polyèdres isolés de borate. Vingt-sept minéraux, dont vingt-cinq types structuraux, contiennent des chaînes de polyèdres de borate. Dix minéraux, dont dix types structuraux distincts, contiennent des chaînes de polyèdres de borate. Quinze minéraux, dont treize types structuraux, contiennent des trames de polyèdres de borate. Seules les structures à empilement compact de polyèdres isolés font preuve d'isotypisme important.

(Traduit par la Rédaction)

Keywords: borates, minéraux, structures cristallines, hiérarchie structurale.

INTRODUCTION

Boron is not a common element in the Earth's crust, but fractionation in crustal processes results in the concentration of boron and fascinatingly complex deposits of borate minerals. For example, Canada's most significant borate deposits, in the Penobsquis and Salt Springs marine evaporites in Sussex, New Brunswick, contain at least twenty borate species, four of which are not known from any other locality (Roulston & Waugh 1981, Rachlin *et al.* 1986, Mandarino *et al.* 1990, Burns *et al.* 1992, Roberts *et al.* 1993, Grice *et al.* 1994, 1996, 1997, Burns & Carpenter 1996). The deposit is even more significant because three of the four new minerals have structures with remarkable affinities to aluminosilicate zeolites (Grice *et al.* 1994, 1996). Such struc-

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tural complexity can occur because the boron cation occurs both as $(B\phi_3)$ triangles and $(B\phi_4)$ tetrahedra (ϕ : O^{2-} , OH⁻); the superscripts indicate the formal charges of anions and cations in the borate minerals. The polymerization of these two distinct types of coordination polyhedra results in exceptionally complex structures. The structures of over 100 borate minerals are now known; here, the structures are compared and arranged into a hierarchy of structures.

Boron-oxygen bonds are of much higher bond-valence than the interstitial bonds, and thus borate minerals are very suitable for hierarchical classification based on the topological character of the FBB (fundamental building block) and the structural unit. There have been several classifications or structural hierarchies of this sort proposed for the borate minerals. Early versions by Edwards & Ross (1960), Ross & Edwards (1967), Christ (1960), Tennyson (1963) and Heller (1970) were reviewed by Christ & Clark (1977), who also produced the scheme in general use until now. The recent solution of several complex borate structures, both minerals (Grice et al. 1994, 1996) and synthetic phases (Behm 1983, 1985, Heller & Pickardt 1985, Hotokka & Pyykkö 1989), prompted further development on the topological character of *FBB*s of the form $[B_n \phi_m]$ with $3 \le n \le 6$ (Burns et al. 1995). The hierarchy presented here is based on the set of FBBs and linkage nomenclature developed by Burns et al. (1995). The general philosophy follows that of Hawthorne (1985, 1986, 1990, 1994): the FBB, a cluster of coordination polyhedra with the strongest bond-valence linkages in the structure, is repeated (usually polymerized) to form the structural unit, a complex (usually) anionic array, the charge of which is balanced by the presence of large low-valence interstitial cations. Hierarchical ordering is a function of the topological character of the FBB and the dimensional and topological character of the polymerization of the FBB to form the structural unit.

Throughout this paper, the descriptor proposed by Burns et al. (1995) for borate clusters and FBBs is used. Each FBB has a descriptor of the form A:B, where A gives the number of borate triangles (Δ) and tetrahedra (\Box) in the *FBB* in the form $i\Delta j\Box$, where *i* and *j* are the numbers of triangles and tetrahedra, respectively. The B part of the descriptor is a character string that contains information on the connectivity of the polyhedra. The string is written such that adjacent Δ or \Box (or both) represent polyhedra that share corners, and the delimiters <> indicate that the included polyhedra share corners to form a ring. The sharing of polyhedra between rings is indicated by the symbols -, =, \equiv , *etc.*, for one, two, three or more polyhedra, respectively. For example, the FBB with the descriptor $2\Delta 2 \square :< \Delta 2 \square > =< \Delta 2 \square >$ contains two triangles and two tetrahedra. There are two three-membered rings of polyhedra, each of which contains one triangle and two tetrahedra, and the rings have two tetrahedra in common. Further details are given by Burns et al. (1995).

STRUCTURES BASED ON ISOLATED POLYHEDRA

There are two possible *FBBs* in this class, Δ and \Box , and this class can be divided into two groups on this basis. Each of these groups can be divided into two subgroups according to the identity of the anions coordinating the central B, O^{2–} or (OH)[–], as this has important structural and paragenetic consequences. Minerals in this class are listed in Table 1.

$FBB = 1\Delta: \Delta, \phi = O^{2-};$ the 3Å wallpaper structures

These structures consist of infinite $[M\phi_4]$ chains of edge-sharing octahedra cross-linked by $T\phi_3$ triangles (T = B) and ($T\phi_4$) tetrahedra (T = S, Cr^{6+} , P, As⁵⁺, V⁵⁺, Si) (Hawthorne 1985, 1986, 1990). The $[M\phi_4]$ chain has an intrinsic repeat-distance of ~3 Å along its length. In the borates, the chains are cross-linked by $B\phi_3$ triangles in the plane perpendicular to the length of the chains, and by edges and vertices shared with adjacent chains. Ignoring ordering along the length of the chains, the graphical (topological) aspects of these structures may be idealized as colorings of the regular 3⁶ net. These structures can be divided into two subsets, the zigzag structures and the miscellaneous structures.

The zigzag structures: Takéuchi et al. (1978) and Takéuchi (1978) introduced the idea of F walls, C walls and S columns to describe the structure of orthopinakiolite and its relation to the structure of pinakiolite. This description works very well for the structures of several other (commonly paragenetically) related borate minerals listed in Table 1. We call these minerals the zigzag borates because of the structures are viewed down their 3n Å axis.

The structures of these minerals are shown in Figure 1. There are three principal elements apparent in this view: (1) straight truncated chains of edge-sharing octahedra extending diagonally through the structures, (2) zigzag truncated chains of octahedra between the chains described in (1), and (3) (BO₃) triangles occupying interstices between the straight and zigzag chains (Fig. 1). Both sets of chains of octahedra share edges with similar chains that are displaced ~3 Å along [001] to form flat sheets and zigzag sheets, respectively. In orthopinakiolite, Takéuchi et al. (1978) called the flat sheet the Fwall; the zigzag sheet was described as a C (corrugated) wall flanked by columns of octahedra designated as S columns. This notation is shown by the shading of polyhedron elements in Figure 1. Each F wall is terminated at each end by an S column. Similarly, each C wall is terminated at each end by sharing octahedron corners with an S column. Note that the terminal octahedra of each F wall also belong to the attached C-wall. There are equal numbers of octahedra in the F wall, the C wall and the S column, and hence we can write each structure as $F_n C_n S_n$, where *n* is the number of octahedra in each wall in the structure (note that when considering

ABLE 1, BORATE MINERALS BASED	ON ISOLATED BO	OF BO.	POLYHEDRA
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1 wynoura	Name	Connectivity	Formula	a (Å)	b (Ā)	c (Å)	α (*)	B (*)	v (*)	Sn Gr	Bet	Fin
Zizwaw have			3 Å v	vallpaper str	uctures			6.1/		op. or	1101	
LIGZAG DOR	ates		Ad an Remark as some as									
1.4	bonaccordito	Δ	Mg ₂ (Fe st , II ^{**} ,Mg)(BO ₃)O ₂	9,26(1)	12.25(1)	3_01(1)	-	-	-	Pbam	(1)	-
1.4	fredrikeconito	<u>A</u>	NI ₂ Fe ^{**} (BO ₃)O ₂	9.213(6)	12,229(7)	3 001(2)	-	-	-	Pbam	(2)	-
1A	ludwigito	4	Mg ₂ Mn ⁴⁴ (BO ₃)O ₂	9,198(2)	12.528(3)	2,965(1)		- 👄	-	Pbam	(3)	-
1 Av	voncenito	4	Mg2Fe ³¹ (BO3)O2	9_257(1)	12 282(1)	3 0234(2	- (-	-	Pbam	(4)	1a
	Vonsenite	Δ	F02 F0- (BO3)O2	9,463(1)	12,305(1)	3,073(1)	~	-	-	Pbam	(5)	-
1∆ ،	chestermanite***	Δ	Mg ₂ (Fe ³⁺ ,Mg,Al,Sb ⁵⁺)(BO ₃)O ₂	18,535(3)	12,273(1)	6.043(1)	-	-	+	Pnnm	(6)	-
1Δ 0	orthopinakiolite**	Δ	Mn ³⁺ (Mn ²⁺ ,Mg,Fe ³⁺ ,□) ₁₇ (BO ₃) ₈ O ₁₆	18.357(4)	12,591(2)	6.068(1)	-	-	-	Pnnm	(7)	1b
1∆ †	takéuchiite**	Δ	Mn ³⁺ (Mn ²⁺ ,Mg,Fe ³⁺ ,□) ₂₅ (BO ₃) ₁₂ O ₂	4 27.585(4)	12.561(3)	6.027(2)	-	-	-	Pnnm	(8)	1c
1A I	blatterite**	Δ	Sb ⁵⁺ Mn ³⁺ (Mn ²⁺ ,Mg) ₃₆ (BO ₂), ₆ O ₂₂	37.654(8)	12 615(3)	6 2472/8				Doom	(0)	ا ما
۱∆ '	'Mg-blatterite'**	Δ	Sb3+Mn3+(Mg,Mn2+)ac(BOa)+00	37 384(11)	12 568(3)	6 200(2)	,		-	Panm	(9)	IG
10 7	ninakiolite		(Ma Ma2t) (Ma2t Ob 30 (DO 10			0,200(2)		2	-	r-111111	(10)	-
·~~ .	printinonito	4	(WQ,WIT*)2(WIT*,SD**)(BO3)O2	21.79(1)	5,977(5)	5.341(5)	+	95,83(5)	-	C2/ m	(11)	1e
Miscellaneo	ous wallpaper bora	ates										
	riuoborite	ΔΙ	Mg ₃ [BO ₃](F,OH) ₃	8_827(3)	8,827(3)	3_085(2)		-	-	P6 ₃ /m	(12)	2a
1Δ p	painite	Δ (CaZrAl ₉ O ₁₅ [BO ₃]	8 715(2)	8,715(2)	8.472(2)	-	-	Ψ.	P63	(13)	-
JA Je	eremejevite	Δ /	Al ₆ [BO ₃]₅F₃	8,56	8.56	8 18	-	-	\sim	P6₃/m	(14)	-
ı∆ v	warwickite	Δ ((Mg,Ti,Fe³⁺,Al)₂[BO₃]O	9,246(1)	3.0927(2)	9.384(1)	-	-		Poma	(15)	26
∆ у	vuanfuliite	Δ Ν	Mg(Fe ³⁺ ,Fe ²⁺ ,Al,Ti,Mg)(BO ₃)O	9,258(6)	3.081(2)	9.351(4)	-	-	_	Pnma	(16)	
iΔ k	karlite	Δ.	Ma-(OH).(BO_)-CI	17 697(1)	17 067(2)	2 10 40/0				-	()	_
Δ 🗤	wightmanite	ΔΜ	Mg-Q(OH)_(BQ.1	13 46(2)	3 102(5)	3,1040(2)	-	-	-	P212121	(19)	20
			35-(10.40(2)	3.102(3)	10,17(2)	-	91.60(5)	7	12/m	(20)	-
	uiste	Δ (Fe,Mg) ₂ (Fe,Sn)O ₂ [BO ₃]	10,695(4)	3,102(1)	5,431(1)	-	94,21(3)	-	P2/m	(17)	-
	nagnesionuisite	Δ (Mg,Fe) ₂ (Fe,Sn)O ₂ [BO ₃]	-	-	-	-	-	-	-	(18)	~
∆ jir	imboite	Δ Ν	νIn ₃ [BO ₃] ₂	5_658(1)	8.740(1)	4 646(2)	÷	-	-	Pnmn	(21)	-
Δ ki	otoite	Δ Ν	/lg ₃ [BO ₃] ₂	5_396(1)	8_297(2)	4,459(1)	-	-	-	Pnmn	(22)	3a
∆ n	ordenskiöldine	Δ 0	CaSn(BO ₃)	4 858(1)	4 858/1)	16 090(2)				00	(00)	
∆ tu	usionite	ΔΝ	InSn[BOa]	4.781(1)	4 781(1)	15 381(7)		-	-	M3 (75	(23)	-
🗆 si	inhalite		VMg[BO₄]	9.878	5.675	4,328	2	2	2	ns Pnma	(24)	_
∆ s;	assolite	Δ [6	B(OH) ₃]	7.039	7.053	6.578	92.58	101.17	119.83	PT	(25)	3h
🗆 bi	andylite	- C	u[B(OH)₄]Cl	6.19	6.19	5.61	_	_	_	 P4/n	(27)	49
🗆 te	eepleite	• N	a,[B(OH),]CI	7,260(2)	7 260(2)	4 847(2)	_			R4/amm	(20)	14
					(2)	1.041 (1)			_	1 4/10/00	1(20)	40
L fro	otovite	- C	Ca[B(OH) ₄] ₂	7.774(2)	5.680(1)	8 136(2)	11_315(1)	101_67(2)	107.87(2)	PT	(29)	4c
🗆 he	exahydroborite	□ C	$a[B(OH)_4]_2(H_2O)_2$	8.006(2)	8.012(2)	6.649(2)	-	-	104,21(2)	P2/a	(30)	4d
	onmilito											

