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A BOND-VALENCE APPROACH TO THE STRUCTURE, CHEMISTRY AND PARAGENESIS OF HYDROXY-HYDRATED OXYSALT MINERALS.
II. CRYSTAL STRUCTURE AND CHEMICAL COMPOSITION OF BORATE MINERALS

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ABSTRACT

The crystal structures and chemical compositions of hydroxy-hydrated borate oxysalt minerals are interpreted in terms of the bond-valence approach to the structure and chemistry of oxysalts developed by Schindler & Hawthorne (2001). The grand mean Lewis basicity of structural units in hydroxy-hydrated borate minerals is 0.21 *vu*. For stable structures to occur, the Lewis acidities of the interstitial complexes must match this value on average. Hence the percentage of transformer (H_2O) groups in borate minerals is strongly positively correlated with the Lewis basicity of the interstitial cation(s), a direct result of the valence-matching principle. Thus on average, interstitial Mg must bond to transformer (H_2O) groups, whereas interstitial Na will not bond to transformer (H_2O) groups. Detailed predictions of the compositions of interstitial complexes are developed for the structural units $[B_3\,O_3\,(OH)_5]^{2-}$, $[B_4\,O_5\,(OH)_4]^{2-}$ and $[B_6\,O_7\,(OH)_6]^{2-}$, and these predictions are in accord with the chemical compositions of inderite, inderborite, inyoite, meyerhofferite, tincalconite, borax, hungchaoite, rivadavite, mcallisterite, admontite and aksaite. General predictions for Cl-free hydroxy-hydrated borate minerals lead to accurate prediction of coordination number of interstitial cations in 90% of the minerals, and 95% have the observed amount of transformer (H_2O) groups within the predicted range for each mineral. This agreement between the predicted and observed values suggests that the general argument developed by Schindler & Hawthorne (2001) is physically realistic and should be applicable to oxysalt minerals in general.

Keywords: bond-valence theory, structural unit, interstitial complex, valence-matching principle, borate minerals, acidity, basicity.

SOMMAIRE

Nous interprétons la structure cristalline et la composition chimique de minéraux boratés hydroxy-hydratés en évaluant les valences de liaison, tel que proposé par Schindler et Hawthorne (2001). La basicité moyenne globale d'unités structurales des minéraux boratés hydroxy-hydratés est égale à 0.21 unités de valence. Pour qu'une structure stable puisse se former, l'acidité de Lewis des complexes interstitiels doit correspondre à cette valeur, en moyenne. La proportion de groupes (H_2O) dits transformateurs dans les minéraux boratés doit donc montrer une forte corrélation positive avec la basicité de Lewis des cations interstitiels, ce qui découle directement du principe de correspondance des valences. En moyenne, le Mg interstitiel doit donc entrer en liaison avec des groupes (H_2O) transformateurs, alors que le Na interstitiel ne pourrait former de telles liaisons. Nous faisons des prédictions détaillées à propos de la composition des complexes interstitiels pour le cas des unités structurales $[B_3\,O_3\,(OH)_5]^{2-}$, $[B_4\,O_5\,(OH)_4]^{2-}$ et $[B_6\,O_7\,(OH)_6]^{2-}$, qui s'avèrent en accord avec la composition chimique des minéraux indérite, inderborite, inyoïte, meyerhofferite, tincalconite, borax, hungchaoïte, rivadavite, mcallisterite, admontite et aksaïte. Des prédictions générales dans le cas des minéraux boratés hydroxy-hydratés sans chlore mènent à une prédiction juste de la coordinence des cations interstitiels dans 90% des minéraux traités, et 95% possèdent un nombre observé de groupes (H_2O) jouant le rôle de transformateur à l'intérieur de l'intervalle prédit pour chaque minéral. D'après cette concordance entre valeurs prédites et observées, l'argument général développé par Schindler et Hawthorne (2001) serait physiquement réaliste et généralement applicable aux minéraux oxysels.

(Traduit par la Rédaction)

Mots-clés: théorie des valences de liaison, unité structurale, complexe interstitiel, principe de la correspondance des valences, minéraux boratés, acidité, basicité.

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INTRODUCTION

Schindler & Hawthorne (2001) have interpreted aspects of the chemical composition of oxysalt minerals on the basis of the *binary structural representation* approach of Hawthorne (1990, 1992, 1994, 1997). A mineral structure is divided into two parts, a *structural unit* and an *interstitial complex*. The structural unit is a (usually anionic) array of strongly bonded polyhedra, and is characterized by its Lewis basicity. The interstitial complex is an array of large low-valence cations, (usually) monovalent anions and (H_2O) groups, and is characterized by its Lewis acidity. The interaction between these two units is subject to the valence-matching principle (Brown 1981); for a structural arrangement to be stable, the Lewis acidity and basicity of the constituent parts must match. The roles of (H_2O) groups are of particular importance in understanding the interaction of the interstitial complex with the structural unit, and (H_2O) groups play a key role in moderating the Lewis acidity of the interstitial complex such that it matches with the Lewis basicity of a specific structural unit. The Lewis acidity of a generalized interstitial complex $\{^{[m]}M^{+}_{a}\ ^{[n]}M^{2+}_{b}\ ^{[l]}M^{3+}_{c}\ (H_2O)_d\ (H_2O)_e\ (OH)_f\ (H_2O)_g\}^{(a+2b+3c-f)+}$ can be expressed graphically as a function of charge and coordination number of the cation and the number of *transformer* (H_2O) groups (Schindler & Hawthorne 2001). A specific structural unit can exhibit a range of Lewis basicity *via* changes in the coordination numbers of its simple anions. Where the Lewis acidity of the generalized interstitial complex overlaps the range of Lewis basicity of a specific structural unit, a stable structure can occur. Here, we examine the structures and chemical compositions of the borate minerals using this approach.

Hawthorne *et al.* (1996) and Grice *et al.* (1999) developed a hierarchy of structures of borate minerals. They divided the borate minerals into two major groups: (a) borates with exclusively ($B\phi_3$) and ($B\phi_4$) oxyanions, and (b) mixed oxyanion borates, in which ($B\phi_3$) and ($B\phi_4$) polyhedra occur with (SiO_4), (SO_4), (PO_4), (BeO_4), (CO_3) or (AsO_4) anion groups. Here, we consider borate minerals with only ($B\phi_3$) and ($B\phi_4$) as oxyanions. Table 1 lists selected borate minerals with

TABLE 1. COMPOSITION OF BORATE MINERALS: STRUCTURAL UNITS AND INTERSTITIAL COMPLEXES, AVERAGE BASICITY OF THE STRUCTURAL UNIT (AB), AND THE AVERAGE O-COORDINATION NUMBER IN THE STRUCTURAL UNIT (CN)

Structural units with examples		Structure mode	Interstitial complex	AB [vu]	CN	Ref.
sinhalite	$Mg\ Al\ [BO_4]$	Isolated polyhedron	$\{^{[6]}Mg\ ^{[6]}Al\}^{5+}$	1.25	4.0	(1)
ludwigite	$(Mg,Fe^{2+})_2\ Fe^{3+}\ O_2\ [BO_3]$	Isolated polyhedron	$\{^{[6]}Mg\ ^{[6]}Fe^{2+}\ ^{[6]}Fe^{3+}\ O_2\}^{3+}$	1.00	4.0	(2)
nordenskiöldine	$Ca\ Sn\ [BO_3]_2$	"	$\{^{[6]}Ca\ ^{[6]}Sn^{4+}\}^{6+}$	"	3.0	(3)
suanite	$Mg_2\ [B_2O_5]$	Dimer	$\{^{[6]}Mg_2\}^{4+}$	0.80	3.6	(4)
kurchatovite	$Ca\ Mg\ [B_2O_5]$	"	$\{^{[7]}Ca\ ^{[6]}Mg\}^{4+}$	"	3.8	(5)
johachidolite	$Ca\ Al\ [B_3O_7]$	Sheet	$\{^{[10]}Ca\ ^{[6]}Al\}^{5+}$	0.71	4.0	(6)
szaibelyite	$Mg_2\ (OH)\ [B_2O_4(OH)]$	Dimer	$\{^{[6]}Mg_2\ ^{[3]}(OH)\}^{3+}$	0.64	3.6	(7)
sussexite	$Mn_2\ (OH)\ [B_2O_4(OH)]$	"	$\{^{[6]}Mn_2\ ^{[3]}(OH)\}^{3+}$	"	"	(8)
calciborite	$Ca\ [B_2O_4]$	Chain	$\{^{[8]}Ca\}^{2+}$	0.50	3.8	(9)
fedorovskite	$Ca_2\ Mg_2\ (OH)_4\ [B_4O_7(OH)_2]$	Cluster	$\{^{[8]}Ca_2\ ^{[6]}Mg_2\ ^{[3]}(OH)_2\ ^{[4]}(OH)_2\}^{4+}$	0.49	4.0	(10)
roweite	$Ca_2\ Mg_2\ (OH)_4\ [B_4O_7(OH)_2]$	"	$\{^{[8]}Ca_2\ ^{[6]}Mg_2\ ^{[3]}(OH)_2\ ^{[4]}(OH)_4\}^{4+}$	"	4.0	(11)
solongoite	$Ca_2\ ^{[6]}Cl\ [B_3O_4(OH)_4]$	Trimer	$\{^{[8]}Ca_2\ ^{[6]}Cl\}^{3+}$	0.48	3.6	(12)
vimsite	$Ca\ [B_2O_2(OH)_4]$	Chain	$\{^{[8]}Ca\}^{2+}$	0.47	4.0	(13)
uralborite	$Ca_2\ [B_4O_4(OH)_8]$	Trimer	$\{^{[8]}Ca\}^{2+}$	0.47	4.0	(13a)
nifontovite	$Ca_3\ (H_2O)_2\ [B_3O_3(OH)_6]_2$	Trimer	$\{^{[8]}Ca\ ^{[9]}Ca_2\ (H_2O)_0\ H_2O)_2\}^{6+}$	0.47	4.1	(14)
pentahydroborite	$Ca\ (H_2O)_1\ [B_2O(OH)_6]\ (H_2O)$	Dimer	$\{^{[7]}Ca\ (H_2O)_0\ (H_2O)_1\}^{2+}$	0.46	3.9	(15)
pinnoite	$Mg\ [B_2O(OH)_6]$	"	$\{^{[6]}Mg\}^{2+}$	"	3.7	(16)
teepleite	$Na_2\ ^{[8]}Cl\ [B(OH)_4]$	Isolated polyhedron	$\{^{[6]}Na_2\ ^{[8]}Cl\}^{1-}$	0.45	4.0	(17)
bandylite	$Cu^{2+}\ ^{[6]}Cl\ [B(OH)_4]$	"	$\{^{[6]}Cu^{2+}\ ^{[6]}Cl\}^{1-}$	"	3.0	(18)
frolovite	$Ca\ [B(OH)_4]_2$	"	$\{^{[8]}Ca\}^{2+}$	"	4.0	(19)
hexahydroborite	$Ca\ [B(OH)_4]_2\ (H_2O)_2$	"	$\{^{[8]}Ca\}^{2+}$	"	4.0	(20)
hydrochlorborite	$Ca_2\ (H_2O)_6\ ^{[8]}Cl\ [B_4O_4(OH)_7]\ (H_2O)_1$	Cluster	$\{^{[8]}Ca_2\ (H_2O)_2\ (H_2O)_4\ ^{[8]}Cl\}^{3+}$	0.40	3.6	(21)
boracite-group	$^{[6]}M_3\ [^{[4]}B_7O_{13}]$, M = Mg, Fe^{2+}, Mn^{2+}	Framework	$\{^{[6]}M_3\ ^{[8]}Cl\}^{5+}$	0.38	2.9	(22)
"	$^{[5]}M_3\ [^{[4]}B_6\ ^{[3]}B\ O_{13}]$, M = Mg, Fe^{2+}, Mn^{2+}	"	$\{^{[5]}M_3\ ^{[3]}Cl\}^{5+}$	"	3.0	(22)

