

A bond topological approach to borate minerals: A brief review

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Here I use bond topology and bond valence theory to examine the structural chemistry of borate minerals. Bond valence theory is briefly reviewed, with particular emphasis on the valence sum rule and the valence matching principle. With regard to the valence matching principle for simple cations and oxyanions, I define a Matching index: $M = (\text{Lewis acidity} - \text{Lewis basicity}) / \text{Lewis basicity}$. Structures with large positive values of M show significant strain in the form of unusual coordination numbers for some cations, and unusual mean bond lengths for other cations. Lewis acidities of geochemically common cations are commonly smaller than Lewis basicities of common oxyanions. This mismatch drives both polymerisation and hydroxylation of oxyanions that reduce the Lewis basicities of the resulting complex oxyanions, enabling a better match with the Lewis acidities of geochemically common cations. More complicated minerals are considered as made up of a (usually anionic) structural unit and a (usually cationic) interstitial complex, and the principle of correspondence of Lewis acidity–basicity (the mean field equivalent of the valence matching principle) is a powerful method for predicting many aspects of the chemical composition and stereochemistry of complicated minerals.

Introduction

Boron is not an abundant element in the Earth. However, because of its crystal-chemical characteristics, it is very susceptible to fractionation in Earth processes, and can become concentrated to a degree not found for other elements of similar abundance. As a result, there are a relatively large number of borate minerals, and borate deposits are of economic importance at many localities around the world. Here, I will use *bond topology* and the *bond valence model* to consider the crystal chemistry of borate minerals, particularly with respect to those factors affecting their chemical compositions and crystal structure arrangements. I will use the terms *cation* and *anion* to differentiate between the more electropositive and electronegative species bonded to one another, with no implication as to the type of chemical bonding involved.

The bond valence model

Bond valence is a measure of the strength of a chemical bond; bond valence is considered as positive if it is directed from a cation to an anion, and negative if it is directed from an anion to a cation. The bond valence model⁽¹⁾ involves relations between the length of a bond and the corresponding value of its bond valence for the constituent ions.^(2–4) There are two separate parts to the bond valence model: *bond valence*

curves and *bond valence theory*. Bond valence curves are based on experimentally observed interatomic distances and the valence sum rule (see below). *Bond valence theory* is based on various theorems (axioms) and is topological (or graph theoretic) in nature. There are three fundamental theorems in bond valence theory:⁽¹⁾ (1) the valence sum rule, (2) the loop rule, and (3) the valence matching principle.

The valence sum rule

The *valence sum rule* states that the sum of the bond valences incident at an ion is equal to the formal ion valence. For any field, Gauss' law relates the flux of the field intensity through a closed surface to the net charge within that surface. The valence sum rule is a corollary of Gauss' theorem applied to the vector electric field, and the fluxes between atoms correlate strongly with the assigned bond valences in the bond valence method.⁽⁵⁾ Long range Coulomb interactions are transmitted inductively through a crystal by the operation of Gauss' law on the Coulomb field at each atom.⁽⁵⁾

The loop rule

The *loop rule* states that the sum of the directed bond valences around any (closed) loop in a structure is zero. Note that this rule is partly a result of assigning positive and negative bond valences as a function of their direction (positive from a cation to an anion, negative from an anion to a cation).

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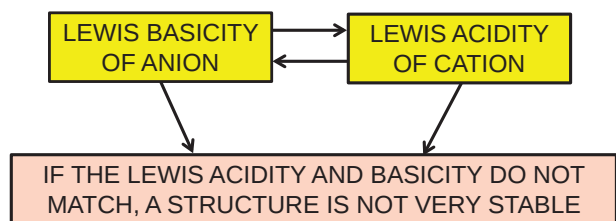


Figure 1. The valence matching principle [Colour available online]

The valence matching principle

The *valence matching principle* involves the relative magnitudes of the Lewis acid strength (acidity) and Lewis base strength (basicity) of the constituent ions in a chemical bond. The *Lewis acid strength* of a cation may be defined as the characteristic valence of its bonds, and this is given by its formal atomic valence divided by its mean (ideal) coordination number;⁽⁶⁾ a comprehensive list of values is given by Gagné & Hawthorne.⁽⁷⁾ The Lewis base strength of an anion can be similarly defined as the characteristic valence of the bonds formed by the anion. The magnitude of the strength of a chemical bond from a cation to an anion is controlled by the Lewis acid strength of the cation, and the magnitude of the strength of the bond from the anion to the cation is controlled by the *Lewis base strength* of the anion. As the chemical bond from the cation to the anion is the same bond as that from the anion to the cation, the magnitudes of the Lewis acid strength and the Lewis base strengths of the constituent ions must be (approximately) the same for that bond to form. This argument leads to the *valence matching principle*.⁽¹⁾ *Stable structures will form where the Lewis acid strength of the cation closely matches the Lewis base strength of the anion* (Figure 1).

These three theorems are based on (1) the handshaking principle in Graph Theory, and (2) Gauss' law (see above), and are bond topological in nature: They deal with the spatial connectivity of chemical bonds rather than the details of electron sharing between atoms.

The Lewis basicity of oxyanions

The definition of Lewis basicity given above is often not useful, as variations in bond valence around anions are commonly much greater than variations in bond valence around cations, and any characteristic bond valence that is assigned has too large a dispersion to be useful. For example, in kotoite, $\text{Mg}_3(\text{BO}_3)_2$,^(8,9) the bond valences to O^{2-} vary between 0.29 vu for $\text{O}^{2-}\text{--Mg}^{2+}$ bonds to 0.99 vu for $\text{O}^{2-}\text{--}^{[3]}\text{B}^{3+}$ bonds (the leading superscript in $^{[3]}\text{B}^{3+}$ indicates the boron coordination number); with this amount of variation in bond valence, it is generally not very useful to define a Lewis base strength for O^{2-} . However, the situation is somewhat different for oxyanions. Consider a complex oxyanion such

