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Understanding the weakly bonded constituents in oxysalt minerals

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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 (H_2O) 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 *principle of correspondence of Lewis acidity-basicity.* 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: $\{^{[m]}M^{+}_{a}{}^{[n]}M^{2+}_{b} \cdot {}^{[l]}M^{3+}_{c}(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}$, where [*m*], [*n*] and [*l*] are coordination numbers, *a, b* and *c* are the numbers of monovalent, divalent and trivalent cations, *d* is the number of *transformer* (H_2O) groups, *e* is the number of (H_2O) 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 (H_2O) groups not bonded to any cation. The number of transformer (H_2O) 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 (H_2O) groups. Where the Lewis acidity of a generalized interstitial complex overlaps the range of Lewis basicity of a specific structural unit, the principle of correspondence of Lewis acidity-basicity is satisfied and a stable structural arrangement is possible. Detailed predictions of the compositions of interstitial complexes are made for the borate, sulfate and uranyl-oxide-hydroxy-hydrate minerals. There is fairly close agreement between the predicted ranges of interstitial complex and those observed in Nature.

Introduction

When we consider variations in chemical composition or stability of minerals, we make certain premises: (1) we assume the stability of the structures with which we are dealing; (2) we do not usually consider the factors that affect the bond topology (the connectivity of the constituent atoms); (3) we observe changes in chemical composition within a given structure type, we observe changes in composition of progressively crystallizing structures, and we relate these changes to variations in intensive thermodynamic parameters. When dealing with rock-forming minerals, this is a very effective *modus operandi*, and allows us to follow petrologic process through variation in chemical composition of the constituent phases. When dealing with most complicated oxysalts, these premises are less effective as the character of the variations in the mineral assemblages is different: rather than responding to change in intensive variables by incremental change in composition and/or mode, structures frequently break down to form new phases of very different bond topology, and the frequent occurrence of large numbers of associated minerals suggests that these parageneses are non-equilibrium. This difference in (i) behaviour, and (ii) our ability to quantitatively describe this behaviour, emphasizes the fact that we do not understand *why* mineral structures have the atomic arrangements and chemical compositions that they do, even though we can, in some cases, describe their behaviour quite accurately using equilibrium thermodynamics. We have been working for some time to try and understand the factors that control bond topology (connectivity of the atoms) and chemical composition in minerals (Hawthorne, 1983, 1985, 1986, 1990, 1992, 1994, 1997, 2007; Schindler and Hawthorne, 2001a, b, c, 2004, 2007; Schindler *et al.*, 2000a, b, 2006), with a particular focus on the weakly bonded constituents in hydroxy-hydrated oxysalt minerals. Here, we review this work and give an outline of our understanding of these minerals, particularly borate, uranyl-oxide hydroxy-hydrate, sulfate

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and uranyl-oxysalt minerals. Many of these minerals are important phases from an environmental perspective, and increased understanding of their behaviour is desirable in order to resolve many environmental problems.

Understanding versus prediction

Why do minerals have the chemical and structural features that they do? From a chemical perspective, this is less of an issue for simple minerals. For example, in the system Na−Cl at surface conditions, Na and Cl can combine in accord with electroneutrality to form NaCl. Of course, there are still issues of its atomic arrangement: why does NaCl have the sodium-chloride arrangement rather than the CsCl or zinc-sulfide arrangements? However, we can answer half of the problem: we know what the chemical formula will be. Consider minerals in the system $MgO-SO_4-H_2O$: electroneutrality indicates that structures may form with the formula $MgSO_4(H_2O)_n$ where $n = 0$, 1, 2, 4, 5, 6, 7, 11 (0: synthetic; 1: kieserite; 2: sanderite; 4: starkeyite; 5: pentahydrite; 6: hexahydrite; 7: epsomite; 11: synthetic). This increase in complexity comes with an increase in ignorance: from a structural perspective, what controls the degree of hydration. Consider more complex minerals, *e.g.*, metavoltine: $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}{}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$; what controls the composition and structure of this mineral? Apart from knowing that the formula must obey the electroneutrality principle, we have no idea what are the controls on the chemical composition and structure of this mineral.

The intent of the above discussion is to emphasize that we have virtually no understanding of the reasons why minerals have the chemical compositions and structural arrangements that they do. Of course, we can state that this is the chemical composition and structural arrangement that has the lowest Gibbs free energy. However, this statement is an article of faith rather that an understanding of (1) the atomic properties of the constituent elements, and (2) the details of their chemical bonding. We wish to understand why minerals are stable in terms of their chemical compositions and structural arrangements; otherwise, why do we analyze minerals and solve/refine their crystal structures?

In this paper, we summarize our recent work on trying to understand the factors that control some aspects of the chemical composition and structural arrangements of oxysalt minerals. We will compare observed and predicted features of these minerals. However, we make no claim of accuracy, as these predictions are not the result of inductive correlation; they result from the proposed mechanisms of structural cohesion (and are impossible to predict by any other approach). The intent of such prediction is to test our ideas and to guide further development: agreement suggests adequate understanding, disagreement indicates that further development is necessary.

A comment on minerals versus synthetic compounds

It is often not realized that minerals do have an intrinsic difference from synthetic compounds: minerals crystallize in a system with a large number of components, whereas synthetic compounds have been grown in chemical systems with a limited number of components. As a consequence, minerals are able to select the most appropriate components when forming, whereas synthetic compounds must make do with what the experimenter has given them. As a result, synthetic compounds are often far more strained than minerals; they often show much higher deviations from the valence-sum rule of bond-valence theory (Brown, 1981, 2002), and they can show very unusual valence states and coordination numbers that are forced on the compounds by the limited chemistry at their disposal, *e.g.*, K_3FeO_2 (Bernhardt and Hoppe, 1993), $K_2S_2O_7$ (Ståhl *et al.*, 2005). We are trying to understand the factors controlling the chemical composition and stability of minerals, and as far as we are aware, this is the only work that is attempting to do this from a structural perspective. We are tending to focus on minerals (rather than synthetic compounds) at the present time, as we expect some (highly strained) synthetic compounds to deviate from our current findings, and it is sensible to avoid highly strained structures until we understand more about what is controlling the chemical composition and stability of complicated phases.

Binary structural representation

Oxysalt minerals are often very difficult to deal with from a stereochemical and paragenetic perspective as there are many different atom interactions, the topological and geometrical characteristics of which are important. However, the same situation applies to an atom: there are protons and neutrons in a nucleus and numerous electrons in a series of orbitals around that nucleus, 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 *etc*. Hawthorne (1983, 1985) adopted this approach to complicated crystal structures, dividing them into two components (Fig. 1). The *structural unit* is the strongly bonded part of the structure, and the *interstitial complex* is an assemblage of (usually monovalent and

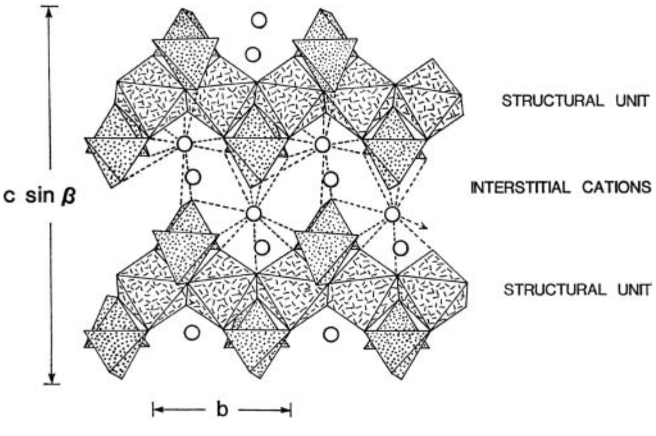

Fig. 1. Partitioning of a complex crystal structure into two units, the strongly bonded *structural unit* (shown as shaded polyhedra) and the weakly bonded *interstitial complex* (shown as individual atoms and chemical bonds).