Structural units with examples		Structure mode	Interstitial complex	AB [vu]	CN	Ref.
inyoite	$Ca (H_2O)_3 [B_3 O_3 (OH)_5] (H_2O)$	Trimer	$\{^{[8]}Ca (H_2O)_1 (H_2O)_2\}^{2+}$	0.38	3.8	(23)
inderite	$Mg (H_2O)_4 [B_3 O_3 (OH)_5] (H_2O)$	"	$\{^{[6]}Mg (H_2O)_4 (H_2O)_0\}$	"	3.9	(24)
kurnakovite	$Mg (H_2O)_4 [B_3 O_3 (OH)_5] (H_2O)$	"	$\{^{[6]}Mg (H_2O)_4 (H_2O)_0 (H_2O)_1\}^{2+}$	"	3.9	(25)
meyerhofferite	$Ca (H_2O) [B_3 O_3 (OH)_5]$	"	$\{^{[8]}Ca (H_2O)_0 (H_2O)_1\}^{2+}$	"	3.6	(26)
inderborite	$Ca Mg (H_2O)_4 [B_3 O_3 (OH)_5]_2 (H_2O)_2$	"	$\{^{[8]}Ca\ ^{[6]}Mg (H_2O)_2 (H_2O)_2\}^{4+}$	"	"	(27)
colemanite	$Ca [B_3 O_4 (OH)_3] (H_2O)$	Chain	$^{[8]}Ca (H_2O)_0 (H_2O)_1\}^{2+}$	0.37	3.6	(28)
hydroboracite	$Ca Mg (H_2O)_3 [B_6 O_8 (OH)_6]$	"	$\{^{[8]}Ca\ ^{[6]}Mg (H_2O)_2 (H_2O)\}^{4+}$	"	3.6	(29)
fabianite	$Ca_2 [B_6 O_{10} (OH)_2]$	Sheet	$\{^{[8]}Ca_2\}^{4+}$	0.37	3.5	(30)
ulexite	$Na Ca (H_2O)_5 [B_5 O_6 (OH)_6]$	Cluster	$\{^{[8]}Ca\ ^{[6]}Na (H_2O) (H_2O)_4\}^{3+}$	0.35	3.8	(31)
probertite	$Na Ca (H_2O)_3 [B_5 O_7 (OH)_4]$	Chain	$\{^{[9]}Ca\ ^{[6]}Na (H_2O)_0 (H_2O)_3\}^{3+}$	0.35	3.7	(32)
tuzlaite	$Na Ca (H_2O)_3 [B_5 O_8 (OH)_2]$	Sheet	$\{^{[9]}Ca\ ^{[7]}Na (H_2O)_0 (H_2O)_3\}^{3+}$	0.34	3.8	(33)
hilgardite-1A	$Ca_2 (H_2O)\ ^{[4]}Cl [B_5 O_9]$	Framework	$\{^{[8]}Ca_2 (H_2O)_0 (H_2O)\ ^{[4]}Cl\}^{3+}$	0.33	2.4	(34)
preobrazhenskite	$Mg_3 [B_{11} O_{15} (OH)_9]$	Sheet	$\{^{[6]}Mg_3\}^{6+}$	0.33	3.2	(35)
pringleite & ruitenbergite	$Ca_9 [B_{26} O_{34} (OH)_{24} Cl_4] (H_2O)_{13}$	Framework	no hydrogen bonding determined	0.32	–	(36)
borax	$Na_2 (H_2O)_8 [B_4 O_5 (OH)_4]$	Cluster	$\{^{[6]}Na_2 (H_2O)_0 (H_2O)_8\}^{2+}$	0.31	3.8	(37)
tincalconite	$Na_2 (H_2O)_{2.67} [B_4 O_5 (OH)_4]$	"	$\{^{[6]}Na_{1.33}\ ^{[5]}Na_{0.67} (H_2O)_0 (H_2O)_4\}^{2+}$	"	3.7	(38)
hungchaoite	$Mg (H_2O)_5 [B_4 O_5 (OH)_4] (H_2O)_2$	"	$\{^{[6]}Mg (H_2O)_4 (H_2O) (H_2O)_2\}^{2+}$	"	3.6	(39)
kernite	$Na_2 (H_2O)_3 [B_4 O_6 (OH)_2]$	Chain	$\{^{[6]}Na\ ^{[5]}Na (H_2O)_0 (H_2O)_3\}^{2+}$	0.30	3.6	(40)
diomignite	$Li_2 [B_4 O_7]$	Framework	$\{^{[5]}Li_2\}^{2+}$	0.28	3.4	(41)
kaliborite	$K Mg_2 (H_2O)_2 [B_{12} O_{15} (OH)_{11}]$	Chain	$\{^{[8]}K\ ^{[6]}Mg_2 (H_2O)_0 (H_2O)_2\}^{5+}$	0.28	3.3	(42)
ezcurrite[1]	$Na_2 (H_2O)_2 [B_5 O_7 (OH)_3]$	Chain	$\{^{[7]}Na\ ^{[6]}Na (H_2O)_0 (H_2O)_4\}^{2+}$	0.26	3.6	(43)
biringuccite	$Na_2 (H_2O)_1 [B_5 O_8 (OH)]$	Sheet	$\{^{[8]}Na_2\ ^{[7]}Na\ ^{[6]}Na (H_2O)_0 (H_2O)_2\}^{4+}$	0.25	3.7	(44)
nasinite	$Na_2 (H_2O)_2 [B_5 O_8 (OH)]$	"	$\{^{[8]}Na_2 (H_2O)_1 (H_2O)_1\}^{2+}$	"	4.0	(45)
ameghinite	$Na_2 [B_6 O_6 (OH)_8]$	Cluster	$\{^{[6]}Na_2\}^{2+}$	0.26	3.4	(46)
mcallisterite[1]	$Mg (H_2O)_3 [B_6 O_7 (OH)_6] (H_2O)_{1.5}$	Cluster	$\{^{[6]}Mg (H_2O)_3 (H_2O)_0\}^{2+}$	0.25	3.2	(47)
admontite	$Mg (H_2O)_3 [B_6 O_7 (OH)_6]$	"	$\{^{[6]}Mg_2 (H_2O)_6 (H_2O)_0\}^{4+}$	"	3.2	(48)
aksaite	$Mg (H_2O)_2 [B_6 O_7 (OH)_6]$	"	$\{^{[6]}Mg (H_2O)\}^{2+}$	"	3.3	(49)
rivadavite[1]	$Na_6 Mg_1 (H_2O)_{10} [B_6 O_7 (OH)_6]_4$	"	$\{^{[6]}Na_6\ ^{[6]}Mg (H_2O)_0 (H_2O)_{10}\}^{8+}$	"	3.4	(50)
aristarainite	$Na_2 Mg (H_2O)_4 [B_6 O_8 (OH)_4]_2$	Chain	$\{^{[6]}Na_2\ ^{[6]}Mg (H_2O)_2 (H_2O)_2\}^{4+}$	0.23	3.3	(51)
nobleite	$Ca (H_2O)_3 [B_6 O_9 (OH)_2]$	Sheet	$\{^{[8]}Ca (H_2O) (H_2O)_2\}^{2+}$	0.22	3.1	(52)
tunellite	$Sr (H_2O)_3 [B_6 O_9 (OH)_2]$	"	$\{^{[10]}Sr (H_2O) (H_2O)_2\}^{2+}$	"	3.3	(53)
gowerite[1]	$Ca (H_2O)_1 [B_5 O_8 (OH)] [B (OH)_3] (H_2O)_2$	Sheet &	$\{^{[9]}Ca (H_2O)_1 (H_2O)_0\}^{2+}$	0.23	3.2	(54)
veatchite	$Sr_2(H_2O)_2[B_5 O_8 (OH)]_2[B (OH)_3]_2(H_2O)_2$	Isolated polyhedron	$\{^{[10]}Sr\ ^{[11]}Sr (H_2O)_0 (H_2O)_0\}^{4+}$	0.20	3.2	(55)
strontioginorite	$Sr Ca (H_2O)_3 [B_{14} O_{20} (OH)_6] (H_2O)_2$	Sheet	$\{^{[10]}Sr\ ^{[8]}Ca (H_2O)_2 (H_2O)_1\}^{4+}$	0.20	3.1	(56)
strontioborite	$Sr [B_8 O_{11} (OH)_4]$	Sheet	$\{^{[9]}Sr\}^{2+}$	0.19	2.9	(57)
sborgite	$Na (H_2O)_3 [B_5 O_6 (OH)_4]$	Cluster	$\{^{[6]}Na (H_2O)_0 (H_2O)_3\}^{1+}$	0.18	3.0	(58)
santite	$K (H_2O)_2 [B_5 O_6 (OH)_4]$	Cluster	$\{^{[8]}K (H_2O)_0 (H_2O)_2\}^{+}$	0.18	3.2	(59)
ammonioborite	$(NH_4)_3 (H_2O)_2 [B_{15} O_{20} (OH)_8] (H_2O)_2$	Cluster	$\{^{[4]}(NH_4)_3 (H_2O)_2 (H_2O)_0\}^{3+}$	0.16	2.8	(60)
larderellite[1]	$NH_4 (H_2O) [B_5 O_7 (OH)_2]$	Chain	$\{^{[4]}(NH_4) (H_2O)_0 (H_2O)\}^{1+}$	0.16	2.7	(61)

[1] hydrogen bonds of some or all H-atoms determined *via* stereochemical argument.

