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A BOND-VALENCE APPROACH TO THE STRUCTURE, CHEMISTRY AND PARAGENESIS OF HYDROXY-HYDRATED OXYSALT MINERALS. I. THEORY

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ABSTRACT

The crystal structure of a mineral may be divided into two parts: (1) the *structural unit*, an array of high-bond-valence polyhedra that is usually anionic in character, and (2) the *interstitial complex*, an array of large low-valence cations, simple anions and (H₂O) groups that is usually cationic in character. Interstitial complexes link the structural units with weak cation–anion and hydrogen bonds into a continuous structure, and the breakdown of a structure is usually controlled by the strengths of the weak bonds that link the structural units together. The interstitial complex is (usually) a complex cation, and can be characterized by its *Lewis acidity*, a measure of the electrophilic character of the complex. The structural unit is (usually) a complex oxyanion, and can be characterized by its *Lewis basicity*. The interaction between the structural unit and the interstitial complex can be examined using the *valence-matching principle* from bond-valence theory. If one examines a series of structures with the same structural unit, it is evident that the average coordination of the O atoms of the structural unit varies slightly from one structure to another, producing a range of Lewis basicity for this specific structural unit. In this way, a specific structural unit can be stable over a range of Lewis basicity (i.e., over a specific pH range). The formula of an interstitial complex may be written in the following way: $\{^{[m]}M^+_a\ ^{[n]}M^{2+}_b\ ^{[l]}M^{3+}_c\ (H_2O)_d\ (H_2O)_e\ (OH)_f\ (H_2O)_g\}^{(a+2b+3c-f)+}$, where $[n]$, $[m]$ and $[l]$ are coordination numbers, a , b and c are the numbers of monovalent, divalent and trivalent cations, d is the number of *transformer* (H₂O) groups, e is the number of (H₂O) groups bonded to two interstitial cations or one interstitial cation and one hydrogen bond, f is the number of interstitial (OH) groups, and g is the number of (H₂O) groups not bonded to any cation. The number of *transformer* (H₂O) groups strongly affects the Lewis acidity of the interstitial complex, and the variation in Lewis acidity of a generalized interstitial complex can be graphically represented as a function of the number of *transformer* (H₂O) groups. 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 structural arrangement is possible. A range of borate minerals is examined from this perspective. These ideas show that there are considerable restrictions on the details of the interstitial complexes in even the most complicated of the borates. The impetus at present is to understand what controls the composition of complex oxysalt minerals, and the present approach takes some steps toward this goal.

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

SOMMAIRE

On peut diviser la structure cristalline d'un minéral en deux parties: (1) l'*unité structurale*, un agencement de polyèdres ayant une valence de liaisons élevée, et généralement à caractère anionique, et (2) le *complexe interstitiel*, un agencement de cations à

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gros rayon et faible valence, d'anions simples, et de groupes (H₂O), généralement à caractère cationique. Les complexes interstitiels rattachent les unités complexes au moyen de liaisons cation-anion et de liaisons hydrogène relativement faibles pour former une structure continue. La décomposition d'une structure est généralement régie par la force des liaisons les plus faibles qui lient les unités structurales les unes aux autres. Le complexe interstitiel est généralement un cation complexe, et on peut le caractériser selon son *acidité de Lewis*, mesure de son affinité pour les électrons. L'unité structurale est généralement un oxyanion complexe, et on peut le caractériser selon sa *basicité de Lewis*. L'interaction entre l'unité structurale et le complexe interstitiel peut se quantifier selon le principe de la correspondance des valences de liaisons. Dans une série de structures ayant la même unité structurale, il est évident que la coordinnence moyenne des atomes d'oxygène dans l'unité structurale varie légèrement d'une structure à l'autre, menant à un intervalle de basicité de Lewis pour cette unité structurale particulière. Ainsi, une telle unité structurale peut être stable sur un intervalle de basicité de Lewis, c'est-à-dire, de pH. On peut écrire la formule d'un complexe interstitiel de la façon suivante: $\{[m]M^+{}_a [n]M^{2+}{}_b [l]M^{3+}{}_c (H_2O)_d (H_2O)_e (OH)_f (H_2O)_g\}^{(a+2b+3c-f)+}$, expression dans laquelle $[n]$, $[m]$ et $[l]$ expriment la coordinnence, a , b et c représentent le nombre de cations monovalents, bivalents et trivalents, d est le nombre de groupes de (H₂O) qui sont *transformateurs*, e est le nombre de groupes de (H₂O) liés à deux cations interstitiels ou un cation interstitiel et participant à une liaison hydrogène, f est le nombre de groupes (OH) interstitiels, et g représente le nombre de groupes (H₂O) non liés à un cation. Le nombre de groupes (H₂O) agissant comme transformateurs influence fortement l'acidité de Lewis d'un complexe interstitiel, et la variation en acidité de Lewis d'un complexe interstitiel généralisé peut se représenter graphiquement en fonction du nombre de groupes de (H₂O) transformateurs. Où l'acidité de Lewis d'une complexe interstitiel généralisé correspond à l'intervalle en basicité de Lewis d'une unité structurale particulière, le principe de correspondance des valences de liaison est satisfait, et un agencement stable est donc possible. Nous examinons une collection de minéraux boratés de ce point de vue. Il y a des restrictions importantes concernant les détails de complexes interstitiels, même dans le cas des borates les plus complexes. Nous essayons de comprendre ce qui contrôle la composition des minéraux du groupe des oxysels complexes, et nous croyons que notre démarche contribue à atteindre cet objectif.

(Traduit par la Rédaction)

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

INTRODUCTION

Hydroxy-hydrated oxysalts constitute the bulk of the mineral kingdom and are by far the most important phases from an environmental perspective. However, we know far less about the factors that control their atomic arrangement, chemical composition and stability than for the (usually) more simple rock-forming minerals. This situation results primarily from the structural complexity of the hydroxy-hydrated oxysalts. Simple oxides (e.g., spinel, Mg Al₂ O₄) and oxysalts (e.g., forsterite, Mg₂ Si O₄) are susceptible to standard theoretical approaches of chemistry and physics: molecular mechanics, molecular-orbital theory, molecular dynamics. When dealing with hydroxy-hydrated oxysalt minerals [e.g., althupite, Al Th [(UO₂)₃ {(UO₂)₃ (PO₄)₂ (OH) O₂}] (OH)₃ (H₂O)₁₅], structural complexity and the difficulty in dealing with (OH) and (H₂O) groups preclude many of these standard approaches. Moreover, numerous additional issues arise when considering complex minerals:

(1) What controls the details of their chemical composition? For example, in inderborite, Ca Mg (H₂O)₄ [B₃ O₃ (OH)₅]₂ (H₂O)₂, why are the interstitial cations Ca and Mg instead of Ca₂ or Mg₂? Why are there four (H₂O) groups bonded to interstitial cations and two interstitial (H₂O) groups not bonded to interstitial cations? Why are there two interstitial (H₂O) groups not bonded to interstitial cations rather than one or three (or any other number of) (H₂O) groups?

(2) Such hydroxy-hydrated oxysalt minerals are normally stable over a small range of external conditions (e.g., Eh, pH, T, P) and are commonly associated with many (e.g., > 20) other complex minerals of similar composition in some parageneses. What factors control their relative stability?

We currently have no way to even approach these questions from a structural perspective.

Detailed paragenetic studies (e.g., Bandy 1938, Fisher 1958) have shown that there are well-defined relations between chemical compositions of hydroxy-hydrated minerals and their position in paragenetic sequences. Moore (1965, 1973) showed that this correlation extended to structural arrangements in minerals, leading to the development of structural hierarchies in minerals (Moore 1975, 1982, 1984, Hawthorne 1979, 1985, 1986, 1990, Burns 1999, Hawthorne *et al.* 1996, 2000, Hawthorne & Huminicki 2001), with the eventual intention of relating structural change to paragenetic sequence. Hawthorne (1985) introduced the idea of *binary structural representation* wherein even the most complex crystal structure is considered as a strongly bonded (usually anionic) *structural unit* and weakly bonded (usually cationic or neutral) *interstitial species*, and examined the interaction of these two components with the *valence-matching principle* (Brown 1981, Hawthorne 1994, 1997). Here, we develop this approach further, particularly in regard to relations among bond topology, bond valence and chemical composition, and show how the valence-matching principle controls many

aspects of the chemical composition of these minerals. Specifically, we consider the hydroxy-hydrated borate minerals; these are light-atom structures, and their atomic arrangements, including details of their hydrogen bonding, are accurately known.

BOND-VALENCE THEORY

As some of this material may not be generally familiar to many readers, we give a preliminary discussion of some of the important ideas before further developing the theory. More extensive treatments have been given by Brown (1981) and Hawthorne (1992, 1994, 1997).

Bond valence and the valence-sum rule

Pauling (1929) defined the strength of an 'electrostatic bond in an ionic crystal' as the formal valence of the cation divided by its coordination number. Pauling's second rule states that the sum of the bond strengths incident at an anion is approximately equal to the formal valence of that anion. Correlations between deviations from Pauling's second rule and bond-length variations in crystals have been parameterized for specific cation-anion bonds, in particular by Brown & Shannon (1973), Brown & Altermatt (1985) and Brese & O'Keeffe (1991):

$$\begin{aligned}s &= s_0 [R / R_0]^{-N}, \\ s &= [R / R_1]^{-n} \text{ or } s = \exp [-(R - R_0) / B]\end{aligned}\quad (1)$$

where s is the bond-valence in vu (valence units), R is the observed bond-length, and R_0 , N , R_1 , n and B are constants characteristic of cation-anion pairs; values for these constants were derived by fitting the equations to a large number of well-refined crystal structures such that the sum of the incident bond-valences at any atom be as close as possible to the formal valence of that atom.

Let us define a crystal, liquid or molecule as a network of atoms connected by chemical bonds. For the materials in which we are interested, any path through this network contains alternating cations and anions, and the total network is subject to the *law of electroneutrality*: the total valence of the cations is equal to the total valence of the anions. A bond valence can be assigned to each bond such that the *valence-sum rule* is obeyed: *the sum of the bond valences at each atom is equal to the magnitude of the atomic valence*. If the interatomic distances are known, then the bond valences can be calculated; if the interatomic distances are not known, then the bond valences can be approximated by Pauling bond-strengths.

Characteristic bond-valence

Brown (1981) introduced a very important idea. He noted that the bond valences around a specific cation in

a wide range of crystal structures lie within ~20% of the mean value; this mean value is thus *characteristic* of that particular cation. If the cation only occurs in one type of coordination, then the mean bond-valence for that cation will be equal to the Pauling bond-strength; thus P (phosphorus) always occurs in tetrahedral coordination to oxygen, and will hence have a mean bond-valence of $5/4 = 1.25\ vu$. If the cation has more than one coordination number, then the mean bond-valence will be equal to the weighted mean of the bond valences in all the observed structures. Thus Fe^{2+} occurs in various coordinations from [4] to [8]; the tendency is for [4]- and [5]-coordinations to be more common than [7]- and [8]-coordinations, and the mean bond-valence is $0.40\ vu$. The mean bond-valence correlates with formal charge and cation size, and varies systematically through the periodic table.