Konev et al. (1970). (2) De Waal et al. (1974). (3) Burns et al. (1994), (4) Bonazzi & Menchetti (1969), (5) Swinnea & Steinlink (1983), (6) Alfredsson et al. (1991), (7) Takéuchi et al. (1976), (8) Norrestam & Bovin (1987), (9) Cooper & Hawthorne (1998) (10) Bovin et al. (1966), (11) Moore & Araki (1974a), (12) Dal Negro & Tadini (1974), (13) Moore & Araki (1976), (14) Sokolova et al. (1987), (15) Bigi et al. (1991), (16) Huang & Wang (1994), (17) Yamanova et al. (1978), (18) Yang et al. (1985), (19) Bonazzi et al. (1986), (20) Moore & Araki (1972a), (21) Bondareva et al. (1978), (22) Eftenberger & Pertik (1994), (23) Eftenberger & Zemann (1986), (24) Cooper et al. (1994), (25) Zachariasen (1954), (26) Fang & Newnham (1965), (27) Collin (1951), (28) Effenberger (1982), (29) Simonov et al. (1976a), (30) Simonov et al. (1976b), (31) Nakai et al. (1986)

the stoichiometries of such structures, it is important to remember that the terminal octahedra of the F wall and the C wall are common to each unit, and should not be counted twice.) For ludwigite, n = 3, for orthopinakiolite, n = 5, for takéuchiite, n = 7, and for blatterite, n = 9. The next (unnamed) member of this series has n = 11; details of the unit cell are given in Table 1. Pinakiolite (Fig. 1) is the end-member of this series: $F_{\infty}C_{\infty}S_{\infty}$.

In all of these structures, the direction of the wall is changed [in the (001) plane] by a glide operation orthogonal to [100]. If $c \approx 3$ Å (as in ludwigite), this operation is a *b* glide; if $c \approx 6$ Å (as in orthopinakiolite, takéuchiite and blatterite, Table 1), this operation is an *n* glide. The type of glide plane is related to the chemical composition and stereochemistry of the *F* wall. The ludwigite minerals have chemically and structurally simple *F*-walls that are compatible with a *c*-repeat of only 3 Å (*i.e.*, one octahedron along the *c* axis). The other zigzag borates have chemically (and structurally) more complicated *F*-walls, and hence require a longer repeat-distance in the *c* direction to incorporate these



more complicated chemical compositions. An n glide gives double the repeat distance in the c direction for the F wall which, when combined with the increase in the a dimension, gives sufficient room for the F wall to incorporate the required combination of different types of cation sites.

The *C* wall in these minerals shows extreme positional disorder of its constituent cations, the degree of which increases with increasing *n* in the formula $F_nC_nS_n$. This makes determination of the correct chemical formula quite difficult. However, it is clear from the structural results that the general formula $M^{2+}_2(M^{3+}, M^{5+})$ (BO₃)O₂ is inappropriate. These structures are not all polymorphs. Indeed, the occurrence of blatterite seems to be due to the need to incorporate Sb⁵⁺ into the *F* wall, and a complicated formula results (Table 1). It is feasible that the structural differences in these $F_nC_nS_n$ structures are driven by slight compositional differences. Certainly, the occurrence of all these structure types at a single locality poses some interesting questions on paragenesis.

Other wallpaper structures: The simplest structure is that of fluoborite, [Mg₃(BO₃)(F,OH)₂], in which chains of octahedra occur in pairs that share vertices to form a triangular tunnel, which contains the $(B\phi_3)$ groups (Fig. 2a); the hexagonal tunnels are empty in fluoborite. Painite, CaZr[BAl9O18], has the same structure in projection despite the very different chemical composition. The octahedra in painite are occupied by Al, reducing the basic repeat-length of the chain from 3.0 to 2.8 Å. In addition, only alternate triangular tunnels are occupied by $(B\phi_3)$ groups; the other triangular tunnels contain Zr in trigonal prismatic coordination, leading to a tripling of the repeat distance along the chain-repeat direction. The hexagonal tunnels, empty in fluoborite, are occupied by [6]-coordinated Ca in painite. Jeremejevite, [Al₆(BO₃)₅(OH)₃], also has a similar framework to that of fluoborite, except that every third octahedral site along the chain-repeat direction is vacant, and the resulting octahedral dimers are linked along the chain direction by BO3 triangles.

In warwickite, [(Mg,Ti)2(BO3)O], the chains of octahedra share edges to form ribbons four octahedra wide; each ribbon is canted at 60° to the adjacent ribbons, and the resulting triangular interstices are bridged by BO3 triangles (Fig. 2b). Karlite, Mg7(OH)4(BO3)4Cl, consists of 2×1 edge-sharing ribbons of $[M\phi_4]$ chains (Fig. 2c) and simple $(1 \times 1) [M\phi_4]$ chains linked in the 3⁶ plane by sharing octahedron vertices to form large octagonal channels parallel to [001]. The sequence of octahedra around each channel is 2-1-1-2-1-1 (Fig. 2c), and the large Cl anion occurs in these channels. Wightmanite, [Mg5(BO3)(OH)5O](H2O)2, consists of 2×2 edge-sharing bundles of $[M\phi_4]$ chains and 1×2 ribbons of edge-sharing chains (Fig. 2d), linked in the 36 plane by sharing vertices of octahedra and by (BO3) groups in the resulting triangular channels

through the framework. Large hexagonal channels through the structure are filled with disordered (H_2O) groups.

$FBB = 1\Delta: \Delta, \ \phi = O^{2-};$ miscellaneous structures

The minerals of the kotoite group are based on a $[M_3(B\phi_3)_2]$ framework of corner-sharing between triangles and octahedra, and edge-sharing between octahedra (Fig. 3a). Two octahedra share edges to form a dimer, and these dimers alternate with single octahedra along [100] to form a chain of edge-sharing octahedra of the form $[M_3\phi_{10}]$. These chains cross-link along [010] by sharing corners with isolated $B\phi_3$ triangles to form sheets parallel to (001) that link into a framework by sharing corners with linking triangles and octahedra.

Nordenskioldine and tusionite are isostructural with dolomite, with Ca and Mn proxying for Ca, and Sn⁴⁺ proxying for Mg in the prototype dolomite structure.

$FBB = 1\Delta : \Delta, \ \phi = OH^{-1}$

Sassolite, $[B(OH)_3]$, is the only mineral in this subgroup. The structure (Fig. 3b) consists of layers of $B(OH)_3$ triangles H-bonded together to form a sheet parallel to (001). Adjacent sheets are separated by 3.16 Å, and the intersheet attraction is assured by weak Van der Waals interactions.

$$FBB = 1 \square : \square, \phi = O^{2}$$

There is only one mineral within this class, sinhalite, $AIMg(BO_4)$. Sinhalite is isostructural with olivine, with Al occupying the *M*1 site and Mg occupying the *M*2 site. It is a compact close-packed structure.

$FBB = 1 \square : \square, \phi = OH^-$

In bandylite, $Cu[B(OH)_4]Cl$, there is one unique Cu²⁺ atom that is octahedrally coordinated by four (OH) groups and two Cl atoms; $(Cu^{2+}\phi_6)$ octahedra and $(B\phi_4)$ tetrahedra link by sharing corners to form a distorted chequerboard of corner-sharing polyhedra (Fig. 4a) parallel to (001). The (Cu²⁺ ϕ_6) octahedra show the usual Jahn-Teller distortion, with Cl as the apical ligand at a distance of 2.8 Å. Sheets adjacent along [001] link through apical Cl atoms of the $(Cu\phi_6)$ polyhedra, forming $[Cu\phi_5]$ chains of corner-sharing octahedra parallel to the c axis. In teeplite, $Na_2[B(OH)_4]Cl$, there is one unique Na atom coordinated by four (OH) groups and two Cl atoms. (Na ϕ_6) octahedra are cross-linked by edge-sharing into a sheet orthogonal to [001]. These sheets stack along the c axis, and adjacent sheets are linked by $(Na\phi_6)$ - $(B\phi_4)$ corner-sharing with layers of $(B\phi_4)$ tetrahedra in the (001) plane (Fig. 4b). The (Na ϕ_6) octahedra have four meridional OH ligands and two apical Cl ligands, and the octahedra are canted such that each Cl atom is coordinated by four Na atoms.





FIG. 2. The isolated Bφ₃ 3 Å wallpaper structures projected down the 3 Å direction: miscellaneous structures: (a) fluoborite, (b) warwickite, (c) karlite, and (d) wightmanite. Divalent- and trivalent-occupant octahedra are random-dot shaded, BO₃ triangles are shown in black.

Frolovite, $Ca\{B(OH)_4\}_2$, has one unique Ca atom that is coordinated by eight (OH) groups. The $(Ca\phi_8)$ polyhedra share edges to form $[Ca_2\phi_{14}]$ dimers that are cross-linked by $\{B(OH)_4\}$ tetrahedra to form $[Ca\{B(OH)_4\}_2]$ sheets parallel to $\{101\}$; an oblique view of this sheet is shown in Figure 4c. These sheets are neutral, and are linked solely by H-bonding, accounting for the prominent $\{101\}$ cleavage of frolovite. Hexahydroborite, $Ca[B(OH)_4]_2(H_2O)_2$, consists of chains of edgesharing $(Ca\phi_8)$ polyhedra extending along [100] and decorated by $\{B(OH)_4\}$ tetrahedra (Fig. 4d). The chains are linked in the other two dimensions by H bonding that involves an interstitial (H_2O) group that is not bonded to any cation. In henmilite, $Ca_2Cu(OH)_4$ $(B(OH)_4)_2$, there is one unique Ca atom coordinated by eight (OH) groups. Pairs of $(Ca\phi_8)$ polyhedra share edges to form $[Ca_2\phi_{14}]$ dimers that are linked into chains along [001] by {B(OH)₄} tetrahedra. These chains are cross-linked by square-planar (Cu ϕ_4) groups (Fig. 4e) into a three-dimensional network that is strengthened by H-bonding.

STRUCTURES BASED ON FINITE CLUSTERS OF POLYHEDRA

At present, there are twelve distinct types of clusters known, and these may be divided into seven sets: (1) 2B:2B, (2) 3B:<3B>, (3) 4B:<3B>B, (4) 5B:<3B>-<3B>, (5) 4B:<3B>=<3B>, (6) 6B: $[\phi]$ <3B> | <3B | <3B> |



FIG 3. Miscellaneous isolated $B\varphi_3$ polyhedra structures: (a) kotoite, and (b) sassolite.