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their chemical compositions, the character of their structural unit, the composition of the interstitial complex and its Lewis acidity, the average basicity of the structural unit, and the average coordination-number of oxygen in the structural unit. There are only a few crystal structures of borate minerals in which the interstitial hydrogen bonding is not resolved. In these cases, we used stereochemical constraints to determine the possible schemes of interstitial hydrogen bonding.

INTERSTITIAL CATIONS IN BORATE MINERALS

The most common interstitial cations in hydrated borate minerals are Mg, Ca, Na, Sr and (NH_4). Table 2 shows the grand mean coordination-number of these interstitial cations in hydrated borate minerals: [6] for Mg, [8.2] for Ca, [6] for Na, [10] for Sr, and [4] for (NH_4), together with the resulting Lewis-acid strengths of the cations. Except for Na, the Lewis acidities are slightly lower than the values of Brown (1981). For interstitial complexes containing (H_2O) groups, we also list in Table 2 the number of cations that bond to (H_2O) groups, the number of (H_2O) groups that bond to the specific cation, the corresponding numbers and percentages of transformer $^{[3]}(H_2O)$ groups, non-transformer $^{[4]}(H_2O)$ groups bonding to two interstitial cations, and non-transformer $^{[4]}(H_2O)$ groups bonding to one cation and also accepting a hydrogen bond.

Inspection of Table 2 shows that Mg (with the highest Lewis-acid strength of all interstitial cations in borates: 0.33 valence units, *vu*) occurs with the highest fraction of transformer $^{[3]}(H_2O)$ groups in interstitial complexes (77%). Only 15% of all (H_2O) groups bonded to Mg also bond to a second cation (not necessarily Mg), and only 10% bond to one Mg and also accept a hydrogen bond. If we consider only interstitial complexes containing Mg, then only two out of seventeen (H_2O) groups bonded to Mg do not act as a bond-valence transformer. For interstitial complexes containing Ca, the connectivity of interstitial (H_2O) groups is significantly different: the majority of (H_2O) groups also accept a hydrogen bond (53%), and only 25% of all (H_2O) groups are transformer (H_2O) groups.

Interstitial Na cations have low Lewis-acid strength (0.17 *vu*), and this is expressed in the occurrence of only 6% transformer (H_2O) groups and 94% non-transformer (H_2O) groups bonded to Na in interstitial complexes. Moreover, 4% of the transformer (H_2O) groups occur with Na and Mg in the interstitial complex of aristarainite, implying that their presence is actually related to the presence of Mg rather than Na. In interstitial complexes with exclusively Na, only 2% of the (H_2O) groups act as bond-valence transformers. The majority of (H_2O) groups bond to two cations (57%, usually two Na atoms, less commonly Na and another cation).

Interstitial K has the lowest Lewis-acid strength of all cations in borate minerals (0.125 *vu*). There is only one potassium borate mineral (santite), and it has no transformer (H_2O) groups in the interstitial complex.

We can summarize the above discussion as follows: (1) ~97% of interstitial (H_2O) groups in Mg borates are transformer (H_2O) groups, (2) ~25% of interstitial (H_2O) groups in Ca borates are transformer (H_2O) groups, (3) ~6% of interstitial (H_2O) groups in Na borates are transformer (H_2O) groups, and (4) 0% of interstitial (H_2O) groups in K borates are transformer (H_2O) groups.

This large compositional variation in the interstitial complexes in borate minerals results from adherence to the valence-matching principle. The grand mean Lewis basicity of structural units in hydrated borate minerals is 0.21 *vu*. For stable structures to occur, the Lewis acidities of the interstitial complexes have to match this value on average. The Lewis acidities of Mg, Ca, Na and K are 0.33, 0.24, 0.17 and 0.125 *vu*, respectively (Table 2). Thus, on average, interstitial Mg will have to bond to interstitial transformer (H_2O) groups to lower the Lewis acidity of the interstitial complex to match the Lewis basicity of the average structural unit. On average, interstitial Na and K will not bond to interstitial transformer (H_2O) groups because their Lewis acidities are somewhat lower than the Lewis basicity of the average structural unit. Calcium, with its intermediate Lewis acidity, exhibits a behavior intermediate between that of Mg and Na.

TABLE 2. DETAILS OF THE HYDROGEN BONDING IN INTERSTITIAL COMPLEXES OF BORATE MINERALS WITH (H_2O) GROUPS

Interstitial cation	Mg	Ca	Na	K	Sr	$(NH_4)^+$
Average coordination number [CN]	[6]	[8.2]	[6]	[8]	[10]	[4]
Average Lewis-acid strength	0.33	0.24	0.17	0.13	0.2	0.25
Number of cations bond to (H_2O) groups	10	15	29	1	2	4
Number of (H_2O) groups bonded to interstitial cations	26	28	49	2	5	3
Transformer $^{[3]}(H_2O)$ groups	20 (77%)	7 (25%)	3(6%)	0	3	2
Non-transformer $^{[4]}(H_2O)$ groups bonded to two cations	4 (15%)	6 (21.5%)	28(57%)	0	1	–
Non-transformer $^{[4]}(H_2O)$ groups bonded to one cation and accepting one hydrogen bond	2 (10%)	15 (53.5%)	18(37%)	2	1	1

INTERACTION BETWEEN (OH) OF THE STRUCTURAL UNIT AND NON-TRANSFORMER (H_2O) GROUPS

As discussed by Schindler & Hawthorne (2001), in structural units containing (OH) groups, hydrogen bonds emanate from the structural unit. Some of these hydrogen bonds may link to anions of the adjacent (or even the same) structural unit, but the hydrogen bonds that do not (most of them) must link to (H_2O) groups of the interstitial complex. This indicates that these (OH) groups of the structural unit control the presence and location of non-transformer (H_2O) groups of the interstitial complex. This is a difficult problem to investigate from a general stereochemical perspective and must be deferred, but the bond-valence approach developed here provides the first indication of a stereochemical reason for the existence of this type of (H_2O) in crystal structures.

INTERSTITIAL COMPLEXES IN Cl-FREE BORATE MINERALS

Schindler & Hawthorne (2001) have shown how to express the Lewis acidity of the interstitial complex in terms of the valence and coordination number of the interstitial cations, and the number of transformer (H_2O) groups, and also how to calculate the range in Lewis basicity of a specific structural unit. Where the Lewis acidity of a generalized interstitial complex overlaps the range of Lewis basicity of a specific structural unit, the valence-matching principle is satisfied, and a stable structure is possible. Now we will consider from this viewpoint some of the borate minerals that have the following structural units in common: $[B_3 O_3 (OH)_5]^{2-}$, $[B_4 O_5 (OH)_4]^{2-}$ and $[B_6 O_7 (OH)_6]^{2-}$; details of these minerals are given in Table 1.

The structural unit $[B_3 O_3 (OH)_5]^{2-}$

This structural unit occurs in inyoite: Ca $(H_2O)_3$ $[B_3 O_3 (OH)_5]$ (H_2O), inderite: Mg $(H_2O)_4$ $[B_3 O_3 (OH)_5]$ (H_2O), kurnakovite: Mg $(H_2O)_4$ $[B_3 O_3 (OH)_5]$ (H_2O), meyerhofferite: Ca (H_2O) $[B_3 O_3 (OH)_5]$, and inderborite: Ca Mg $(H_2O)_4$ $[B_3 O_3 (OH)_5]_2$ $(H_2O)_2$, and contains one ($B\phi_3$) and two ($B\phi_4$) groups. The modified charge of this structural unit is $(2 + 0.2 \times 5)^- = 3.0^-$, and the number of O atoms in the structural unit is 8; hence the average basicity is 3.0 / 8 = 0.38 *vu*. Inspection of Figure 1 shows that the corresponding range in average coordination-number of oxygen is [3.55]–[3.95]. Now let us calculate the corresponding range in Lewis basicity. For an average coordination number of oxygen of [3.55], the total number of bonds involving the structural unit is $3.55 \times 8 = 28.4$ bonds. The number of bonds within the structural unit is $3 \times 1 + 4 \times 2 + 1 \times 5 = 16$ bonds, and therefore there needs to be $28.4 - 16 = 12.4$ bonds external to the structural unit. The corresponding Lewis basicity is the effective charge ($s = t$) / the num-

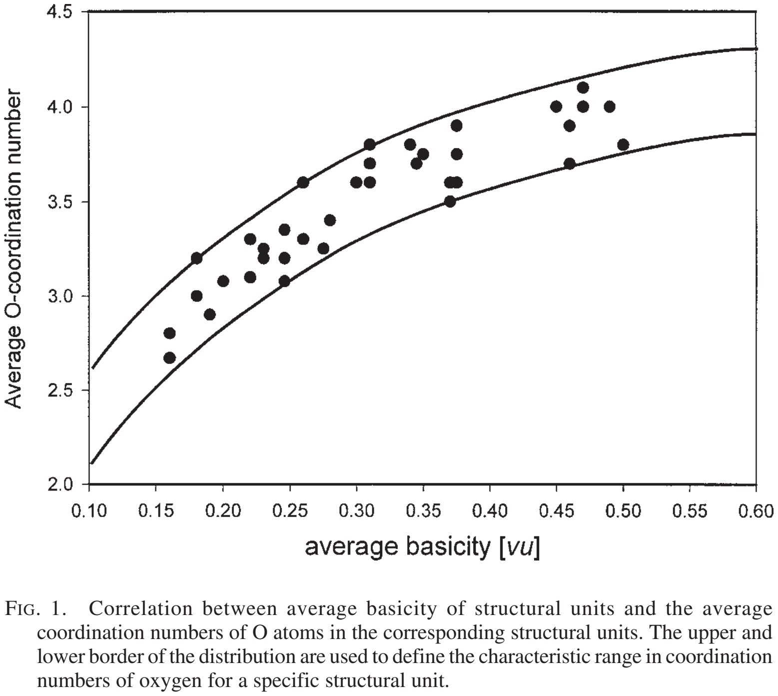

FIG. 1. Correlation between average basicity of structural units and the average coordination numbers of O atoms in the corresponding structural units. The upper and lower border of the distribution are used to define the characteristic range in coordination numbers of oxygen for a specific structural unit.

ber of bonds required = 3 / 12 = 0.24 *vu*. For an average coordination-number of oxygen of [3.95], the total number of bonds involving the structural unit is 3.9 × 8 = 31.6 bonds, and hence there needs to be 31.6 – 16 = 15.6 bonds external to the structural unit. The corresponding Lewis basicity ($s = t$) = 3 / 15.6 = 0.19 *vu*. Thus the range in Lewis basicity of the $[B_3O_3(OH)_5]^{2-}$ structural unit is 0.19–0.24 *vu*.