Lewis-acid and Lewis-base strengths

The concept of bond valence can be generalized in the following way. The mean bond-valence of a cation correlates strongly with its *electronegativity*. Electronegativity is a measure of the electrophilic strength (electron-accepting capacity) of the cation; the correlation with characteristic bond-valence indicates that the latter is a measure of the *Lewis-acid strength* of the cation (see also Brese & O'Keeffe 1991). Thus we have the following definition (Brown 1981):

The Lewis-acid strength of a cation may be defined as the characteristic bond-valence = atomic (formal) valence / (mean coordination-number).

The *Lewis-base strength* of an anion can be defined in exactly the same way, as the characteristic valence of the bonds formed by the anion. However, bond-valence variations around anions are much greater than those around cations; in minerals, the valence of bonds to O^{2-} can vary between nearly zero and $2.0\ vu$. For example, in sodium alum, $Na [Al (SO_4)_2] (H_2O)_{12}$, the bond valence to the O atoms of sulfate groups varies between $1.50\ vu$ from the [4]-coordinated S atom and $0.08\ vu$ from the [12]-coordinated Na atom. With this range of values, it is obviously not useful to designate a Lewis basicity for oxygen: the range of values is too great for a single predicted value to be useful. However, if we examine the $(SO_4)^{2-}$ group as an oxyanion, each oxygen atom receives $1.50\ vu$ from the central S^{6+} cation and needs an additional $0.50\ vu$ from other cations. In sodium alum, the oxygen atoms of the sulfate group are [4]-coordinated, and hence need an additional three bonds when we consider the sulfate group as an oxyanion; this gives a value for the additional bond-strength needed of $0.17\ vu$ for each of the oxygen atoms of the $(SO_4)^{2-}$ group. If this process is repeated for all $(SO_4)^{2-}$ groups in minerals, we get a mean value of the characteristic bond-strength (and bond valence) required

of 0.17 *vu* with a spread of $\sim\pm 0.10$ *vu*; this is a useful value for the $(\text{SO}_4)^{2-}$ group. In this way, we can define the *Lewis basicity* of an oxyanion. Tables 1 and 2 list Lewis acidities and Lewis basicities for some geochemically common inorganic cations and oxyanions, respectively.

The valence-matching principle

The definitions of Lewis-acid and Lewis-base strengths lead to a specific criterion for chemical bonding, the *valence-matching principle* (Brown 1981):

Stable structures will form when the Lewis-acid strength of the cation closely matches the Lewis-base strength of the anion.

This is the chemical analogue of the handshaking principle in combinatorial mathematics. As a chemical bond contains two constituents, then the properties of the constituents must match for a stable configuration to form.

BINARY STRUCTURAL REPRESENTATION

One of the problems in dealing with mineral structures is the complexity of the atom interactions; there are many of them, and their topological and geometrical characteristics are important. However, the same situation applies to an atom: there is a nucleus and numerous electrons, all interacting in a very complex manner; nevertheless, we can still usefully consider an atom as a single unit with simple properties such as size, charge and electronegativity. Hawthorne (1985) took this approach with the structural unit and considered it as a very complex oxyanion with intrinsic characteristic properties. If this is done (*e.g.*, Hawthorne 1985, 1986, 1990), we can define a Lewis basicity for the

structural unit in exactly the same way as we do for a more conventional oxyanion.

The interstitial components may be cations (*e.g.*, alkalis or alkaline earths), anions (*e.g.*, OH, Cl), and (H_2O) groups. The interstitial components of a structure can usually be considered in a simple additive fashion to produce an aggregate set of properties (*e.g.*, charge, Lewis acidity). Thus we have essentially factored the structure into two components, and this approach enables us to use the valence-matching principle to examine the interaction of the *structural unit* with the *interstitial species*. It is worth emphasizing here that we have developed a *binary representation* that gives a simple quantitative model of even the most complicated structure, and allows us quantitative insight into the weak bonding between interstitial species and the structural unit.

INTERSTITIAL COMPLEXES IN MINERALS

As discussed above, the binary representation of a structure divides it into two parts, (1) a structural unit, and (2) the interstitial species. The structural unit is an (internally) strongly bonded part of the structure that we treat as a single entity. Until now, the interstitial component has been considered as a collection of species [alkali and alkaline-earth cations, (OH) and (H_2O) groups and other anions, *e.g.*, Cl]. However, to apply the idea of binary representation completely, we need to consider the interstitial species as a single component and characterize its properties in the same way as has been done for the structural unit in previous studies (*e.g.*, Hawthorne 1985, 1986, 1990, 1992, 1994, 1997). Thus we denote the collection of interstitial species as the *interstitial complex*. Having specifically identified the interstitial complex in this way, we can now consider its properties from a much more general perspective than has been done in the past.

Determination of coordination number of interstitial cations

The determination of cation coordination-numbers has been discussed by many authors. There are different strategies to determine a coordination number: one can define the minimum strength of a bond *via* bond-valence calculation, or one can determine a first coordi-

TABLE 1. LEWIS ACID STRENGTHS (*vu*) FOR CATIONS

Li	0.22	Sc	0.50	Cu ²⁺	0.45
Be	0.50	Ti ³⁺	0.50	Zn	0.36
B	0.88	Ti ⁴⁺	0.75	Ga	0.50
C	1.30	V ³⁺	0.50	Ge	0.75
N	1.75	V ⁵⁺	1.20	As	1.02
Na	0.16	Cr ³⁺	0.50	Se	1.30
Mg	0.36	Cr ⁶⁺	1.50	Rb	0.10
Al	0.63	Mn ²⁺	0.36	Sr	0.24
Si	0.95	Mn ³⁺	0.50	Sn	0.66
P	1.30	Mn ⁴⁺	0.67	Sb	0.86
S	1.65	Fe ²⁺	0.36	Te	1.06
Cl	2.00	Fe ³⁺	0.50	Cs	0.08
K	0.13	Co ²⁺	0.40	Ba	0.20
Ca	0.29	Ni ²⁺	0.50	Pb ²⁺	0.20

Values taken from Brown (1981), except Pb²⁺ which was estimated from several oxysalt mineral structures.

TABLE 2. LEWIS BASICITIES (*vu*) FOR SOME MINERALOGICALLY IMPORTANT OXYANIONS

(BO ₃) ³⁻	0.33	(CO ₃) ²⁻	0.25
(SiO ₄) ⁴⁻	0.33	(NO ₃) ³⁻	0.12
(AlO ₄) ³⁻	0.42	(VO ₄) ³⁻	0.25
(PO ₄) ³⁻	0.25	(SO ₄) ²⁻	0.17
(AsO ₄) ³⁻	0.25	(CrO ₄) ²⁻	0.17

nation sphere on the basis of any gap that occurs in the distribution of interatomic distances around a cation. Here, we do not want to follow a strict strategy for the determination of a cation coordination-number. We partly apply bond-valence calculations (*i.e.*, omitting interactions with bond valences smaller than 0.05 vu), geometrical considerations (*i.e.*, another cation is closer to the interstitial cation than the corresponding anions), and coordination gaps.

(H₂O) AS AN INTERSTITIAL SPECIES

Hawthorne (1992) described the different possible roles of (H₂O) groups in crystal structures, and drew a strong distinction between (H₂O) as part of the structural unit and (H₂O) as an interstitial species. In particular, Hawthorne (1992) described the role of (H₂O) as a bond-valence transformer in minerals, and showed that the amount of interstitial (H₂O) can, in some cases, be quantitatively predicted on this basis. However, he did not consider all possible stereochemistries involving (H₂O), and we need to reconsider this issue. Thus here we begin further development of the previous ideas of Hawthorne (1992).

Interstitial (H₂O) not bonded to interstitial cations

Where (H₂O) is not bonded to an interstitial cation, it is usually involved in a hydrogen-bond network [this is not always the case; (H₂O) also may be occluded in the structure, but this situation is fairly rare]. Where involved in a hydrogen-bond network, the O atom of an (H₂O) group is usually [4]-coordinated, with two O–H (donor-hydrogen) bonds and two H...O (hydrogen-acceptor $\equiv$ hydrogen) bonds. In this case (Fig. 1a), two hydrogen bonds of strength $v \text{ vu}$ are incident at the O atom of the (H₂O) group. The bond-valence requirements of the central O atom are satisfied by two O–H bonds of strength $(1 - v) \text{ vu}$. In order to satisfy the bond-valence requirements about the H atoms, each H forms a hydrogen bond of strength $v \text{ vu}$ to another (H₂O) group or to an anion of the structural unit. Hence (H₂O) groups not bonded to any interstitial cations normally do not change the strengths of the chemical bonds; they merely propagate them through space. Hence we designate this type of (H₂O) group as *non-transformer* (H₂O) and denote it by the subscript g , (H₂O) _{g} .

Interstitial H₂O bonded to one interstitial cation

Let a cation, M , bond to an anion S (Fig. 1b); the anion S receives a bond-valence of $v \text{ vu}$ from the cation M . Consider a cation, M , that bonds to an (H₂O) group, which, in turn, bonds to an anion S (Fig. 1c). In the second case, the oxygen atom of the (H₂O) group receives a bond valence of $v \text{ vu}$ from the cation M , and its bond-valence requirements are satisfied by two short O–H bonds of valence $(1 - v/2) \text{ vu}$. To satisfy the bond-val-

ence requirements around each H atom, each H forms at least one hydrogen bond with its neighboring anions. In Figure 1c, one of these hydrogen bonds involves the S anion, which thus receives a bond valence of one half what it received where it was bonded directly to the M cation (Fig. 1b). Thus the (H₂O) group acts as a *bond-*

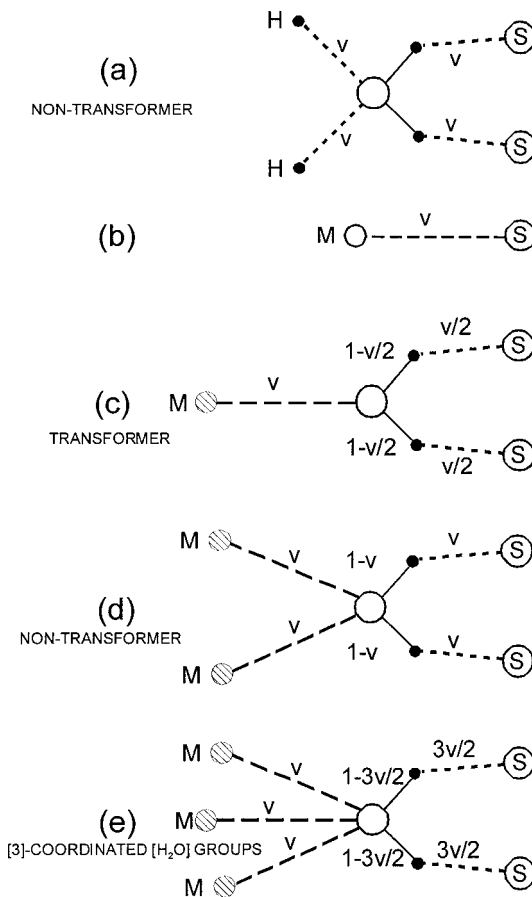


FIG. 1. (a) An (H₂O) group held in a structure solely by H-bonds; the O atom, X, is an acceptor anion for two H-bonds of valence $v \text{ vu}$, and a donor anion for two H atoms; (b) the interstitial cation M bonds to a ligand S with the bond valence v ; (c) the anion, M , bonds to an (H₂O) group, which, in turn, bonds to two anions S and thus, one bond (bond valence = $v \text{ vu}$) is split into two weaker bonds (bond valence = $v/2 \text{ vu}$); (d) two cations, M , bond to an (H₂O) group, which, in turn, bonds to two anions S , which thus receive the same bond-valence as when each was bonded directly to one M cation; (e) three cations, M , bond to an (H₂O) group, which, in turn, bonds to two anions S , which thus receive more bond-valence per bond than if bonded directly to the M cations. Cation–oxygen bonds are shown by broken lines, H bonds are shown as dotted lines, bond valences are in vu .

valence transformer, causing one bond (bond valence = v *vu*) to be split into two weaker bonds (bond valence = $v/2$ *vu*); we designate this type of (H_2O) as *transformer* (H_2O), and denote it by the subscript *d*, (H_2O)_d.