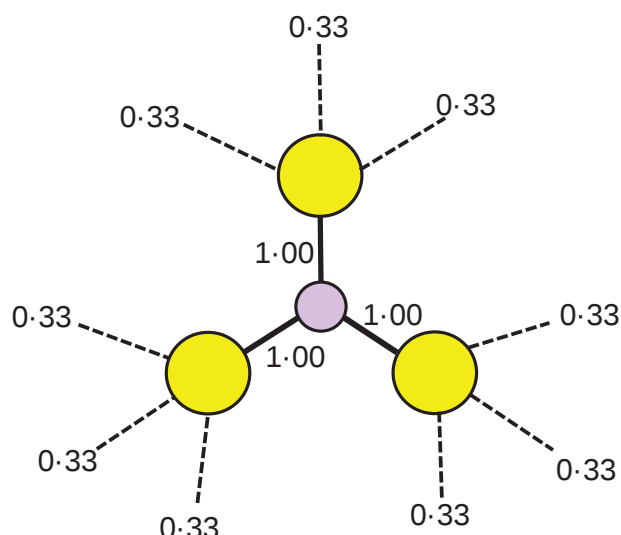


Figure 2. The bond valence structure of the $(\text{BO}_3)^{2-}$ oxyanion, with the individual bond valences shown in valence units; the Lewis basicity of the $(\text{BO}_3)^{2-}$ oxyanion is 0.33 vu [Colour available online]

as $(\text{BO}_3)^{3-}$ (Figure 2): The central B^{3+} cation provides 1.00 vu to each coordinating O^{2-} ion and these need an additional 1.00 vu from other neighboring cations. If the coordination number of O^{2-} is $[n]$, then the average valence of the bonds to O^{2-} (exclusive of the $\text{B}^{3+}\text{--O}^{2-}$ bond) is $1.00/(n-1)$ vu; where $n=2, 3, 4$, or 5 ; however, a bond valence of 1.00 vu corresponds to linking the $(\text{BO}_3)^{3-}$ group to another $(\text{BO}_3)^{3-}$ group (polymerisation), hence changing the oxyanion (to be discussed later). For $3 \leq n \leq 5$, the corresponding bond valences to each O^{2-} of the $(\text{BO}_3)^{3-}$ group are 0.50, 0.33 and 0.25 vu, respectively. The average bond valence received by the $(\text{BO}_3)^{3-}$ group is the same as the average bond valence received by each individual O^{2-} anion, and allows us to define a Lewis basicity for the oxyanion group. For the $(\text{BO}_3)^{3-}$ oxyanion, the possible bond valences are quite tightly constrained (0.50 to 0.25 vu) and give an average value of 0.36 vu. The Lewis basicity for an oxyanion is actually calculated from the average coordination number for the oxyanion group; for the $(\text{BO}_3)^{3-}$ group, Brown⁽¹⁾ assigned a mean anion coordination number of $[4]$ and the resulting Lewis basicity is $1.0/(4-1)=0.33$ vu. Lewis basicities of selected oxyanions are listed in Table 1.

The valence matching principle is the most powerful idea in bond valence theory: it allows us

Table 1. Lewis basicities* for some oxyanions

Oxyanion	LB (vu)	Oxyanion	LB (vu)
$(\text{BO}_3)^{3-}$	0.33	$(\text{AsO}_4)^{3-}$	0.25
$(\text{BO}_4)^{5-}$	0.42	$(\text{CO}_3)^{2-}$	0.22
$(\text{SiO}_4)^{4-}$	0.33	$(\text{CO}_2\text{OH})^-$	0.17
$(\text{AlO}_4)^{5-}$	0.42	$(\text{NO}_3)^-$	0.11
$(\text{PO}_4)^{3-}$	0.25	$(\text{VO}_4)^{3-}$	0.25
$(\text{PO}_3\text{OH})^{2-}$	0.22	$(\text{SO}_4)^{2-}$	0.17
$(\text{PO}_2(\text{OH})_2)^-$	0.17	$(\text{CrO}_4)^{2-}$	0.17

*values from Brown (2009) and Hawthorne (2012)