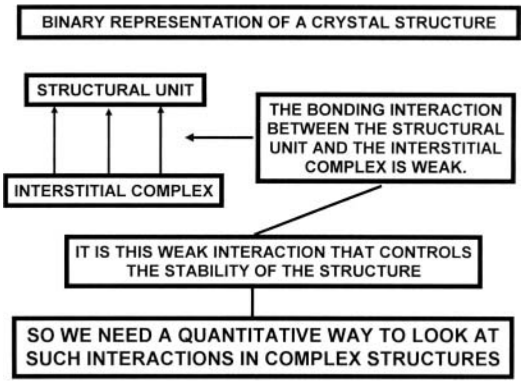

Fig. 2. Representation of the key features of the *binary representation* of a crystal structure.

divalent) cations, anions and neutral groups that weakly bind the structural units into a continuous crystal structure. The important issue is that it is the weak interaction between the structural unit and the interstitial complex that controls the stability of the structural arrangement (Fig. 2). When the structure breaks down, it generally does so by breaking the weakest bonds; this allows the structure to disaggregate into component molecular and atom fragments that can then reform to produce other structural arrangements.

Here, we have developed a *binary representation* that gives a simple but structurally quantitative model of even the most complicated structure, and allows us insight into the weak interactions that control the stability of the structure. In order to exploit this type of structural representation, we now need a quantitative way to look at the interaction between structural unit and interstitial complex.

Bond-valence theory

Bond-valence theory is a “back-of-an-envelope” theory of atom interaction that allows considerable physical and chemical insight into even the most complicated mineral structure. The development of bond-valence theory is discussed in detail by Hawthorne (2007), and the fundamental details are given by Brown (1981, 2002). Here, we assume some familiarity with this approach; a list of definitions is given in Appendix I.

Lewis-acid strength

The mean bond-valence of a cation correlates strongly with its *electronegativity* (Fig. 3), a measure of the electrophilic strength (electron-accepting capacity) of the cation. A Lewis acid is defined as a species that can receive electron density from another species. The correlation of characteristic bond-valence with electronegativity for cations indicates that the characteristic bond-valence is a measure of the *Lewis-acid strength* of the cation. 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)*

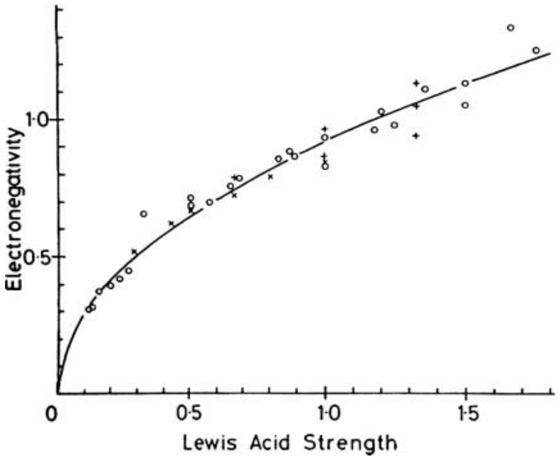

Fig. 3. Variation in electronegativity as a function of the characteristic strength of bonds for common cations (after Brown, 1981).

where the mean coordination number is derived from a large number of crystal structures containing the relevant cation. Lewis-acid strengths of mineralogically relevant cations are given in Table 1.

Lewis-base strength

The *Lewis-base strength* of an anion can be defined in a similar fashion, as the characteristic strength of the bonds formed by the anion. However, bond-valence variations around simple anions are much greater than those around cations; in minerals, the bond valences (strengths of bonds) to O^{2-} can vary between nearly zero and 2.0 *v.u.* For example, in thenardite, $Na_2(SO_4)$, the bond valence to the sulfate O-atoms varies between 1.50 *v.u.* from the [4]-coordinated S^{6+} cation and 0.17 *v.u.* from the [6]-coordinated Na^+ cation. With this range of values, it is obviously not useful to designate a Lewis basicity for O^{2-}: the range of values is too great for a single predictive value to be useful. However, if we examine the $(SO_4)^{2-}$ group as an oxyanion, each O^{2-} anion receives 1.50 *v.u.* from the central S^{6+} cation and needs an additional

Table 1. Lewis acid strengths (*v.u.*) 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^{5+}	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+}	0.34	Te	1.06
Cl^{7+}	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 V^{5+} (Schindler *et al.*, 2000), Fe^{2+} (Brown, 2002) and Pb^{2+} which was estimated from several oxysalt mineral structures.

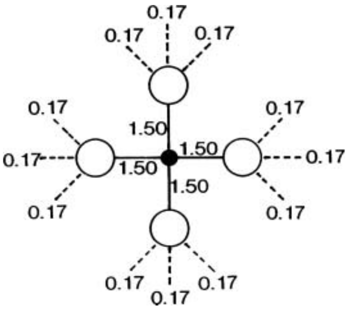

Fig. 4. Bond valences incident at the (SO_4) group in thenardite, $Na_2(SO_4)$.

0.50 *v.u.* from the Na^+ cations. In thenardite, the O^{2-} ligands of the sulfate group are [4]-coordinated, and hence accept three additional bonds when we consider the sulfate group as an oxyanion; this gives a value for the additional bond-valence needed of 0.17 *v.u.* for each O^{2-} anion of the $(SO_4)^{2-}$ group (Fig. 4). If this process is repeated for all $(SO_4)^{2-}$ groups in minerals, we get a mean (characteristic) value of the required bond-valence of 0.17 *v.u.* with a spread of $\sim \pm 0.10$ *v.u.* This is a useful value for the $(SO_4)^{2-}$ group, as unlike the constituent O^{2-} anions, the variation in bond valence to the $(SO_4)^{2-}$ group is small, and may be predicted with a much higher degree of accuracy. In this way, we can define the *Lewis basicity* of an oxyanion. Table 2 lists Lewis basicities for some geochemically common inorganic oxyanions.

The valence-matching principle

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

> *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. The Lewis acidity is a measure of the electron-attracting capacity of the cation, and Lewis basicity is a measure of the electron-donating capacity of the anion. As a chemical bond involves both a cation and an anion, then the electron-attracting capacity of the cation must match the electron-donating capacity of the anion for a chemical bond to form (Fig. 5). We will consider three simple examples to illustrate the operation of this principle.

Consider the composition Na_2SO_4. The Lewis acidity of Na is 0.17 *v.u.* (Table 1) and the Lewis basicity of the (SO_4) group is 0.17 *v.u.* (Table 2). The Lewis basicity of the anion matches the Lewis acidity of the cation, the valence-matching principle is satisfied, and Na_2SO_4 is the mineral thenardite.

Table 2. Lewis basicities (*v.u.*) 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

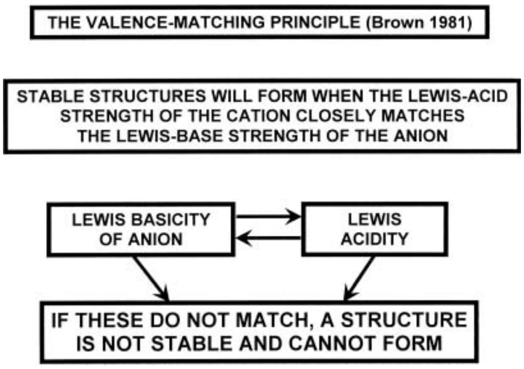

Fig. 5. The valence-matching principle.