Interstitial H_2O bonded to two interstitial cations

Consider next the situation where two cations, *M*, bond to an (H_2O) group, which, in turn, bonds to an anion *S* (Fig. 1d). In this case, the O atom receives a bond valence of $2v$ *vu* from the two cations, and its bond-valence requirements are satisfied by two short O–H bonds, each of valence $(1 - v)$ *vu*. To satisfy the bond-valence requirements of each H atom, each H forms at least one hydrogen bond with its neighboring anions. In Figure 1d, one of these hydrogen bonds involves the *S* anion, which thus receives the same bond-valence (v *vu*) as where it is bonded directly to one *M* cation (Fig. 1b). Thus, in this case, the (H_2O) group does not act as a bond-valence transformer; we designate this also as *non-transformer* (H_2O) and denote it by the subscript *e*, (H_2O)_e.

Interstitial H_2O bonded to three interstitial cations

Consider next the situation where three cations, *M*, bond to an (H_2O) group, which, in turn, bonds to an anion *S* (Fig. 1e). In this case, the O atom receives a bond valence of $3v$ *vu* from the three cations, and its bond-valence requirements are satisfied by two short O–H bonds, each of valence $(1 - 3v/2)$ *vu*. To satisfy the bond-valence requirements of each H atom, each H forms (at least) one hydrogen bond with its neighboring anions. In Figure 1e, one of these hydrogen bonds involves the *S* anion, which thus receives $3v/2$ *vu* as compared with v *vu* where it is bonded directly to one *M* cation (Fig. 1b). Thus, in this case, the (H_2O) group acts as a reverse bond-valence transformer, increasing the strength of the bonds between the cations and the structural unit. This type of (H_2O) is very unusual, and has not (yet) been found in borate minerals.

MONOVALENT INTERSTITIAL ANIONS

In most minerals, the structural unit bears a negative charge and the interstitial components have a net positive charge as required by the electroneutrality principle (a few minerals have the reverse situation, but may be dealt with using the same reasoning). In the majority of minerals, the interstitial components consist of simple cations and neutral (H_2O) groups. However, some minerals contain interstitial anionic species, where the net charge of the interstitial species is positive. Of particular importance in this regard are the monovalent anions (OH) and Cl. The role of these two anions is similar: they receive bond valence from surrounding interstitial cations and hydrogen atoms [both interstitial and belonging to (OH) groups of the structural unit], essen-

tially acting as *bond-valence absorbers*. Their presence decreases the net charge of the interstitial components by 1^- per anion and usually strongly affects the number of chemical bonds from the interstitial components to the structural unit; thus they can affect the Lewis acidity of the interstitial components.

The role of (OH) as an interstitial species

The (OH) group is a very polar anion and can act as a bond-valence transformer. However, its role as a bond-valence transformer is very different from that of (H_2O). Where it is an interstitial species, the O anion of the (OH) group receives ≤ 1.0 *vu* (usually ~ 0.8 *vu*) from its companion H atom, and hence requires ≥ 1.0 *vu* from the interstitial cations to which it is bonded. By definition, bonds involving interstitial cations are weak, and this feature puts considerable constraints on the occurrence of (OH) as an interstitial species. The average bond-valences for octahedrally coordinated monovalent, divalent and trivalent cations are 0.17, 0.33 and 0.50 *vu*, respectively. For monovalent interstitial cations, this means that interstitial (OH) must bond to (at least) six cations. This arrangement is very crowded, and occurs in halite-type structures; in the open arrangements typical of interstitial environments, (OH) cannot occur with [6]- or higher-coordination monovalent cations.

For divalent interstitial cations, (OH) must bond to (at least) three cations to satisfy its bond-valence requirements. For (OH) to bond to three octahedrally coordinated cations, there must be a cluster of three edge-sharing octahedra. It is very unusual to find such a close-packed arrangement as an interstitial species, presumably because of the space requirements of incorporating the (H_2O) groups required to complete the coordination(s) of the interstitial cations, together with the resulting network of hydrogen bonding. Higher coordinations merely exacerbate this problem. Thus (OH) groups are unlikely to occur as interstitial species where accompanied by divalent cations.

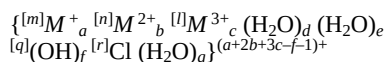
For trivalent interstitial cations, (OH) must bond to two octahedrally coordinated cations. Thus two (AlF_6) octahedra linking through a vertex, edge or face can share one, two or three (OH) groups, respectively. Although the face-sharing arrangement may be unlikely, the other two arrangements are compact and may be compatible with the occurrence of an embedding network of hydrogen bonds. Thus we come to the conclusion that (OH) is unlikely to occur as an interstitial species except with trivalent interstitial cations.

Let us consider two (AlF_6) octahedra linked through a shared edge (Fig. 2a). Both anions involved in the shared edge are (OH), and their bonding is shown more explicitly in Figure 2b. Two $^{[6]}\text{Al}$ atoms each bond to the O atom with bond valence of v *vu*. To satisfy the bond-valence requirements of the O atom, the H must link to the O with a bond valence of $2 - 2v$ *vu*. In turn, to satisfy its own bond-valence requirements, the H

atom forms a hydrogen bond of $1 - (2 - 2v) = 2v - 1$ *vu* to a neighboring anion, S. For a trivalent cation, *v* is approximately equal to 0.5 *vu*. Hence the OH anion takes two very strong bonds (≥ 0.5 *vu*) and transforms them into one weak bond (~ 0.2 *vu*). Also, it “absorbs” two strong bonds, radically changing the overall Lewis acidity of the interstitial complex. In calculating the aggregate Lewis acidity of interstitial species that include (OH), one can subtract the charge of the (OH) group(s) from a charge of the cations to get the net charge of the interstitial species, and allow for the reduction in the number of bonds to the structural unit caused by the presence of (OH).

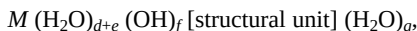
A GENERALIZED INTERSTITIAL COMPLEX

A general interstitial complex can be written as



where *M* is any type of interstitial mono-, di- and trivalent cation, [*m*], [*n*], [*l*] and [*q*] denote coordination numbers, *d* denotes the number of transformer (H_2O) groups, *e* denotes the number of non-transformer (H_2O) groups bonded to two interstitial cations or bonded to one interstitial cation and receiving one hydrogen bond from another interstitial (H_2O) group, and *g* denotes the number of (H_2O) groups not bonded to any interstitial cation; note that the different types of non-transformer (H_2O) groups all affect calculation of the Lewis acidity of the interstitial complex in the same way. Interstitial (OH) groups are bonded to more than one interstitial cation. The O atoms of the structural unit that are directly bonded to interstitial cations are not shown in the general formula.

We may write the overall composition of a mineral in the general form



where the (H_2O) and (OH) groups before the structural unit bond to an interstitial cation, and the (H_2O) group after the structural unit does not bond to an interstitial cation. For example, tunellite has the composition $Sr (H_2O)_3 [B_6 O_9 (OH)_2]$, and all (H_2O) groups bond to interstitial Sr. The Sr atom is coordinated by four interstitial (H_2O) groups and six O atoms of the structural unit. One of the three interstitial (H_2O) groups bonds to two Sr cations and another bonds to one Sr and also is a hydrogen-bond acceptor; one (H_2O) group bonds to one Sr cation only. Thus there is one transformer (H_2O) group and two non-transformer (H_2O) groups in tunellite, and the interstitial complex is written as $\{^{[10]}Sr (H_2O)_1 (H_2O)_2 (OH)_0\}^{2+}$, i.e., $d = 1$ and $e = 2$. Here, there is no information about the number of ligands in the structural unit that bond to the interstitial cation(s). Their number can only be derived if the type and coordination

of the non-transformer (H_2O) groups are known.

Bonds from the interstitial complex to the structural unit

The number of bonds from an interstitial $\{[m]M^{+a}_a [n]M^{2+b}_b [l]M^{3+c}_c (H_2O)_d (H_2O)_e [q](OH)_f (H_2O)_g\}^{(a+2b+3c-f)+}$ complex to the structural unit can be written as follows: $\Sigma \text{ bonds} = (a \times m + b \times n + c \times l) + d - (q - 1) \times f$. The interstitial (OH) groups must bond to at least two trivalent cations (or three divalent cations) in order to satisfy their own bond-valence requirements. Furthermore, depending on how many cations, *q*, coordinate each (OH) group, the number of bonds from the complex to the structural unit is reduced for every additional (OH) group.

HYDROGEN BONDS EMANATING FROM THE STRUCTURAL UNIT

Consider an interstitial complex with the chemical formula $M^{k+} (H_2O)_2$ in which both (H_2O) groups bond to the *M* cation. This situation is shown in Figure 3a, where it can be seen that there are four bonds from the interstitial complex to the structural unit; there are two transformer (H_2O) groups, and the interstitial complex is written as $\{^{[2]}M^{k+} (H_2O)_2 (H_2O)_0\}^{k+}$. The general

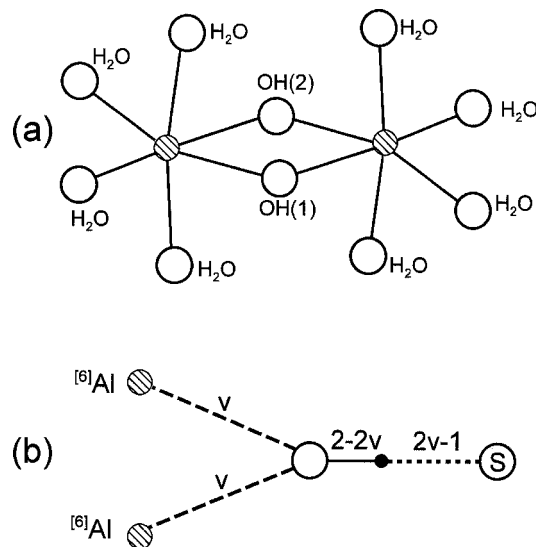


FIG. 2. (a) Two interstitial ($Al\Phi_6$) octahedra sharing an edge: $\{Al_2 (H_2O)_8 (H_2O)_0 (OH)_2\}^{4+}$; H atoms are shown as small black circles. (b) The arrangement of bond valences around an (OH) group in (a); the large unshaded circle is an O atom of an (OH) group, and the broken lines indicate a H-bond.

expression for the interstitial complex is $\{[m]M^{+a} [n]M^{2+b} [l]M^{3+c} (H_2O)_d (H_2O)_e [q](OH)_f [r]Cl (H_2O)_g\}^{(a+2b+3c-f-1)+}$, and the number of bonds from the interstitial complex to the structural unit is $(a \times m + b \times n + c \times l) + d - (q - 1) \times f$ (see above). For the interstitial complex in Figure 3a, this reduces to 2×1 (bonds involving the M cation) + 2 ($d = 2$) = 4 bonds from the interstitial complex to the structural unit.