Figure 2a shows the variation in Lewis acidity of a general interstitial complex as a function of charge of the cation, its coordination number, and the number of transformer (H_2O) groups, with the range of Lewis basicity of the $[B_3O_3(OH)_5]^{2-}$ structural unit marked. Where the Lewis acidity curves intersect the range of Lewis basicity of the structural unit, the valence-matching principle is satisfied, and a stable structure can form. First, consider interstitial monovalent cations. For coordination numbers [6] and above, monovalent cations cannot occur. For a coordination number of [5], a monovalent cation can occur only with zero transformer (H_2O) groups present (Table 3). Compound monovalent cations [*e.g.*, $(NH_4)^+$] typically have low coordination numbers (*e.g.*, [3] or [4]), and their Lewis acidity curves (not shown in Fig. 2a) overlap the range in Lewis basicity, indicating that structures with these interstitial species are possible. For divalent interstitial cations, $^{[5]}M^{2+}$ is possible with 2–5 transformer (H_2O) groups, $^{[6]}M^{2+}$ is possible with 1–4 transformer (H_2O) groups, $^{[7]}M^{2+}$ is possible with 0–3 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–2 transformer (H_2O) groups. Trivalent interstitial cations are possible only for coordination numbers of [6] with 5–6 transformer (H_2O) groups, [7] with 4–7 transformer (H_2O) groups, and [8] with 3–7 transformer (H_2O) groups. As indicated in Table 3, all minerals of this group conform to these predictions: both inderite and kurnakovite have interstitial complexes $\{^{[6]}Mg\,(H_2O)_4\,....\}^{2+}$, and both inyoite and meyerhofferite have interstitial complexes $\{^{[8]}Ca\,(H_2O)\,....\}^{2+}$. Inderborite has interstitial $^{[8]}Ca$ and $^{[6]}Mg$; combining the above predictions results in a possible variation of 0–2 plus 1–4 transformer (H_2O) groups, for a total possible variation of 0–4; the observed value is 2.

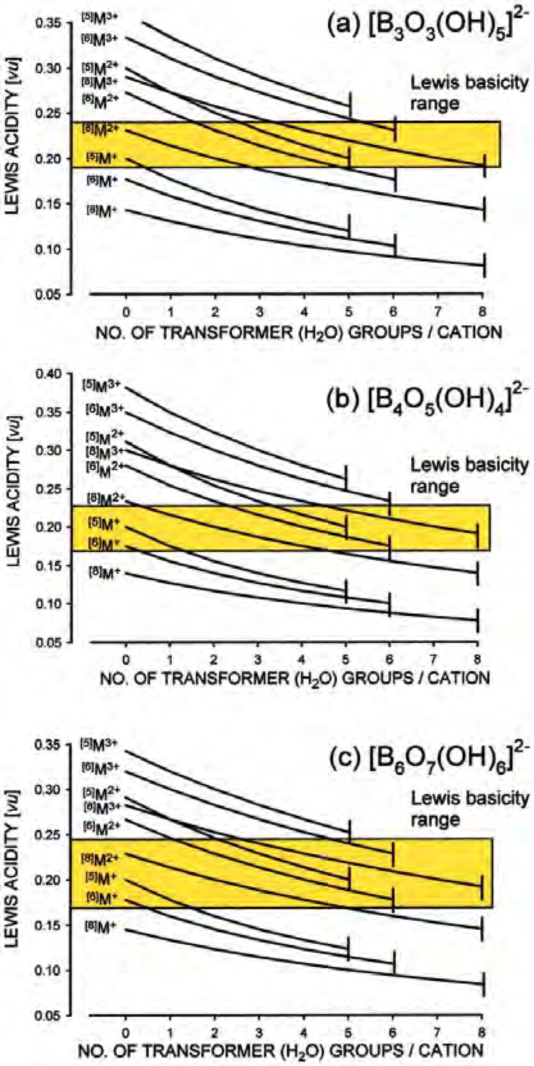

FIG. 2. The Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The range in Lewis basicity for specific structural units are marked: (a) for $[B_3O_3(OH)_5]^{2-}$, (b) $[B_4O_5(OH)_4]^{2-}$, and (c) $[B_6O_7(OH)_6]^{2-}$.

The structural unit $[B_4O_5(OH)_4]^{2-}$

This structural unit occurs in borax: $Na_2(H_2O)_8[B_4O_5(OH)_4]$, tincalconite: $Na_2(H_2O)_{2.67}[B_4O_5(OH)_4]$, and hungchaoite: $Mg(H_2O)_5[B_4O_5(OH)_4](H_2O)_2$, and contains two $(B\phi_3)$ and two $(B\phi_4)$ groups. The modified charge of this structural unit is $(2 + 0.2 \times 4)^- = 2.8^-$, and the number of O atoms in the structural unit is 9; hence the average basicity is 2.8 / 9 = 0.31 *vu*, and the corresponding range in average coordination-number of oxygen is [3.35]–[3.8] (Fig. 2). For an average coordination-number of oxygen of [3.35], the total number of bonds involving the structural unit is 3.4 × 9 = 30.4 bonds. The number of bonds within the structural unit is 3 × 2 + 4 × 2 + 1 × 4 = 18 bonds, and therefore there need to be 30.4 – 18 = 12.4 external bonds to the structural unit. The corresponding Lewis basicity is 2.8 / 12.4 = 0.23 *vu*. Following the same calculation for the higher coordination number gives the range in Lewis basicity of the $[B_3O_3(OH)_5]^{2-}$ structural unit as 0.17–0.23 *vu*.

Using Figure 2b, we predict the range in chemical composition for possible interstitial complexes. Interstitial monovalent cations are possible only for coordination numbers [3] to [6] with 1–2, 0–1 and 0

TABLE 3. THE $[B_3O_3(OH)_5]^{2-}$, $[B_4O_4(OH)_4]^{2-}$ and $[B_6O_7(OH)_6]^{2-}$ STRUCTURAL UNITS: PREDICTED AND OBSERVED INTERSTITIAL COMPLEXES

Structural unit	Lewis-basicity range	Predicted interstitial complexes	Observed interstitial complexes	Mineral
$[B_3O_3(OH)_5]^{2-}$	0.19–0.24	$\{^{[3]}M^{+}(H_2O)_{1-2}(H_2O)_{0-2}\}$		
		$\{^{[4]}M^{+}(H_2O)_{0-1}(H_2O)_{0-4}\}$		
		$\{^{[5]}M^{+}(H_2O)_{0}(H_2O)_{0-5}\}$		
		$\{^{[6]-[8]}M...\}$: not possible		
		$\{^{[6]}M^{2+}(H_2O)_{1-4}(H_2O)_{0-5}\}$	$\{^{[6]}Mg(H_2O)_4(H_2O)_0(H_2O)_1\}^{2+}$	inderite
		$\{^{[7]}M^{2+}(H_2O)_{0-3}(H_2O)_{0-7}\}$	$\{^{[8]}Ca\,^{[6]}Mg(H_2O)_2(H_2O)_2\}^{4+}$	inderborite
		$\{^{[8]}M^{2+}(H_2O)_{0-2}(H_2O)_{0-8}\}$	$\{^{[8]}Ca(H_2O)_1(H_2O)_2\}^{2+}$	inyoite, meyerhofferite
		$\{^{[6]}M^{3+}(H_2O)_{5-6}(H_2O)_{0-1}\}$		
		$\{^{[6]}M^{3+}(H_2O)_{3-4}(H_2O)_{0-1}(OH)_1\}$		
		$\{^{[7]}M^{3+}(H_2O)_{4-7}(H_2O)_{0-3}\}$		
		$\{^{[8]}M^{3+}(H_2O)_{3-7}(H_2O)_{0-5}\}$		
$[B_4O_5(OH)_4]^{2-}$	0.17–0.23	$\{^{[3]}M^{+}(H_2O)_{1-3}(H_2O)_{0-2}\}$		
		$\{^{[4]}M^{+}(H_2O)_{0-2}(H_2O)_{0-4}\}$		
		$\{^{[5]}M^{+}(H_2O)_{0-1}(H_2O)_{0-5}\}$	$\{^{[6]}Na_{1.33}\,Na_{0.67}(H_2O)_0(H_2O)_4\}^{3+}$	tincalconite
		$\{^{[6]}M^{+}(H_2O)_{0}(H_2O)_{0-6}\}$	$\{^{[6]}Na_2(H_2O)_0(H_2O)_8\}^{2+}$	borax
		$\{^{[7],[8]}M\}$: not possible		
		$\{^{[6]}M^{2+}(H_2O)_{2-6}(H_2O)_{0-3}\}$	$\{^{[6]}Mg(H_2O)_4(H_2O)_1(H_2O)_2\}^{2+}$	hungchaoite
		$\{^{[7]}M^{2+}(H_2O)_{1-5}(H_2O)_{0-5}\}$		
		$\{^{[8]}M^{2+}(H_2O)_{0-4}(H_2O)_{0-5}\}$		
		$\{^{[6]}M^{3+}(H_2O)_{6}(H_2O)_{0}(OH)_1\}$		
		$\{^{[7]}M^{3+}(H_2O)_{5-7}(H_2O)_{0-1}\}$		
		$\{^{[8]}M^{3+}(H_2O)_{4-8}(H_2O)_{0-3}\}$		
$[B_6O_7(OH)_6]^{2-}$	0.17–0.25	$\{^{[3]}M^{+}(H_2O)_{1-3}(H_2O)_{0-2}\}$		
		$\{^{[4]}M^{+}(H_2O)_{0-3}(H_2O)_{0-4}\}$		
		$\{^{[5]}M^{+}(H_2O)_{0-2}(H_2O)_{0-5}\}$		
		$\{^{[6]}M^{+}(H_2O)_{0-1}(H_2O)_{0-6}\}$	$\{^{[6]}Na_6\,^{[6]}Mg_1(H_2O)_0(H_2O)_{10}\}^{8+}$	rivadavite
		$\{^{[7]}M^{+}\}$: not possible		
		$\{^{[8]}M\}$: not possible		
		$\{^{[6]}M^{2+}(H_2O)_{1-6}(H_2O)_{0-3}\}$	$\{^{[6]}Mg(H_2O)_3(H_2O)_0\}^{2+}$	mcallisterite
		$\{^{[7]}M^{2+}(H_2O)_{0-6}(H_2O)_{0-5}\}$	$\{^{[6]}Mg(H_2O)_3(H_2O)_0\}^{2+}$	admontite
		$\{^{[8]}M^{2+}(H_2O)_{0-5}(H_2O)_{0-7}\}$	$\{^{[6]}Mg(H_2O)_1\}^{2+}$	aksaite
		$\{^{[6]}M^{3+}(H_2O)_{4-5}(H_2O)_{0}\}$		
		$\{^{[6]}M^{3+}(H_2O)_{4}(H_2O)_{0}(OH)_1\}$		
		$\{^{[7]}M^{3+}(H_2O)_{4-7}(H_2O)_{0-1}\}$		
		$\{^{[8]}M^{3+}(H_2O)_{3-8}(H_2O)_{0-3}\}$		