ABLE 2 BORATE MINERALS BASE	ON FINITE CLUSTERS OF BO	AND BO POLYHEDRA
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Polyhedra	Name	Connectivity	Formula	a (Ă)	b (Ă)	c (Ă)	β (°)	Sp Gr	Ref. Fig
			3Å wallpaper struc	tures					
2Δ	suanite	2Δ	Mg ₂ [B ₂ O ₆]	12 10(5)	3 12(2)	9 36(5)	104 3(5)	P21/a	(1) 6a
2∆	száibélyite	2∆	Mg ₂ (OH)[B ₂ O ₄ (OH)]	3 139(1)	10 393(2)	12 577(2)	95 88(2)	P2,/c	(2) 6b
2Δ	sussexite	2Δ	$Mn_2(OH)[B_2O_4(OH)]$	3 287(1)	10 718(2)	12 866(3)	94 75(3)	P2,/c	(2) -
20	kurchatovite	2Δ	CaMg[B ₂ O ₅]	12,331(4)	5 489(1)	11 092(4)	-	P2,/b	(3) 6c
20	pentahydroborite	20	Ca[B ₂ O(OH) ₆](H ₂ O) ₂	7.875(2)	6 534(2)	8 104(2)	111 33	PT	(4) 6d
20	pinnoite	20	Mg[B ₂ O(OH) ₆]	7.614(1)	7.614(1)	8.1898(8)	_	P42	(5) 6e
2∆1⊡	ameghinite	(2∆□)	Na[B ₃ O ₃ (OH) ₄]	18.428(3)	9.882(2)	6_326(2)	104 38(1)	C2/c	(6) 6f
1∆2⊡	inderite	$\left< \Delta 2 \Box \right>$	Mg[B ₃ O ₃ (OH) ₅](H ₂ O) ₅	6 8221(3)	13_1145(13)	12.0350(8)	104.552(8)	P21/c	(7) 7a
1∆2⊡	kurnakovite	⟨∆2□⟩	Mg[B ₃ O ₃ (OH) ₅](H ₂ O) ₅	8.3479	10 6068	6 4447	108 891	PT	(8) 7b
1∆2⊡	inyoite	< Δ2]	Ca[B ₃ O ₃ (OH) ₆](H ₂ O) ₄	10.63	12.06	8.405	114 03(8)	P2,/a	(9) 7c
1∆2⊡	meyerhofferite	< <u>∆2</u> □>	Ca[B ₃ O ₃ (OH) ₆](H ₂ O)	6.632(1)	8 337(1)	6 4748(6)	101.97(1)	P1	(10) 7d
1∆2⊡	solongoite		Ca ₂ [B ₃ O ₄ (OH) ₄]Cl	7 955(3)	12.570(5)	7 241(3)	-	P21/b	(11) 7e
1∆2□	Inderborite		CaMg[B ₃ O ₃ (OH) ₅] ₂ (H ₂ O) ₈	12,137(2)	7 433(1)	19,234(3)	90.29(1)	C2/c	(12) 7f
30	nifontovite	⟨3□⟩	Ca ₃ [B ₃ O ₃ (OH) ₆] ₂ (H ₂ O) ₂	13.119(4)	13 445(5)	9.526(3)	-	B2/b	(13) 8a
2∆2□	hydrochlorborite	⟨∆2□)∆	Ca2[B3O3(OH)4][BO(OH)3]CI(H2O)7	22.783(3)	8.745(1)	17,066(1)	96 705(1)	1 2/a	(14) 8b
4🗆	uralborite	(30)	Ca ₂ [B ₄ O ₄ (OH) ₈]	6 927(3)	9 836(3)	12 331(3)	-	P2,/n	(15) 8c
4∆1⊡	sborgite	$\langle 2\Delta\Box\rangle - \langle 2\Delta\Box\rangle$	Na[B ₅ O ₆ (OH) ₄](H ₂ O) ₃	11.119	16 474	13.576	112.83	C2/c	(16) 8d
2∆3⊡	ulexite	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	NaCa[B ₅ O ₆ (OH) ₈](H ₂ O) ₅	8 816(3)	12 870(7)	6.678(1)	109.05(2)	PT	(17) 8e
2∆2⊡	borax	⟨∆2□⟩≖⟨∆2□⟩	Na ₂ [B ₄ O ₅ (OH) ₄](H ₂ O) ₈	11,885(1)	10 654(1)	12 206(1)	106 623(5)	C2/c	(18) 9a
2∆2⊡	tincalconite	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$	Na ₂ [B ₄ O ₅ (OH) ₄](H ₂ O) ₃	11 097(2)	11.097(2)	21 114(4)	-	R32	(19) 9b
2 <u>∆2</u> ⊡	hungchaoite	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$	Mg[B ₄ O ₅ (OH) ₄](H ₂ O) ₇	8 807(1)	10 657(1)	7.897(1)	108 53(1)	PT	(20) 9c
2∆2□	fedorovskite	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$	Ca2Mg2(OH)4[B4O2(OH)2]	8.96(2)	13.15(2)	8,15(1)	-	Pbam	(21) –
2∆2⊡	roweite	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$	Ca2Mn2(OH)4[B4O2(OH)2]	9,057(1)	13 357(2)	8,289(1)	-	Pbam	(22) 9d
3∆3⊡	mcallisterite	$[\varphi]\langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle $	Mg ₂ [B ₆ O ₇ (OH) ₆] ₂ (H ₂ O) ₉	11.549(2)	11,549(2)	35,567(8)		Rāc	(23) 10a
3∆3⊡	aksaite	$[\varphi]\langle \Delta 2\Box\rangle \langle \Delta 2\Box\rangle \langle \Delta 2\Box\rangle $	Mg[B ₆ O ₇ (OH) ₆](H ₂ O) ₂	12 540(6)	24.327(11)	7_480(3)	-	Pbca	(24) 10b
3∆3⊡	rivadavite	$[\phi] \langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle $	Na ₆ Mg[B ₆ O ₇ (OH) ₆] ₄ (H ₂ O) ₁₀	15 870	8 010	22 256	116.43	P2,/c	(25) -
12∆3⊡	ammonioborite	3((2Δ□)-(2Δ□))	(NH ₄) ₃ [B ₁₅ O ₂₀ (OH) ₈](H ₂ O) ₄	25.27	9 65	11.56	94 28	C2/c	(26) 10c

kurchatovite: $\gamma = 78.7(2)^\circ$; pentahydroborite: $\alpha = 111 \cdot 53^\circ$, $\gamma = 72 \cdot 70^\circ$; kurnakovite: $\alpha = 98 \cdot 846^\circ$, $\gamma = 105 \cdot 581^\circ$; meyerhofferite: $\alpha = 90 \cdot 81(1)^\circ$; $\gamma = 86 \cdot 76(1)^\circ$; solongoite: $\alpha = 86 \cdot 18(5)^\circ$; nifontovite: $\gamma = 118 \cdot 40(2)^\circ$; uralborite: $\gamma = 97 \cdot 81(3)^\circ$; ulexite: $\alpha = 90 \cdot 36(2)^\circ$, $\gamma = 104 \cdot 98(4)^\circ$; hungchaoite: $\alpha = 103 \cdot 39(1)^\circ$, $\gamma = 97 \cdot 18(1)^\circ$

(1) Takéuchi (1952), (2) Takéuchi & Kudoh (1975), Hoffman & Armbruster (1995), (3) Yakubovich et al. (1976), (4) Kazanskaya et al. (1977), (5) Genkina & Malinovskii (1983), (6) Dal Negro et al. (1975), (7) Corazza (1976), (8) Corazza (1974), (9) Clark et al. (1964), (10) Burns & Hawthorne (1993b), (11) Yamanova et al. (1977) (12) Burns & Hawthorne (1994o), (13) Simonov et al. (1978), (14) Brown & Clark (1978), (15) Simonov et al. (1977), (16) Merlino & Sartori (1972), (17) Ghose & Clark (1978), (18) Evors & (1977), (12) Levor & Lisensky (1978), (19) Powell et al. (1991), (20) Wan & Ghose (1977), (21) Malinko et al. (1977), (22) Moore & Araki (1974b), (23) Dal Negro et al. (1969), (24) Dal Negro et al. (1971), (25) Dal Negro et al. (1973), (26) Merlino & Sartori (1971)



⊢b sin a -/



⊢-c sinα ---

FIG. 4. The isolated B\$\phi_4\$ polyhedra structures: (a) bandylite,(b) teepleite, (c) frolovite, (d) hexahydroborite, and (e) henmilite.

this class are listed in Table 2; the clusters are illustrated in Figure 5.

 $FBB = 2\Delta:2\Delta$

This *FBB* (Fig. 5a) occurs as an isolated cluster in four minerals. Two minerals of this set have wallpaper structures and show very strong affinities with the *FBB* = $1\Delta:\Delta$ wallpaper structures (Figs. 1, 2). Suanite consists of ribbons of parallel edge-sharing octahedra, four octahedra wide, that extend in the [010] direction and are cross-linked in the (101) plane by [B₂O₅] groups (Fig. 6a). Száibélyite and sussexite are isostructural, and consist of 1×2 ribbons of edge-sharing octahedra that link by sharing vertices to form corrugated sheets of octahedra perpendicular to [100] (Fig. 6b); these sheets are cross-linked into a framework by [B₂O₅] groups.

In kurchatovite, $CaMgB_2O_5$, (MgO_6) octahedra share corners to form a chequerboard pattern resembling a slice through the perovskite structure. These $[MgO_4]$ sheets are linked along [001] by $[B_2O_5]$ groups. One (BO_3) group links to two apical vertices of octahedra from adjacent sheets, and the other (BO_3) group links to two meridional vertices of octahedra from the same sheet (Fig. 6c). Seven-coordinated Ca further links the $[MgO_4]$ sheets to form a fairly dense-packed structure.



FIG. 5. The twelve distinct clusters that occur as FBBs in the finite-cluster borate minerals.

 $FBB = 2\Box:2\Box$

Two minerals contain this FBB (Fig. 5b) as an isolated cluster in their structure. In both cases, two $(B\phi_4)$ groups share a vertex to form a $[B_2O(OH)_6]$ cluster. In pentahydroborite, $Ca[B_2O(OH)_6](H_2O)_2$, there is one unique Ca atom coordinated by one O atom, three (OH) groups and one (H₂O) group. The (Ca ϕ_7) polyhedra share edges to form $[Ca_2\phi_{12}]$ dimers that are crosslinked by $[B_2\phi_7]$ groups to form corrugated sheets parallel to (100) (Fig. 6d). These sheets are linked directly via H-bonds involving the (OH) anions of the pyroborate group and the (H_2O) groups that bond directly to the Ca atoms. In pinnoite, Mg[B₂O(OH)₆], there is one unique Mg atom octahedrally coordinated by O atoms and (OH) groups. The (Mg ϕ_6) octahedra and [B₂ ϕ_7] pyroborate groups cross-link into a framework. Each (OH) ligand of the borate group links directly to one $(Mg\phi_6)$ octahedron (Fig. 6e), and H-bonds to the bridging O anion of adjacent pyroborate groups.

 $FBB = 2\Delta 1 \square : < 2\Delta \square >$

This *FBB* occurs in ameghinite, Na[B₃O₃(OH)₄], as an isolated $<2\Delta\square>$ cluster of the form [B₃O₃(OH)₄] (Fig. 5c). There is one unique Na atom octahedrally coordinated by one O atom and five (OH) groups, and each pair of (Na\u03c6₆) octahedra share an edge to form [Na\u03c6₁₀] dimers. Each (Na\u03c6₆) octahedron links to five $<2\Delta\square>$ clusters to form a framework (Fig. 6f). This framework has a distinctly layered aspect, with sheets at $y \approx \pm \frac{1}{4}$, and extensive H-bonding provides further inter-cluster linkage.

$$FBB = 1\Delta 2 \square :< \Delta 2 \square >$$

There are six finite-cluster structures with this *FBB* (Fig. 5d), which also occurs polymerized into chains (see below). Inderite and kurnakovite are polymorphs of composition $Mg[B_3O_3(OH)_5](H_2O)_5$. In inderite (Fig. 7a), there is one unique Mg site that is coordinated



FIG. 6. Finite-cluster borate structures containing the *FBBs* $2\Delta:2\Delta$, $2\Box 2\Box$ and $2\Delta 1\Box:<2\Delta\Box>:$ (a) suanite, (b) száibélyite, (c) kurchatovite, (d) pentahydroborite, (e) pinnoite, and (f) ameghinite.

by two (OH) groups and four (H₂O) groups. Each $<\Delta 2 \square >$ ring links to one (Mg φ_6) octahedron by sharing two vertices of different (BO₄) groups with an edge of the octahedron; the result is a cluster of composition Mg[B₃O₃(OH)₅](H₂O)₄. These clusters are linked only by H-bonding, both directly *via* the (OH) and (H₂O) ligands of the cluster, and through the single interstitial (H₂O) group. In kurnakovite, there is one unique Mg site octahedrally coordinated by two (OH) groups and four (H₂O) groups. Each $<\Delta 2 \square >$ ring links to two (symmetrically equivalent) (Mg φ_6) octahedra to form chains

that extend parallel to [001] (Fig. 7b); the chain in kurnakovite has the same stoichiometry as the cluster in inderite. Interchain linkage is *via* direct H-bonding and also *via* H-bonding involving the single interstitial (H_2O) group.

In inyoite, Ca[B₃O₃(OH)₅](H₂O)₄, there is one unique Ca atom coordinated by two O atoms, three (OH) groups and three (H₂O) groups. Two (Ca ϕ_8) polyhedra share an edge to form a dimer of composition [Ca₂ ϕ_{14}]. Each $<\Delta 2$]> cluster shares two tetrahedron edges with one (Ca ϕ_8) polyhedron and one tetrahedron vertex with



FIG. 7. Finite-cluster borate structures containing the *FBB* $1\Delta 2:<\Delta 2$: (a) inderite, (b) kurnakovite, (c) inyoite, (d) meyerhofferite, (e) solongoite, and (f) inderborite.

the other $(Ca\phi_8)$ polyhedron of the dimer (Fig. 7c). These clusters are joined solely by H-bonding. In meyerhofferite, $Ca[B_3O_3(OH)_5](H_2O)$, there is one unique Ca atom coordinated by three O atoms, four (OH) groups and one (H₂O) group, and (Ca ϕ_8) polyhedra share edges to form zigzag chains parallel to [001] (Fig. 7d). Each $<\Delta 2\square>$ ring attaches to three (Ca ϕ_8) polyhedra, each of which is adjacent in the same chain. Each (BO₄) tetrahedron shares edges with two different (Ca ϕ_8) polyhedra, and the (BO₃) triangle attaches to a (Ca ϕ_8) polyhedron by corner-sharing (Fig. 7d). There are no interstitial (H₂O) groups, and interchain linkage involves H-bonding directly between the chains. In solongoite, Ca₂[B₃O₄(OH)₄]Cl, there are two unique Ca atoms; one Ca is coordinated by two O atoms, four (OH) groups and two Cl atoms, and the other Ca is coordinated by four O atoms and four (OH) groups. The (Ca ϕ_8) groups polymerize to form sheets of edge-sharing (Ca ϕ_8) polyhedra parallel to (010) (Fig. 7e) that are cross-linked by $<\Delta 2\square$ > rings. Both (BO₄) tetrahedra share edges with the (Ca ϕ_8) polyhedra, and the (BO₃) triangle extends outward from the sheet to link by corner-sharing to the adjacent sheet. Inderborite, CaMg[B₃O₃(OH)₅]₂(H₂O)₆, is the most complex structure of this particular group. The borate tetrahedra of two $<\Delta 2\square$ > rings each share a corner with the $(Mg\phi_6)$ octahedron (Fig. 7f); one tetrahedron shares a non-bridging anion, and both tetrahedra share a bridging anion with a single $(Ca\phi_8)$ polyhedron, forming infinite rods parallel to [001] that cross-link *via* cornersharing between (BO₃) and (Ca\phi_8) groups (Fig. 7f). These sheets are then cross-linked by H-bonding both directly between the sheets and *via* interstitial (H₂O) groups.