Consider next the situation where there is a hydrogen bond from the structural unit to an interstitial (H_2O) group (Fig. 3b). As one of the interstitial (H_2O) groups is a hydrogen-bond acceptor as well as bonding to the M cation, it is no longer a transformer (H_2O) group,

and the corresponding interstitial complex is written as $\{[2]M^{k+} (H_2O)_1 (H_2O)_1\}^{k+}$. According to the formula given above, the number of bonds from the interstitial complex to the structural unit is $2 \times 1 + 1$ ($d = 1$) = 3. Inspection of Figure 3b shows that there are four bonds from the interstitial complex to the structural unit, and hence the formula given above needs to be modified to include the effect of hydrogen bonds from the structural unit to the interstitial complex. Each hydrogen bond to the interstitial complex will change a transformer (H_2O) group to a non-transformer (H_2O) group, and hence will decrease the value of d in the above formula by one. Thus the expression for the number of bonds from the

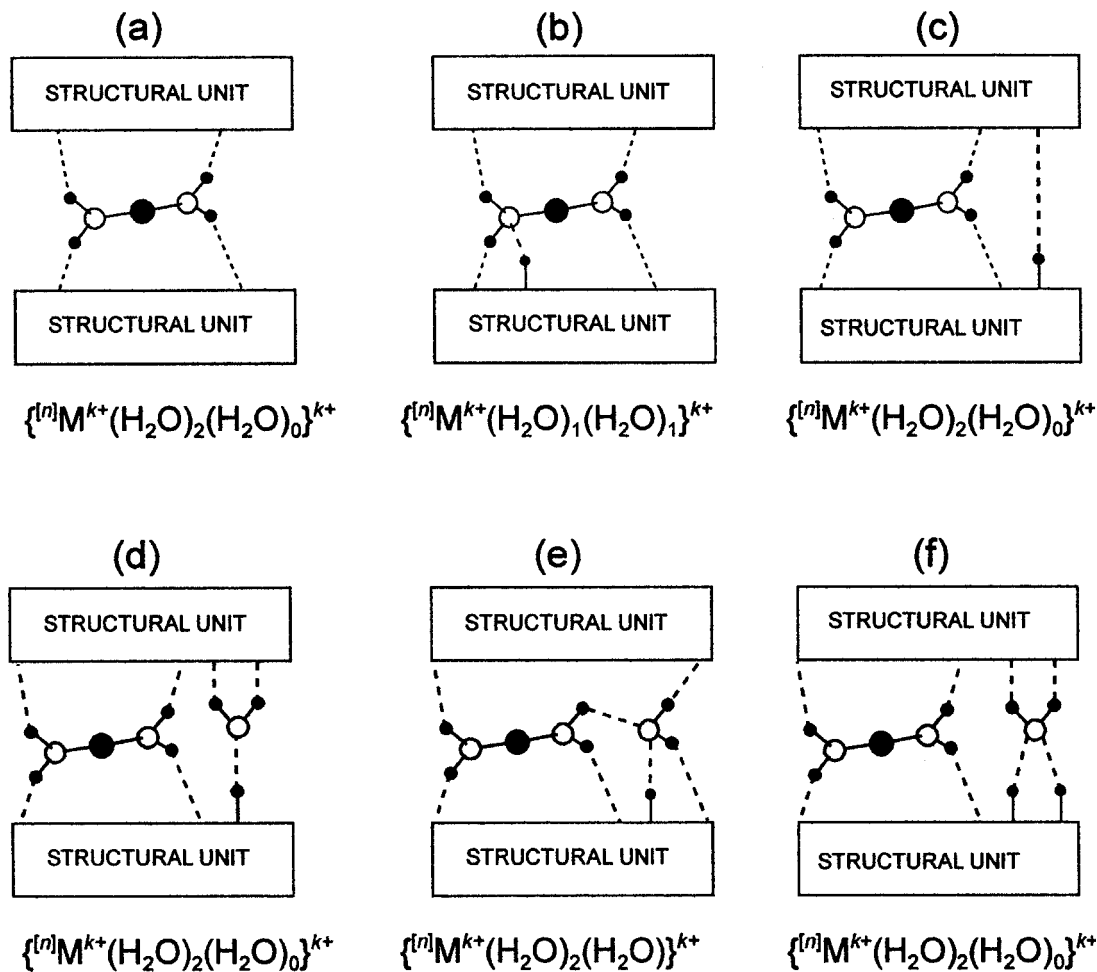


FIG. 3. Different possible configurations for hydrogen bonds emanating from the structural unit: (a) there are no such hydrogen bonds present; (b) there is one hydrogen bond from the structural unit to a non-transformer (H_2O) group of the interstitial complex; (c) there is one hydrogen bond from one structural unit to another; (d) there is one hydrogen bond from the structural unit to an interstitial (H_2O) group otherwise not bonded to anything; (e) there is one hydrogen bond from the structural unit to a non-transformer interstitial (H_2O) group not bonded to an interstitial cation; (f) there are two hydrogen bonds from the structural unit to an interstitial (H_2O) group not bonded to an interstitial cation.

structural unit to the interstitial complex must be modified by adding an additional term, s , the number of hydrogen bonds from the structural unit to the interstitial complex, to compensate for the corresponding reduction in the number of transformer (H_2O) groups: $(a \times m + b \times n + c \times l) + d - (q - 1) \times f + s$. One might ask why we need to make this modification, as if we ignored the effect of the hydrogen bonds from the structural unit to the interstitial complex, the arithmetic of calculating the number of hydrogen bonds from the structural unit to the interstitial complex would still give the correct answer. This view obviates our main intention here, which is not primarily to predict aspects of mineral composition, but to understand the stereochemical details of these complex structures. Moreover, there are other configurations for such hydrogen bonds for which the arithmetic of bond counting needs to be complete.

Consider the situation where there is a hydrogen bond from the structural unit to an adjacent structural unit (Fig. 3c). Here, the number of bonds from the interstitial complex to the structural unit is still four. However, the number of bonds received by the structural unit is five, the bonds from the interstitial complex to the structural unit *plus* the hydrogen bond from the adjacent structural unit. Thus it is important (1) to identify the acceptor anions for the hydrogen atoms of the structural unit and to count the bonds appropriately, and (2) to specify whether one is dealing with (a) the number of bonds from the interstitial complex to the structural unit, or (b) the number of bonds received by the structural unit, as these two values may be different.

Consider next the situation where a hydrogen bond from the structural unit bonds to an (H_2O) group that otherwise receives bonds only from its constituent H atoms (Fig. 3d). Without the hydrogen bond, this (H_2O) group is an occluded group and does not bond to any atom in the structure. When receiving a hydrogen bond, this (H_2O) group is a transformer (H_2O) group relative to the situation in Figure 3c: the hydrogen bond from one structural unit to another is split into two hydrogen bonds of half the bond valence. The number of bonds received by the structural unit in Figure 3d is six.

Consider the situation where a hydrogen bond from the structural unit bonds to an (H_2O) group that already accepts a hydrogen bond from a transformer (H_2O) group (Fig. 3e). Without the hydrogen bond from the structural unit, this (H_2O) group is a transformer (H_2O) group; with the hydrogen bond from the structural unit, this (H_2O) group is a non-transformer (H_2O) group, and hence the number of bonds received by the structural unit is five.

Consider last the situation where two hydrogen bonds from the structural unit bond to an (H_2O) group that is otherwise an occluded (H_2O) group (Fig. 3f). The (H_2O) group is now [4]-coordinated and is a non-transformer (H_2O) group. Thus its role is to propagate the bonds from one structural unit to the next without chang-

ing their number. Hence there are six bonds to the structural unit in Figure 3e.

AVERAGE BASICITY OF A STRUCTURAL UNIT

It is of interest to revisit our earlier discussion of the calculation of the Lewis-base strength of the $(\text{SO}_4)^{2-}$ oxyanion in sodium alum, $\text{Na} [\text{Al} (\text{SO}_4)_2] (\text{H}_2\text{O})_{12}$. In the $(\text{SO}_4)^{2-}$ oxyanion, each oxygen anion receives 1.50 *vu* from the central S^{6+} cation, and requires an additional 0.50 *vu* from other cations in the structure. In sodium alum, the oxygen atoms are [4]-coordinated, and hence each requires an additional three bonds of 0.17 *vu* to satisfy their individual bond-valence requirements. Thus the Lewis basicity of the $(\text{SO}_4)^{2-}$ oxyanion in sodium alum is 0.17 *vu*. If we repeat this process in all sulfate structures, we get a mean value for the Lewis basicity of $(\text{SO}_4)^{2-}$ that we can use without requiring any knowledge of the mean coordination of oxygen in the specific structure of interest.

In the approach proposed by Hawthorne (1985), which we are largely following here, we define the structural unit as a complex oxyanion and calculate its Lewis basicity. To do this, we need to specify a mean coordination-number for oxygen. Hawthorne (1985, 1986, 1990) postulated a coordination number (usually [4]) for specific (large) groups of structures, recognizing that, for some structures within these groups, the value chosen was inappropriate. However, if we wish to be in a position to predict *all* of the information concerning the interstitial complex, we obviously cannot use the observed mean coordination of oxygen in the structure of interest as input to that process; we need to be able to *predict* the mean coordination number of oxygen in the structural unit.

Schindler *et al.* (2000) introduced the notion of the average basicity of a structural unit: *The average basicity of a structural unit is defined as the average bond-valence sum per O atom contributed by the interstitial species and other structural units.*

This is a very easy quantity to calculate: it is the formal charge of the structural unit modified by any charge transferred by the t hydrogen bonds that emanate from the structural unit, $(Z + ht)^-$, divided by the number of oxygen atoms in the structural unit. For example, consider the structural unit $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$. The *modified charge* is $(2 + 0.2 \times 4)^- = 2.8^-$, and the number of O atoms in the structural unit is 9; the resulting average basicity is $2.8 / 9 = 0.31$ *vu*. As we will see next, there is a close relation between the average basicity of a structural unit and its average coordination number of oxygen.

DERIVATION OF THE COORDINATION NUMBER OF OXYGEN FOR STRUCTURAL UNITS

Let us consider what a specific value of average basicity implies from a structural perspective. The bonds

of the structural unit contribute most of the bond valence required by the O atoms of the structural unit, and hence the average basicity is a measure of the bond valence required by each O atom of the structural unit from the interstitial complex. Thus the O atoms in a structural unit with a low average basicity require only a small amount of bond valence from the interstitial complex, whereas the O atoms in a structural unit with a high average basicity require more bond valence from the interstitial complex. As the bonds of the structural unit are strong and the bonds of the interstitial complex are weak, differences in average basicity will have a greater effect on the number of interstitial bonds than on the number of bonds within the structural unit; hence there must be a positive correlation between the average basicity and the mean coordination-number of the O atoms in the structural unit. Figure 4 shows that this is indeed the case for borate minerals. The data define a band rather than a single line, in accord with the observation that a specific structural unit usually exhibits a range of mean coordination-numbers for the O atoms of the structural unit (e.g., $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$, Table 3). Note that three data points fall outside of the general trend. The points for biringuccite and nasinite (hollow squares) lie above the trend. Inspection of the Na–O distances suggests that the coordination numbers of the interstitial Na cations can be redefined such that these minerals now accord with the general trend (black squares). The point for preobraz-

henskite falls below the trend of Figure 4. This may be a result of the fact that preobrazhenskite contains a symmetrical hydrogen bond (Burns & Hawthorne 1994), and our method of calculating the modified charge of the structural unit is not valid in this case.