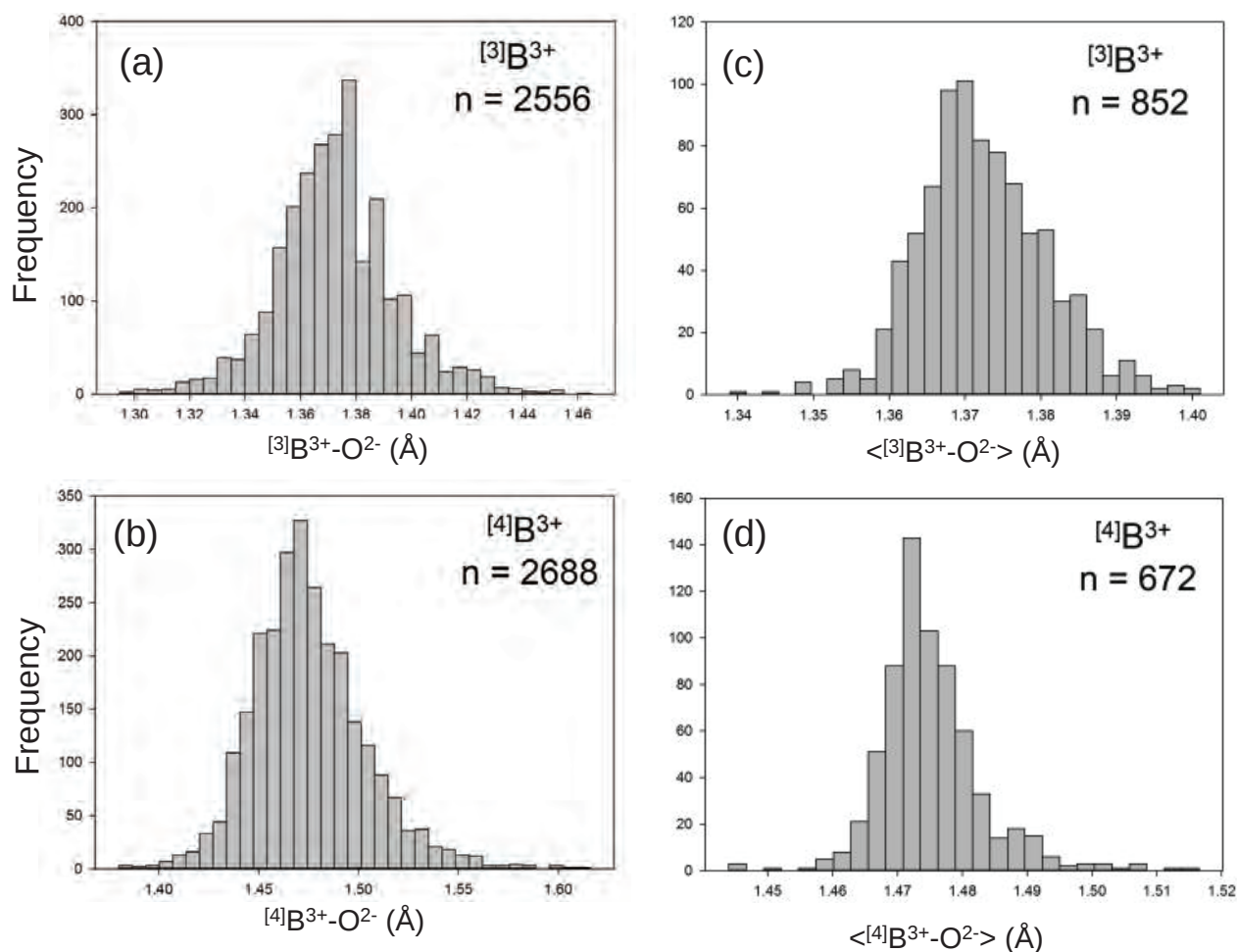


Figure 3. The variation in B³⁺-O²⁻ distances in inorganic borate crystal structures: (a) [³]B³⁺-O²⁻ distances; (b) [⁴]B³⁺-O²⁻ distances; (c) <[³]B³⁺-O²⁻> mean distances; (d) <[⁴]B³⁺-O²⁻> mean distances. Modified from Gagné & Hawthorne⁽¹⁰⁾

not just to interpret known atomic arrangements; we can test the relative stability of *possible* compounds, which moves us from *a-posteriore* to *a-priori* analysis.

Bond lengths and bond valences in borates

Gagné & Hawthorne⁽¹⁰⁾ examined the variation in B³⁺-O²⁻ bond lengths as a function of coordination number, and their results are shown in Figure 3. B³⁺ occurs in three coordination numbers [2], [3] and [4], with a slight preference for [3] relative to [4]. Linear BO₂ groups occur in four structures^(11,12) and the presence of B in these crystals was confirmed by chemical analysis and ¹¹B NMR. [³]B³⁺-O²⁻ distances (Figure 3(a)) are in the range 1.298 to 1.464 Å with a grand mean value of 1.372 Å, and the skewness of the distribution is very low, as expected for an ion with high bond valences and small coordination number. [⁴]B³⁺-O²⁻ distances (Figure 3(b)) are in the range 1.380 to 1.616 Å with a grand mean value of 1.475 Å, and again the skewness of the distribution is very low. The variation of mean distances for coordination numbers [3] and [4] are shown in Figure 3(c) and (d), respectively. <[³]B³⁺-O²⁻> distances are in the range 1.339 to 1.401 Å with a grand mean-value of 1.372

Å, and <[⁴]B³⁺-O²⁻> distances are in the range 1.444 to 1.517 Å with a grand mean value of 1.475 Å. These variations in bond lengths should provide a guide for what B³⁺-O²⁻ may be observed in borate glasses.

The valence matching principle in borate crystals

As noted above, the valence matching principle allows us to test the relative stability of *possible* compounds, and hence also the relative stability of *possible* local arrangements in glasses. We will briefly consider [⁴]B³⁺-O²⁻ and [³]B³⁺-O²⁻ arrangements in turn.

(BO₃)³⁻ groups

The valence matching principle states that stable structures will form where the Lewis acid strength of the cation closely matches the Lewis base strength of the anion. Let us look at this matching in a more quantitative way. We will define a *Matching Index*, *M*, in the following way:

$$M = (LA - LB) / LB$$

where LA and LB are the Lewis acidity and Lewis

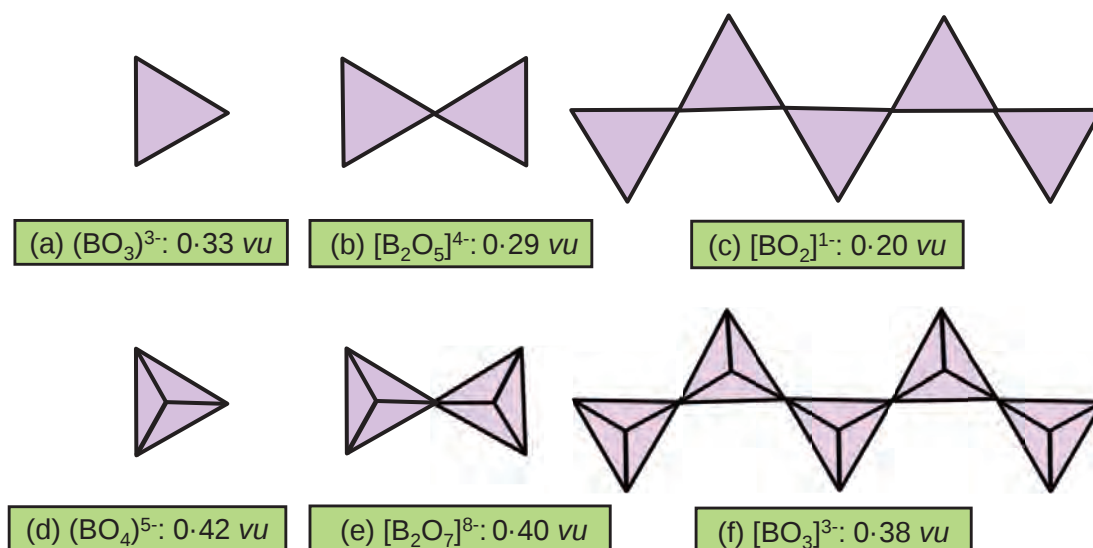


Figure 4. The effect of polymerisation on the Lewis basicities of (a)–(c) $(\text{BO}_3)^{3-}$ and (d)–(f) $(\text{BO}_4)^{5-}$ polyhedra [Colour available online]