transformer (H_2O) groups, respectively (Table 3). For divalent interstitial cations, $^{[5]}M^{2+}$ is possible with 3–5 transformer (H_2O) groups, $^{[6]}M^{2+}$ is possible with 2–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ (not shown in Fig. 2b) is possible with 1–5 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–4 transformer (H_2O) groups. For trivalent interstitial cations, $^{[6]}M^{3+}$, $^{[7]}M^{3+}$ (not shown in Fig. 2b) and $^{[8]}M^{3+}$ are possible with one (OH) group and 4 transformer (H_2O) groups or with 6 transformer (H_2O), 5–7 and 4–8 transformer (H_2O) groups, respectively. As indicated in Table 3, all minerals of this group conform to these predictions: borax has an interstitial complex $\{^{[6]}Na(H_2O)_0 ....\}^{+}$, and hungchaoite has an interstitial complex $\{^{[6]}Mg(H_2O)_4 ....\}^{2+}$. Tincalconite has interstitial $^{[5]}Na$ and $^{[6]}Na$; combining the above predictions results in a possible variation of 0–1 plus 0 transformer (H_2O) groups, for a total possible variation of 0–1; the observed value is 0.

The structural unit $[B_6O_7(OH)_6]^{2-}$

This structural unit occurs in mcallisterite: $Mg(H_2O)_3[B_6O_7(OH)_6](H_2O)_{1.5}$, admontite: $Mg(H_2O)_3[B_6O_7(OH)_6](H_2O)$, aksaite: $Mg(H_2O)_2[B_6O_7(OH)_6](H_2O)$, and rivadavite: $Na_6Mg(H_2O)_{10}[B_6O_7(OH)_6]$. It contains three ($B\phi_3$) and three ($B\phi_4$) groups. The modified charge of this structural unit is $(2 + 0.2 \times 6)^{-} = 3.2^{-}$, and the number of O atoms in the structural unit is 13; the average basicity is 3.2 / 13 = 0.25 *vu*, and the corresponding range in average coordination-number of oxygen is [3.05]–[3.55] (Fig. 2). The corresponding range in Lewis basicity of the $[B_6O_7(OH)_6]^{2-}$ structural unit is 0.17–0.25 *vu*.

Using Figure 2c, we predict the range in chemical composition for possible interstitial complexes. For interstitial monovalent cations, $^{[5]}M^{+}$ is possible with 0–1.5 transformer (H_2O) groups, $^{[6]}M^{+}$ is possible with

0–0.5 transformer (H_2O) groups, $^{[7]}M^+$ (not shown in Fig. 2c) and $^{[8]}M^+$ are not possible (Table 3). For divalent interstitial cations, $^{[5]}M^{2+}$ is possible with 2–5 transformer (H_2O) groups, $^{[6]}M^{2+}$ is possible with 1–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ (not shown in Fig. 2c) is possible with 0–6 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–5 transformer (H_2O) groups. For trivalent interstitial cations, $^{[6]}M^{3+}$ is possible with 4.5 transformer (H_2O) groups, $^{[7]}M^{3+}$ (not shown in Fig. 2c) is possible with 3.5–7 transformer (H_2O) groups, and $^{[8]}M^{3+}$ is possible with 2.5–8 transformer (H_2O) groups. As indicated in Table 3, all minerals of this group conform to these predictions: mcallisterite and admontite have interstitial complexes $\{^{[6]}\mathrm{Mg}\ (H_2O)_3\ ....\}^{2+}$, and aksaite has an interstitial complex $\{^{[6]}\mathrm{Mg}\ (H_2O)_1\ ....\}^{2+}$.

Prediction of interstitial complexes for Cl-free hydroxy-hydrated borate minerals

The above calculations for the structural units $[B_3\,O_3\,(OH)_5]^{2-}$, $[B_4\,O_5\,(OH)_4]^{2-}$ and $[B_6\,O_7\,(OH)_6]^{2-}$ illustrate how we can predict aspects of the interstitial complex of a mineral, given its structural unit. The results of calculations for all Cl-free hydroxy-hydrated borate minerals are shown in Table 4, where they are compared with the observed interstitial complexes. This approach is quite successful in predicting the coordination numbers of the interstitial cations. This aspect of the predictions is examined in Figure 3, where it can be seen that coordination numbers from [4] to [11] are predicted accurately. Five examples lie off the 1:1 line in the central region between [6] and [8], but this amounts to only 9% of the data.

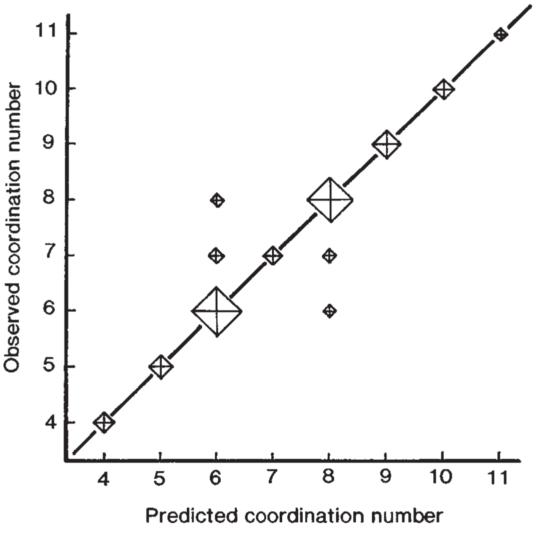

FIG. 3. Comparison of the predicted and observed coordination-numbers of interstitial cations in borate minerals; the size (area) of the squares are proportional to the number of data defining each point.

Prediction of the number of transformer (H_2O) groups in the interstitial complex is also reasonably successful. Omitting microporous structures such as pringleite and ruitenbergite, 95% of the borate minerals of Table 4 have the observed amount of transformer (H_2O) groups falling within the predicted range. Moreover, the mean value of the predicted ranges is 2.4 (H_2O) [*i.e.,* transformer (H_2O) varies between n and $(n + 2.4)$]. There is a range in predicted transformer (H_2O) groups because a structural unit has a range in Lewis basicity (reflecting its stability over a range of pH). The factors that dictate the amount of transformer (H_2O) *within* the predicted range are not yet understood, but may relate to geometrical details of the interaction between the interstitial complex and the structural unit.

The agreement between the predicted and observed values suggests that the general argument developed here is physically realistic and should be applicable to oxysalt minerals in general, and we are currently extending this work to include sulfates, vanadates and uranium-based oxysalt minerals.

INTERSTITIAL COMPLEXES IN CL-BEARING BORATE MINERALS

Schindler & Hawthorne (2001) showed that [3]-, [4]-, [6]- and [8]-coordinated Cl anions occur as interstitial constituents in borate minerals. The dominant coordination number of Cl is [8]; it occurs in teepleite: $^{[8]}\mathrm{Na}_2\ ^{[8]}\mathrm{Cl}\ [B\,(OH)_4]$, hydroclorborite: $^{[8]}\mathrm{Ca}_2\,(H_2O)_6\ ^{[8]}\mathrm{Cl}\ [B_4\,O_4\,(OH)_7]\ (H_2O)$, and in the cubic modification of boracite: $^{[6]}M_3\ ^{[8]}\mathrm{Cl}\ [^{[4]}B_4\,O_{13}]$, M = Mg, Fe^{2+}, Mn^{2+} (Table 1). Schindler & Hawthorne (2001) showed that Cl may be incorporated (conceptually) into an interstitial complex in two ways: (1) $^{[m]}M^+ + {}^{[8]}\mathrm{Cl}^- \rightarrow \square + \square$, and (2) $^{[8]}M^{2+} + {}^{[8]}\mathrm{Cl}^- \rightarrow {}^{[m]}M^+ + \square$. In the first case, Cl is incorporated, together with sufficient additional interstitial cations to maintain electroneutrality. In the second case, Cl is incorporated and a lower-valence interstitial cation is replaced by a higher-valence interstitial cation such that electroneutrality is maintained. Now let us consider some structural units that are associated with interstitial Cl.