THE IMPORTANCE OF A *PRIORI* PREDICTION OF AVERAGE COORDINATION NUMBER OF OXYGEN ATOMS OF THE STRUCTURAL UNIT

If we wish to have any predictive power, we need to be able to derive the average coordination-number of such O atoms *a priori*, without recourse to a known structure. The relation between average basicity and average coordination-number of O-atoms in structural units shown for borates in Figure 4 allows such prediction, and for this reason, Figure 4 is a key feature of the theory developed here.

There is an even more important issue associated with Figure 4. As well as predicting an average coordination-number for O atoms in a given structural unit,

TABLE 3. DETAILS OF SELECTED STRUCTURAL UNITS

Structural unit	AB	Structure type	${}^{\text{t}}\text{B} = \square$ ${}^{\text{b}}\text{B} = \Delta$	Average O-CN	Lewis basicity (νu)
$[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$	0.31	Cluster	2□2Δ	3.4–3.8	0.17–0.22
$[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$	0.25	Chain	3□3Δ	3.15–3.6	0.16–0.23

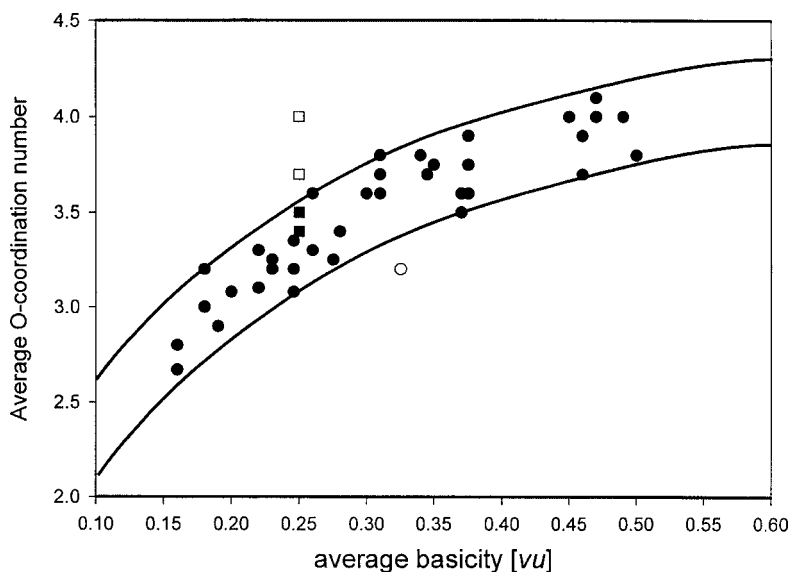


FIG. 4. Correlation between average basicity of structural units and the average coordination-numbers of O atoms in the corresponding structural units. The upper and lower border of the distribution are used to define the characteristic range in coordination numbers of oxygen for a specific structural unit. Minerals deviating from the trend are shown in unshaded symbols (see text).

this relation also predicts the *range* of possible average coordination-numbers of oxygen in a given structural unit. Where a specific structural unit (e.g., $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$, $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$) occurs in a series of structures, the O atoms of the structural unit show a range of mean coordination-numbers (e.g., [3.6]–[3.8], [3.15–3.35], respectively, for the structural units mentioned above). As discussed in the following papers (Schindler & Hawthorne 2001a, b), this range of average coordination-numbers for the O atoms of the structural unit reflects the range in pH over which the mineral is stable. Indeed, it is by varying the coordination numbers of the O atoms in the structural unit that the structural unit maintains its stability as the pH of its environment changes. Moreover, it allows calculation of the range of possible Lewis-base strength for specific structural units.

CALCULATION OF LEWIS BASICITY OF STRUCTURAL UNITS

Hawthorne (1985, 1990, 1997) described a method for calculating the Lewis basicity of a structural unit as the formal charge of the structural unit divided by the number of bonds required by the structural unit. This number of bonds was calculated by specifying the ideal coordination-number of an anion and subtracting the number of bonds within the structural unit. This works reasonably well, but (1) requires “guessing” the ideal coordination-number, and (2) cannot deal with minerals whose structural units have zero charge. Here, we have overcome the first problem by developing a relation between the average basicity and coordination number (Fig. 4). Now let us examine the second problem.

Consider kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The structural unit of kaolinite is the sheet $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]^0$. Sheets are linked by hydrogen bonds from the (OH) groups of one sheet to the bridging O atoms of the adjacent sheet. From a bond-valence perspective, we can regard the hydrogen bonds as transferring charge from one sheet to the next, and imparting a polar character to the sheet, which acts as a cation on the hydroxyl side and as an anion on the aluminosilicate side. There are two types of transfer of charge: (1) hydrogen bonds link to anions of the interstitial complex (e.g., Fig. 3b); (2) hydrogen bonds link to anions within the same structural unit or to anions in adjacent structural units (e.g., Fig. 3c). Where hydrogen bonds link to anions of the interstitial complex, there is a net transfer of charge from the structural unit to the interstitial complex. Where hydrogen bonds link to anions within the same structural unit or to anions in adjacent structural units, a polar character is developed but there is no net transfer of charge from the structural unit.

Let us define the *effective charge* of the structural unit as the formal charge of the structural unit as modified by the hydrogen bonds to the interstitial complex,

taking the average bond-valence of a hydrogen bond as *h vu*. Let there be *t* hydrogen bonds emanating from the structural unit, and let *s* of these hydrogen bonds link to the interstitial complex. In this case, the charge of *s* hydrogen bonds is transferred to the interstitial complex; the effective charge of the interstitial complex becomes $(Z + hs)^+$, and the effective charge of the structural unit is $(Z + hs)^-$.

We now define the Lewis basicity of a structural unit as its effective charge divided by the number of bonds required by the structural unit. Above, we show that each structural unit has a range in average coordination-number of oxygen and that we can derive this range from the average basicity of the structural unit *via* Figure 4. Thus we can calculate the corresponding range in Lewis basicity for any structural unit.

Example: Consider meyerhofferite, $\{\text{Ca}(\text{H}_2\text{O})_0(\text{H}_2\text{O})_1\} [\text{B}^{13}\text{B}^{14}\text{B}_2\text{O}_3(\text{OH})_5]$ (Burns & Hawthorne 1993). The modified charge of the structural unit is $[3 \times 3 - 3 \times 2 - 5 \times 1 - h \times 5] = 3.0^-$ (setting *h* = 0.20 *vu*, the average strength of a hydrogen bond; Brown 1981). The average basicity of the structural unit is thus $3.2 / 8 = 0.375$ *vu*. From Figure 4, the corresponding range in coordination number of O for this structural unit is 3.5–4.0. Thus the total numbers of bonds involved in the structural unit (where part of a mineral) are $3.5 \times 8 = 28$ and $4.0 \times 8 = 32$ bonds. The number of bonds within the structural unit is $3 \times 1 (^{13}\text{B}_3) + 4 \times 2 (^{14}\text{B}_3) + 1 \times 5 [(\text{OH})_6] = 16$ bonds. Therefore, the structural unit needs between $28 - 16 = 12$ and $32 - 16 = 16$ bonds. Now we must calculate the effective charge of the structural unit (note that this is different from the modified charge involved in calculating the average basicity of the structural unit). The effective charge of the structural unit is its formal charge as modified by the hydrogen bonds *to the interstitial complex*: $(Z + hs)^-$ *vu*. So what is the value of *s*? Inspection of the structure of meyerhofferite shows that *t* = 5 and *s* = 1. Hence the effective charge is $2 + 1 \times 0.20 = 2.2^-$. The number of bonds needed by the structural unit is from 12 to 16; however, the structural unit receives $(t - s)$ bonds from hydrogen atoms of the structural unit that do not hydrogen-bond to the interstitial complex, and hence the additional numbers of bonds needed are $12 - (t - s) = 8$ and $16 - (t - s) = 12$. Thus the range in Lewis basicity is $2.2 / 12$ to $2.2 / 8$: 0.183–0.275 *vu*.

CALCULATION OF THE LEWIS ACIDITY OF INTERSTITIAL COMPLEXES

Hawthorne (1997) described a method for calculating the Lewis acidity of a “complex cation” (= interstitial complex) as the formal charge of the interstitial cation(s) divided by the number of bonds to the structural unit. However, this method (1) ignores any hydrogen bonds emanating from the structural unit, and (2) cannot deal with minerals whose interstitial complexes

have zero charge. Here, we have overcome these problems by explicitly considering the hydrogen bonds emanating from the structural unit and the charge transferred by these hydrogen bonds.

Consider an interstitial complex containing a M cations of coordination number $[m]$ and formal charge Z/a . There are $a \times m$ bonds emanating from the interstitial cations and there are d transformer (H_2O) groups in the interstitial complex; hence there are $a \times m + d$ bonds emanating from the $\{^{[m]}M_a (\text{H}_2\text{O})_d\}^{z-}$ part of the interstitial complex. The non-transformer (H_2O) groups are [4]-coordinated. They receive two bonds from cations or act as hydrogen-bond acceptors, and also two hydrogen bonds emanate from their constituent H atoms; hence the role of non-transformer (H_2O) groups is to propagate bonds through space. Counting the bonds from the interstitial complex to the structural unit, we have the number of bonds emanating from the $\{^{[m]}M_a (\text{H}_2\text{O})_d\}^{z-}$ part of the interstitial complex, $am + d$. The total number of bonds to the structural unit is the number of bonds from the interstitial complex augmented by the hydrogen bonds emanating from the structural unit that bond to the interstitial complex, $am + d + s$, as illustrated in Figure 5.

We now define the Lewis acidity of an interstitial complex as its effective charge divided by the number of bonds from the interstitial complex to the structural unit. Now, we give a general expression for the calculation of Lewis acidity. The Lewis acidity of the interstitial complex $\{^{[m]}M^+ a^{[n]}M^{2+} b^{[l]}M^{3+} c (\text{H}_2\text{O})_d (\text{H}_2\text{O})_e (\text{OH})_f (\text{H}_2\text{O})_g\}^{(a+2b+3c-f)^+}$ can be written as

$$\frac{(a + 2b + 3c - f + h \times s)}{[m \times a + n \times b + l \times c + d - f \times (q - 1) + s]} \quad (2)$$

where h is the average bond-valence of the hydrogen bonds emanating from the structural unit.

Example: Consider the interstitial complex $\{^{[7]}Ca_2 (\text{H}_2\text{O})_7 (\text{H}_2\text{O})_3\}^{4+}$ interacting with a structural unit with

three constituent (OH) groups; two of these (OH) groups hydrogen-bond to the interstitial complex and one (OH) group hydrogen-bonds to an adjacent structural unit (Fig. 6), and hence $t = 3$ and $s = 2$. The interstitial complex has seven transformer (H_2O) groups, three non-transformer (H_2O) group bonded to Ca, no (OH) groups, and no (H_2O) groups not bonded to any cation. The effective charge of the interstitial complex is 4 (the formal charge of the interstitial cations) + 2×0.20 (the charge transferred by the s hydrogen bonds to the interstitial complex) = 4.4^+ . The number of bonds from the interstitial complex to the structural unit is 7×2 (from Ca) + 7 [from transformer (H_2O) groups] + 2 (resulting from the hydrogen bonds to the interstitial complex) = 25. Thus the Lewis acidity of the interstitial complex is $4.4 / 25 = 0.191 \text{ vu}$.