basicity of the constituent ions or oxyanions. Consider the composition $\text{Al}(\text{BO}_3)$. The Lewis basicity of the $(\text{BO}_3)^{3-}$ group is 0.33 vu (Table 1) and the Lewis acidity of Al^{3+} is 0.583 vu.⁽⁷⁾ The Lewis acidity of the cation does not match the Lewis basicity of the anion, the valence matching principle is not satisfied, and M is 0.77. Consider the composition $\text{Mn}^{2+}\text{Sn}^{4+}(\text{BO}_3)_2$, the mineral tusionite.^(13,14) The Lewis basicity of the $(\text{BO}_3)^{3-}$ group is 0.33 vu (Table 1) and the aggregate Lewis acidity of Mn^{2+} and Sn^{4+} is $(0.334+0.69)/2=0.51$ vu.⁽⁷⁾ The Lewis acidity of the cation does not match the Lewis basicity of the anion, the valence matching principle is not satisfied, and M is 0.55. Consider the composition $\text{Mg}_3(\text{BO}_3)_2$. The Lewis basicity of the $(\text{BO}_3)^{3-}$ group is 0.33 vu (Table 1) and the Lewis acidity of Mg^{2+} is 0.33 vu.⁽⁷⁾ The Lewis acidity of the cation matches the Lewis basicity of the anion, the valence matching principle is satisfied, and M is 0.00. Consider the compositions $\text{Na}_3(\text{BO}_3)$ and $\text{Cs}_3(\text{BO}_3)$. The Lewis basicity of the $(\text{BO}_3)^{3-}$ group is 0.33 vu (Table 1) and the Lewis acidities of Na^+ and Cs^+ are 0.159 and 0.084 vu.⁽⁷⁾ The Lewis acidity of the cation does not match the Lewis basicity of the anion in either case, the valence matching principle is not satisfied, and the M values are -0.52 and -0.75 , respectively.

$(\text{BO}_4)^{5-}$ groups

Consider the compositions $\text{Nb}(\text{BO}_4)$ and $\text{Ta}(\text{BO}_4)$. The Lewis basicity of the $(\text{BO}_4)^{5-}$ group is 0.42 vu (Table 1) and the Lewis acidities of Nb^{5+} and Ta^{5+} are 0.835 and 0.822 vu.⁽⁷⁾ The Lewis acidity of the cation does not match the Lewis basicity of the anion, the valence matching principle is not satisfied, and the M values are 0.988 and 0.957. Consider the composition $\text{MgAl}(\text{BO}_4)$. The Lewis basicity of the $(\text{BO}_4)^{5-}$ group

is 0.42 vu (Table 1) and the aggregate Lewis acidity of Mg^{2+} and Al^{3+} is $(0.337+0.583)/2=0.460$ vu.⁽⁷⁾ The Lewis acidity of the cation shows a poor match with the Lewis basicity of the anion, the valence matching principle is not satisfied, and M is 0.393. Consider the compositions $\text{Na}_5(\text{BO}_4)$ and $\text{Cs}_5(\text{BO}_4)$. The Lewis basicity of the $(\text{BO}_4)^{5-}$ group is 0.42 vu (Table 1) and the Lewis acidities of Na^+ and Cs^+ are 0.159 and 0.084 vu.⁽⁷⁾ The Lewis acidity of the cation does not match the Lewis basicity of the anion in either case, the valence matching principle is not satisfied, and the M values are -0.518 and -0.745 , respectively.

How do these structures that have large M values accommodate the mismatch in their Lewis acidities and Lewis basicities? $\text{Al}(\text{BO}_3)$ has a $\langle^{[6]}\text{Al}-\text{O}\rangle$ distance of 1.930 Å which is much larger than the grand mean $\langle^{[6]}\text{Al}-\text{O}\rangle$ distance of 1.903 Å given by Gagné & Hawthorne⁽¹⁵⁾ for 453 Al^{3+} octahedra in inorganic structures, indicating that the structure is highly strained. Schiavinitoite, $\text{Nb}(\text{BO}_4)$,⁽¹⁶⁾ and behierite, $\text{Ta}(\text{BO}_4)$,⁽¹⁷⁾ have the zircon structure, and both Nb^{5+} and Ta^{5+} have [8]-coordination which is extremely uncommon for these two cations. Thus it seems that structures with high positive values of M typically show very strained structures, i.e. unusual mean bond lengths or unusual coordination numbers.

Polymerisation and hydration

Inspection of Table 1 shows that the Lewis basicity of the oxyanions listed are commonly higher in magnitude than the Lewis acidities of many of the abundant cations in the crust of the Earth (e.g. Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Pb^{2+}), and hence the valence matching principle would tend to limit the number of minerals that could crystallise with these simple oxyanions. However, there are other processes that