$FBB = 3 \square :< 3 \square >$

This *FBB* (Fig. 5e) occurs as isolated clusters in nifontovite, $Ca_3[B_3O_3(OH)_6](H_2O)_2$, and it also polymerizes to form a framework structure in metaborite (see below). In nifontovite, there are two distinct Ca atoms, each of which is [8]-coordinated by O atoms, (OH) groups and (H₂O) groups. The (Ca ϕ_8) polyhedra share edges to form chains extending along [101]. These chains are cross-linked by <3 \Box > rings, which share both edges and corners with (Ca ϕ_8) polyhedra (Fig. 8a), together with a network of H-bonds.

$FBB = 1\Delta 3 \square :< \Delta 2 \square > \square$

This FBB occurs only in hydrochlorborite, Ca₂[B₃O₃ (OH)₄][BO(OH)₃]Cl(H₂O)₇, the only example of a cluster mineral with a decorated $\langle \Delta 2 \rangle$ ring (Fig. 5f). There are two unique Ca atoms, each coordinated by two O atoms, three (OH) groups and three (H_2O) groups. The $(Ca\phi_8)$ polyhedra link to form a four-membered linear cluster, two central polyhedra sharing an edge and the two outer polyhedra linking to the central edge-sharing dimer by corner-sharing. Each (Ca ϕ_8) polyhedron shares two edges with borate tetrahedra of the $<\Delta 2$ ring, and the (BO_3) triangle bridges to an adjacent $(Ca\phi_8)$ polyhedron (Fig. 8b). The resulting structural unit consists of heteropolyhedral chains extending along a. Cross-linkage of these chains occurs via H-bonding, both directly from one chain to another, and also via an interstitial (H₂O) group and a Cl anion that is an acceptor for eight H-bonds.



 $FBB = 4 \square : < 3 \square > \square$

This *FBB* (Fig. 5g) is a $\langle 3] >$ ring decorated with an additional (BO₄) group and occurs only in uralborite, Ca₂[B₄O₄(OH)₈] (Fig. 8c). There are two distinct Ca atoms; one is coordinated by two O atoms and six (OH) groups, and the other is coordinated by three O atoms and five (OH) groups. The (Ca ϕ_8) polyhedra share edges to form dimers that join with the $\langle 3] >]$ decorated rings to form a heteropolyhedral framework. There is extensive H-bonding that further strengthens linkage across the large cavities in the structure.

$FBB = 4\Delta 1 \square : <2\Delta \square > - <2\Delta \square >$

This *FBB* (Fig. 5h) consists of two $<2\Delta$ > rings that link *via* a common (B φ_4) tetrahedron. It occurs as an isolated cluster in sborgite, Na[B₅O₆(OH)₄](H₂O)₃, and also in larderellite, where it polymerizes to form chains. In sborgite, there are two distinct Na atoms: one is coordinated by two (OH) groups and four (H₂O) groups, and the other is coordinated by two (OH) groups, two (H₂O) groups at 2.298 Å and a further two (H₂O) groups at 2.998 Å (Merlino & Sartori 1972). The (Na φ_6) polyhedra and the $<2\Delta$ >– $<2\Delta$ >– clusters link to form a three-dimensional network (Fig. 8d) that is strengthened by extensive H-bonding involving both direct OH...O interaction between borate clusters and interactions involving the (H₂O) group.

$FBB = 2\Delta 3 \square : <\Delta 2 \square > - <\Delta 2 \square >$

This FBB occurs in the finite-cluster mineral ulexite, as well as in polymerized form; chains in probertite and sheets in the structures of tuzlaite and the hilgardite polymorphs (see below). The FBB (Fig. 5i) consists of two $(B\phi_3)$ groups and three $(B\phi_4)$ groups that link by sharing corners to form two $\langle \Delta 2\phi \rangle$ rings that fuse through a common $(B\phi_4)$ group. In ulexite, NaCa[B₅O₆ (OH)₆](H₂O)₅, there is one distinct Ca cation coordinated by three O atoms, three (OH) groups and two (H₂O) groups, and one distinct Na cation coordinated by two (OH) groups and four (H₂O) groups. The (Na ϕ_6) octahedra form edge-sharing $[Na\phi_4]$ chains, and the $(Ca\phi_8)$ polyhedra share edges to form chains, both extending along the c axis (seen end-on in Fig. 8e). These chains link the polyborate anions into sheets parallel to (110), and these sheets are linked via H bonding.

$$FBB = 2\Delta 2\square :<\Delta 2\square > = <\Delta 2\square >$$

The $<\Delta 2$ > ring is the dominant motif for the isolated-ring structures of this class (Fig. 5d) and, in accord with this, also the dominant component for the dimerized-ring structures of this class (Fig. 5j). In addition to five isolated-cluster structures, the *FBB* also polymerizes to form a framework in diomignite. Borax, Na₂[B₄O₅(OH)₄](H₂O)₈, has two distinct Na atoms, each of which is [6]- coordinated by (H₂O) groups. The (Na ϕ_6) polyhedra share edges to form chains that are cross-linked by the $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ clusters into heteropolyhedral sheets parallel to {100} (Fig. 9a). These sheets are linked by an extensive network of H-bonds.

In tincalconite, Na₂[B₄O₅(OH)₄](H₂O)₃, there are three crystallographically distinct Na cations, all of which are in octahedral coordination by (OH) and (H₂O). The octahedra share edges and corners to form a discontinuous sheet parallel to (001) that is linked to adjacent sheets by edge-sharing of octahedra out of the plane of the sheet (Fig. 9b). The resultant framework has large interstices that contain the $<\Delta 2\square>=<\Delta 2\square>$ clusters, and there is no interstitial H₂O. The structure shows prominent compositional layering and has strong affinities with the structure of borax (Fig. 9a). At 20– 25°C and 60% relative humidity, borax and tincalconite convert to one another rapidly and reversibly (Christ & Garrels 1959).

In hungchaoite, Mg[B₄O₅(OH)₄](H₂O)₇, there is one unique Mg atom that is coordinated by one (OH) group and five (H₂O) groups. The resulting (Mg ϕ_6) octahedron links by corner-sharing to a (B ϕ_4) group of a $<\Delta 2$]>= $<\Delta 2$]> cluster (Fig. 9c). The resultant Mg[B₄O₅(OH)₄](H₂O)₅ cluster is neutral, and links to other clusters by direct H-bonding and by a H-bond network involving the two additional interstitial (H₂O) groups.

Fedorovskite, $Ca_2Mg_2(OH)_4[B_4O_7(OH)_2]$, and roweite, $CaMn^{2+}(OH)_4[B_4O_7(OH)_2]$, are isostructural minerals. In roweite, there are three unique Mn atoms; one is coordinated by four O atoms and two (OH) groups, one is coordinated by two O atoms and four (OH) groups, and the third is coordinated by six (OH) groups. The octahedra share *cis* edges to form $[M\phi_4]$ chains that extend along [010], and these chains link together by sharing opposing apical vertices to form an open sheet of octahedra that resembles a distorted $[M\phi_3]$ chequerboard; these sheets are cross-linked by $<\Delta 2\square >= <\Delta 2\square >$ clusters (Fig. 9d) in the [001] direction. There is one unique Ca atom occupying the interstices of this framework; it is coordinated by three O atoms and five (OH) groups.

$$FBB = 3\Delta 3 \Box : [\phi] < \Delta 2 \Box > | < \Delta 2 \Box > | < \Delta 2 \Box > |$$

This *FBB* (Fig. 5k) consists of three $\langle \Delta 2 \Box \rangle$ rings that link to a common central anion through their tetrahedrally coordinated B atoms. It occurs in three isolatedcluster minerals, mcallisterite, aksaite and rivadavite, as well as in polymerized form: chains in aristarainite and sheets in tunellite and nobleite (see below). In mcallisterite, Mg₂[B₆O₇(OH)₆]₂(H₂O)₉, there is one unique Mg cation that is octahedrally coordinated by three (OH) and three (H₂O) groups. This octahedron links to three tetrahedra of the [φ] $\langle \Delta 2 \Box \rangle$ | $\langle \Delta 2 \Box \rangle$ | $\langle \Delta 2 \Box \rangle$ | cluster by sharing corners (Fig. 10a). The resulting



FIG. 9. Finite-cluster borate structures containing the *FBB* $2\Delta 2\square:<\Delta 2\square:<\Delta 2\square::$ (a) borax, (b) tincalconite, (c) hungchaoite, and (d) roweite

 $Mg[B_6O_7(OH)_6]$ finite clusters are linked solely by Hbonding both directly from cluster to cluster and indirectly *via* interstitial (H₂O) groups.

Aksaite, Mg[B₆O₇(OH)₆](H₂O)₂, contains the same Mg[B₆O₇(OH)₆] clusters as mcallisterite, but the lower hydration state (four H₂O as compared to nine H₂O in mcallisterite) indicates a higher connectivity in aksaite than in mcallisterite. In aksaite, the Mg[B₄O₇(OH)₇] clusters link by sharing one vertex between an (Mg ϕ_6) group of one cluster and a (B ϕ_3) group of the next cluster to form chains extending along [001] (Fig. 10b). The chains are linked directly *via* H-bonds; there are no interstitial (H₂O) groups as in mcallisterite.

Complete details of the structure of rivadavite, Na₆Mg[B₆O₇(OH)₆]₄(H₂O)₁₀, are not available, but a preliminary report (Dal Negro & Ungaretti 1973) shows the presence of $[\phi]<\Delta 2\square> |<\Delta 2\square> |<\Delta 2\square> |$ clusters linked into a framework by [6]-coordinated Mg and [6]-coordinated Na, with only one interstitial (H₂O) group present.

$$FBB = 12\Delta 3 \square : 3(\langle 2\Delta \square \rangle - \langle 2\Delta \square \rangle)$$

Ammonioborite, $(NH_4)_3[B_{15}O_{20}(OH)_8](H_2O)_4$, is the only mineral with this very complex *FBB*. Two $<2\Delta$ rings link *via* a common (BO₄) group, and then three of these units link by sharing two triangular vertices to

form a large and very flexible *FBB*, $[B_{15}O_{20}(OH)_8]$ (Fig. 5l). These clusters are linked *via* H-bonding involving interstitial (NH₄) groups, and the complete structure has strong compositional layering (Fig. 10c).

Structures Based on Infinite Chains of Polyhedra

There are seven distinct types of cluster in this class, and these may be divided into six sets: (1) B:B, (2) 3B:<3B>, (3) 5B:<3B>-<3B>, (4) 6B:<3B>-<3B>B, (5) 7B:<3B>-<3B>-<3B>, and (6) $6B:[\varphi]<3B>|<3B>|<3B>|<3B>|<3B>|$. All but one of the sets involve a three-member ring of polyhedra. The minerals in this class are listed in Table 3, and the clusters are illustrated in Figure 11.

 $FBB = 1 \square : \square$

This *FBB* occurs in vimsite, $Ca[B_2O_2(OH)_4]$, as a single (BO₄) group (Fig. 11a) that polymerizes by sharing two vertices with adjacent (BO₄) groups to form a pyroxene-like chain that extends in the [001] direction. These chains are cross-linked into a heteropolyhedral framework by columns of (Ca ϕ_8) polyhedra that also extend parallel to [001] (Fig. 12a).



FIG. 10. Finite-cluster borate structures containing the *FBBs* $3\Delta 3 \square: [\phi] < \Delta 2 \square > | < \Delta 2 \square > | < \Delta 2 \square > | and 12\Delta 3 \square: 3$ (<2 $\Delta \square$): (a) mcallisterite, most BO₃ triangles are unshaded here for clarity, (b) aksaite, and (c) ammonioborite.