Graphical representation of Lewis acidity in interstitial complexes

We can represent the variation in Lewis acidity of an interstitial complex graphically as a function of the number of transformer (H_2O) groups for specific charges and coordination-numbers of cations (Fig. 7). Obviously, the Lewis acidity of the interstitial complex decreases as the number of transformer (H_2O) groups increases, as the coordination-numbers of cation increase, and as the cation charge decreases. Figure 7 contains all relevant information concerning variation in Lewis-acid strength of interstitial complexes. If more than one cation species is present in an interstitial complex, we may use the weighted arithmetic mean of their salient characteristics (charge and coordination number). Second, in cases where interstitial (OH) is present, we can sum the charges of the cation(s) and the interstitial (OH), and treat the complex as if it contained a cation of the resulting net charge [i.e., $M^{3+} + (\text{OH})^- \equiv M^{2+}$].

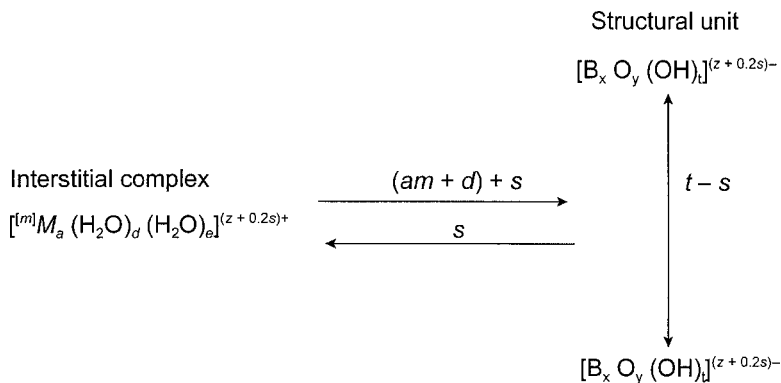


FIG. 5. Bonding between a structural unit and an interstitial complex (for details see text).

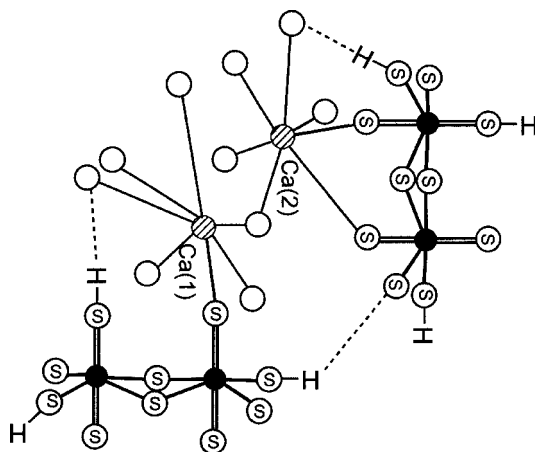


FIG. 6. An example of an interstitial $\{^{[7]}Ca_2(H_2O)_7(H_2O)_3\}^{4+}$ complex. In the structural unit, the central cations are indicated by large black circles, and the corresponding anions, by circles marked S. In the interstitial complex, the interstitial (H_2O) groups are shown as large white circles, the hydrogen atoms are shown as H, the Ca atoms are shown as line-shaded circles, and hydrogen bonds are shown as broken lines.

STRUCTURAL UNITS, INTERSTITIAL COMPLEXES AND THE VALENCE-MATCHING PRINCIPLE

As noted previously (Hawthorne 1990, 1994, 1997), the *binary representation* approach factors a structure into a (usually anionic) *structural unit* and a (usually cationic) *interstitial complex*. We may use the *valence-matching principle* to examine the interaction between these two components. More specifically, we have shown how each structural unit has a range of Lewis basicity (controlled by variations in coordination numbers of simple anions), and we have seen how we can represent the variation in Lewis acidity of an interstitial complex as a function of the amount of transformer (H_2O) , the valence of the cation(s) and the coordination number(s) of the cations. We may now combine these two representations of basicity and acidity *via* the valence-matching principle by plotting the range of basicity of a specific structural unit on a graph that shows the variation in Lewis acidity of cation complexes (*i.e.*, Fig. 8). Where the properties of the structural unit and the interstitial complexes intersect, the valence-matching principle is satisfied, and structures of those specific compositions are stable. Where the properties of the structural unit and interstitial complexes do not overlap, the valence-matching principle is not satisfied, and structures of those compositions are not stable.

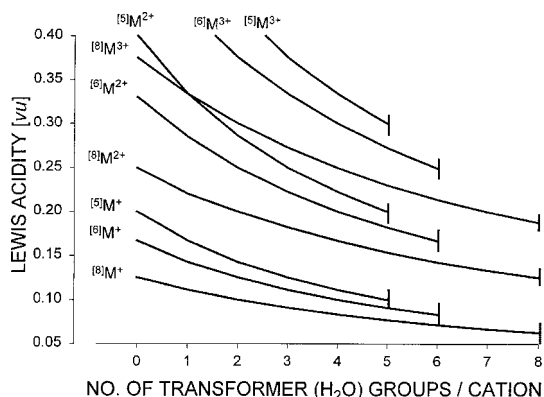


FIG. 7. The Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The lines shown are for interstitial cations with formal charges and coordination numbers shown to the left of the plot.

The effect of hydrogen bonding on Lewis-basicity – Lewis-acidity relations

A key issue in the calculation of Lewis basicity and Lewis acidity is the number of hydrogen bonds from the structural unit to the interstitial complex and the number of hydrogen bonds between anions of the structural unit. As indicated by the formulae given above, *t* and *s* play an important role in calculating the effective charge and numbers of bonds involving the interstitial complex and structural units. When considering the interaction of an arbitrary structural unit or interstitial complex (*viz.* when considering a hypothetical structure), we know *t* (the number of hydrogen atoms in the structural unit), but we do not know *s* (the number of hydrogen bonds from the structural unit to the interstitial complex). So let us examine the effect of different values of *s* (for a specific value of *t*) on the Lewis basicity and Lewis acidity.

Consider the structural unit $[^{[3]}B_3\ ^{[4]}B_3O_8(OH)_4]^{2-}$. We need to (1) calculate its average basicity, (2) calculate its range in coordination number of O atoms in the structural unit, and (3) calculate its corresponding range in Lewis basicity for different values of *s*, the number of hydrogen bonds that link to an interstitial complex. (1): The modified charge of the structural unit is $(2 + 0.2 \times 4) = 2.8$, and there are 12 O atoms in the structural unit. Hence the average basicity is $2.8 / 12 = 0.233$ *vu*. (2): From Figure 4, the range in O coordination number is 3.0–3.5. (3): From the coordination numbers and the number of O atoms in the structural unit, we can calculate the total number of bonds required by the

structural unit: $3.0 \times 12 = 36.0$ and $3.50 \times 12 = 42.0$. The number of (strong) bonds within the structural unit is $3 \times 3 + 4 \times 3 + 1 \times 6 = 25$, and hence the number

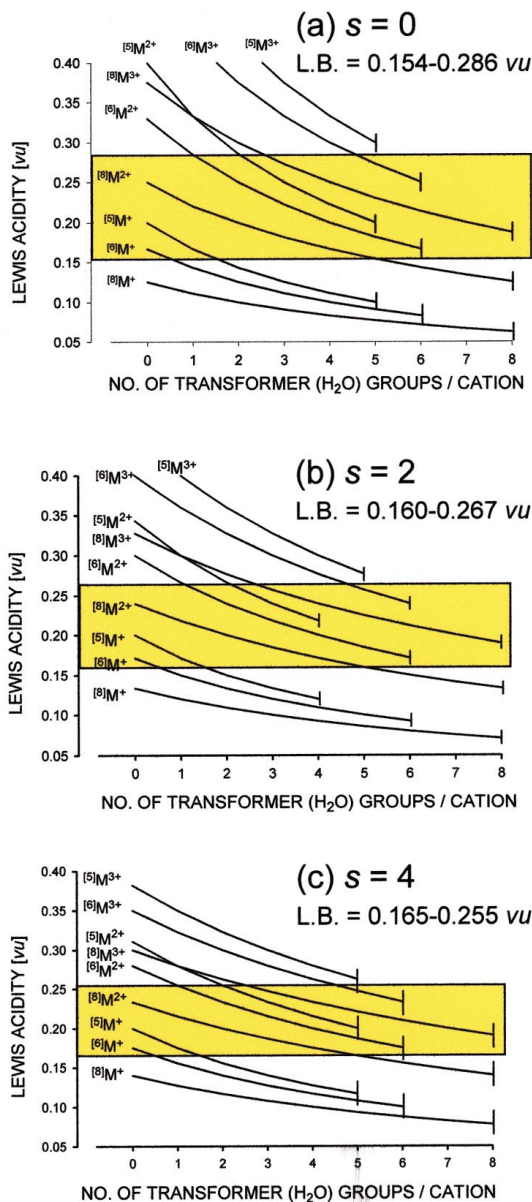


FIG. 8. The Lewis acidity of a general interstitial complex as a function of the number of transformer (H₂O) groups per cation and the formal valence and coordination number of the interstitial cations, with the corresponding ranges in Lewis basicity of the structural unit $[\text{B}_3\text{B}_3\text{O}_8(\text{OH})_4]^{2-}$ marked by the shaded bands: (a) calculated with s (the number of hydrogen bonds to the interstitial complex) = 0; (b) calculated with $s = 2$; (c) calculated with $s = 4$.

of weak bonds required to satisfy the coordination requirements of the O atoms of the structural unit is in the range $36.0 - 25$ to $42.0 - 25 = 11.0$ to 17.0 . As discussed above, if there are t hydrogen atoms in the structural unit and s of them hydrogen-bond to an interstitial complex, this leaves $(t - s)$ hydrogen bonds that bond to O atoms of the same or an adjacent structural unit. These $(t - s)$ hydrogen bonds contribute toward the number of bonds required by the structural unit. Hence for our example, $t = 4$ and the number of bonds required by the structural unit is $11.0 - (4 - s)$ to $17.0 - (4 - s)$: $(7.0 + s)$ to $(13.0 + s)$.

$s = 0$: In this case, none of the hydrogen bonds go to an interstitial complex, all of them go to the (or an adjacent) interstitial complex. The effective charge of the structural unit is $(2 + 0.2 \times 0) = 2^-$, and the range in bonds needed by the structural unit is 7.0 – 13.0 . Hence the range in Lewis basicity of the structural unit is $2.0 / 13.0$ to $2.0 / 7.0 = 0.154$ – 0.286 vu.

$s = 2$: In this case, two of the hydrogen bonds go to an interstitial complex and two of the hydrogen bonds go to the (or an adjacent) interstitial complex. The effective charge of the structural unit is $(2 + 0.2 \times 2) = 2.4^-$, and the range in bonds needed by the structural unit is 9.8 – 15.0 . Hence the range in Lewis basicity of the structural unit is $2.4 / 15.0$ to $2.4 / 9.0 = 0.160$ – 0.267 vu.

$s = 4$: In this case, four of the hydrogen bonds go to an interstitial complex and none go to the interstitial complex. The effective charge of the structural unit is $(2 + 0.2 \times 4) = 2.8^-$, and the range in bonds needed by the structural unit is 11.8 – 17.0 . Hence the range in Lewis basicity of the structural unit is $2.8 / 17.0$ to $2.8 / 11.0 = 0.165$ – 0.255 vu.