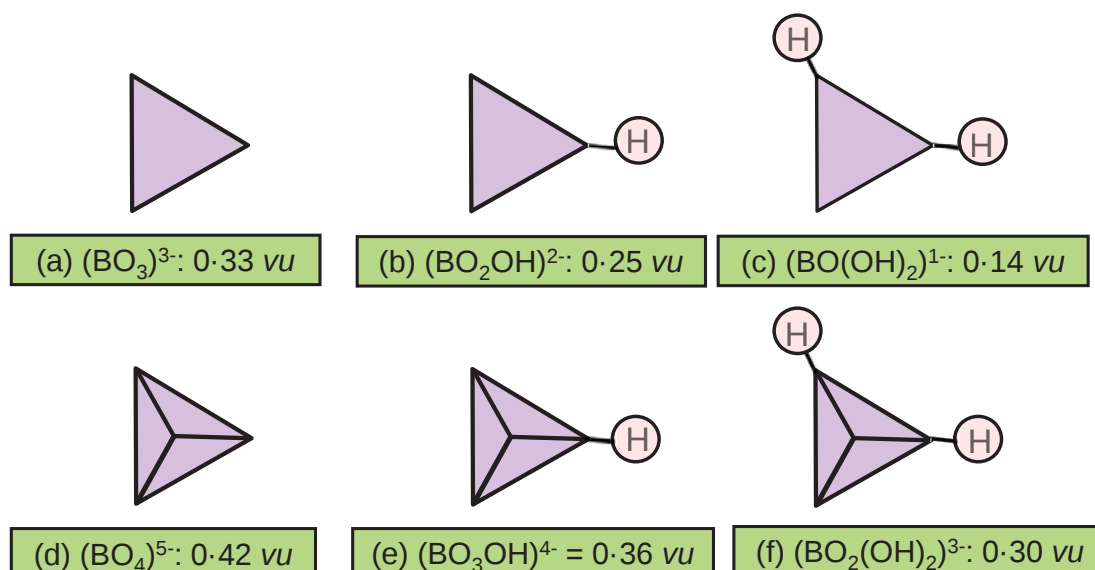


Figure 5. The effect of hydroxylation on the Lewis basicities of (a)–(c) $(\text{BO}_3)^{3-}$ and (d)–(f) $(\text{BO}_4)^{5-}$ polyhedra [Colour available online]

reduce the magnitudes of the Lewis basicities of oxyanions; these are (1) polymerisation, and (2) hydroxylation.

Polymerisation

Various examples of polymerisation of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ groups are shown in Figure 4. Following Brown,⁽¹⁾ all simple anions have an ideal coordination number of [4] (see above). For the (BO_3) group (Figure 4(a)), each anion receives one bond from B^{3+} and three bonds from ions external to the (BO_3) group. The Lewis basicity is the magnitude of the net charge, 3^- , divided by the total number of external bonds, $3 \times 3 / (3 \times 3) = 0.33$ vu. For the $[\text{B}_2\text{O}_5]^{4-}$ dimer (Figure 4(b)), the Lewis basicity is $4 / (4 \times 3 + 1 \times 2) = 0.29$ vu. For the infinite $[\text{BO}_2]$ metaborate chain (Figure 4(c)), the Lewis basicity is $1 / (1 \times 3 + 2 \times 1) = 0.20$ vu. For the (BO_4) group (Figure 4(d)), the Lewis basicity is $5 / (4 \times 3) = 0.42$ vu. For the $[\text{B}_2\text{O}_7]^{8-}$ dimer (Figure 4(e)), the Lewis basicity is $8 / (6 \times 3 + 1 \times 2) = 0.40$ vu. For the infinite $[\text{BO}_3]^{3-}$ metaborate chain (Figure 4(f)), the Lewis basicity is $3 / (2 \times 3 + 1 \times 2) = 0.38$ vu. For the $[\text{B}_2\text{O}_5]^{4-}$ sheet (not shown), the Lewis basicity is $4 / (2 \times 3 + 3 \times 2) = 0.33$ vu. Mixed polymerisations are also common. For example, the three-membered ring of one $(\text{BO}_3)^{3-}$ group and two $(\text{BO}_4)^{5-}$ groups, $[\text{B}_3\text{B}_4\text{O}_{13}]^{7-}$, has a Lewis basicity of $7 / (5 \times 3 + 3 \times 2) = 0.33$ vu.

Hydroxylation

Various examples of hydroxylation of $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ groups are shown in Figure 5. For the $(\text{BO}_2\text{OH})^{2-}$ group (Figure 5(b)), the Lewis basicity is $2 / (2 \times 3 + 1 \times 2) = 0.25$ vu. For the $(\text{BO}(\text{OH})_2)^{1-}$ group (Figure 5(c)), the Lewis basicity is $1 / (1 \times 3 + 2 \times 2) = 0.14$ vu. For the $(\text{BO}_3\text{OH})^{4-}$ group (Figure

5(e)), the Lewis basicity is $4 / (3 \times 3 + 1 \times 2) = 4/11 = 0.36$ vu. For the $(\text{BO}_2(\text{OH})_2)^{3-}$ group (Figure 5(f)), the Lewis basicity is $3 / (2 \times 3 + 2 \times 2) = 3/10 = 0.30$ vu. For the $[\text{B}_2\text{O}_3(\text{OH})_2]^{2-}$ dimer (not shown), the Lewis basicity is $2 / (2 \times 3 + 3 \times 2) = 2/12 = 0.16$ vu.

Thus both polymerisation and hydroxylation reduce the Lewis basicity of the oxyanion and promote matching of the Lewis acidity and Lewis basicity of the cation and anion components of a structure. These values of Lewis basicity now approach the range of Lewis basicity of water, and this accord has a major impact on the behaviour of B in the Earth's surficial environment.

The principle of correspondence of Lewis acidity–basicity

Above, we saw how the valence matching principle enables assessment of the structure stability of particular chemical compositions via the interaction of the acid and basic ions of the structure. However, many minerals have very complicated structures and compositions, and looking at the interaction of single ions is not useful. In this case, we use a *binary representation* of the structure where we partition the structure into a strongly bonded *structural unit*, and a weakly bonded *interstitial complex* that links the structural units into a complete crystal structure. Thus, in the structure of aristarainite, $\text{Na}_2\text{Mg}(\text{H}_2\text{O})_4[\text{B}_6\text{O}_8(\text{OH})_4]_{2z}$,⁽¹⁸⁾ the structural unit is $[(\text{B}_6\text{O}_8(\text{OH})_4)_2]^{4-}$ and the interstitial complex is $\{\text{Na}_2\text{Mg}(\text{H}_2\text{O})_4\}^{4+}$ (Figure 6). If we can derive Lewis basicities and acidities for the structural unit and the interstitial complex, then we can examine the interaction of these two structural constituents. However, the valence matching principle applies to individual ions, whereas both the structural unit and