The structural unit $[B\,(OH)_4]^-$

This structural unit occurs in teepleite: $\mathrm{Na}_2\ ^{[8]}\mathrm{Cl}\ [B\,(OH)_4]$, bandylite: $\mathrm{Cu}^{2+}\ ^{[6]}\mathrm{Cl}\ [B\,(OH)_4]$, and frolovite: $\mathrm{Ca}\ [B\,(OH)_4]_2$, and Cl is present as an interstitial constituent in two of these minerals. The calculated range in Lewis basicity for the structural unit is 0.21–0.27 *vu*. This range overlaps with the Lewis acidity of Ca (Table 2), and hence $\mathrm{Ca}\ [B\,(OH)_4]_2$ is a stable arrangement: frolovite. However, monovalent cations, particu-

TABLE 4. STRUCTURAL UNITS WITH AVERAGE BASICITIES SMALLER THAN 0.50 *vu*: AVERAGE COORDINATION NUMBER RANGE, LEWIS BASICITY RANGE, PREDICTED AND OBSERVED INTERSTITIAL COMPOSITIONS

Structural unit	AB	Structure type	$^{[4]}$B = □ $^{[3]}$B = Δ	Average O-CN	Lewis basicity (*vu*)	Predicted interstitial composition without Cl-anions	Observed interstitial composition
$[B_2O_4]^{2-}$	0.50	Chain	1□1Δ	3.7–4.1	0.21–0.26	$\{^{[8]}M (H_2O)_{0-2} (H_2O)_{0-6}\}^{2+}$	$\{^{[8]}Ca\}^{2+}$
$[B_4O_7(OH)_2]^{4-}$	0.49	Cluster	2□2Δ	3.7–4.1	0.21–0.25	$\{^{[8]}M^{2+}_2\ ^{[6]}M^{2+}_2 (H_2O)_{0-3} (H_2O)_{0-12} (OH)_4\}^{4+}$	$\{^{[8]}Ca_2\ ^{[6]}Mg_2\ ^{[4]}(OH)_4\}^{4+}$
$[B_3O_4(OH)_4]^{3-}$	0.475	Trimer	2□Δ	3.7–4.1	0.21–0.26	$\{^{[8]}M^{2+}_2 (H_2O)_{4-10} (H_2O)_{0-8}\ ^{[4]}(OH)\}^{3+}$	$\{^{[8]}Ca_2\ ^{[6]}Cl\}^{3+}$
$[B_2O_2(OH)_4]^{2-}$	0.47	Chain	2□	3.7–4.1	0.22–0.27	$\{^{[8]}M (H_2O)_0 (H_2O)_{0-8}\}^{2+}$	$\{^{[8]}Ca\}^{2+}$
$[B_3O_3(OH)_6]^{3-}$	0.47	Trimer	3□	3.7–4.1	0.22–0.28	$\{^{[8]}M\ ^{[9]}M^{2+}_2 (H_2O)_0 (H_2O)_{0-26}\}^{6+}$	$\{^{[8]}Ca^{[9]}\ Ca_2 (H_2O)_0 (H_2O)_2\}^{6+}$
$[B_2O(OH)_6]^{2-}$	0.46	Dimer	2□	3.7–4.1	0.22–0.27	$\{^{[8]}M^{2+} (H_2O)_0 (H_2O)_{0-6}\}^{2+}$ $\{^{[8]}M^{2+} (H_2O)_{0-2} (H_2O)_{0-6}\}^{2+}$	$\{^{[7]}Ca (H_2O)_0 (H_2O)_1\}^{2+}$ $\{^{[6]}Mg\}^{2+}$
$[B(OH)_4]^{-}$	0.45	Isolated polyhedron	1□	3.7–4.1	0.21–0.27	$\{^{[6]}M^{+}\}$: not possible $\{^{[6]}M^{2+} (H_2O)_{0-3} (H_2O)_{0-6}\}^{2+}$ $\{^{[8]}M^{2+} (H_2O)_{0-1} (H_2O)_{0-8}\}^{2+}$	$\{^{[6]}Na_2\ ^{[8]}Cl\}^{1+}$ $\{^{[6]}Cu\ ^{[6]}Cl\}^{1+}$ $\{^{[8]}Ca\}^{2+}$
$[B_4O_4(OH)_7]^{3-}$	0.40	Cluster	3□1Δ	3.55–4.0	0.20–0.26	$\{^{[8]}M^{2+}_2 (H_2O)_{0-2} (H_2O)_{0-12}\ ^{[4]}(OH)\}^{3+}$	$\{^{[8]}Ca_2 (H_2O)_2 (H_2O)_4\ ^{[8]}Cl\}^{3+}$
$[B_7O_{13}]^{5-}$	0.38	Framework	7□/6□1Δ	3.55–3.95	0.205–0.275	$\{^{[6]}M^{2+}_3 (H_2O)_{3-9} (H_2O)_{0-12}\ ^{[4]}(OH)\}^{5+}$ $\{^{[5]}M^{2+}_3 (H_2O)_{5-11} (H_2O)_{0-6}\ ^{[4]}(OH)\}^{5+}$	$\{^{[6]}M_3\ ^{[8]}Cl\}^{5+}$ $\{^{[5]}M_3\ ^{[3]}Cl\}^{5+}$
$[B_3O_3(OH)_5]^{2-}$	0.38	Trimer	2□1Δ	3.55–3.95	0.19–0.24	$\{^{[8]}M^{2+} (H_2O)_{0-3} (H_2O)_{0-8}\}^{2+}$ $\{^{[6]}M^{2+} (H_2O)_{1-5} (H_2O)_{0-5}\}^{2+}$ $\{^{[7]}M^{2+} (H_2O)_{0-4} (H_2O)_{0-7}\}^{2+}$	$\{^{[8]}Ca (H_2O)_1 (H_2O)_2\}^{2+}$ $\{^{[8]}Ca (H_2O)_1 (H_2O)_0\}^{2+}$ $\{^{[6]}Mg (H_2O)_4 (H_2O)_0 (H_2O)_1\}^{2+}$ $\{^{[6]}Ca\ ^{[6]}Mg (H_2O)_2 (H_2O)_2\}^{4+}$
$[B_3O_4(OH)_3]^{2-}$	0.37	Chain	2□1Δ	3.5–3.95	0.19–0.25	$\{^{[8]}M^{2+} (H_2O)_{0-2} (H_2O)_{0-8}\}^{2+}$ $\{^{[8]}M^{2+}\ ^{[6]}M^{2+} (H_2O)_{0-3} (H_2O)_{0-14}\}^{4+}$	$\{^{[8]}Ca (H_2O)_0 (H_2O)_1\}^{2+}$ $\{^{[8]}Ca\ ^{[6]}Mg (H_2O)_2 (H_2O)_1\}^{4+}$
$[B_6O_{10}(OH)_2]^{4-}$	0.37	Sheet	4□2Δ	3.5–3.9	0.19–0.24	$\{^{[8]}M^{2+}_2 (H_2O)_{0-5} (H_2O)_{0-16}\}^{4+}$	$\{^{[8]}Ca_2\}^{4+}$
$[B_5O_6(OH)_6]^{3-}$	0.35	Cluster	3□2Δ	3.5–3.9	0.18–0.23	$\{^{[8]}M^{2+}\ ^{[6]}M^{+} (H_2O)_{0-3} (H_2O)_{0-14}\}^{3+}$	$\{^{[8]}Ca\ ^{[6]}Na (H_2O)_1 (H_2O)_4\}^{3+}$
$[B_5O_7(OH)_4]^{3-}$	0.35	Chain	3□2Δ	3.5–3.9	0.18–0.23	$\{^{[9]}M^{2+}\ ^{[6]}M^{+} (H_2O)_{0-2} (H_2O)_{0-15}\}^{3+}$	$\{^{[9]}Ca\ ^{[6]}Na (H_2O)_0 (H_2O)_3\}^{3+}$
$[B_5O_8(OH)_2]^{3-}$	0.34	Sheet	3□2Δ	3.45–3.9	0.18–0.24	$\{^{[9]}M^{2+}\ ^{[6]}M^{+} (H_2O)_{0-2} (H_2O)_{0-15}\}^{3+}$	$\{^{[9]}Ca\ ^{[7]}Na (H_2O)_0 (H_2O)_3\}^{3+}$
$[B_5O_9]^{3-}$	0.33	Framework	3□2Δ	3.4–3.85	0.18–0.24	$\{^{[8]}Ca_2 (H_2O)_{0-3} (H_2O)_{0-12}\ ^{[4]}(OH)\}^{3+}$	$\{^{[8]}Ca_2 (H_2O)_0 (H_2O)_1\ ^{[4]}Cl\}^{3+}$
$[B_{11}O_{15}(OH)_9]^{6-}$	0.33	Sheet	7□4Δ	3.4–3.85	0.18–0.24	$\{^{[6]}M^{2+}_3 (H_2O)_{6-16} (H_2O)_{0-13}\}^{6+}$	$\{^{[6]}Mg_3\}^{6+}$
$[B_{26}O_{34}(OH)_{24}]^{14-}$	0.32	Framework	14□12Δ	3.4–3.85	0.175–0.23	$\{^{[8]}M_7 (H_2O)_{2-24} (H_2O)_{0-54}\}^{14+}$	no hydrogen bonding determined
$[B_4O_5(OH)_4]^{2-}$	0.31	Cluster	2□2Δ	3.35–3.8	0.17–0.23	$\{^{[6]}M^{+} (H_2O)_0 (H_2O)_{0-6}\}$ $\{^{[6]}M^{+}_2\ ^{[5]}M^{+} (H_2O)_{0-1} (H_2O)_{0-17}\}^{3+}$ $\{^{[6]}M^{2+} (H_2O)_{2-6} (H_2O)_{0-3}\}$	$\{^{[6]}Na_2 (H_2O)_0 (H_2O)_8\}^{2+}$ $\{^{[6]}Na_2\ ^{[5]}Na (H_2O)_0 (H_2O)_4\}^{3+}$ $\{^{[6]}Mg (H_2O)_4 (H_2O)_1 (H_2O)_2\}^{2+}$
$[B_4O_6(OH)_2]^{2-}$	0.30	Chain	2□2Δ	3.3–3.75	0.17–0.23	$\{^{[6]}M^{+}\ ^{[5]}M^{+} (H_2O)_{0-1} (H_2O)_{0-11}\}^{2+}$	$\{^{[6]}Na\ ^{[5]}Na (H_2O)_0 (H_2O)_3\}^{2+}$
$[B_4O_7]^{2-}$	0.28	Framework	2□2Δ	3.3–3.7	0.17–0.22	$\{^{[5]}M^{+}_2 (H_2O)_{0-2} (H_2O)_{0-10}\}^{2+}$	$\{^{[5]}Li_2\}^{2+}$
$[B_{12}O_{15}(OH)_{11}]^{5-}$	0.275	Chain	6□6Δ	3.25–3.68	0.17–0.24	$\{^{[8]}M^{+}\ ^{[6]}M^{2+}_2 (H_2O)_{0-12} (H_2O)_{0-20}\}^{5+}$	$\{^{[8]}K\ ^{[6]}Mg_2 (H_2O)_0 (H_2O)_2\}^{5+}$
$[B_5O_7(OH)_3]^{2-}$	0.26	Chain	2□3Δ	3.15–3.65	0.16–0.23	$\{^{[7]}M^{+}\ ^{[6]}M^{+} (H_2O)_0 (H_2O)_{0-13}\}^{2+}$	$\{^{[7]}Na\ ^{[6]}Na (H_2O)_0 (H_2O)_4\}^{2+}$
$[B_6O_6(OH)_8]^{2-}$	0.26	Cluster	2□4Δ	3.15–3.65	0.16–0.22	$\{^{[6]}M^{+}_2 (H_2O)_{0-3} (H_2O)_{0-12}\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$
$[B_5O_8(OH)]^{2-}$	0.25	Sheet	2□3Δ	3.05–3.55	0.16–0.23	$\{^{[6]}M^{+}_2 (H_2O)_{0-1} (H_2O)_{0-12}\}^{2+}$ $\{^{[8]}M^{+}_2\}^{2+}$: not possible	$\{^{[8]}Na_2\ ^{[7]}Na\ ^{[6]}Na (H_2O)_0 (H_2O)_2\}^{4+}$ $\{^{[8]}Na_2 (H_2O)_1 (H_2O)_1\}^{2+}$
$[B_6O_7(OH)_6]^{2-}$	0.25	Cluster	3□3Δ	3.05–3.55	0.17–0.25	$\{^{[6]}M^{2+} (H_2O)_{2-6} (H_2O)_{0-3}\}$ $\{^{[6]}M^{+}_6\ ^{[6]}M^{2+}_1 (H_2O)_{0-10} (H_2O)_{0-42}\}$	$\{^{[6]}Mg (H_2O)_3 (H_2O)_0\}^{2+}$ $\{^{[6]}Mg_2 (H_2O)_3 (H_2O)_0\}^{2+}$ $\{^{[6]}Mg (H_2O)_1\}^{2+}$ $\{^{[6]}Na_6\ ^{[6]}Mg_1 (H_2O)_0 (H_2O)_{10}\}^{8+}$
$[B_6O_8(OH)_4]^{2-}$	0.23	Chain	3□3Δ	3.0–3.45	0.17–0.25	$\{^{[6]}M^{+}_2\ ^{[6]}M^{2+} (H_2O)_{0-3} (H_2O)_{0-18}\}^{4+}$	$\{^{[6]}Na_2\ ^{[6]}Mg (H_2O)_2 (H_2O)_2\}^{4+}$
$[B_6O_9(OH)_2]^{2-}$	0.22	Sheet	3□3Δ	2.95–3.4	0.17–0.25	$\{^{[8]}M^{2+} (H_2O)_{0-4} (H_2O)_{0-8}\}^{2+}$ $\{^{[10]}M^{2+} (H_2O)_{0-2} (H_2O)_{0-10}\}^{2+}$	$\{^{[8]}Ca (H_2O]_1 (H_2O)_2\}^{2+}$ $\{^{[10]}Sr (H_2O]_1 (H_2O)_2\}^{2+}$
$[B_5O_8(OH)]^{2-}$ x $[B(OH)_3]$	0.23	Sheet & isolated polyhedron	2□3Δ1Δ	3.0–3.45	0.16–0.23	$\{^{[9]}M^{2+} (H_2O)_{1-4} (H_2O)_{0-8}\}^{2+}$ $\{^{[10]}M^{2+}\ ^{[11]}M^{2+} (H_2O)_{0-5} (H_2O)_{0-22}\}^{4+}$	$\{^{[9]}Ca (H_2O)_1 (H_2O)_0\}^{2+}$ $\{^{[10]}Sr\ ^{[11]}Sr (H_2O)_0 (H_2O)_0\}^{4+}$
$[B_{14}O_{20}(OH)_6]^{4-}$	0.20	Sheet	6□8Δ	2.85–3.35	0.16–0.26	$\{^{[8]}M^{2+}\ ^{[10]}M^{2+} (H_2O)_{0-9} (H_2O)_{0-18}\}^{2+}$	$\{^{[8]}Ca\ ^{[10]}Sr (H_2O)_2 (H_2O)_1\}^{4+}$
$[B_8O_{11}(OH)_4]^{2-}$	0.19	Sheet	3□5Δ	2.75–3.25	0.16–0.27	$\{^{[9]}M^{2+} (H_2O)_{0-5} (H_2O)_{0-9}\}^{2+}$	$\{^{[9]}Sr\}^{2+}$
$[B_5O_6(OH)_4]^{1-}$	0.18	Cluster	1□4Δ	2.7–3.2	0.15–0.26	$\{^{[6]}M^{+}\ ^{[4]}M^{+} (H_2O)_{0-3} (H_2O)_{0-10}\}^{2+}$, $\{^{[8]}M^{+}\}$	$\{^{[6]}Na\ ^{[4]}Na (H_2O)_0 (H_2O)_6\}$, $\{^{[8]}K^{+}\}$
$[B_5O_7(OH)_2]^{1-}$	0.16	Chain	1□4Δ	2.8–3.1	0.14–0.26	$\{^{[4]}M^{+} (H_2O)_{0-4} (H_2O)_{0-4}\}^{+}$	$\{^{[4]}(NH_4) (H_2O)_0 (H_2O)_1\}^{1+}$
$[B_{15}O_{20}(OH)_8]^{3-}$	0.16	Cluster	3□12Δ	2.6–3.1	0.15–0.27	$\{^{[4]}M^{+}_3 (H_2O)_{0-11} (H_2O)_{0-12}\}^{3+}$	$\{^{[4]}(NH_4)_3 (H_2O)_2 (H_2O)_0\}^{3+}$