а

 $FBB = 1\Delta 2 \square :< \Delta 2 \square >$

This FBB (Fig. 11b) is quite common; it occurs in six finite-cluster structures (above) and in polymerized form as chains in the structures of colemanite, calciborite and hydroboracite (Table 3). In colemanite, Ca[B₃O₄(OH)₃](H₂O), $<\Delta 2\square$ > rings share two vertices between triangles and tetrahedra of adjacent rings to form a chain extending along [100]. There is one unique Ca atom coordinated by eight anions in an irregular dodecahedral arrangement. The (Ca ϕ_8) polyhedra share corners to form chains parallel to [100] (Fig. 12b). The $[Ca\phi_7]$ chains cross-link the borate chains into a heteropolyhedral sheet of composition [Ca₂B₃O(OH)] (H₂O)] parallel to (010). These sheets, seen "edge-on" in Figure 12b, link via corner-sharing between (BO₄) tetrahedra and $(Ca\phi_8)$ dodecahedra, and through an extensive network of H-bonds.

In calciborite, Ca[B₂O₄], $<\Delta 2$ > rings link *via* common (BO₄) groups to form [^[3]B^[4]B φ_4] chains extending along [001] (Fig. 12c). The single Ca atom is coordinated by eight anions in a dodecahedral arrangement, and the resulting (Ca φ_8) polyhedra link to form columns along [001]. Each column of dodecahedra is surrounded by six borate chains, and these link directly to form a heteropolyhedral framework.

Hydroboracite, CaMg[B₃O₄(OH)₃](H₂O)₃, consists of $<\Delta 2$] > rings that link through sharing triangle and tetrahedron vertices to form chains parallel to the *c* direction (Fig. 12d). There is a single Mg cation that is octahedrally coordinated by two (OH) groups and four (H₂O) groups, and the Mg φ_6 octahedra link *via* sharing of *trans* vertices to form an [Mg φ_5] chain, also extending in the *c* direction. Each [Mg φ_5] chain is flanked by two borate chains (Fig. 12d). There is one unique Ca cation coordinated by eight anions in a dodecahedral arrangement. The (Ca φ_8) dodecahedra polymerize to form chains parallel to *c*, and the borate chains link the [Mg φ_5] and [Ca φ_7] chains into a heteropolyhedral framework.

$FBB = 4\Delta 1 \square : < 2\Delta \square > - < 2\Delta \square >$

This FBB (Fig. 11c) consists of pairs of $\langle 2\Delta \Box \rangle$ rings that link through a common (BO₄) group. It is uncommon, and occurs in the finite-cluster mineral sborgite, as well as polymerized to form chains in larderellite. In larderellite, (NH₄)[B₅O₇(OH)₂](H₂O), the *FBBs* link through a triangle vertex to form a complex modulated chain extending along the *b* axis (Fig. 12e); the chain resembles the complex $3\{\langle 2\Delta \Box \rangle - \langle 2\Delta \Box \rangle\}$ cluster in ammonioborite. These chains are linked *via* H-bonds involving interstitial (NH)₄ and (H₂O) groups. From the view in Figure 12e, it appears that individual $\langle 2\Delta \Box \rangle - \langle 2\Delta \Box \rangle$ groups polymerize only by sharing two triangle vertices, but further linkage is provided by H-bonds between the (OH) groups of each (B φ_3) triangle.



FIG. 11. The eight distinct clusters that occur as FBBs in the chain-borate minerals.

$FBB = 2\Delta 3 \square : <\Delta 2 \square > - <\Delta 2 \square >$

This *FBB* (Fig. 11d) consists of two $<\Delta 2 \square >$ rings that link through a shared (B φ_4) tetrahedron. It occurs in the finite-cluster mineral ulexite, and is polymerized to form chains in probertite, sheets in tuzlaite, and frameworks in the hilgardite polymorphs. In probertite, NaCa[B₅O₇(OH)₄](H₂O)₃, the *FBBs* link by sharing a vertex between (B φ_3) and (B φ_4) groups to form an infinite chain extending along [001], with chains adjacent along [010] pointing in opposing directions (Fig. 12f).

The Ca atom is coordinated by five O atoms, three (OH) groups and an (H₂O) group, and the Na atom is coordinated by one O atom, two (OH) groups and three (H₂O) groups. Two (Ca ϕ_9) polyhedra share an edge to form a dimer, and each end of the dimer shares an edge with an (Na ϕ_6) polyhedron to form a large-cation tetramer. These tetramers cross-link the borate chains that weave between them, and this linkage is strengthened by a network of H-bonds involving both (OH) and (H₂O) groups.

TABLE 3. BORATE MINERALS BASED ON INFINTE CHAINS OF BO	D BOA POLYHEDRA
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Polyhedra	Name	Connectivity	Formula	a (Å)	b (Å)	c (Å)	β (°)	Sp. Gr.	Ref.	Fig.
10	vimsite	9	Ca[B ₂ O ₂ (OH) ₄]	10.026(2)	4,440(1)	9 558(3)	-	B2/b	(1)	12a
1∆2□	colemanite	$\left< \Delta 2 \Box \right>$	Ca[B ₃ O ₄ (OH) ₃](H ₂ O)	8,712(2)	11.247(3)	6.091(1)	110,12(2)	P2,/a	(2)	12b
1∆2⊡	calciborite	$\left< \Delta 2 \Box \right>$	Ca[B ₂ O ₄]	8.38	13.82	5.006	-	Pccn	(3)	12c
1∆2□	hydroboracite	$\langle \Delta 2 \alpha \rangle$	CaMg[B ₃ O ₄ (OH) ₃](H ₂ O) ₃	11.769(2)	6.684(2)	8,235(4)	102.59(2)	P2/c	(4)	12d
4∆1⊡	larderellite	$\langle 2\Delta \Box \rangle - \langle 2\Delta \Box \rangle$	(NH ₄)[B ₅ O ₇ (OH) ₂](H ₂ O)	9_47	7.63	11.65	97.08	P2,/c	(5)	12e
2∆3□	probertite	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	NaCa[B507(OH)4](H2O)3	6_588(1)	12.560(2)	13.428(2)	99,97(1)	P2,/c	(6)	12f
3∆2□	ezcurrite	< <u>Δ2</u>]-< <u>2</u>]	Na ₂ [B ₅ O ₇ (OH) ₃](H ₂ O) ₂	8.598(2)	9.570(2)	6 576(2)	107.50(5)	PT	(7)	13a
3∆3□	kaliborite	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle \Delta$	Kmg ₂ H[B ₈ O ₈ (OH) ₅] ₂ (H ₂ O) ₄	18_572(6)	8.466(3)	14.689(5)	100.02(3)	C2/c	(8)	13b
3∆4⊐	kernite	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	Na ₂ [B ₄ O ₆ (OH) ₂](H ₂ O) ₃	7_0172(2)	9 1582(2)	15.6774(5)	108,861(2)	P2,/c	(9)	13c
3∆3⊓	aristarainite	$[\varphi]\langle\Delta2\Box\rangle \langle\Delta2\Box\rangle \langle\Delta2\Box\rangle$	Na2Mg[B808(OH)4]2(H2O)4	18.886(4)	7.521(2)	7_815(1)	97.72(1)	P2,/a	(10)	13d,e

vimsite: γ = 91,32(2)°; ezcurrite: α=102.75(5)°; γ=71.52(5)°

Simonov et al. (1976c), (2) Burns & Hawthorne (1993a), (3) Egorov-Tismenko et al. (1980), (4) Sabelli & Stoppioni (1978), (5) Merlino & Sartori (1969), (6) Menchetti et al. (1982), (7) Cannillo et al. (1973), (8) Burns & Hawthorne (1994e), (9) Cooper et al. (1973), (10) Ghose & Wan (1977)



FIG. 12. Infinite-chain borate structures containing the *FBBs* $1 \square: \square, 1\Delta 2 \square:<\Delta 2 \square>, 4\Delta 1 \square:<2\Delta \square>-<2\Delta \square>, and 2\Delta 3 \square:<\Delta 2 \square>-<\Delta 2 \square>: (a) vimsite, (b) colemanite, (c) calciborite, (d) hydroboracite, (e) larderellite, and (f) probertite.$

$FBB = 3\Delta 2 \square : <\Delta 2 \square > - <2\Delta \square >$

This *FBB* (Fig. 11e) has two different types of rings, $<2\Delta$ > and $<\Delta 2$ > that link through a common tetrahedron. It is a common *FBB* that occurs polymerized to form chains in ezcurrite, as well as sheets in several structures (see below). In ezcurrite, Na₂[B₄O₅(OH)₃] (H₂O)₂, the *FBB* shares two vertices between tetrahedra and triangles of adjacent clusters to form a chain parallel to the *c* axis (Fig. 13a). There are two distinct Na atoms in ezcurrite, one is [6]-coordinated by two O atoms, two (OH) groups and two (H₂O) groups, and one is [7]-coordinated by five O atoms, one (OH) group and one (H₂O) group. Pairs of (Na ϕ_7) polyhedra share an edge to form an [Na₂ ϕ_{12}] dimer, and pairs of (Na ϕ_6)

polyhedra share an edge to form an $[Na_2\phi_{10}]$ dimer. These dimers link by sharing vertices to form chains extending along [111]. The skewed chains link by sharing edges and vertices to form an extremely complex arrangement (Fig. 13a) that is further linked by a network of H-bonds.

$FBB = 3\Delta 3 \square : <\Delta 2 \square > - <\Delta 2 \square > \Delta$

This *FBB* (Fig. 11f) occurs only in kaliborite, KMg₂H[B₆O₈(OH)₅]₂(H₂O)₄, and is a decorated variety of the *FBB* in probertite: two $<\Delta 2\square>$ rings link through a common (B φ_4) group, and an additional (B φ_3) group is attached to a tetrahedron vertex. These clusters link by sharing vertices between triangles and tetrahedra to form convoluted chains extending along [010] (Fig. 13b). The rigidity of the chain is reinforced by $(Mg\phi_6)$ octahedra; each octahedron shares four vertices with borate polyhedra of the chain, the remaining pair of anions being interstitial (H₂O) groups. These heteropolyhedral chains are linked *via* interstitial [8]-coordinated K cations, each of which links to four separate chains. A complex network of H-bonds provides further linkage between the chains.

$$FBB = 3\Delta 4 \square : <\Delta 2 \square > - <\Delta 2 \square > - <\Delta 2 \square >$$

This *FBB* (Fig. 11g) occurs only in kernite, Na₂[B₄O₆(OH)₂](H₂O)₃, and consists of a $<\Delta 2 \square >$ ring that links to form a chain along [010] *via* sharing of a common tetrahedron between adjacent rings. There are two distinct Na sites; Na(1) is coordinated by five O atoms and one (H₂O) group, and Na(2) is coordinated by two O atoms and three (H₂O) groups. All (H₂O) groups are bonded to Na atoms, and the borate chains (Fig. 13c) are linked by both Na atoms and a complex network of H bonds.

$$FBB = 3\Delta 3\Box: [\phi] < \Delta 2\Box > | < \Delta 2\Box > | < \Delta 2\Box > |$$

This *FBB* (Fig. 11h) consists of three $<\Delta 2 \square$ > rings that link to a central anion ([ϕ] in the *FBB* descriptor). It is a common *FBB* that occurs in the isolated-cluster minerals mcallisterite, aksaite and rivadavite, as well as polymerized to form chains in aristarainite and sheets in tunellite and nobleite. This *FBB* polymerizes to other *FBBs* in aristarainite, Na₂Mg[B₆O₈(OH)₄]₂(H₂O)₄, by linkage between (B ϕ_3) and (B ϕ_4) groups to form chains parallel to the *b*-axis (Fig. 13d). These chains are cross-linked into sheets parallel to (001) by (Mg ϕ_6) octahedra (Fig. 13e), and these sheets are linked into a three-dimensional arrangement by (Na ϕ_5) polyhedra and a network of H-bonds.



a $sin\beta$

STRUCTURES BASED ON INFINITE SHEETS OF POLYHEDRA

There are nine distinct types of clusters in this class, and these may be divided into eight sets: (1) 5B:<3B>-<3B>, (2) $6B:[\phi]<3B> | <3B> | <3B> | <3B> | <3B> | , (3) <math>8B:[\phi]$ <3B> | <3

TA

 $<3B> | -[\phi]<3B> | <3B> | <3B> | 2B, (5) 6B:<3B>= <4B>=<3B>, (6) 8B:<6B>=<4B>, (7) 11B:B<3B>-<3B>-<3B>-<3B>-<3B>-<3B>B, and (8) 12B:<12B>. All but one of the sets involve a three-membered ring of polyhedra. The minerals in this class are listed in Table 4, and the clusters are illustrated in Figure 14.$



FIG. 14. The nine distinct clusters that occur as *FBB*s in the sheet-borate minerals.