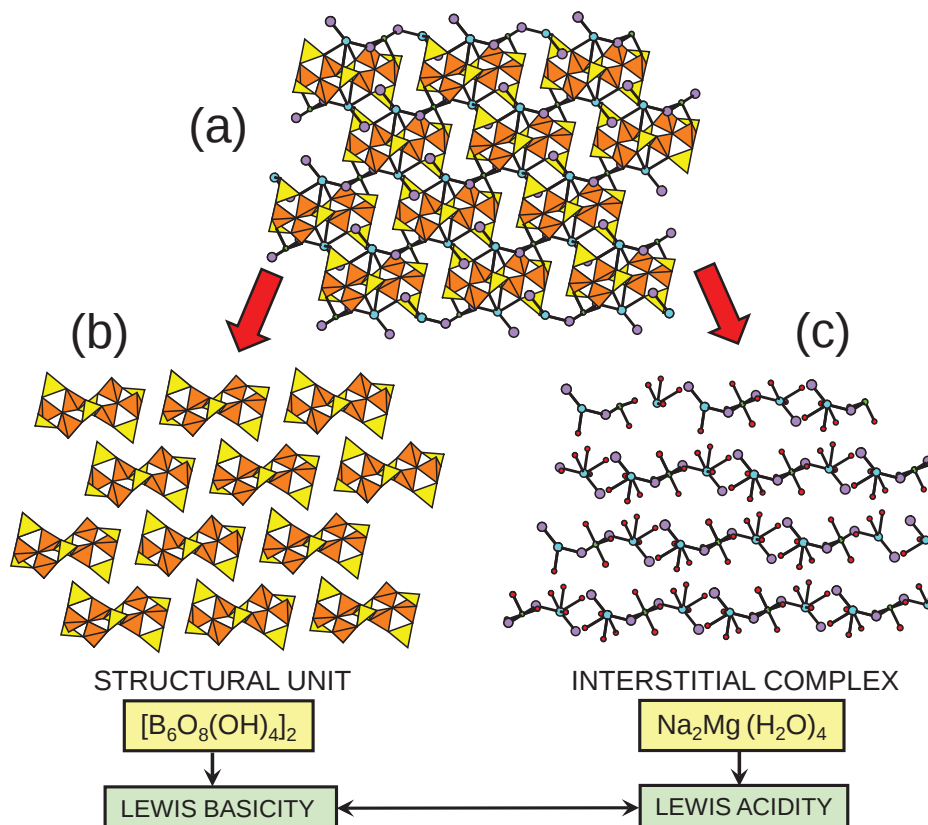


Figure 6. Binary representation of the crystal structure of aristarainite.⁽¹⁸⁾ (a) The complete structure, (b) the structural unit, and (c) the interstitial complex. $(\text{BO}_3)^{3-}$ polyhedra: yellow; $(\text{BO}_4)^{5-}$ polyhedra: orange; Mg^{2+} : small blue circle; Na^+ : large blue circle; O^{2-} : small red circle; H_2O : large mauve circle [Colour available online]

the interstitial complex are commonly aggregates of ions, and hence we need a mean field equivalent of the valence matching principle to deal with such aggregate constituents: this is formulated as *the principle of correspondence of Lewis acidity–basicity*.^(19,20) The next step is to calculate the mean Lewis basicity and Lewis acidity of these constituents.

Calculation of the Lewis basicity of a structural unit

For simple ions, the Lewis acidities are calculated by dividing the formal charge by the mean observed coordination number, the latter being derived from a large number of crystal structures.^(6,7) For simple (mononuclear) oxyanions, the Lewis basicities are calculated by dividing the formal charge by the mean estimated coordination number (as the mean observed coordination numbers have not been experimentally derived for oxyanions). For a structural unit, the Lewis basicity is calculated by dividing the *effective charge of the structural unit* by the *number of bonds to the structural unit from the interstitial complex and adjacent structural units*. The effective charge of the structural unit is the formal charge as modified by transfer of charge from the structural unit by any hydrogen bonds to the interstitial complex and adjacent structural units. Thus for the structural unit

$[(\text{B}_6\text{O}_8(\text{OH})_4)_2]^{4-}$, the effective charge is $-4 - 0.2 \times 8 = -5.6$ vu (assuming an average hydrogen bond valence of 0.2 vu). Next, we need to know the number of

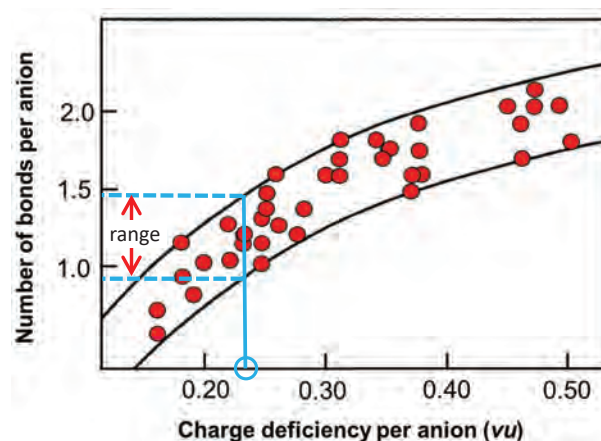


Figure 7. The variation in the number of bonds to the structural unit from the interstitial complex and adjacent structural units versus the CDA (charge deficiency per anion) of the structural unit for several dozen well-refined borate crystal structures; the data follow a band defined by the curved solid black lines. The blue circle on the abscissa shows the CDA of aristarainite, 0.23 vu. The dashed blue lines show the range of data at this CDA value, and define the numbers of bonds to the structural unit: 0.85 to 1.42 per anion of the structural unit [Colour available online]

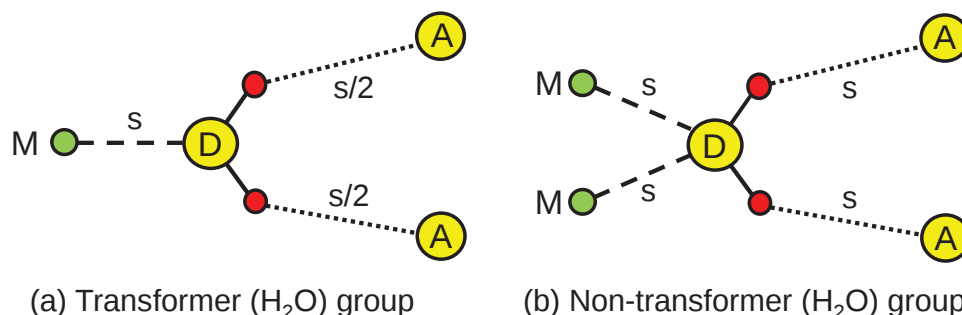


Figure 8. The bond valence structure of (a) transformer (H₂O), and (b) non-transformer (H₂O). Green circles: Mⁿ⁺ cations; yellow circles: O_{donor} and O_{acceptor} anions; red circles: H⁺ ions; bond valences are shown as lowercase letters [Colour available online]