larly Na, have Lewis acidities much lower than the range of Lewis basicity of $[B(OH)_4]^-$, and hence cannot occur as interstitial cations in the absence of Cl.

The effective charge of the structural unit is $1 + 4h = 1.8^-$ (for $h = 0.20$ *vu*), and hence the maximum and minimum numbers of bonds from the interstitial complex to the structural unit are 1.8 / 0.21 = 8.6 and 1.8 / 0.27 = 6.7, respectively. Schindler & Hawthorne (2001) showed that the number of bonds from an interstitial complex $\{^{[l]}M^{n+}\,^{[m]}M^{n+}_a\,(H_2O)_d\,(H_2O)_e\,^{[r]}Cl_n]^{(a \times n)+}$ containing Cl to the structural unit is $l + am + d + s - r$, where l and m are the coordination numbers of the interstitial cations, a is the number of interstitial cations in the conceptual Cl-free interstitial complex (*i.e.*, one less than in the interstitial complex containing Cl), d is the number of transformer (H_2O) groups, s is the number of hydrogen bonds from the structural unit, and r is the coordination number of Cl. For the structural unit $[B(OH)_4]^-$, $6.7 < l + am + d + s - r < 8.6$. It is interesting that this expression is independent of the formal charge of the interstitial cation. For an interstitial complex with no transformer (H_2O) groups and [8]-coordinated Cl, $l + am + d + s - r = l + m - 4$. If $l = m$, $5.4 < m < 6.3$; thus the interstitial cation will have a coordination number of [6], in accord with the structure of teepleite (Table 1). For bandylite, the number of bonds to the structural unit is $l + (a - 1) \times m + d + s - r$, where $a = 1$, m is the coordination number of the original putative cation in mechanism (2) (Schindler & Hawthorne 2001), $s = 4$ and $r = 6$. Following the procedure given above, the number of bonds reduces to $l - 2$, and hence $6.7 < l - 2 < 8.6$; thus l = [9] or [10]. In bandylite, $l = 6$, and the scheme does not work well here. This discrepancy may be connected with the fact that Cu^{2+} has additional electronic effects (Jahn–Teller distortion) affecting its geometry.

The structural unit $[B_4O_4(OH)_7]^{3-}$

This structural unit occurs in hydrochlorborite, $^{[8]}Ca_2\,(H_2O)_6\,^{[8]}Cl\,[B_4O_4(OH)_7]\,(H_2O)$. The calculated range in Lewis basicity for the structural unit is 0.20–0.26 *vu*. This range overlaps with the Lewis acidity of Ca (Table 2), and hence Ca could occur as an interstitial cation with no transformer (H_2O) groups. However, the formal charge of this structural unit is 3^-, and hence electroneutrality forces the smallest Cl-free unit formula to have three interstitial Ca atoms and a double-sized structural unit. However, incorporation of Cl into the interstitial complex allows a simpler formula, that observed for hydrochlorborite. The effective charge of the structural unit is $3 + 2h = 3.4^-$ (for $h = 0.20$ *vu*), and hence the maximum and minimum numbers of bonds from the interstitial complex to the structural unit are 3.4 / 0.20 = 17.0 and 3.4 / 0.26 = 13.0, respectively. As above, the number of bonds from an interstitial complex containing Cl to the structural unit is $m\,(a + 1) + s - r$, where, for $[^{[8]}Ca_2\,(H_2O)_2\,(H_2O)_4\,^{[8]}Cl]^{3+}$, m is the coordination number of the interstitial cation, a is 1, d is the number of transformer (H_2O) groups, s is 7, and r is the coordination number of Cl. The number of bonds from an interstitial complex with [8]-coordinated Cl^- is $2m + d - 8$, and $13.0 < 2m + d - 6 < 17.0$; this simplifies to $9.5 - d/2 < m < 11.5 - d/2$. For $d = 2$ [*i.e.*, two transformer (H_2O) groups in the interstitial complex], the predicted coordination-numbers are [8.5] and [10], in reasonable accord with the observed value of [8].

The structural unit $[B_3O_4(OH)_4]^{5-}$

This structural unit occurs in solongoite, $Ca_2\,^{[6]}Cl\,[B_3O_4(OH)_4]$. The effective charge is $(3 + 0.2 \times 4)^- = 3.8^-$, and hence the average basicity = 3.8 / 8 = 0.475 *vu*. From Figure 1, the minimum and maximum coordination-numbers of the O atoms in the structural unit are 3.7 and 4.1, respectively, and the corresponding range in the number of bonds required in total by the structural unit is 29.4–32.9. The number of bonds in the structural unit is $4 \times 2 + 3 \times 1 + 4 + 15$, and hence the number of bonds required from the interstitial complex is in the range 29.4 – 15 = 14.4 and 32.9 – 15 = 17.9. Dividing the effective charge of the structural unit by these numbers of bonds gives the range in Lewis basicity: 3.8 / 14.4 to 3.8 / 17.9: 0.21–0.26 *vu*. The number of bonds from the interstitial complex may be calculated from the expression of Schindler & Hawthorne (2001): $2(m - 1)$, where m is the coordination number of the interstitial cation. Thus $14.4 < 2(m - 1) < 17.9$, from which m = [8], [9] or [10]. This is in accord with the [8]-coordination of Ca in solongoite.