BLE 4	BORATE MINERALS	BASED ON INFINITE	SHEETS OF BO	3 OR BOA POLYHEDR
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Polyhedra	Name	Connectivity	Formula	a (Å)	b (Å)	c (Å)	β (°)	Sp Gr	Ref.	Fig
3∆2□	biringuccite	(Δ2□)-(2Δ□)	Na ₂ [B ₆ O ₈ (OH)](H ₂ O)	11,1955	6 5607	20.7566	93.891	P2,/c	(1)	15a,b
3∆2⊡	nasinite	(Δ20)-(2Δ0)	Na ₂ [B ₅ O ₈ (OH)](H ₂ O) ₂	12,015(2)	6,518(1)	11,173(1)	-	Pna2,	(2)	15c
3∆2¤,1∆	gowerite	$\langle \Delta 2 \Box \rangle - \langle 2 \Delta \Box \rangle, \Delta$	Ca[B ₅ O ₈ (OH)][B(OH) ₃](H ₂ O) ₃	12,882(4)	16,360(7)	6,558(4)	121_62(5)	P2,/a	(3)	15d
3∆2¤,1∆	veatchite	$\langle \Delta 2 \Box \rangle - \langle 2 \Delta \Box \rangle, \Delta$	$Sr_2[B_5O_8(OH)]_2[B(OH)_3](H_2O)$	20.860(5)	11.738(3)	6,625(2)	92 10(3)	Aa	(4)	15e
3∆2¤,1∆	p-veatchite	$\langle \Delta 2 \Box \rangle - \langle 2 \Delta \Box \rangle, \Delta$	$Sr_2[B_sO_8(OH)]_2[B(OH)_3](H_2O)$	6.70	20.80	6 60	119 25	P2,	(5)	_
3∆2⊡,1∆	volkovskite	$\langle \Delta 2 \Box \rangle \cdot \langle 2 \Delta \Box \rangle, \Delta$	KCa4[B608(OH)]4[B(OH)3]2CI(H2O)4	6.500	23,960	6 620	119.60	<i>P</i> 1	(6)	15f
2∆3⊡	tuzlaite	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	NaCa[B ₆ O ₈ (OH) ₂](H ₂ O) ₃	6.506(1)	13 280(3)	11 462(3)	92 97(2)	P2,/c	(7)	16a,b
3∆3□	nobleite	$[\Phi]\langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle $	$Ca[B_{s}O_{9}(OH)_{2}](H_{2}O)_{3}$	14 56(5)	8.02(2)	9 84(2)	111 8(2)	P2,/a	(8)	-
3∆3⊡	tunellite	$[\Phi]\langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle $	Sr[B ₆ O ₉ (OH) ₂](H ₂ O) ₃	14,415(3)	8.213(1)	9 951(2)	114,05(1)	P2,/a	(9)	16c,d
5∆3□	strontioborite	$[\varphi]\langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle \langle \Delta 2 \Box \rangle 2 \Delta$	Sr[B ₈ O ₁₁ (OH) ₄]	9,909(5)	8,130(10)	7 623(1)	108 4(2)	P21	(10)	16e
8∆6□	ginorite	$[\varphi]\langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle -[\varphi]\langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle \langle\Delta 2\Box\rangle 2\Delta$	Ca ₂ [B ₁₄ O ₂₀ (OH) ₆](H ₂ O) ₆	12.74(1)	14.36(2)	12.82(2)	100 77(3)	P2,/a	(11)	- 1
8∆6□	strontioginorite	$[\varphi]\langle\Delta 2 n\rangle \langle\Delta 2 n\rangle \langle\Delta 2 n\rangle -[\varphi]\langle\Delta 2 n\rangle \langle\Delta 2 n\rangle \langle\Delta 2 n\rangle \Delta 2 n\rangle A n\rangle A$	Sr ₂ [B ₁₄ O ₂₀ (OH) ₆](H ₂ O) ₅	12.817(8)	14,488(8)	12,783(8)	101 42(8)	P2,/a	(11)	17a
2∆4⊡	fabianite	$\langle \Delta 2 \Box \rangle = \langle 4 \Box \rangle = \langle \Delta 2 \Box \rangle$	$Ca_2[B_6O_{10}(OH)_2]$	6.593	10,488	6.365	113.38	P2,/a	(12)	17b
80	johachidolite	(6□)⇒(4□)	Ca ₂ Al ₂ [B ₈ O ₁₄]	7 970	11,722	4.374	-	Cnma	(13)	17c
4∆7⊡	preobrazhenskite	$\Box \langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle \Box$	Mg ₃ [B ₁₁ O ₁₅ (OH) ₈]	16 291(4)	9,181(2)	10 571(2)		Pbcn	(14)	17d
6460	brianroulstonite	<∆□+>=	Ca ₃ [B ₅ O ₆ (OH) ₆](OH)Cl ₂ (H ₂ O) ₈	17_42(4)	8.077(5)	8.665(6)	121,48(7)	Pa	(15)	17e

volkovskite: α = 95.68°, γ = 90.59°

(1) Corazza et al. (1974), (2) Corazza et al. (1975), (3) Konnert et al. (1972), (4) Clark & Christ (1971): (5) Rumanova & Gandymov (1971), (6) Rastsvetaeva et al. (1992), (7) Bermanec et al. (1994), (8) Erd et al. (1961), (9) Burns & Hawthorne (1994a), (10) Brovkin et al. (1975), (11) Konnert et al. (1970a), (12) Konnert et al. (1970b), (13) Moore & Araki (1972b), (14) Burns & Hawthorne (1994b), (15) Grie et al. (1997)

$FBB = 3\Delta 2 \square : <\Delta 2 \square > - < 2\Delta \square >$

This *FBB* (Fig. 14a) has five [1]-coordinated anions, three of which are bonded to ^[3]B and two of which are bonded to ^[4]B. This is a common *FBB* that occurs polymerized to form chains in ezcurrite, as well as sheets in seven minerals. In nasinite and biringuccite, the basic $3\Delta 2$: $<2\Delta$]>- $<\Delta 2$]> *FBB* links to form a sheet by sharing two triangle vertices with two tetrahedron vertices of neighboring *FBBs* and two tetrahedron vertices of neighboring *FBBs* and two tetrahedron vertices with two triangle vertices of neighboring *FBBs* (Fig. 15a). In biringuccite, all the (BO₃) groups not involved with linkage between *FBBs* point one way (Fig. 15b), whereas in nasinite, the corresponding (BO₃) groups point in opposing directions in adjacent *FBBs* (Fig. 15c). Thus, the structural units in nasinite and biringuccite are geometrical isomers (Hawthorne 1983, 1985). There are four independent Na cations in biringuccite, Na₂[B₅O₈ (OH)](H₂O). Two of the independent Na cations are coordinated by eight and seven O and OH anions, respectively, all of which belong to the structural unit; the resultant coordination polyhedra share edges and corners to form chains. The other two Na atoms are coordinated by anions belonging to the structural unit and by interstitial (H₂O) groups, and are [7]- and [6]-coordinated, respectively. Two equivalent [7]-coordinated polyhedra share an edge to form a dimer, and these dimers bridge chains of (Na ϕ_8) polyhedra to form sheets orthogonal to [100]. (Na ϕ_6) polyhedra link these sheets to other chains of (Na ϕ_8)



polyhedra, forming a continuous framework that intercalates the $[B_5O_8(OH)]$ sheets. In nasinite, Na₂ $[B_5O_8$ $(OH)](H_2O)_2$, there are two independent Na cations. both of which are [8]-coordinated and link to interstitial (H_2O) groups. The $(Na\phi_8)$ polyhedra share edges to form a framework that encloses the $[B_5O_8(OH)]$ sheets. The reason for the more complex arrangement of interstitial cations in biringuccite is related to the conformation of the borate sheets. In biringuccite (Fig. 15b), there are two types of interstitial space, one bounded by straight parallel sides and one bounded by zigzag parallel sides. In nasinite (Fig. 15c), there is only one type of interstitial space, bounded by the convoluted surface of the structural unit. Thus in biringuccite, the interstitial space occupied by Na and (H₂O) is far more varied in local environment, accounting for the more complicated array of interstitial species.

$FBB = 3\Delta 2\Box, 1\Delta: <\Delta 2\Box > -< 2\Delta\Box >, \Delta$

This *FBB* consists of two separate (*i.e.*, not linked) units, a sheet that contains a $\langle \Delta 2 \Box \rangle \langle 2 \Delta \Box \rangle$ cluster, and an isolated Δ group. There are four minerals with this combination of two *FBBs*: gowerite, veatchite, pveatchite and volkovskite (Table 4). In gowerite, Ca[B₅O₈(OH)][B(OH)₃](H₂O)₃, the sheet of $\langle \Delta 2 \Box \rangle \rangle$ - $\langle 2\Delta \Box \rangle$ clusters is of the nasinite type (*cf.* Figs. 15c, d). There is one unique Ca site coordinated by nine anions, including one of the three distinct (H₂O) groups. The Ca atoms lie within the plane of the borate sheet (Fig. 15d), and the (Ca ϕ_9) polyhedron shares an edge with the isolated (B ϕ_3) group. The sheets stack along [010] and are linked solely by H-bonding, both directly and *via* the two additional interstitial (H₂O) groups that do not bond directly to any cation.

In veatchite and p-veatchite, Sr₂[B₅O₈(OH)]₂ $[B(OH)_3](H_2O)$, the FBB $<\Delta 2$ $> -<2\Delta$ > connects to form a sheet of the biringuccite type (Fig. 15a), in which the neighboring $\langle \Delta 2 \Box \rangle$ groups within the same sheet point in the same direction, together with an isolated Δ group. In each structure, there are two distinct Sr sites, one of which is [10]-coordinated, and the other of which is [11]-coordinated. The Sr atoms lie in the plane of the borate sheets (Fig. 15e) and link two sheets together to form a thick slab that has the bulk composition of the mineral; these slabs are then linked together by H-bonding. The difference between the structures of veatchite and p-veatchite involves only a slight shift in the relative positions of adjacent sheets (Clark & Christ 1971) that result from the difference in space group: Aa for veatchite (Clark & Christ 1971) and P2 for p-veatchite (Rumanova & Gandymov 1971).

In volkovskite, $KCa_4[B_5O_8(OH)]_4[B(OH)_3]_2$ Cl(H₂O)₄, the structural unit consists of two unconnected parts, a biringuccite-like sheet of $<\Delta 2\square >$ - $<2\Delta\square >$ clusters and an isolated Δ group. This arrangement is somewhat similar to those of veatchite and p-veatchite. However, the Δ groups point in opposing directions in volkovskite (Fig. 15f), whereas they all point the same way in veatchite and p-veatchite (Fig. 15e). The Ca atoms occur in the plane of the sheets of $<\Delta 2$]>- $<2\Delta$]> clusters and link back-to-back sheets into thick slabs (Fig. 15f), as is the case for veachite and p-veatchite. However, the additional K cation is displaced from the plane of the sheet and links adjacent slabs together, supplemented by extensive H-bonding.

$$FBB = 2\Delta 3 \square : <\Delta 2 \square > - <\Delta 2 \square >$$

This FBB (Fig. 14b) occurs in the finite-cluster mineral ulexite, as well as polymerized to form chains in probertite, sheets in tuzlaite, and frameworks in the hilgardite polymorphs. It consists of two $\langle \Delta 2 \Box \rangle$ rings that link together through a common $(B\phi_4)$ group. In tuzlaite, NaCa[B5O8(OH)2](H2O)3, the FBB links to other clusters by sharing triangle vertices with neighboring tetrahedra and tetrahedron vertices with neighboring triangles to form a sheet perpendicular to [001] (Fig. 16a). In addition to the three-membered rings, there are prominent ten-membered rings that consist of alternating corner-sharing tetrahedra and triangles (Fig. 16b). Each ten-membered ring consists of four FBBs, and each FBB links in a topologically unique manner. As there is only one symmetrically unique FBB in the sheet, each FBB must belong to four ten-membered rings, and inspection of Figure 16b shows this to be the case. This topological diversity offers the possibility of extensive geometrical isomerism (Hawthorne 1983) in this particular type of sheet. The sheet is quite corrugated in both the a and b directions, and the corrugations of adjacent sheets intermesh (Fig. 16a). There is one Ca atom, coordinated by six O atoms and two (H₂O) groups, and one Na atom, coordinated by four O atoms and three (H₂O) groups. The (Ca ϕ_8) and (Na ϕ_7) polyhedra share a face to form a dimer, and adjacent dimers link through edge-sharing of like polyhedra to form chains approximately orthogonal to the borate sheets; Na atoms occur close to the plane of the borate sheet (Fig. 16a), whereas Ca atoms occupy a position intermediate between adjacent sheets.

$$FBB = 3\Delta 3\Box : [\phi] < \Delta 2\Box > | < \Delta 2\Box > | < \Delta 2\Box > |$$

This *FBB* (Fig. 14c) is quite common, and occurs in three finite-cluster minerals, as well as in polymerized linkages to form chains in aristarainite and sheets in nobleite and tunellite. Three $\langle \Delta 2 \Box \rangle$ rings link by sharing tetrahedra; each ring shares one tetrahedron with each of the other two rings. This produces a cluster with three triangles and three tetrahedra, and the tetrahedra all link together *via* a common vertex denoted by $[\phi]$ in the designation for the *FBB*. In the isostructural minerals tunellite, Sr[B₆O₉(OH)₂](H₂O)₃, and nobleite, Ca[B₆O₉(OH)₂](H₂O)₃, each *FBB* shares anions with four other *FBB*s, and each of these *FBB*s points in a direction opposite to that of the central *FBB*. This ar-







FIG. 16 Infinite-sheet borate minerals containing the *FBBs* $2\Delta 3$: $\Delta 2$, $\Delta 2$, $\Delta 2$, $\Delta 3$, $\Delta 3$, $\Delta 2$, Δ

rangement results in sheets that contain alternating rows of *FBBs*, with all *FBBs* pointing either up (central row parallel to [001] in Fig. 16c) or down (peripheral rows parallel to [001] in Fig. 16c). Each *FBB* shares two tetrahedron vertices with two *FBBs* on one side, and two triangle vertices with two *FBBs* on the other side. This leaves vertices of one triangle and one tetrahedron that do not bridge between borate polyhedra. There is one unique Sr position that is coordinated by ten anions. The Sr cations are centered in the holes of the borate sheet (Fig. 16d) and do not link adjacent sheets directly. The linkage between adjacent sheets occurs *via* Sr–(H₂O)– Sr vertex-sharing, together with a network of H-bonds involving both (OH) and (H₂O) groups.