Consider next the composition Na_4SiO_4. The Lewis acidity of Na is 0.17 *v.u.* and the Lewis basicity of the (SiO_4) group is 0.33 *v.u.* (Table 2). The Lewis basicity of the anion does not match the Lewis acidity of the cation, the valence-matching principle is not satisfied, and Na_4SiO_4 is not a stable mineral.

Consider next the composition Na $[AlSiO_4]$. The Lewis acidity of Na is 0.17 *v.u.* and the Lewis basicity of the $[AlSiO_4]$ group is 0.13 *v.u.* The Lewis basicity of the anion matches (approximately) the Lewis acidity of the cation, the valence-matching principle is satisfied, and $NaAlSiO_4$ is the mineral nepheline.

The principle of correspondence of Lewis acidity-basicity

We may characterize the interaction of the structural unit and the interstitial complex in a manner similar to the application of the valence-matching principle to simple chemical compositions:

> *Stable structures will form when the Lewis-acid strength of the interstitial complex closely matches the Lewis-base strength of the structural unit (Fig. 6).*

We may illustrate the basis of binary structural representation and the correspondence of Lewis acidity and Lewis basicity by considering the sulfate mineral metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}{}_3O(S)_4)_6(H_2O)_3]_2(H_2O)_6$, from this

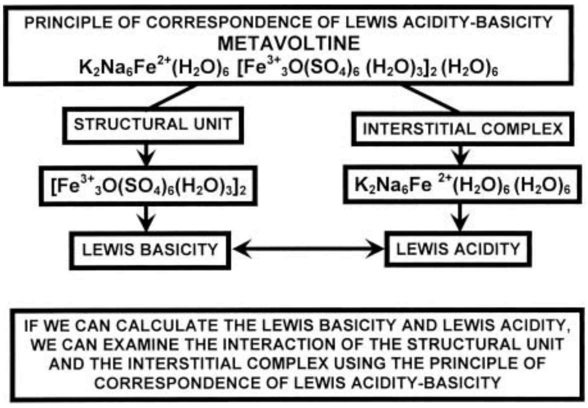

Fig. 6. The principle of correspondence of Lewis acidity-basicity and the structural unit and interstitial complex for the complex sulfate mineral metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}{}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$.

perspective (Fig. 6). Although the chemical formula is quite complicated, we may partition it into a strongly bonded structural unit and a weakly bonded interstitial complex. The structural unit is a cluster of Fe^{3+} and sulfate polyhedra, and the interstitial complex consists of K, Na and Fe^{2+} cations, together with their associated (H_2O) groups. If we can calculate a Lewis basicity for a structural unit and a Lewis acidity for an interstitial complex, we can examine the interaction of the structural unit and the interstitial complex using the principle of correspondence of Lewis acidity-basicity, a mean-field equivalent of the valence-matching principle.

Calculation of Lewis basicity

The Lewis basicity of the structural unit is the average bond-valence of bonds to that structural unit from surrounding interstitial complexes and neighbouring structural units. The electroneutrality principle requires that the bonds to the structural unit neutralize the charge of the structural unit, and hence we can define the Lewis basicity of the structural unit as *the charge on the structural unit divided by the number of bonds to the structural unit.* What we need to know for this calculation is

(1) the charge on the structural unit, and
(2) the number of bonds from the interstitial complex and adjacent structural units needed by the structural unit.

The effective charge of the structural unit

It is not necessarily appropriate to use the formal charge of a structural unit in the calculation of Lewis basicity. This issue is particularly apparent for structures with formally neutral structural units; if the formal charge of the structural unit is used (zero), there is no mechanism for the structure to link together. Consider lizardite, $Mg_3Si_2O_5(OH)_4$ (Fig. 7), the structural unit of which is the sheet $[Mg_3Si_2O_5(OH)_4]^0$. Sheets are linked by hydrogen bonds from the (OH) groups of the octahedral layer of one sheet to the bridging O atoms in the tetrahedral layer of the adjacent sheet. From a bonding 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 silicate side (see + and − signs in Fig. 7). Thus we have to factor this transfer of charge into the calculation of the charge of the structural unit if we are to describe correctly the interaction between adjacent structural units. For lizardite, the effective charge is 0 (the formal charge of the structural unit) -4×0.20 (the charge transferred by hydrogen bonding, assuming a hydrogen bond-valence of 0.20 *v.u.*, Brown, 1981) $= 0.80^-$. Such transfer of charge to modify the effective charge of the structural unit can only involve cations which show very asymmetric coordinations (commonly H, less commonly lone-pair-stereoactive cations such as Pb^{2+} and Bi^{3+}).

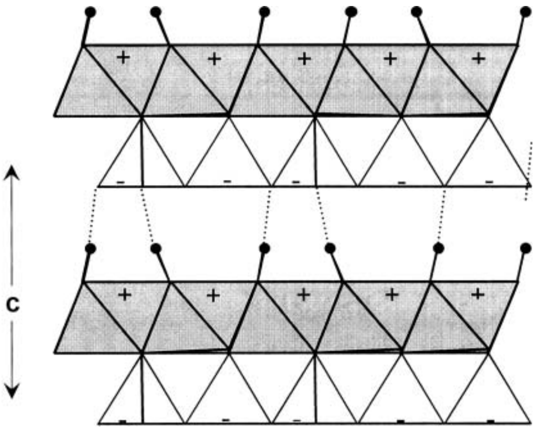

Fig. 7. Representation of the crystal structure of lizardite, showing the polar nature of the structural unit; dark grey:octahedra; unshaded: tetrahedra; dark circles: H atoms; broken lines: hydrogen bonds. The acidic (+) and basic (−) parts of the structural unit are indicated.

The polar nature of the structural unit in lizardite is very apparent because its formal charge is zero. However, minerals with formally charged structural units may still be polar, and the role of polarity must be built in to the calculation of Lewis basicity. In borate minerals, the structural units generally consist of (BO_3) and (BO_4) groups commonly linked by sharing vertices. Following Brown (1981, 2002), Schindler and Hawthorne (2001a, b) assumed an average hydrogen-bond valence of 0.20 *v.u.* and calculated the effective charge accordingly as the formal charge minus the charge transferred by any hydrogen bonding. Thus for borax, $Na_2(H_2O)_8[B_4O_5(OH)_4]$, the effective charge of the structural unit, $[B_4O_5(OH)_4]^{2-}$, is 2 (the formal charge) -4×0.20 (the charge transferred by hydrogen bonding) $= 2.8^-$. For sulfate minerals, Schindler *et al.* (2006) developed a detailed argument to show how the hydrogen-bond valences differ between locally acid and basic parts of the structural unit. However, the numerical arguments are not significantly affected by assuming a hydrogen-bond valence of 0.20 *v.u.* Thus for metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}{}_3O(SO)_4)_6(H_2O)_3]_2(H_2O)_6$, the effective charge of the structural unit is -10 (the formal charge) -12×0.20 (the charge transferred by hydrogen bonding) $= 12.4^-$. Thus *the effective charge* of the structural unit is the formal charge as modified by charge transferred by hydrogen bonding from donor anions within the structural unit.

The number of bonds needed by the structural unit

First, we will examine how we may calculate this number if we know everything about the structure of interest. The total number of chemical bonds in a structure may be calculated as the sum of the cation-coordination numbers multiplied by the numbers of those cations in the formula unit. Also, we may calculate the number of bonds in the structural unit in the same fashion. The difference between these two values, the number of bonds in the structure minus the number of bonds within the structural unit, is the number of bonds needed by the structural unit. This calculation is quite trivial if we know the details of the coordinations of all the atoms in the structure. However, we wish to predict information about crystal structures, and we do not know such details as anion coordination in a structure or proposed structure *a priori*. We must be able to predict this information if we want *a priori* analysis of crystal structures.