bonds to the structural unit from the interstitial complex and adjacent structural units. At first sight this seems impossible to know in advance. However, let us define the CDA (charge deficiency per anion) as the effective charge of the structural unit divided by the number of anions in the structural unit, i.e. $-5.6/24 = 0.233$ vu in the above example of aristarainite. Figure 7 shows the variation in the number of bonds per anion to the structural unit from the interstitial complex and adjacent structural units versus the CDA for several dozen well refined crystal structures of borate minerals, where the number of bonds to the structural unit from the interstitial complex and adjacent structural units was counted from the refined crystal structure for each data point. The data conform to a well defined nonlinear band across the plot that is bounded by the curved black lines (Figure 7). Using a CDA of 0.233 vu, we get a range in the number of bonds per anion to the structural unit of 0.85 to 1.42 (see blue lines in Figure 7). There are 24 anions in the structural unit of aristarainite, and hence the number of bonds to the structural unit is 24×0.85 to $24 \times 1.42 = 20.4$ to 34.1 , i.e. there is a range in the possible number of bonds to the structural unit. The Lewis basicity of the structural unit of aristarainite is $-5.6/20.4$ to $-5.6/34.1 = 0.16$ to 0.27 vu; there is a range in the Lewis basicity that reflects the range in pH over which the structural unit $[(B_6O_8(OH)_4)_2]^{4-}$ is stable.

Calculation of the Lewis acidity of an interstitial complex

In order to calculate the Lewis acidity of an interstitial complex, we need to understand the role of (H₂O) in interstitial complexes.⁽²¹⁾ Consider an (H₂O) group bonded to a single cation M (Figure 8(a)) with a bond valence of s vu. Requiring adherence to the valence sum rule at O_{donor} and H⁺ results in H...O_{acceptor} bond valences of $s/2$ vu. These are exactly half the bond valence from M to O_{donor}; in effect, the (H₂O) group has transformed a single bond of bond valence s vu into two bonds each of bond valence $s/2$ vu. For this reason, an (H₂O) group of the local stereochemistry shown in Figure 8(a) is known as a *transformer* (H₂O)

group as it transforms a single bond into two bonds of half the bond valence. Now consider an (H₂O) group bonded to two cations (Figure 8(b)) each with a bond valence of s vu. Requiring adherence to the valence sum rule at O_{donor} and H⁺ results in H...O_{acceptor} bond valences of s vu. An (H₂O) group of the local stereochemistry shown in Figure 8(b) is known as a *non-transformer* (H₂O) group as it does not change a bond, it merely propagates it further through space. As a transformer (H₂O) group affects the number of bonds and the strength of the bonds in an interstitial complex, it affects the Lewis acidity of that interstitial complex; a *non-transformer* (H₂O) group does not.

With regard to aristarainite, Na₂Mg(H₂O)₄[B₆O₈(OH)₄]₂, the Lewis basicity of the structural unit is 0.16 to 0.27 vu; what is the Lewis acidity of the interstitial complex? We may write the interstitial complex of aristarainite in a bit more detail as $\{^{[5]}Na_2^{[6]}Mg(H_2O)_4\}^{4+}$ where the superscript t on the (H₂O) groups shows that they are all transformer (H₂O) groups. The coordination of Mg²⁺ is MgO₄(H₂O)₂ ^{t_{2r}} and hence there are $4 + 2 \times 2 = 8$ bonds from Mg²⁺ to the structural unit. The coordination of Na⁺ is NaO₃(H₂O)₂ ^{t_{2r}} , and hence there are $3 + 2 \times 2 = 7$ bonds from each Na⁺ to the structural unit. There is a total of $8 + 2 \times 7 = 22$ bonds emanating from the structural unit, and hence the Lewis acidity of aristarainite is $4/22 = 0.18$ vu. The range in Lewis basicity of the structural unit of aristarainite is 0.16 to 0.27 vu; as this range includes the Lewis acidity of aristarainite (0.18 vu), aristarainite accords with the principle of correspondence of Lewis acidity–basicity.

The principle of correspondence of Lewis acidity–basicity: Predictive capabilities

The whole point of the principle of correspondence of Lewis acidity–basicity (and the valence matching principle) is that we can (and should) use it for *a-priori* prediction of structures and chemical compounds. So how do we approach prediction from the principle of correspondence of Lewis acidity–basicity?

We may write a general formula for an interstitial

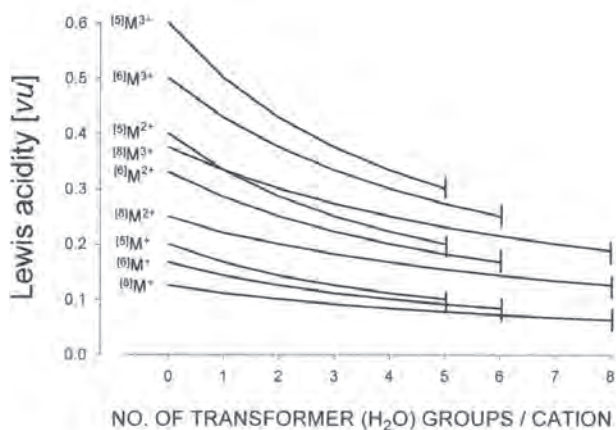
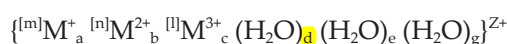


Figure 9. Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation (along the abscissa) and the formal valence and coordination number of the interstitial cations (the family of curves across the plot). From Hawthorne & Schindler⁽¹⁹⁾

complex as follows:



where M are cations with coordination numbers $[m]$, $[n]$ and $[l]$ and:

d =amount of transformer (H_2O);

e =amount of non-transformer (H_2O);

g =amount of (H_2O) not bonded to any interstitial cation.