These ranges are significantly different, showing that the calculated ranges of Lewis basicity of a structural unit are sensitive to the configuration of the hydrogen bonds associated with the structural unit. However, the value of s also affects the Lewis acidity of an interstitial complex [see discussion above, expression (2)], and hence both Lewis basicity and Lewis acidity are sensitive to this parameter. We may calculate the variation in Lewis acidity as a function of the number of transformer (H₂O) groups and the valence and coordination number of the interstitial cation(s) (as in Fig. 7) for different values of s . These graphs are shown in Figure 8 for $s = 0, 2$ and 4 , together with the corresponding ranges in Lewis basicity (shown in yellow) of the structural unit $[\text{B}_3\text{B}_3\text{O}_8(\text{OH})_4]^{2-}$ as calculated above. Careful comparison of Figures 8a, b, and c show that the valence-matching principle is satisfied for the same compositions of the interstitial complex in all three figures, notwithstanding the fact that the numerical values of the Lewis basicity and Lewis acidity are different in all three figures. For example, consider ^[6]M²⁺. In Figure 8a, the curve for ^[6]M²⁺ intersects the upper range of the Lewis basicity, 0.286 vu, at d (the number of transformer (H₂O) groups) = 1; in Figure 8b, the curve for ^[6]M²⁺ intersects

the upper range of the Lewis basicity, 0.267 *vu*, at $d = 1$; in Figure 8c, the curve for $^{[6]}M^{2+}$ intersects the upper range of the Lewis basicity, 0.255 *vu*, at $d = 1$. Next, consider $^{[8]}M^{2+}$. In Figure 8a, the curve for $^{[8]}M^{2+}$ intersects the lower range of the Lewis basicity, 0.154 *vu*, at $d = 5$; in Figure 8b, the curve for $^{[8]}M^{2+}$ intersects the lower range of the Lewis basicity, 0.160 *vu*, at $d = 5$; in Figure 8c, the curve for $^{[8]}M^{2+}$ intersects the lower range of the Lewis basicity, 0.165 *vu*, at $d = 5$. This indicates that the operation of the valence-matching principle is independent of the configuration of the hydrogen bonds emanating from O atoms of the structural unit. This is a conclusion of major practical importance, as it allows us to calculate Lewis basicity and Lewis acidity without knowing of the configuration of the hydrogen bonds emanating from O atoms of the structural unit. We will calculate Lewis basicity and Lewis acidity with $s = t$ (thus the modified and effective charges of the structural unit are identical).

Prediction of transformer and non-transformer H_2O groups

For a stable mineral to form, the valence-matching principle requires that the Lewis acidity of the interstitial complex lies within the characteristic range of Lewis basicity for a given structural unit. Thus the range in Lewis basicity determines the type of interstitial cation and the number of transformer (H_2O) groups. We may express the Lewis acidity of a general interstitial complex in terms of the numbers of transformer (H_2O)_{*d*} and non-transformer (H_2O)_{*e*} groups, in an attempt to understand the mechanism controlling the function and amount of these interstitial components.

Let us consider a structural unit with a formal charge of 2[−], four (OH) groups and a range in Lewis basicity of 0.17 to 0.22 *vu* (Fig. 9). The Lewis acidities of all possible stable interstitial complexes must match this range, and thus we can formulate the following restrictions for interstitial complexes with only one type of interstitial cation from equation (2):

$$(a) \{^{[m]}M^{2+} (H_2O)_d (H_2O)_e\}^{2+} 0.17 < 2(1 + 2h) / (2m + d + 4) < 0.22 \quad (3)$$

$$(b) \{^{[n]}M^{2+} (H_2O)_d (H_2O)_e\}^{2+} 0.17 < 2(1 + 2h) / (n + d + 4) < 0.22 \quad (4)$$

$$(c) \{^{[l]}M^{3+} (H_2O)_d (H_2O)_e [^3]OH\}^{2+} 0.17 < 2(1 + 2h) / (l + d - 1 \times 2 + 4) < 0.22 \quad (5)$$

Thus, for mono-, di- and trivalent cations in different coordinations (m, n, l), we can predict the possible range in transformer (H_2O) groups and the possible coordination-numbers for the interstitial cations.

Consider interstitial complex (a). For cation coordination-numbers $m > [6]$, expression (3) does not hold,

and hence there can be no minerals with interstitial monovalent cations of coordination number $> [6]$. Where $m = [6]$, expression (3) holds only for $d = 0$ and 1, and hence there can be 0–1 transformer (H_2O) groups for two [6]-coordinated monovalent cations. Where $m = [5]$, expression (3) holds for $0 < d < 3$, and hence there can be 0–3 transformer (H_2O) groups for two [5]-coordinated monovalent cations.

Consider interstitial complex (b). For $n = [5]$, expression (4) holds for $4 < d < 7$; as the maximum possible number of (H_2O) groups coordinating a [5]-coordinated cation is five, then for $n = [5]$, interstitial complex (b) can have 4–5 transformer (H_2O) groups. For $n = [6]$, there are 3–6 transformer (H_2O) groups, changing monotonically to zero transformer (H_2O) groups for $n = [12]$.

Consider interstitial complex (c). For $l = [6]$, expression (5) holds for $5 < d < 6$, the number of possible transformer (H_2O) groups is 5 only [although $d = 6$ is a numerically possible solution, one of the ligands to Al must be (OH), and hence there cannot be six transformer (H_2O) groups bonded to $^{[6]}M^{3+}$]. For $l = [8]$, the number of possible transformer (H_2O) groups is in the range 3–6. There will be some stereochemical restrictions on these numbers, as the ligands of $^{[8]}M^{3+}$ that are not (OH) or transformer (H_2O) groups must be non-transformer (H_2O) groups (*i.e.*, they must link to two $^{[8]}M^{3+}$ cations). Hence the details of the (H_2O) groups carry implications as to the polymerization of the coordination polyhedra of the interstitial complex.

Non-transformer (H_2O) groups

Consider an [N]-coordinated interstitial cation. There are N vertices that can be occupied by non-transformer (H_2O) groups [*i.e.*, those (H_2O) groups designated as e

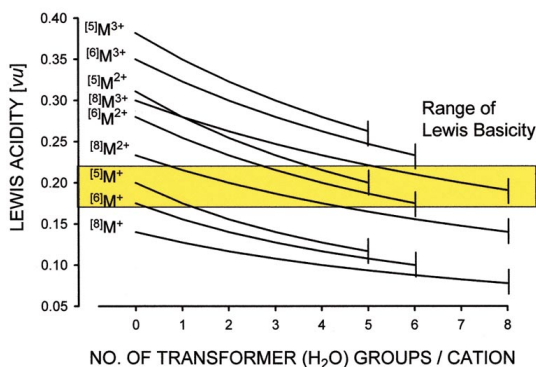


FIG. 9. Variation in Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups for mono-, di- and trivalent cations in [5]-, [6]- and [8]-coordination, with the range in Lewis basicity 0.17–0.22 *vu*.

in the interstitial complex]. If each (H₂O) group is shared by two cations or linked to one cation and receives one hydrogen bond, there is a maximum of N non-transformer (H₂O) groups per interstitial cation. If we now consider d transformer (H₂O) groups at vertices of the polyhedron, then the $(N - d)$ remaining vertices of the octahedron could be occupied by a maximum of $(N - d) = e$ non-transformer (H₂O) groups, giving $(N - d) = e$ non-transformer (H₂O) groups per cation. In this way, the maximum number of non-transformer (H₂O) groups per $[N]$ -coordinated cation is $(N - d)$, and the maximum number of (H₂O) groups bonded to one interstitial cation is given by $d + (N - d) = N$. The minimum number of non-transformer and transformer (H₂O) groups is always zero, because every interstitial $[N]M$ cation can be bonded to N O atoms of the structural unit.

For example, let us consider an interstitial $[6]Mg$ cation coordinated by two transformer (H₂O) groups. The maximum number of non-transformer (H₂O) groups per $[6]Mg$ cation is $(6 - 2) = 4$. This would occur, for example, in a chain of vertex-sharing $\{Mg(H_2O)_6\}$ octahedra or an edge-sharing dimer. The minimum number of non-transformer (H₂O) groups is zero, which would be the case if the $[6]Mg$ cation were bonded to four O atoms of the structural unit. Thus, in this case, the range of chemical composition of possible interstitial complexes is $[Mg(H_2O)_2(H_2O)_{0-4}]$, and the range in chemical composition of the corresponding mineral would be $Mg(H_2O)_{2-6}$ [structural unit] $(H_2O)_g$, where g is the number of interstitial (H₂O) groups that do not bond to Mg atoms. Note that g , the number of (H₂O) groups that do not bond to any interstitial cation, can neither be predicted or calculated at the present time.

THE ROLE OF Cl^- AS AN INTERSTITIAL SPECIES

Several borate minerals contain Cl as an interstitial anion. It is notable that known borate minerals never contain more than one Cl anion per interstitial cation. Consider the case for no interstitial Cl (Fig. 5), an interstitial complex of the form $\{[m]M^{n+}_a(H_2O)_d(H_2O)_e\}^{(a \times n)^+}$ that receives s hydrogen bonds from the structural unit. The Lewis acidity of this complex is $[a \times n + h \times s] / (a \times m + d + s)$. Now consider incorporation of Cl into this interstitial complex. This may be done in two ways: (1) $M^{n+} + Cl_n \rightarrow \square + \square$, i.e., incorporation of Cl, together with more interstitial cations to maintain electroneutrality, producing the interstitial complex $\{[l]M^{n+}_{a-1}[m]M^{n+}_a(H_2O)_d(H_2O)_e[r]Cl_n\}^{(a \times n)^+}$; (2) $M^{(n+1)+} + Cl \rightarrow M^{n+} + \square$, i.e., incorporation of Cl and replacement of an interstitial cation by a higher-valence interstitial cation, producing the complex $\{[l]M^{(n+1)+}_{a-1}[m]M^{n+}_a(H_2O)_d(H_2O)_e[r]Cl\}^{(a \times n)^+}$, where $[r]$ is the coordination number of Cl. Note that the charge of the interstitial complex is maintained in all cases as $(a \times n)^+$. First, mechanism (1): the number of bonds from the interstitial complex to the structural unit is $l + am + d + s - r$, and the Lewis acidity of the interstitial com-

plex is $[(a + 1) \times n - n + h \times s] / (l + am + d + s - (n \times r)) = [a \times n + h \times s] / (l + am + d + s - (n \times r))$, where the hydrogen bonds emanating from the structural unit have a bond valence of $h = 0.20$ vu. Next, mechanism (2): the number of bonds from the interstitial complex to the structural unit is $l + (a - 1) \times m + d + s - r$, and the Lewis acidity of the interstitial complex is $[(n + 1) + n \times (a - 1) - 1 + h \times s] / (l + \{a - 1\} \times m + d + s - r) = (a \times n + h \times s) / (l + \{a - 1\} \times m + d + s - r)$. Thus we have three expressions for the Lewis acidity of these interstitial complexes:

$$\{[m]M^{n+}_a(H_2O)_d(H_2O)_e\}^{(a \times n)^+} \\ \text{Acidity} = [a \times n + h \times s] / (a \times m + d + s) \quad (6) \\ = A / B$$

$$\{[m]M^{n+}_{a+1}(H_2O)_d(H_2O)_e[r]Cl_n\}^{(a \times n)^+} \\ \text{Acidity} = [a \times n + h \times s] / (l + am + d + s - n \times r) \quad (7) \\ = A / (B + l - n \times r)$$

$$\{[m]M^{(n+1)+}_{a-1}[m]M^{n+}_a(H_2O)_d(H_2O)_e[r]Cl\}^{(a \times n)^+} \\ \text{Acidity} = (a \times n + h \times s) / (l + (a - 1) \times m + d + s - r) \quad (8) \\ = A / (B + l - m - r)$$

Consider mechanism (1): the Lewis acidity of the interstitial complex changes from A / B to $A / (B + l - n \times r)$. Thus the Lewis acidity will change in the following manner: (a) if $l < (n \times r)$, then the denominator (the number of bonds from the interstitial complex to the structural unit) decreases and the Lewis acidity increases; (b) if $l = (n \times r)$, then the Lewis acidity does not change; (c) if $l > (n \times r)$, then the Lewis acidity decreases. Consider mechanism (2): the Lewis acidity of the interstitial complex changes from A / B to $A / (B + l - \{m + r\})$. Thus the Lewis acidity will change in the following manner: (a) if $l < (m + r)$, then the denominator (the number of bonds from the interstitial complex to the structural unit) decreases and the Lewis acidity increases; (b) if $l = (m + r)$, then the Lewis acidity does not change; (c) if $l > (m + r)$, then the Lewis acidity decreases.