The charge deficiency per anion: CDA

A quantity designated as the *average basicity* and defined as *the average bond-valence per O-atom contributed by the interstitial species and adjacent structural units* was introduced by Schindler *et al.* (2000b). This is an extremely important quantity as it correlates strongly with the average O-coordination number of the structural unit, and hence plays a crucial role in the predictive aspects of our approach. However, the name "average basicity" is inappropriate as it implies that each O-atom of the structural unit receives on average only one bond from the interstitial complex and adjacent structural units; this is not the case, and the name was not meant to imply this restriction. As indicated by its definition, this quantity is the average bond-valence per O-atom required by the structural unit to satisfy the principle of correspondence of Lewis acidity-basicity. As such, we rename this quantity the *charge deficiency per anion*, or CDA.

As we will see, the charge deficiency per anion of a structural unit or a complex in aqueous solution is extremely important as it correlates strongly with (1) the numbers of bonds to those structural units from the interstitial complex and adjacent structural units, and (2) the pH at maximum concentration of that species in aqueous solution, and it is these correlations that play a major role in *a priori* prediction of structural features.

Calculation of the charge deficiency per anion

The charge deficiency per anion of the structural unit is a simple 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 O atoms in the structural unit.

Example 1: Consider the structural unit in borax, $Na_2(H_2O)_8[B_4O_5(OH)_4]$. The effective charge is $(2 + 0.2 \times 4)^- = 2.8^-$ and the number of O atoms in the structural unit is 9; thus CDA = 2.8/9 = 0.32 *v.u.*

Example 2: Consider the structural unit in becquerelite, $[(UO_2)_3O_2(OH)_3]^-$. The effective charge is $(1 + 0.2 \times 3)^- = 1.6^-$ and the number of O atoms in the structural unit is $2 \times 3 + 2 + 1 \times 3 = 11$; thus CDA = 1.6/11 = 0.145 *v.u.* As we will see next, there is a close relation between the charge deficiency per anion of a structural unit and the average number of bonds to those anions from the interstitial complex and adjacent structural units. Note that in becquerelite itself, the structural unit has a multiplicity of 2 in the unit formula: *i.e.*, $[(UO_2)_3O_2(OH)_3]^-{}_2 = [(UO_2)_6O_4(OH)_6]^{2-}$. However, the average basicity and Lewis basicity are not affected in that these quantities have the multiplicity in both the numerator and the denominator of their expressions and hence the multiplicity cancels out in the calculation of these properties. Note, however, that one must be careful with this issue when considering the numbers of bonds between the structural unit and the interstitial complex for interstitial cations of differing charge.

Derivation of the number of bonds required by the structural unit and calculation of Lewis basicity of the structural unit

The bonds of the structural unit contribute most of the bond valence required by the O atoms of the structural unit, and hence the charge deficiency per anion is a measure of the bond valence required by each O atom of the structural unit from the interstitial complex and adjacent structural units. The O atoms in a structural unit with a low CDA value require only a small amount of additional bond-valence to satisfy the valence-sum rule, whereas O atoms in a structural unit with a high CDA value require more additional bond-valence. As the bonds of the structural unit are strong and the bonds involving the interstitial complex and adjacent structural units are weak, differences in the charge deficiency per anion 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 charge deficiency per anion of the structural unit and the average number of bonds received by O atoms of the structural unit from the interstitial complex and adjacent structural units, $\langle NB \rangle_{in}$. Such a correlation is shown in Fig. 8. This is an extremely important relation as it allows us to predict a range for the number of bonds from the interstitial complex and adjacent structural units to a specific structur-

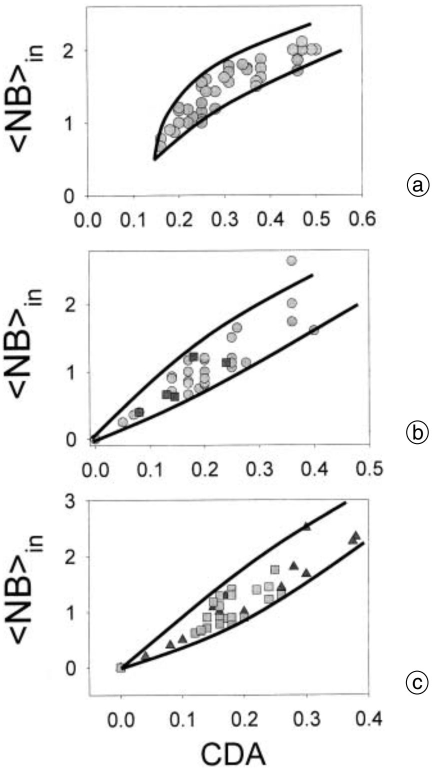

Fig. 8. Correlation between the CDA of structural units and the average number of bonds from the interstitial complex and adjacent structural units, $\langle NB \rangle_{in}$, to O-atoms in the corresponding structural units of oxysalt minerals. The upper and lower borders of the distribution are used to define the characteristic range in O-coordination numbers for a specific structural unit. Minerals deviating from the trend are shown in unshaded symbols (**a**) borates; (**b**) uranyl-oxide hydroxy-hydrates; (**c**) sulfates.

al unit, and in turn, this allows us to calculate a range in Lewis basicity for that structural unit.

Example: Consider borax, $Na_2(H_2O)_8[B_4O_5(OH)_4]$: above, we saw that the effective charge is $(2 + 0.2 \times 4)^-$ $= 2.8^-$, the number of O atoms in the structural unit is 9, and CDA = 2.8/9 = 0.0.32 *v.u.* Using this value of CDA, we may use Fig. 8a to read off the range for the number of bonds to anions of the structural unit: 1.35–1.85. The corresponding range in the total number of bonds to the structural unit is $(1.35–1.85) \times 9 = 12.2–16.7$, and the resulting range in Lewis basicity of the $[B_3O_3(OH)_5]^{2-}$ structural unit is the effective charge divided by the range in the number of bonds to the structural unit: 2.8/(12.2–16.7) = 0.17–0.23 *v.u.*

The variation of $\langle NB \rangle_{in}$ as a function of CDA is shown in Fig. 8 for the oxysalt minerals considered here; it seems apparent that $\langle NB \rangle_{in}$ is the salient parameter when trying to establish a relation between O-coordination number and CDA. If we wish to have any predictive power, we need to be able to derive the number of bonds required by such O atoms *a priori*, without recourse to a known structure. The relations shown in Fig. 8 allow such prediction.

There is an even more important issue associated with Fig. 8. The data form bands rather than monotonic trends, indicating that the structural units are compatible with a range in the number of bonds from the interstitial complex to the anions of the structural unit. Indeed, we propose that *it is by varying the number of bonds to the structural unit from the interstitial complex and adjacent structural units that the structural unit maintains its stability as the pH of its environment changes*. Thus the range in numbers of bonds from the interstitial complex and adjacent structural units to the O atoms of the structural unit reflects the range in pH over which the mineral is stable. Moreover, the relations of Fig. 8 allow calculation of the range of possible Lewis-base strength for a specific structural unit.

Example: Consider becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3 \cdot O_2(OH)_3]_2(H_2O)_4$. The effective charge of the structural unit is $[3 \times 2 - 2 \times 2–3 \times 1 - h \times 3] = 1.6^-$ (setting $h = 0.20$ *v.u.*, the average strength of a hydrogen bond, Brown, 1981). The charge deficiency per anion of the structural unit is thus $1.6/[2 \times 3 + 2 + 3] = 1.6/11$ $= 0.145$ *v.u.* From Fig. 8b, the corresponding range in the average number of bonds to O for this structural unit is 0.65–1.05. Thus the minimum and maximum possible numbers of bonds from the interstitial complex (and adjacent structural units) to the structural unit are $0.65 \times 11 = 7$ and $1.05 \times 11 = 11.5$ bonds, respectively. This results in a range in Lewis basicity of 1.6/11.5 to 1.6/7 = 0.14–0.23 *v.u.*

(H_2O) as an interstitial species

Here, we examine the possible stereochemical arrangements adopted by interstitial (H_2O), and consider its effect in moderating the Lewis acidity of the interstitial complex.