$FBB = 5\Delta3\Box: [\phi] < \Delta2\Box > | < \Delta2\Box > | < \Delta2\Box > | 2\Delta$

This *FBB* (Fig. 14d) occurs only in strontioborite, Sr[B₈O₁₁(OH)₄], although it is similar to the *FBB* in tunellite and nobleite, and the finite-cluster minerals mcallisterite, aksaite and rivadavite. Three $<\Delta 2$]> rings link by sharing tetrahedra. Each ring shares one tetrahedron with the adjacent two rings, producing a cluster of three triangles and three tetrahedra in which the three tetrahedra link together *via* a common vertex, as is the case for the *FBB* in tunellite and nobleite (Fig. 14c). However, the *FBB* in strontioborite is decorated with a 2Δ cluster, a [B₂O₅] pyro-group similar to those found in the finite-cluster minerals suanite, száibélyite, sussexite and kurchatovite (Fig. 14d). The linkage of *FBBs* to form a sheet (Fig. 16e) is similar to that in tunellite (Fig. 16c). The strontioborite sheet shows the same alternating rows of *FBB* pointing in different directions (compare Figs. 16c, e), but this feature is exaggerated in strontioborite by the decoration of the sheet by the 2Δ cluster. The Sr cation is centered (in projection) in the holes of the borate sheet (Fig. 16e), and adjacent sheets are linked by Sr cations and by a network of H-bonds.

$$FBB = 8\Delta6\square: [\phi] < \Delta2\square > | < \Delta2\square > | < \Delta2\square > | -[\phi] < \Delta2\square > | < \Delta2\square > | < \Delta2\square > | 2\Delta$$

The isostructural minerals ginorite, $Ca_2[B_{14}O_{20}(OH)_6](H_2O)_5$, and strontioginorite, $Sr_2[B_{14}O_{20}(OH)_6](H_2O)_5$, have this *FBB*, which combines the *FBB* in nasinite and strontioborite, a $[\phi]<\Delta 2\square> |<\Delta 2\square> |<\Delta$

1970), there are two distinct sites, one of which is occupied by Sr and the other of which is occupied by Ca. Sr is coordinated by six O atoms, two (OH) groups and two (H₂O) groups; Ca is coordinated by six O atoms, one (OH) group and one (H₂O) group. The Sr and Ca atoms are arranged in planes parallel to {010}, but do not link together directly; they bond to the FBBs to form very complex heteropolyhedral sheets parallel to {010} (Fig. 17a). These sheets are cross-linked solely by Hbonding; note that two (H₂O) groups do not link directly to any cations, but do play an important role in the Hbond network.

$FBB = 2\Delta 4 \square : <\Delta 2 \square > = <4 \square > = <\Delta 2 \square >$

This FBB (Fig. 14f), known only in fabianite, Ca₂[B₆O₁₀(OH)₂], consists of a four-membered ring of tetrahedra, $<4\square>$, that shares two *trans* edges with two three-membered rings, $\langle \Delta 2 \square \rangle$; the resulting cluster consists of four tetrahedra and two triangles. These clusters link by sharing two tetrahedron and two triangle vertices with adjacent clusters to form a sheet (Fig. 17b). The sheet is corrugated, and linkage of the FBBs produces ten-membered borate rings. There is one distinct Ca atom that is coordinated by six O atoms and two (OH) groups. The (Ca ϕ_8) polyhedra share edges to form chains that extend along [100]. Rows of these chains occur between the borate sheets and bind them in stacks along [001], with additional inter-sheet linkage from Hbonds involving the OH anion.

$FBB = 8 \square : <6 \square > = <4 \square >$

Johachidolite, Ca₂Al₂[B₆O₁₄], is the only mineral that contains this FBB, which consists of a six-membered ring of tetrahedra that shares an edge with a fourmembered ring of tetrahedra (Fig. 14g). The FBBs link by sharing edges between the six-membered rings and between the six- and four-membered rings, and by sharing vertices between six-membered rings and between four-membered rings (Fig. 17c) to form a sheet parallel to (001). The Al atom is centered in the four-membered ring and has octahedral coordination, and the Ca atom is centered in the six-membered ring and has [8]-coordination. Adjacent sheets are linked via both Al and Ca atoms.



FIG. 17. Infinite-sheet borate minerals containing the FBBs $8\Delta 6 : [\phi] < \Delta 2 : | < \Delta 2 : | < \Delta 2 : | - [\phi] < \Delta 2 : |$ $<\Delta 2 \square > | <\Delta 2 \square > | 2\Delta, 2\Delta 4 \square : <\Delta 2 \square > = <4 \square > = <\Delta 2 \square >,$ $8 \square: <\!\! 6 \square\!\! > = <\!\! 4 \square\!\! >, \ 4 \Delta 7 \square: \square <\!\! \Delta 2 \square\!\! > -\!\! <\!\! <\!\! \Delta 2 \square\!\! > -\!\! <\!\! <\!\! \Delta 2 \square\!\! > -\!\! <\!\! <\!\! <\!\! \Delta 2 \square\!\! > -\!\! <\!\! <\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! > -\!\! <\!\! <\!\! > -\!\! <\!\! <\!\! >$ $<\Delta 2 \square > \square$, and $6\Delta 6 \square :< \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square > :$ (a) strontioginorite, (b) fabianite, (c) joachidolite, (d) preobrazhenskite, and (e) brianroulstonite.

$$FBB = 4\Delta7 \square: \square < \Delta2 \square > - < \Delta2 \square > - < \Delta2 \square >$$

Preobrazhenskite, Mg₃[B₁₁O₁₅(OH)₉], is the only mineral that contains this *FBB*. It consists of four threemembered $<\Delta 2 \square$ > rings, each of which links to one or two other rings *via* a common tetrahedron. The resulting arrangement is topologically linear, although the terminal ([1]-connected) rings are joined *via* a symmetrical H-bond, and this tetrameric group is decorated by the addition of a tetrahedron at each end (Fig. 14h). The *FBB* clusters link by sharing corners between triangles and tetrahedra to form a corrugated borate sheet parallel to (010) (Fig. 17d). There are two distinct Mg sites, each of which is octahedrally coordinated by both O and (OH) anions and links the sheets into a strongly bonded arrangement that is reinforced by extensive Hbonding,

$FBB = 6\Delta6\square: <\Delta\square\Delta\square\Delta\square\Delta\square\Delta\square\Delta\square>$

Brianroulstonite, $Ca_3[B_5O_6(OH)_6](OH)Cl_2(H_2O)_8$, is the only sheet mineral that contains this *FBB* (which also occurs in the framework minerals pringleite, ruitenbergite and penobsquisite). The *FBB* consists of a twelve-membered ring of alternating triangles and tetrahedra (Fig. 14i) that may be written in condensed form as $6\Delta 6 \square :< \Delta \square \bullet >$. The *FBB* clusters meld to form a sheet of twelve-membered rings, the centers of which define a 3^6 net (Fig. 17e). These sheets are linked through H-bonding, Ca and Cl atoms to form a sheet structure. The decorated sheets of the related framework borates form frameworks because the decorations (three-membered borate rings) promote direct linkage of the sheets to form frameworks.

STRUCTURES BASED UPON FRAMEWORKS OF POLYHEDRA

There are fifteen species (Table 5) that are based upon frameworks of borate polyhedra. There are seven distinct clusters that form *FBBs* (Fig. 18), and these may be divided into the following seven sets: (1) 3B:<3B>, (2) 4B:<3B>=<3B>, (3) 5B:<3B>-<3B>, (4) $4B:[\phi] B | B | B | B |, (5) 7B:[\phi]<3B> | <3B> | <3B> | <3B> | B, (6) 15B:<B•>=<3B>A, and (7) 16B:<B•> = <3B>-<3B>.$

$$FBB = 3 \square : < 3 \square >$$

Metaborite, $[B_3O_3(OH)_3]$, is the only framework mineral with this FBB. The structure is based upon the *FBB* 3::<3::>> (Fig. 18a), which also occurs in the



FIG. 18. The seven distinct clusters that occur as FBBs in the framework-structure borate minerals.

TABLE 5. BORATE MINERALS BASED ON INFINITE FRAMEWORKS OF BO3 OR BO4 POLYHEDRA

Polyhedra	Name	Connectivity	Formula	a (Å)	b (Å)	c (Å)	β (°)	Sp. Gr.	. Ref.	Fig.
30	metaborite	(3□)	B ₃ O ₃ (OH) ₃	8,886(1)		4	-	P43n	(1)	-
2 <u>0</u> 20	diomignite	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$	Li₂[B₄O ₇]	9.47	9.47	10.26	-	I4,cd	(2)	19a
2∆3□	hilgardite-1A	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	Ca ₂ [B ₅ O ₃]Cl(H ₂ O)	6.452(1)	6.559(1)	6,286(1)	118.72(1)	Pl	(3)	19b
2∆3□	hilgardite-4M	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	Ca ₂ [B ₅ O ₉]Cl(H ₂ O)	11.438(2)	11,318(2)	6.318(1)	90,06(1)	Aa	(4)	_
2∆3□	hilgardite-3A	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	Ca ₆ [B ₅ O ₉] ₃ Cl ₃ (H ₂ O) ₃	17.495(4)	6.487(1)	6,313(1)	79,56(1)	<i>P</i> 1	(5)	-
2∆3□	tyretskite-1A	$\langle \Delta 2 \Box \rangle - \langle \Delta 2 \Box \rangle$	Ca ₂ [B ₅ O ₉](OH)(H ₂ O)	6.44	6.45	6.41	60.3	-	(6)	-
1∆6⊡	boracite (low)	[φ]⟨3□⟩ ⟨3□⟩ ⟨3□⟩ ∆	Mg ₃ [B ₆ O ₁₀][BO ₃]Cl	8.5496	8.5496	12.0910(9)	-	Pca2,	(7)	19c
1∆6□	chambersite	[φ]⟨3□⟩ ⟨3□⟩ ⟨3□⟩ Δ	Mn ₃ [B ₆ O ₁₀][BO ₃]Cl	8.68(1)	8.68(1)	12,26(1)	-	Pca2	(8)	_
1∆6□	congolite	[∲](3¤) (3¤) (3¤) ∆	Fe ₃ [B ₆ O ₁₀][BO ₃]Cl	8.622(1)	8,622(1)	21.054(5)	-	R3c	(7)	-
1∆6□	ericaite	$[\![\varphi]\!\langle 3\Box\rangle \langle 3\Box\rangle \langle 3\Box\rangle \Delta$	Fe ₃ [B ₆ O ₁₀][BO ₃]Cl	8.58	8.65	12.17	-	Pca2,	(9)	-
1∆6□	trembathite	[φ]⟨3□⟩ ⟨3□⟩ ⟨3□⟩ ∆	Mg ₃ [B ₆ O ₁₀][BO ₃]Cl	8.588(2)	8.588(2)	21,050(6)	-	R3c	(10)	-
40	boracite (high)	[þ]¤ ¤ ¤	Mg _a [B ₇ O ₁₃]Cl	12.0986(2)	a	a	-	F43c	(11)	-
7∆8□	pringleite	$\langle \Delta \Box \bullet \rangle = \langle \Delta 2 \Box \rangle \Delta$	Ca ₉ [B ₂₀ O ₂₈ (OH) ₁₈][B ₈ O ₆ (OH) ₆]Cl ₄ (H ₂ O) ₁₃	12.746(2)	13.019(3)	9.693(2)	102,1(2)	<i>P</i> 1	(12)	19ď
7∆8□	ruitenbergite	$\langle \Delta \Box \bullet \rangle = \langle \Delta 2 \Box \rangle \Delta$	Ca ₉ [B ₂₀ O ₂₈ (OH) ₁₈][B ₈ O ₈ (OH) ₈]Cl ₄ (H ₂ O) ₁₃	19.857(7)	9.708(4)	17,522(6)	114.68(3)	P2,	(12)	-
8∆8□	penobsquisite	<Δ□•>=<Δ2□><Δ2□>	Ca ₂ Fe[B ₉ O ₁₃ (OH) ₈]Cl(H ₂ O) ₄	11.63(4)	9,38(1)	8,735(9)	98.40(7)	P21	(13)	19e

metaborite: α =92.58°, γ =119.83°; hilgardite-1A: α =61_60(1)°, γ =105.86(1)°; hilgardite-3A: α =60.77(1)°, γ =83.96(1)°; tyretskite-1A: α = 61_8°, γ = 73.5°; pringleite: α =102.2(2)°, γ =85.6(1)°

(1) Zachariasen (1963), (2) Krogh-Moe (1962), (3) Burns & Hawthorne (1994d), (4) Ghose & Wan (1979), (5) Wan & Ghose (1983), (6) Kondrat'eva (1964), Ghose (1985), (7) Wendling et al. (1972), (8) Honea & Beck (1962), (9) Kühn & Schaacke (1955), (10) Burns et al. (1992), Schindler & Hawthorne (1998), (11) Sueno et al. (1973), (12) Grice et al. (1994), (13) Grice et al. (1996)

structure of nifontovite, and in decorated form in the structure of uralborite. The structure of metaborite is a simple ${}^{[4]}T\phi_2$ framework in which the B is [4]-coordinated and the anions are [2]-coordinated. However, there is extensive hydrogen bonding present that provides further linkage between the framework anions and that satisfies their local bond-valence requirements.