Example: In hydrochlorborite, $Ca_2(H_2O)_6[8]Cl[B_4O_4(OH)_7]$ (Brown & Clark 1978), the Cl anion accepts seven hydrogen bonds from (OH) groups of the structural unit and one hydrogen bond from interstitial (H₂O) groups. The Ca atom is [8]-coordinated and bonds to two transformer (H₂O) groups and four non-transformer (H₂O) groups. The interstitial complex is $\{[8]Ca_2(H_2O)_2(H_2O)_4[8]Cl\}^{3+}$, and the number of bonds from the interstitial complex to the structural unit is as follows: $2 \times 8 + 2 + 7 - 8 = 17$ bonds. Thus the Lewis acidity of the interstitial complex is $(3 + 0.2 \times 7) / 17 = 0.26$ vu.

Consider the putative interstitial complex $\{[8]Na[8]Ca(H_2O)_2(H_2O)_4\}^{3+}$ for the same structural unit: $[B_4O_4(OH)_7]^{3-}$ (note that the electroneutrality principle is satisfied). The number of bonds from the interstitial

complex to the structural unit is $8 + 8 + 2 + 7 = 25$ bonds. The Lewis acidity of this interstitial complex is $(3 + 0.2 \times 7) / 25 = 0.18$ *vu*, significantly less than that of the structural unit in hydrochlorborite.

SUMMARY

(1) A mineral structure can be divided into two parts: a *structural unit* and an *interstitial complex*.

(2) The interstitial complex is an array of large low-valence cations, usually monovalent anions and (H₂O) groups, that is usually cationic in character and is characterized by its Lewis acidity, a measure of its electrophilic strength. The structural unit is usually an anionic array of strongly bonded polyhedra and is characterized by its *Lewis basicity*.

(3) Interaction between these two units is subject to the *valence-matching principle*: for a structural arrangement to be stable, the Lewis acidity and basicity of its constituent parts must match.

(4) The Lewis basicity of the structural unit can be moderated by change in the coordination numbers of its constituent simple anions, subject to the valence-sum rule. Thus a specific structural unit is stable over a range of Lewis basicities.

(5) A general interstitial complex can be written as $\{[m]M^+{}_a [n]M^{2+}{}_b [l]M^{3+}{}_c (H_2O)_d (H_2O)_e [q](OH)_f (H_2O)_g\}^{(a+2b+3c-f)+}$, where $[n]$, $[m]$, $[l]$ and $[q]$ are coordination numbers, a , b and c are the numbers of monovalent, divalent and trivalent cations, d is the number of *transformer* (H₂O) groups, e is the number of (H₂O) groups bonded to two interstitial cations or one interstitial cation and one hydrogen bond, f is the number of interstitial (OH) groups, and g is the number of (H₂O) groups not bonded to any cation.

(6) A *transformer* (H₂O) group takes a chemical bond and splits it into two weaker bonds, thereby altering the effective Lewis acidity of the constituent cation.

(7) The number of *transformer* (H₂O) groups in an interstitial complex has a strong effect on its Lewis acidity, and the variation in Lewis acidity of a general interstitial complex can be graphically represented as a function of the number of *transformer* (H₂O) groups in the complex.

(8) The *modified charge* of a structural unit is defined as the formal charge of the structural unit as modified by the hydrogen bonds emanating from it.

(9) The *average basicity* of a structural unit is defined as the modified charge divided by the number of O atoms in the structural unit.

(10) The average basicity correlates with the mean coordination-number of O atoms in the structural unit. This correlation defines a band that allows prediction of the range in average coordination-number of the O atom (by which the structural unit responds to small changes in pH while remaining stable).

(11) The “effective charge” of the structural unit is the formal charge of the structural unit as modified by the hydrogen bonds to the interstitial complex. Similarly, the effective charge of the interstitial complex is the formal charge of the interstitial complex as modified by the hydrogen bonds to the interstitial complex. It is important to note the difference between the “modified charge” (used to calculate the average basicity) and the *effective charge* (used to calculate the Lewis basicity) of a structural unit. The modified charge incorporates all hydrogen bonds emanating from the structural unit, whereas the effective charge incorporates only those hydrogen bonds from the structural unit to the interstitial complex; the effective charge does not include hydrogen bonds that link directly to adjacent structural units.

(12) The range in Lewis basicity of the structural unit may be calculated from the maximum and minimum values of the average coordination-number of the O atoms of the structural unit. The maximum and minimum coordination-numbers are multiplied by the number of O atoms in the structural unit to give the minimum and maximum numbers of bonds required by the O atoms. The minimum and maximum numbers of bonds required by the structural unit from the interstitial complex are the minimum and maximum total numbers of bonds minus the number of bonds within the structural unit. The range in Lewis basicity of the structural unit is its effective charge divided by the maximum and minimum numbers of bonds required by the structural unit from the interstitial complex.

(13) 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 structural arrangement is possible.

(14) Application of this approach to the borate minerals shows that there are significant restrictions on the chemical and structural details of the interstitial complexes.

(15) The Lewis basicities of some structural units do not allow certain types of cations to occur as interstitial components.

(16) The overlap of Lewis basicity and acidity required for structural stability by the valence-matching principle leads to an explanation and prediction of the number of *transformer* (H₂O) groups in the interstitial complexes of these minerals. These predictions can be precise or imprecise, but in all cases, they are accurate.

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REFERENCES

- BANDY, M.C. (1938): Mineralogy of three sulphate deposits of northern Chile. *Am. Mineral.* **23**, 669-760.
- BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BROWN, G.E. & CLARK, J.R. (1978): Crystal structure of hydrochlorborite $\text{Ca}_2[\text{B}_2\text{O}_3(\text{OH})_4 \cdot \text{OB}(\text{OH})_3]\text{Cl} \cdot 7\text{H}_2\text{O}$, a seasonal evaporite mineral. *Am. Mineral.* **63**, 814-823.
- BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. In *Structure and Bonding in Crystals II* (M. O'Keeffe and A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- _____, & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.
- _____, & SHANNON, R.D. (1973): Empirical bond-strength – bond-length curves for oxides. *Acta Crystallogr.* **A29**, 266-282.
- BURNS, P.C. (1999): The crystal chemistry of uranium. In *Uranium: Mineralogy, Geochemistry and the Environment* (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 23-90.
- _____, & HAWTHORNE, F.C. (1993): Hydrogen bonding in meyerhofferite: an X-ray and structure energy study. *Can. Mineral.* **31**, 305-312.
- _____, & _____ (1994): Structure and hydrogen bonding in preobrazhenskite, a complex heteropolyhedral borate. *Can. Mineral.* **32**, 387-396.
- FISHER, D.J. (1958): Pegmatite phosphates and their problems. *Am. Mineral.* **43**, 181-207.
- HAWTHORNE, F.C. (1979): The crystal structure of morinite. *Can. Mineral.* **17**, 93-102.
- _____, (1985): Towards a structural classification of minerals: the $^{\text{VI}}\text{M}^{\text{IV}}\text{T}_2\text{O}_n$ minerals. *Am. Mineral.* **70**, 455-473.
- _____, (1986): Structural hierarchy in $^{\text{VI}}\text{M}_x^{\text{III}}\text{T}_y\text{O}_z$ minerals. *Can. Mineral.* **24**, 625-642.
- _____, (1990): Structural hierarchy in $\text{M}^{[6]}\text{T}^{[4]}\text{O}_n$ minerals. *Z. Kristallogr.* **192**, 1-52.
- _____, (1992): The role of OH and H_2O in oxide and oxysalt crystals. *Z. Kristallogr.* **201**, 183-206.
- _____, (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.
- _____, (1997): Structural aspects of oxide and oxysalt minerals. In *Modular Aspects of Minerals* (S. Merlino, ed.). *Eur. Mineral. Union, Notes in Mineralogy* **1**, 373-429.
- _____, BURNS, P.C. & GRICE, J.D. (1996): The crystal chemistry of boron. In *Boron: Mineralogy, Petrology and Geochemistry* (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 41-115.
- _____, & HUMINICKI, D.M.C. (2001): The crystal chemistry of beryllium. *Rev. Mineral.* (in press).
- _____, KRIVOVICHEV, S.V. & BURNS, P.C. (2000): The crystal chemistry of sulfate minerals. In *Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance* (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 1-112.
- MOORE, P.B. (1965): A structural classification of Fe–Mn orthophosphate hydrates. *Am. Mineral.* **50**, 2052-2062.
- _____, (1973): Bracelets and pinwheels: a topological-geometrical approach to the calcium orthosilicate and alkali sulfate structures. *Am. Mineral.* **58**, 32-42.
- _____, (1975): Laueite, pseudolaueite, stewartite and metavauxite: a study in combinatorial polymorphism. *Neues Jahrb. Mineral., Abh.* **123**, 148-159.
- _____, (1982): Pegmatite minerals of P(V) and B(III). *Mineral. Assoc. Can., Short Course Handbook* **8**, 267-291.
- _____, (1984): Crystallochemical aspects of the phosphate minerals. In *Phosphate Minerals* (J.O. Nriagu & P.B. Moore, eds.). Springer-Verlag, Berlin, Germany (155-170).
- PAULING, L. (1929): The principles determining the structure of complex ionic crystals. *J. Am. Chem. Soc.* **51**, 1010-1026.
- SCHINDLER, M. & HAWTHORNE, F.C. (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.* **39**, 1243-1256.
- _____, & _____ (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. III. Paragenesis of borate minerals. *Can. Mineral.* **39**, 1257-1274.
- _____, _____ & BAUR, W.H. (2000): A crystal-chemical approach to the composition and occurrence of vanadium minerals. *Can. Mineral.* **38**, 1443-1456.
- SIMONOV, M.A., EGOROV-TISMENKO, YU.K., KAZANSKAYA, E.V., BELOKONEVA, E.L. & BELOV, N.V. (1978): Hydrogen bonds in the crystal structure of nifontovite $\text{Ca}_2[\text{B}_5\text{O}_3(\text{OH})_6]_2 \cdot 2\text{H}_2\text{O}$. *Sov. Phys. Dokl.* **23**, 159-161.

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