Interstitial (H_2O) not bonded to interstitial cations

Where (H_2O) is not bonded to an interstitial cation, it is usually involved in a hydrogen-bond network [this is not always the case, but this situation is fairly rare]. Where involved in a hydrogen-bond network, the O atom of an (H_2O) group is usually [4]-coordinated, with two O—H (donor-hydrogen) bonds and two H...O (hydrogen-acceptor ≡ hydrogen) bonds. In this case (Fig. 9a), two hydrogen bonds of strength v *v.u.* are incident at the O atom of the (H_2O) group. The bond-strength requirements of the central O atom are satisfied by two O—H bonds of strength (1 − v) *v.u.* In order to satisfy the bond-strength requirements about the H atoms, each H forms a hydrogen bond of strength v *v.u.* to another (H_2O) group or to an anion of the structural unit. Hence (H_2O) groups not bonded to any interstitial cations normally do not change the strengths of the chemical bonds; they merely propagate them through space. We designate this type of (H_2O) group as *non-transformer* (H_2O) and denote it by the subscript *g*, $(H_2O)_g$.

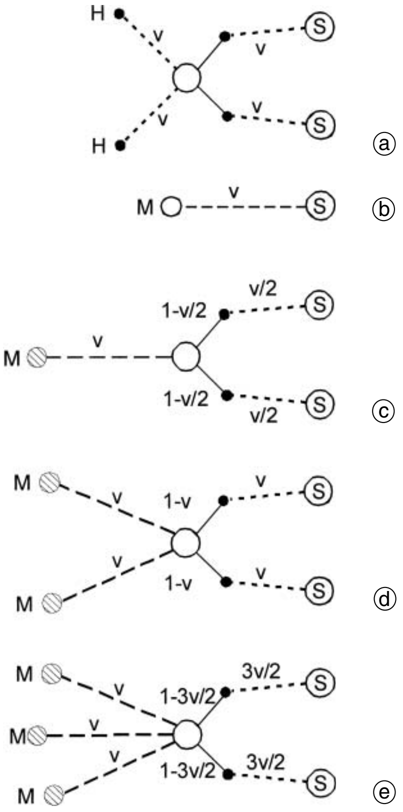

Fig. 9. (**a**) an (H_2O) group held in a structure solely by hydrogen bonds; the O atom of the (H_2O) group is an acceptor anion for two hydrogen bonds of valence v *v.u.*, and a donor anion for two H atoms; (**b**) the interstitial cation, *M*, bonds to an anion, *S*, with bond valence v; (**c**) bond-valence transformer effect of an (H_2O) group: the anion, *M*, bonds to an (H_2O) group which, in turn, bonds to two anions, *S*; thus one bond (bond valence = v *v.u.*) is split into two weaker bonds (bond valence = v/2 *v.u.*); (**d**) the (H_2O) group does not act as a bond-valence transformer: two cations, *M*, bond to an (H_2O) 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**) the (H_2O) group bonds to three cations, and is an inverse bond-valence transformer. Cation-oxygen bonds are shown by broken lines, H bonds are shown as dotted lines, bond valences are in *v.u.*.

Interstitial H_2O bonded to one interstitial cation

Let a cation, *M*, bond to an anion *S* (Fig. 9b); the anion *S* receives a bond-strength of v *v.u.* from the cation *M*. Consider a cation, *M*, that bonds to an (H_2O) group, which, in turn, bonds to an anion *S* (Fig. 9c). In the second case, the oxygen atom of the (H_2O) group receives a bond-strength of v *v.u.* from the cation *M*, and its bond-strength requirements are satisfied by two short O—H bonds of strength (1 − v/2) *v.u.* To satisfy the bond-strength requirements around each H atom, each H forms at least one hydrogen bond with its neighbouring anions. In Fig. 9c, one of these hydrogen bonds involves the *S* anion which thus receives a bond-strength of one half what it received where it was bonded directly to the *M* cation. Thus the (H_2O) group acts as a *bond-strength transformer*, causing one bond (bond strength = v *v.u.*) to be split into two weaker bonds (bond strength = v/2 *v.u.*); 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. 9d). In this case, the O atom receives a bond strength of 2v *v.u.* from the two cations, and its bond-strength requirements are satisfied by two short O–H bonds, each of strength (1 − v) *v.u.* To satisfy the bond-strength requirements of each H atom, each H forms at least one hydrogen bond with its neighbouring anions. In Fig. 9d, one of these hydrogen bonds involves the *S* anion, which thus receives the same bond-strength (v *v.u.*) as where it is bonded directly to one *M* cation (Fig. 9b). Thus, in this case, the (H_2O) group does not act as a bond-strength 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. 9e). In this case, the O atom receives a bond strength of 3v *v.u.* from the three cations, and its bond-strength requirements are satisfied by two short O—H bonds, each of strength (1−3v/2) *v.u.* To satisfy the bond-strength requirements of each H atom, each H forms (at least) one hydrogen bond with its neighbouring anions. In Fig. 9e, one of these hydrogen bonds involves the *S* anion, which thus receives 3v/2 *v.u.* as compared with v *v.u.* where it is bonded directly to one *M* cation (Fig. 9b). Thus, in this case, the (H_2O) group acts as a reverse bond-strength transformer, increasing the strength of the bonds between the cations and the structural unit. This type of (H_2O) is fairly uncommon, and is included for completeness.

Monovalent interstitial anions: OH, F, Cl

In most minerals, the structural unit bears a negative charge and the interstitial complex has 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. 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], essentially 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 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 *v.u.* (usually ~0.8 *v.u.*) from its companion H atom, and hence requires ~1.0 *v.u.* 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 *v.u.*, 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-coordinated monovalent cations.

For divalent interstitial cations, (OH) must bond to (at least) three cations to satisfy its bond-valence requirements, and hence 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. Thus (OH) groups are unlikely to

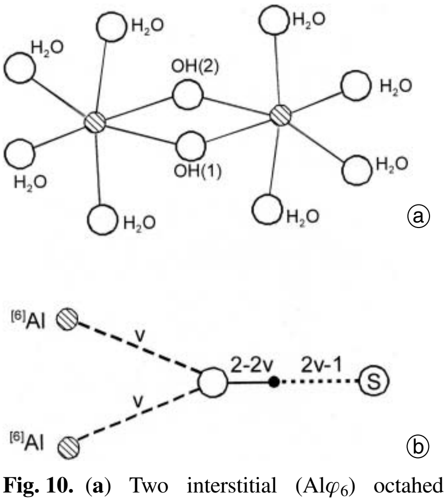

Fig. 10. (**a**) Two interstitial ($Al\varphi_6$) octahedra sharing an edge: $\{Al_2(H_2O)_8(H_2O)_0(OH)_2\}^{4+}$; H atoms are shown as small black circles; (**b**) the arrangement of bond valences around an (OH) group in (a); the large unshaded circle is an O atom of an (OH) group, and the broken lines indicates an H-bond.

occur as interstitial species where accompanied by divalent cations.