$FBB = 2\Delta 2\Box : <\Delta 2\Box > = <\Delta 2\Box >$

Diomignite, $Li_2B_4O_7$, is a rare anhydrous borate that has only been identified as a daughter mineral in a fluid inclusion in spodumene (London et al. 1987). The structure of diomignite contains the *FBB* $2\Delta 2\square :<\Delta 2\square >=$ $<\Delta 2$ (Fig. 18b), which also occurs in a hydrated form in the finite-cluster minerals borax, tincalconite, hungchaoite, fedorovskite and roweite. The energetics of borate clusters with the general form 4B:<3B>=<3B> were investigated by Burns (1995); the $2\Delta 2 \square :< \Delta 2 \square >=$ $<\Delta 2 \square > FBB$ was found to be the most stable owing to local bonding constraints. In the structure of diomignite, the *FBB*s polymerize such that each $(B\phi_3)$ group shares an anion with a $(B\phi_4)$ group of an adjacent FBB, resulting in a framework structure that is composed of two interlocking networks of polmerized FBBs (Fig. 19a). Additional bond-valence requirements of the anions are met by bonds to Li cations, which occur coordinated by six anions in voids in the framework.

$FBB = 2\Delta 3 \square : <\Delta 2 \square > - <\Delta 2 \square >$

Four minerals contain this *FBB*, the three polymorphs of hilgardite, $Ca_2[B_5O_9]Cl(H_2O)$, and tyretskite,

 $Ca_2[B_5O_9]OH(H_2O)$, which is isostructural with hilgardite-1A. The borate FBB (Fig. 18c) is anhydrous in all four structures, in which it occurs in two distinct stereo-isomers. Note that hydrated versions of this FBB occur in the structures of ulexite, probertite and tuzlaite. The structures of the hilgardite polymorphs and tyretskite consist of open zeolite-like borate frameworks, with Cl and OH⁻ anions and H₂O groups occurring in open channels in the structures (Fig. 19b). A detailed discussion of the stereochemistry of these structures is given by Ghose (1982). In brief, the FBBs link by sharing $(B\phi_4)$ corners to form chains that extend along the c axis; each chain connects to adjacent chains by sharing corners between a $(B\phi_3)$ group of one chain and a $(B\phi_4)$ group of the adjacent chain. This connectivity results in a framework structure with open channels parallel to the a, b and c axis, with channel diameters of up to ~ 6 Å (Ghose & Wan 1979). The frameworks of the three polymorphs of hilgardite are distinct in the orientation of the $(\mathbf{B}\phi_3)$ groups along the *a* and *b* axes; otherwise, the frameworks are very similar.

 $FBB = 4 \square : [\phi] \square | \square | \square | \square | \square$ and $\Delta 6 \square : [\phi] < 3 \square > | < 3 \square > | < 3 \square > | \Delta$

Boracite-group minerals are the naturally occurring subset of the boracite-type phases that have the general formula $M_3B_7O_{13}X$, where *M* is a divalent metal (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd), and *X* is a halogen atom (Cl, Br, I). Boracite-type phases have been prepared synthetically and extensively studied, owing to the ferroelastic, ferroelectric and magnetic properties of the crystals (*e.g.*, Nelmes 1974, Schmid & Tippmann 1978,



(b) hilgardite-1A, (c) low boracite, (d) pringleite, and (e) penobsquisite.

Tolédano *et al.* 1985, Moopenn & Coleman 1990, Crottaz *et al.* 1995). There are five boracite-group minerals; all contain Cl as the halogen, and the divalent metals are Mg, Fe and Mn.

The four boracite-group minerals boracite, $Mg_3B_7O_{13}Cl$, trembathite, $(Mg,Fe)_3B_7O_{13}Cl$, congolite, $(Fe,Mg)_3B_7O_{13}Cl$, and ericaite, $(Fe,Mg)_3B_7O_{13}Cl$, are each members of a complete $Mg_3B_7O_{13}Cl$ – $Fe_3B_7O_{13}Cl$ solid-solution series. Chambersite, $Mn_3B_7O_{13}Cl$, is the fifth boracite-group mineral. Only very limited solid-solution occurs between chambersite and the Mg–Fe boracite-group minerals. Boracite, ericaite and chambersite have structures with orthorhombic symmetry (space group *Pca2*₁), whereas the structures of trembathite and congolite have rhombohedral symmetry (space group *R3c*). The phase relations in the series boracite – trembathite – congolite have been reported by Burns & Carpenter (1996) (Fig. 20). At 25°C, the

orthorhombic boracite structure ($Pca2_1$) is stable for compositions from Mg₃B₇O₁₃Cl to Mg₁₉Fe₁₁B₇O₁₃Cl, and the rhombohedral congolite structure (R3c) occurs for compositions ranging from Mg_{1.9}Fe₁ 1B₇O₁₃Cl to Fe₃B₇O₁₃Cl. Ericaite (Fe > Mg, $Pca2_1$) does not occur at room temperature.

The crystal structures of all boracite-group minerals have cubic symmetry (space group F3c) at high temperature (Burns & Carpenter 1996, 1997). The structure of cubic boracite (Ito *et al.* 1951, Sueno *et al.* 1973) consists of a framework of corner-sharing BO₄ tetrahedra, with the metal and halogen atoms located within cavities in the borate framework. The *FBB* for this structure is $4\Box:[\phi] \Box | \Box | \Box | \Box |$, indicating that a central oxygen atom is connected to four BO₄ tetrahedra (Fig. 18e). This situation is very unusual; cubic boracite is the only known structure that contains an oxygen atom [O(1) using the notation of Sueno *et al.* 1973] that is



FIG. 20. The stability of the boracite – trembathite – congolite series as a function of temperature (from Burns & Carpenter 1996).

bonded to four boron atoms. The O(1) atom is located on a site with 23 point symmetry, and in cubic boracite each of the four B(3)–O(1) bond-lengths is 1.693(5) Å (Sueno et al. 1973), a value considerably longer than $<^{[4]}B-O> = 1.476$ Å found in minerals (Hawthorne et al. 1996). Significant anisotropic thermal motion of the B(3) and O(1) atoms, most likely about single potential-energy minima, is observed by diffraction techniques. An infrared spectroscopic study of crystals in the series Mg₃B₇O₁₃Cl-Fe₃B₇O₁₃Cl suggests that there are BO3 triangles locally present in the structure (Burns & Carpenter 1997), in contrast to the long-range structure obtained using diffraction techniques. The metal site is coordinated by six ligands; four equidistant equatorial oxygen atoms and two equidistant halogen atoms in a trans arrangement.

For all boracite-group minerals, cooling of the cubic structure results in a phase transition, or a series of phase transitions, to a structure with lower symmetry (Fig. 20).

Evidence that crystals have undergone these phase transitions may be present as transformation-induced twins and anomalous optical properties. In the low-temperature structures, the O(1) position is bonded to three boron atoms only, and the borate framework contains both BO₄ tetrahedra and BO₃ triangles (Fig. 18d). The borate *FBB* of both the *Pca2*₁ and *R3c* structures is $\Delta 6 \square : [\phi] < 3 \square > | < 3 \square > | < 3 \square > | \Delta$ (Fig. 19c). The *Pca2*₁ and *R3c* structures contain three and one symmetry-distinct metal sites, respectively. In each case, the coordination geometry of the cation is significantly distorted from the arrangement of the cubic structure.

$FBB = 7\Delta 8 \square : <\Delta \square > = <\Delta 2 \square > \Delta$

Pringleite and ruitenbergite are dimorphs of $Ca_9[B_{20}O_{28}(OH)_{18}][B_6O_6(OH)_6Cl_4(H_2O)_{13}$; together with penobsquisite (below), these borates display a new level of structural complexity in borate minerals. These

structures have borate frameworks that are remarkably open and that resemble aluminosilicate zeolites, raising the possibility of using borates in technological applications. To date, these extraordinary zeolite-like borates are only known from the marine-evaporite-hosted borate deposits of Sussex, New Brunswick (Roberts *et al.* 1993, Grice *et al.* 1996).

The structures of pringleite and ruitenbergite are closely related; each contains the unusually large FBB $7\Delta 8 := <\Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box > = <\Delta 2 \Box > \Delta$ (abbreviated $7\Delta 8 :< \Delta \square = < \Delta 2 \square > \Delta$). The *FBB* contains a 12-membered ring of alternating $(B\phi_3)$ and $(B\phi_4)$ groups that share corners, with one of the $(B\phi_4)$ tetrahedra also a component of a $<\Delta 2\square$ > ring that is in turn decorated with a single $(B\phi_3)$ group (Fig. 18f). These large FBBs are connected by sharing corners through the $<\Delta 2 \square > \Delta$ component of the FBB, resulting in an open framework with channels along c and [110] (Fig. 19d) (Grice et al. 1994). The Ca cations are located in these channels, along with Cl- anions and H2O groups. Of these, some H₂O groups bond directly to Ca, others are only connected to the structure through hydrogen bonds. Each of the Cl- anions is held in place in the channels by hydrogen bonds only. The distinction between pringleite and ruitenbergite involves subtle variations in the mode of polymerization of the FBBs (Grice et al. 1994).

 $FBB = 8\Delta 8 \square : <\Delta \square > = <\Delta 2 \square > - <\Delta 2 \square >$

Penobsquisite, Ca₂Fe[B₉O₁₃(OH)₆]Cl(H₂O)₄, is the third zeolite-like borate to be discovered from the marine-evaporite-hosted borate deposits in Sussex, New Brunswick; the others are pringleite and ruitenbergite (above). The structure of penobsquisite contains the $FBB \ 8\Delta 8 \square :< \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square > - < \Delta 2 \square > <\Delta 2 \square >$ (Grice *et al.* 1996). The *FBB* $6\Delta 6 \square :<\Delta \square \bullet >$ is a twelve-membered ring of alternating, corner-sharing $(B\phi_3)$ and $(B\phi_4)$ groups (Fig. 18g), and also occurs as a component of the larger FBB of the structures of pringleite and ruitenbergite. In the penobsquisite structure, the $6\Delta 6 \square :< \Delta \square \bullet >$ are connected to form sheets of 12-membered rings parallel to (100) at height a/2, whereas the $2\Delta 3 \square :< \Delta 2 \square > -< \Delta 2 \square > FBBs$ share corners to form crankshaft chains along c at height a = 0(Fig. 19e). The sharing of corners between the layer of $6\Delta 6 \square :< \Delta \square \bullet >$ at a/2 and the chains of $2\Delta 3 \square :< \Delta 2 \square > <\Delta 2$ > at height a = 0 results in an open, zeolite-like framework. The Ca and Fe cations occur in channels in the borate framework, the single Cl⁻ anion bonds to Fe and accepts hydrogen bonds, some H₂O groups are bonded to Ca or Fe, and two H2O groups are only hydrogen-bonded in the structure.

SUMMARY

Ninety-eight borate minerals have been arranged in a structural hierarchy based on the characteristics of

polymerization of their constituent (BO_3) and (BO_4) tetrahedra. There is a tendency for structure types to adopt a simple pattern of polymerization, and there is only significant isotypism among minerals based on isolated (BO_3) and (BO_4) groups. The hierarchy developed here should be of importance in interpreting the chemical and paragenetic features of borate minerals.

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