The General Chemical Composition of Borate Minerals

The ranges in Lewis basicity for structural units in Cl-free hydroxy-hydrated borate minerals vary from 0.14 to 0.275 *vu* and have individual widths between 0.04 and 0.12 *vu*. Figure 4 shows the variation of these ranges in Lewis basicity as a function of average basicity. For structural units with an average basicity between 0.16 and 0.26 *vu,* the spread of the range of Lewis basicity decreases with increasing average basicity. For structural units with an average basicity greater than 0.26 *vu*, the total range in Lewis basicity is smaller. Furthermore, the minimum value of the range increases with increasing average basicity, up to a maximum value of 0.45 *vu*.

Figures 4a–d show the ranges in Lewis basicity for structural units in Cl-free hydroxy-hydrated borate minerals, together with the maximum, minimum and average Lewis acidities of (Cl-free) interstitial complexes with Mg, Ca, Na and K, respectively, as interstitial cations. Also shown in Figures 4a–d are the average Lewis acidities of the corresponding cations in borate minerals (Table 2). The average Lewis acidity of Mg, 0.33 *vu*, does not match any range in Lewis basicity for hy-

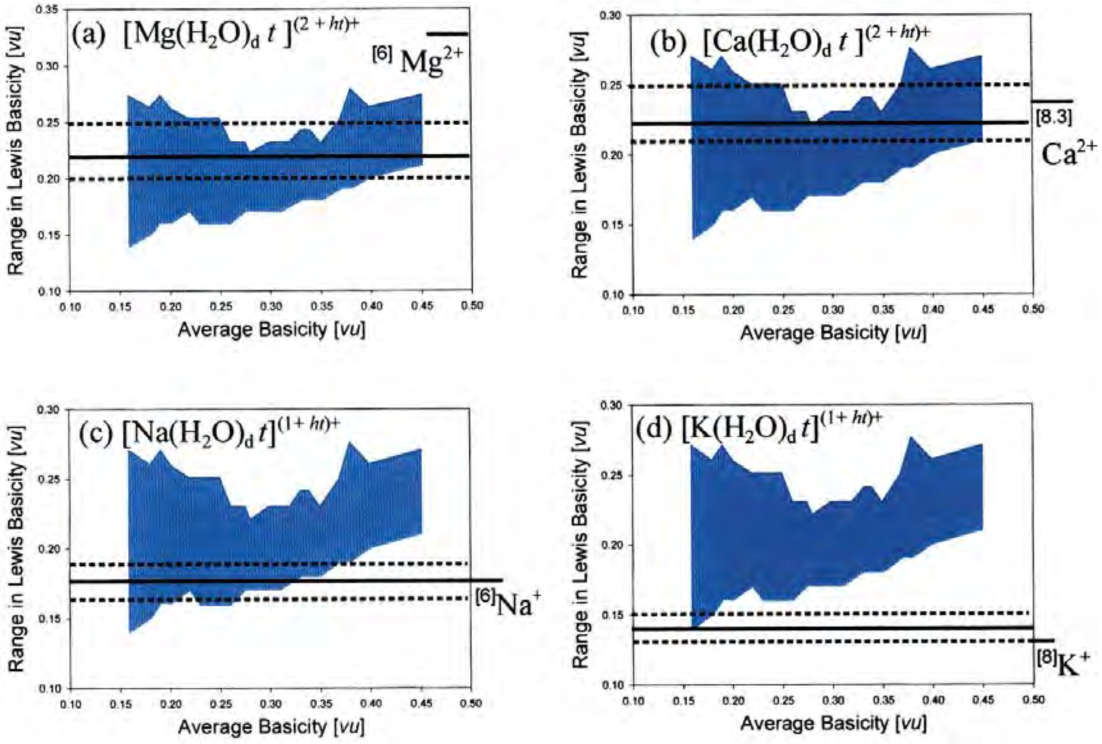

FIG. 4. Variation in range of Lewis basicity (shaded area) as a function of average basicity for structural units in borate minerals; the Lewis acidities for common cations are shown on the right.

droxy-hydrated borate minerals (Fig. 4a). However, when the effects of transformer (H_2O) groups and $s = t$ hydrogen bonds are factored into the calculation of the Lewis acidity of the interstitial complex, the average value of the latter is 0.22 *vu*, and the range in Lewis acidity of the interstitial complexes overlaps the range in Lewis basicity of the structural units (Fig. 4a), as required by the valence-matching principle. Thus every interstitial complex with exclusively $^{[6]}$Mg as its interstitial cation requires transformer (H_2O) groups, monovalent anions such as (OH), or non-transformer (H_2O) groups transferring *s* (*t*) hydrogen bonds; an exception is preobrazhenskite, which contains a symmetrical hydrogen bond (Schindler & Hawthorne 2001).

The average Lewis acidity of Ca, 0.24 *vu*, is between the upper limit and average range in Lewis basicity (Fig. 4b). When the effects of transformer (H_2O) groups and transferred hydrogen bonds are factored into the calculation of the Lewis acidity of the interstitial complex, the average value of the latter is 0.23 *vu*, similar to that of the naked cation, but the range in Lewis acidity of the interstitial complexes is extended to overlap more of the range in Lewis basicity of the structural units (Fig. 4b), increasing the range of structural units able to combine with interstitial Ca to form minerals.

The average Lewis acidity of Na, 0.17 *vu*, matches the lower limit of the range in Lewis basicity below an average basicity of 0.32 *vu* (Fig. 4c). When the effects of transformer (H_2O) groups and transferred hydrogen bonds are factored into the calculation of the Lewis acidity of the interstitial complex, the average value of the latter is 0.17 *vu*, the same as that of the interstitial cation, and the range in Lewis acidity of the interstitial complexes is extended slightly to overlap more of the range in Lewis basicity of the structural units (Fig. 4c), but there is still a wide range of structural units incompatible with Na as an interstitial cation (in the absence of Cl, see later discussion).

The average Lewis acidity of K, 0.13 *vu*, does not overlap the range in Lewis basicity of borate minerals at all (Fig. 4d). The only K borate mineral is santite, K $(H_2O)_2$ $[B_5\ O_6\ (OH)_4]$ (Ashmore & Petch 1970), in which the interstitial complex has a Lewis acidity of 0.15 vu and the structural unit has an average basicity of 0.18 *vu* (Table 1). In order to calculate a more representative average Lewis acidity of interstitial complexes with only K as the interstitial cation, we used additional structural data for synthetic compounds: K (H_2O) $[B_3\ O_3\ (OH)_4]$ (Salentine 1987) with an interstitial complex $\{^{[8]}K\ (H_2O)_0\ (H_2O)_1\}^+$ and a corresponding Lewis acidity of 0.15 *vu*, $K_2 (H_2O)_2 [B_4 O_5 (OH)_4]$ (Marezio *et al.* 1963) with $\{^{[8]}K_2 (H_2O)_0 (H_2O)_2\}^{2+}$ and 0.14 *vu*, $K_2 (H_2O)_2 [B_5 O_8 (OH)]$ (Marezio 1969) with $\{^{[8]}K_2 (H_2O)_0 (H_2O)_2\}^{2+}$ and 0.13 *vu*, and $K (H_2O)_2 [B_5 O_6 (OH)_4]$ (Zachariasen & Plettinger 1968) with $\{^{[8]}K (H_2O)_0 (H_2O)_2\}^{+}$ and 0.15 *vu*. The resulting average Lewis acidity of the interstitial complexes is 0.14 *vu* with a range of 0.13 to 0.15 *vu* (Fig. 4d). The average Lewis acidity of these interstitial complexes and the maximum Lewis acidity match the range in Lewis basicity of structural units, with an average basicity of 0.16 and 0.16 to 0.18 *vu*, respectively. In all above-listed K borate compounds, K is in [8]-coordination and has a Lewis acidity of 0.125 vu. The higher Lewis acidity of the corresponding interstitial complexes is the result of the transference of bond valence *via* hydrogen bonds emanating from the structural unit and affecting the effective charge of the interstitial complex (Schindler & Hawthorne 2001). Thus the occurrence of the one K borate mineral, santite, is in accord with the distribution of ranges and Lewis basicity and Lewis acidity in Figure 4d. Moreover, Figure 4d accounts for the general lack of hydroxy-hydrated K borate minerals in Nature.

Interstitial complexes containing monovalent cations and Cl

Figure 4c shows that the range in Lewis acidity of interstitial complexes with only Na as the interstitial cation does not match the range in Lewis basicity of structural units with an average basicity larger than 0.35 *vu*. However, Na occurs in teepleite, $Na_2 Cl [B (OH)_4]$, in which the structural unit $[B (OH)_4]^-$ has an average basicity of 0.45 *vu*; how can this happen? The range in Lewis basicity of the structural unit $[B (OH)_4]^-$ is 0.21–0.27 *vu* (Table 4). A putative interstitial complex $\{^{[6]}Na\}^+$ in $^{[6]}Na [B (OH)_4]$ would have a Lewis acidity of $(1 + 4 \times 0.20) / 10 = 0.18$ *vu*, which does not match the range in Lewis basicity. However, for teepleite, the interstitial complex is $\{^{[6]}Na_2 \, ^{[8]}Cl\}^+$, and this has a Lewis acidity of $(1 + 4 \times 0.20) / (2 \times 6 + 4 - 8) = 0.23$ *vu*; this value matches the range in Lewis basicity of the structural unit $[B (OH)_4]^-$: 0.21–0.27 *vu*, and a stable structure can form.

A Comment on Minerals *Versus* Synthetic Compounds

Minerals usually crystallize in a chemically complicated system in which Nature provides a wide variety of cations and anions from which crystals may form. As a result, one expects the most stable structural arrangements to occur. In the vocabulary of the ideas presented here, sufficient chemical species are usually available for crystallization such that the valence-matching principle is satisfied and exotic coordination numbers (*e.g.*, [3]-coordinated Na, [1]-coordinated O) are avoided. Synthetic compounds crystallize in a chemically restricted system, and the resultant atomic arrangements are restricted by what chemical species are available during crystallization. In some cases, the atomic arrangements that result may be relatively unstable; they may show exotic coordination-numbers or large deviations from the valence-matching principle. For this reason, the arguments developed here are likely to work better for minerals than for synthetic compounds. Nevertheless, examination of synthetic compounds from this perspective, and comparison with analogous natural systems, may give significant insight into less stable atomic arrangements.

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