We may represent the Lewis acidity of this generalized interstitial complex in terms of variations in chemical composition and stereochemistry by the graph in Figure 9; this graph contains all information concerning the possible variation in Lewis acid strength of interstitial complexes. Consider the interstitial cation $[5]M^{3+}$. The average bond valence of bonds involving this cation (i.e. its effective Lewis acidity) is its formal charge divided by its coordination number: $3/5=0.60$ vu; hence for

zero transformer (H_2O) groups (i.e. a coordination of $M^{3+}\text{O}_5$), the curve for $[5]M^{3+}$ starts at 0.60 vu for zero transformer (H_2O) groups. For a coordination of $M^{3+}\text{O}_4(\text{H}_2\text{O})_1$, the average bond valence of bonds involving this cation is $3/(4+2\times 1)=0.50$ vu; with increasing number of transformer (H_2O) groups, the effective Lewis acidity of the $[5]M^{3+}$ cation decreases down the curve to the right until it terminates at $M^{3+}(\text{H}_2\text{O})_5$ where the effective Lewis acidity is $3/(2\times 5)=0.30$ vu. Cations of other coordinations and formal charges give rise to a family of curves across the graph.

Above, we showed that each structural unit has a range of Lewis basicity. If we mark that range on the graph of the Lewis acidity of the generalized interstitial complex, the intersection of the Lewis acidity curves with the range of Lewis basicity (Figure 10) defines those compositions and stereochemistry that accord with the principle of correspondence of Lewis acidity–basicity, and hence are capable of giving rise to stable structures. Consider the structural unit $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$. This has an effective charge of $-2-0.2\times 5=-3$ and 8 constituent anions, and thus the $\text{CDA}=-3/8=-0.375$. This corresponds to a number of bonds per cation (from Figure 7) of 1.5 to 2.0, and a range in Lewis basicity of $3/8\times 1.5$ to $3/8\times 2.0=0.19$ to 0.25 vu. This range is marked on Figure 10(a) by the yellow box; all compositions within that box are potential minerals. The structural unit $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ occurs in inderite: $[6]\text{Mg}(\text{H}_2\text{O})_4[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})$; inderborite: $[8]\text{Ca}[6]\text{Mg}(\text{H}_2\text{O})_4[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_2$; inyoite: $[8]\text{Ca}(\text{H}_2\text{O})_3[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})$; kurnakovite: $[6]\text{Mg}(\text{H}_2\text{O})_4[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})$; and meyerhofferite: $[8]\text{Ca}(\text{H}_2\text{O})[\text{B}_3\text{O}_3(\text{OH})_5]$. All these minerals are predicted stable compositions for this structural unit, and their compositions are shown by the red circles in Figure 10(a). Now consider the structural unit $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$. This has an effective charge of $-2-0.2\times 4=-2.8$ and 9 constituent anions, and thus the $\text{CDA}=-2.8/9=-0.311$. This corresponds to a number of bonds per cation

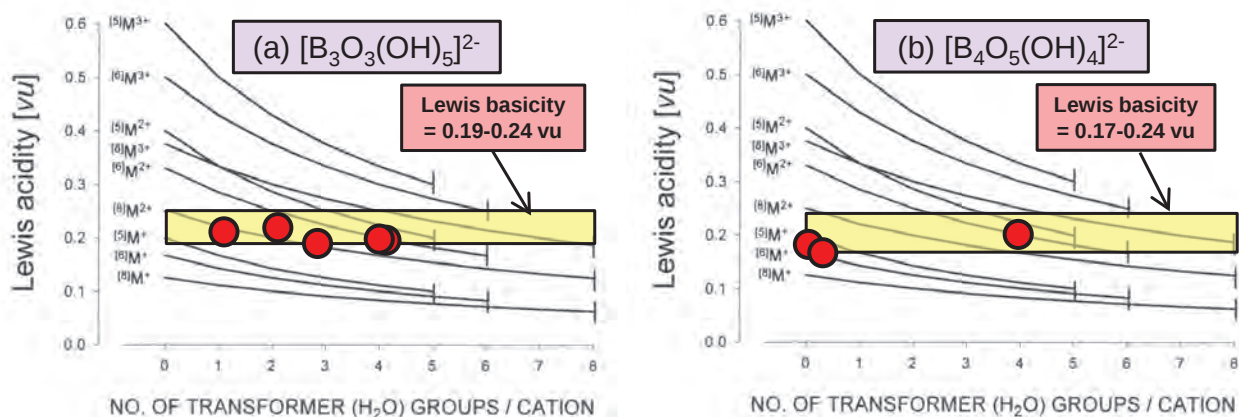


Figure 10. Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The yellow boxes show the range in Lewis basicity for the structural units (a) $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ and (b) $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$. The red circles show the compositions of interstitial complexes observed in minerals with these structural units [Colour available online]

(from Figure 7) of 1.3 to 1.8 and a range in Lewis basicity of $2.8/9 \times 1.3$ to $2.8/9 \times 1.8 = 0.17$ to 0.24 vu. This range is marked on Figure 10(b) by the yellow box; all compositions within that box are potential minerals. The structural unit $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ occurs in borax: $^{[6]}\text{Na}_2(\text{H}_2\text{O})_0[\text{B}_4\text{O}_5(\text{OH})_4](\text{H}_2\text{O})_8$; tincalconite: $^{[6]}\text{Na}_2(\text{H}_2\text{O})_{0.67}[\text{B}_4\text{O}_5(\text{OH})_4](\text{H}_2\text{O})_2$; and hungchaoite: $^{[6]}\text{Mg}(\text{H}_2\text{O})_4[\text{B}_4\text{O}_5(\text{OH})_4](\text{H}_2\text{O})_2$. All these minerals are predicted stable compositions for this structural unit, and their compositions are shown by the red circles in Figure 10(b).

Summary

Bond topology and bond valence theory are very effective in understanding the structural chemistry of borate minerals, and they should also be effective in examining local atomic arrangements in borate glasses. Lewis acidities of geochemically common cations are commonly smaller than Lewis basicities of common oxyanions. This mismatch drives both polymerisation and hydroxylation of oxyanions that reduce the Lewis basicities of the resulting complex oxyanions, enabling a better match with the Lewis acidities of geochemically common cations. The principle of correspondence of Lewis acidity–basicity is a powerful method for understanding and predicting many aspects of the chemical composition and stereochemistry of complicated hydroxy-hydrated borate minerals.

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