For trivalent interstitial cations, (OH) must bond to two octahedrally coordinated cations. Thus two $(Al\varphi_6)$ 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.* Consider two $(Al\varphi_6)$ octahedra linked through a shared edge (Fig. 10a). Both anions involved in the shared edge are (OH), and their bonding is shown more explicitly in Fig. 10b. The OH anion accepts two very strong bonds (≥ 0.5 *v.u.*) and transforms them into one weak bond (~ 0.2 *v.u.*). 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 general interstitial complex

A general interstitial complex can be written as

$$\{^{[m]}M^{+}{}_{a}{}^{[n]}M^{2+}{}_{b}{}^{[l]}M^{3+}{}_{c}(H_2O)_d(H_2O)_e{}^{[q]}(OH)_f \cdot (H_2O)_g\}^{(a+2b+3c-f)+}$$

where M is any type of interstitial mono-, di- and tri-valent 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 overall composition of a mineral may be expressed in the general form

$$M(H_2O)_d(H_2O)_e(OH)_f \text{ [structural unit] } (H_2O)_g$$

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.

Example 1: In copiapite, $Fe^{2+}(H_2O)_6[Fe^{3+}{}_2O(SO_4)_3 \cdot (OH)(H_2O)_4]_2(H_2O)_6$, interstitial Fe^{2+} bonds to six transformer (H_2O) groups, and there are six (H_2O) not bonded to any interstitial cations. The interstitial complex is written in its complete form as $\{^{[6]}Fe^{2+}(H_2O)_6(H_2O)_0(OH)_0 \cdot (H_2O)_6\}^{2+}$, *i.e.*, $d = 6$, $e = 0$, $f = 0$ and $g = 6$ in the general formula of an interstitial complex.

Example 2: In becquerelite, $Ca(H_2O)_4[(UO_2)_3O_2 \cdot (OH)_3]_2(H_2O)_4$, interstitial Ca bonds to four (H_2O) groups and three O-atoms of the structural unit. All interstitial (H_2O) groups bonded to Ca link only to one Ca atom, and hence there are four transformer (H_2O) groups. In addition, there are four non-transformer (H_2O) groups that do not bond to any interstitial cation, and the interstitial complex is written in its complete form as $\{^{[7]}Ca(H_2O)_4(H_2O)_0(OH)_0(H_2O)_4\}^{2+}$, *i.e.*, $d = 4$, $e = 0$, $f = 0$ and $g = 4$. 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.

Calculation of the Lewis acidity of interstitial complexes

The interstitial complex is written as $\{^{[m]}M^{+}{}_{a} \cdot {}^{[n]}M^{2+}{}_{b}{}^{[l]}M^{3+}{}_{c}(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}$. We 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. The effective charge of the interstitial complex is the formal charge, $a + 2b + 3c - f$, modified by the charge transferred *via* hydrogen bonds emanating from the structural unit, $h \times s$ where h is the strength of the hydrogen bonds and s is their number: effective charge $= a + 2b + 3c - f + h \times s$. The number of bonds from the interstitial complex to the structural unit is the product of all interstitial cations times their coordination numbers, $m \times a + n \times b + l \times c$, plus the additional bonds from d transformer (H_2O) groups, d, minus the number of bonds removed by the presence of f (OH) groups, $f \times (q - 1)$, plus the number of hydrogen bonds emanating from the structural unit, s: $m \times a + n \times b + l \times c + d - f \times (q - 1) + s$. Thus the *Lewis acidity* of the interstitial complex $\{^{[m]}M^{+}{}_{a}{}^{[n]}M^{2+}{}_{b} \cdot {}^{[l]}M^{3+}{}_{c}(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}$ can be written as

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

where s is the number and h is the strength of the hydrogen bonds emanating from the structural unit. In order to know s, the number of hydrogen bonds emanating from the structural unit, we need to know the structural unit to be considered. At first sight, this requirement seems unnecessary, as one might expect that the effective charge should be affected only by the number of hydrogen bonds incident to the interstitial complex. However, this fails to consider the effect of polarity of the structural unit. For example, consider lizardite, $[Mg_3Si_4O_{10}(OH)_4]^0$, where four hydrogen-bonds emanate from the structural unit (Fig. 7) to bond to the adjacent structural unit. No charge is transferred to the (virtual) interstitial complex, but the charge transferred to the next structural unit must be incorporated into the calculated effective charge for the structural units to link together. As shown above, the effective charge of the structural unit in lizardite is 0.8^-, and using the observed structure, the Lewis basicity $= 0.8/4 = 0.20$ *v.u.* The formal charge of the (virtual) interstitial complex is 0 and hence the effective charge is $0 + 0.8^+ = 0.8^+$; the number of bonds from this virtual

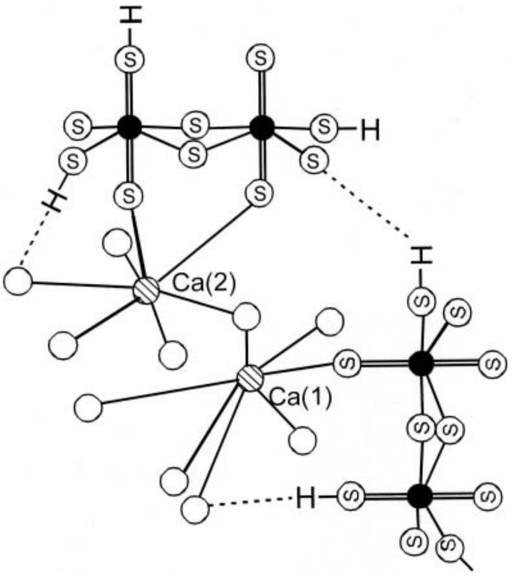

Fig. 11. An example of an interstitial $\{^{[7]}Ca_2(H_2O)_7(H_2O)_3\}^{4+}$ complex. In the structural unit, the central cations are indicated by large black circles and the corresponding anions by circles marked *S*; in the interstitial complex, the interstitial (H_2O) groups are shown as large white 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.

interstitial complex is 4, and hence the Lewis acidity is 0.20 *v.u.* This simple argument is given to show the operation of the above expression for a virtual structural unit (*i.e.*, structural units held together by hydrogen bonds from one unit directly to the next). For this situation, $a = b = c = d = f = 0$, and the Lewis acidity becomes $h \times s/s = h$, which is the strength of the hydrogen bonds emanating from the structural unit.

Example: Consider the interstitial complex $\{^{[7]}Ca_2(H_2O)_7(H_2O)_3\}^{4+}$ interacting with a structural unit containing three (OH) groups (Fig. 11). 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) $+ 3 \times 0.20 = 4.6^+$. The number of bonds from the interstitial complex to the structural unit is 7×2 (from Ca) $+ 7$ [from transformer (H_2O) groups] $+ 3$ (resulting from the hydrogen bonds to the interstitial complex) $= 24$. Thus the Lewis acidity of the interstitial complex is $4.6/24 = 0.192$ *v.u.*

Graphical representation of Lewis acidity

The variation in Lewis acidity of an interstitial complex may be shown graphically as a function of the number of transformer (H_2O) groups for specific cation charges and cation-coordination numbers (Fig. 12a). Obviously, the Lewis acidity of the interstitial complex decreases (1) as the number of transformer (H_2O) groups increases, (2) as the cation-coordination numbers increase, and (3) as the cation charge decreases. Figure 12a 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.*, $M^{3+} + (OH)^- \equiv M^{2+}$).

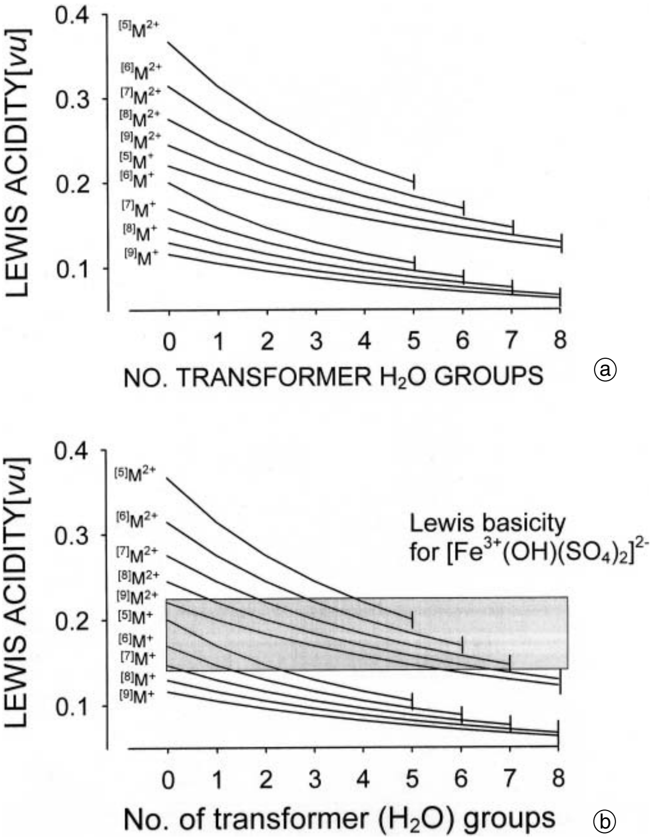

Fig. 12. (**a**) The Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The lines shown are for interstitial cations with formal charges and coordination numbers shown to the left of the plot. (**b**) as Fig. 12a with the corresponding range in Lewis basicity of the structural unit $[Fe^{3+}(OH)(SO_4)_2]^{2-}$ marked by the shaded band.

Structural units, interstitial complexes and the principle of correspondence of Lewis acidity-basicity

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 interstitial cation(s), and the coordination number(s) of those cations. We may now combine these two representations of basicity and acidity *via* the principle of correspondence of Lewis acidity-basicity by plotting the range of Lewis basicity of a specific structural unit on a graph that shows the variation in Lewis acidity of the generalized interstitial complex (Fig. 12b). Where the properties of the structural unit and the interstitial complexes intersect, the principle of correspondence of Lewis acidity-basicity is satisfied and structures of those specific compositions are stable. Where the properties of the structural unit and interstitial complexes do not overlap, the principle of correspondence of

Lewis acidity-basicity is not satisfied and structures of those compositions are not stable.

Prediction of transformer H_2O groups

As the principle of correspondence of Lewis acidity-basicity requires that the Lewis acidity of the interstitial complex lies within the characteristic range of Lewis basicity for a given structural unit for a stable crystal-structure to form, 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.

Example: Consider a structural unit of formal charge 2^-, four (OH) groups and a range in Lewis basicity of 0.17 to 0.22 *v.u.* The Lewis acidities of all possible stable interstitial complexes must match this range, and thus we can formulate the following restrictions derived from expression (1) for interstitial complexes with only one type of interstitial cation:

(i) $\{^{[m]}M^{+}{}_2(H_2O)_d(H_2O)_e\}^{2+}$

$$0.17 < 2(1 + 2h)/(2m + d + 4) < 0.22\ v.u. \qquad (1)$$

(ii) $\{^{[n]}M^{2+}(H_2O)_d(H_2O)_e\}^{2+}$

$$0.17 < 2(1 + 2h)/(n + d + 4) < 0.22\ v.u. \qquad (2)$$

(iii) $\{^{[l]}M^{3+}(H_2O)_d(H_2O)_e{}^{[3]}(OH)\}^{2+}$

$$0.17 < 2(1 < 2h)/(l < d - 1 \times 2 + 4) < 0.22\ v.u. \qquad (3)$$

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 (i). For cation coordination numbers $m > [6]$, expression (1) does not hold, and hence there can be no minerals with interstitial monovalent cations of coordination number > [6]. Where $m = [6]$, expression (1) 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 (1) 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 (ii). For $n = [5]$, expression (2) 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 (iii). For $l = [6]$, expression (3) 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.

Hydroxy-hydrated borate minerals

Boron occurs in triangular and tetrahedral coordination by O [this includes O and (OH)], and considerable structural variation arises *via* polymerization of (BO_3) and (BO_4) polyhedra. Hawthorne *et al.* (1996) described the structural hierarchy developed in borate minerals, Burns *et al.* (1995) described the polyhedron clusters used as fundamental building blocks, and Burns (1995) examined factors affecting the relative stability of borate clusters. With this work as a background, Schindler and Hawthorne

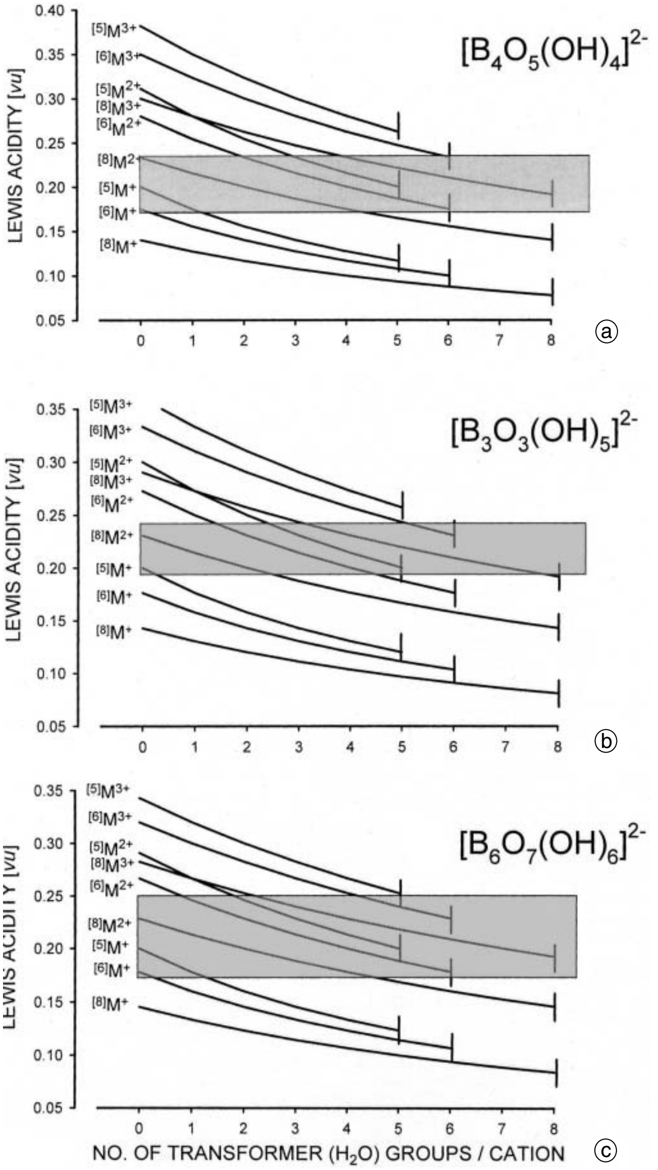

Fig. 13. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in basicity of the structural units of selected borate minerals are shown by the shaded fields: (**a**) $[B_4O_5(OH)_4]^{2-}$; (**b**) $[B_3O_3(OH)_5]^{2-}$; (**c**) $[B_6O_7(OH)_6]^{2-}$.

(2001a, b, c) examined the stability of borate structures within the theoretical framework described above, and showed how many crystal-chemical features of borate minerals may be understood in terms of the principle of correspondence of Lewis-acidity – Lewis-basicity. Below, we examine selected structural units in borate minerals with this approach, and see how well we can predict some of their structural and chemical features.

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

The structural unit $[B_4O_5(OH)_4]^{2-}$ occurs in borax: $Na_2(H_2O)_8[B_4O_5(OH)_4]$; tincalconite: $Na_2(H_2O)_{2.67} \cdot [B_4O_5(OH)_4]$; and hungchaoite: $Mg(H_2O)_5[B_4O_5(OH)_4] \cdot (H_2O)_2$, and contains two $(B\varphi_3)$ and two $(B\varphi_4)$ groups. The effective charge of this structural unit is $(2 + 0.2 \times 4)^- = 2.8^-$, and the number of O atoms in the structural unit is 9; hence the charge deficiency per anion of the structural unit is $2.8/9 = 0.31$ *v.u.* and the corresponding range in $\langle NB \rangle_{in}$, the number of bonds per anion of the structural unit to the structural unit from the interstitial complex and adjacent structural units is 1.30–1.80 (Fig. 9a). As there are nine anions in the structural unit, the range in the total number of bonds to the structural unit is $9 \times (1.3–1.8) = 11.7–16.2$. The range in Lewis basicity of the structural unit is the effective charge, 2.8^-, divided by the range in the number of bonds to the structural unit: 2.8/11.7 and 2.8/16.2 = 0.17–0.24 *v.u.*

We may predict the range in chemical composition for possible interstitial complexes using Fig. 13a. Interstitial monovalent cations are possible only for coordination numbers [5] and [6] with 0–1 and 0 transformer (H_2O) groups, respectively (Table 3). For divalent interstitial cations, $^{[6]}M^{2+}$ is possible with 2–6 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–4 transformer (H_2O) groups. For trivalent interstitial cations, $^{[6]}M^{3+}$, and $^{[8]}M^{3+}$ are possible with one (OH) group and 4 transformer (H_2O) groups, or with 6 transformer (H_2O) and 4–8 transformer (H_2O) groups, respectively. As indicated in Table 3, all minerals of this group conform to these predictions: borax has an interstitial complex $\{^{[6]}Na(H_2O)_0 \ldots\}^+$ and hungchaoite has an interstitial complex $\{^{[6]}Mg(H_2O)_4 \ldots\}^{2+}$. Tincalconite has interstitial $^{[5]}Na$ and $^{[6]}Na$; combining the above predictions results in a possible variation of 0–1 plus 0 transformer (H_2O) groups, for a total possible variation of 0–1; the observed value is 0.

$[B_3O_3(OH)_5]^{2-}$

The structural unit $[B_3O_3(OH)_5]^{2-}$ occurs in inyoite: $Ca(H_2O)_3[B_3O_3(OH)_5](H_2O)$; inderite: $Mg(H_2O)_4[B_3O_3 \cdot (OH)_5](H_2O)$; kurnakovite: $Mg(H_2O)_4[B_3O_3(OH)_5](H_2O)$; meyerhofferite: $Ca(H_2O)[B_3O_3(OH)_5]$; and inderborite: $CaMg(H_2O)_4[B_3O_3(OH)_5]_2(H_2O)_2$, and contains one $(B\varphi_3)$ and two $(B\varphi_4)$ groups. The effective charge of this structural unit is $(2 + 0.2 \times 5)^- = 3.0^-$, and the number of O atoms in the structural unit is 8; hence the charge deficiency per anion of the structural unit is $3.0/8 = 0.38$ *v.u.* Inspection of Fig. 9a shows that the corresponding range in $\langle NB \rangle_{in}$ is 1.55–2.00. The corresponding range in Lewis basicity is $0.38/2.00 - 0.38/1.55 = 0.19–0.24$ *v.u.*.

Figure 13b shows the variation in Lewis acidity of a general interstitial complex and the range of Lewis basicity of the $[B_3O_3(OH)_5]^{2-}$ structural unit. Where the Lewis-acidity curves intersect the range of Lewis basicity of the structural unit, the principle of correspondence of Lewis-acidity – Lewis-basicity is satisfied and a stable structure can form. First, consider interstitial monovalent cations. For coordination numbers [6] and above, monovalent cations cannot occur. For a coordination number of [5], a monovalent cation can occur only with zero transformer (H_2O) groups present (Table 3). Compound

Table 3. The $[B_4O_4(OH)_4]^{2-}$, $[B_3O_3(OH)_5]^{2-}$ and $[B_6O_7(OH)_6]^{2-}$ structural units: predicted and observed interstitial complexes.

Structural unit	Lewis basicity (*v.u.*)	Predicted interstitial complex	Observed interstitial complex	Mineral
$[B_4O_5(OH)_4]^{2-}$	0.17–0.24	$\{^{[5]}M^+(H_2O)_{0-1}\}$	$\{^{[6]}Na_{1.33}{}^{[5]}Na_{0.67}(H_2O)_0\}^{3+}$	tincalconite
		$\{^{[6]}M^+(H_2O)_0\}$	$\{^{[6]}Na_2(H_2O)_0\}^{2+}$	borax
		$\{^{[7],[8]}M\}$: not possible	none observed	
		$\{^{[6]}M^{2+}(H_2O)_{2-6}\}$	$\{^{[6]}Mg(H_2O)_4\}^{2+}$	hungchaoite
		$\{^{[7]}M^{2+}(H_2O)_{1-5}\}$		
		$\{^{[8]}M^{2+}(H_2O)_{0-4}\}$		
		$\{^{[6]}M^{3+}(H_2O)_6(OH)_1\}$		
		$\{^{[8]}M^{3+}(H_2O)_{4-8}\}$		
$[B_3O_3(OH)_5]^{2-}$	0.19–0.24	$\{^{[6]-[8]}M^+ \ldots\}$: not possible	none observed	
		$\{^{[6]}M^{2+}(H_2O)_{2-4}\}$	$\{^{[6]}Mg(H_2O)_4\}^{2+}$	inderite
		$\{^{[7]}M^{2+}(H_2O)_{1-3}\}$	$\{^{[8]}Ca^{[6]}Mg(H_2O)_2\}^{4+}$	inderborite
		$\{^{[8]}M^{2+}(H_2O)_{0-2}\}$	$\{^{[8]}Ca(H_2O)_1\}^{2+}$	inyoite
			$\{^{[8]}Ca(H_2O)_1\}^{2+}$	meyerhofferite
		$\{^{[6]}M^{3+}(H_2O)_{5-6}\}$		
		$\{^{[6]}M^{3+}(H_2O)_{3-4}(OH)_1\}$		
		$\{^{[7]}M^{3+}(H_2O)_{4-7}\}$		
		$\{^{[8]}M^{3+}(H_2O)_{3-7}\}$		
$[B_6O_7(OH)_6]^{2-}$	0.17–0.25	$\{^{[6]}M^+(H_2O)_{0-1}\}$	$\{^{[6]}Na_6{}^{[6]}Mg_1(H_2O)_0\}^{8+}$	rivadavite
		$\{^{[7]}M^+\}$: not possible		
		$\{^{[8]}M\}$: not possible		
		$\{^{[6]}M^{2+}(H_2O)_{1-6}\}$	$\{^{[6]}Mg(H_2O)_3\}^{2+}$	mcallisterite
		$\{^{[7]}M^{2+}(H_2O)_{0-6}\}$	$\{^{[6]}Mg(H_2O)_3\}^{2+}$	admontite
		$\{^{[8]}M^{2+}(H_2O)_{0-5}\}$	$\{^{[6]}Mg(H_2O)_1\}^{2+}$	aksaite

monovalent cations [*e.g.*, $(NH_4)^+$] typically have low coordination numbers (*e.g.*, [3] or [4]), and their Lewis acidity curves (not shown in Fig. 13b) overlap the Lewis basicity range, indicating that structures with these interstitial species are possible. For divalent interstitial cations, $^{[6]}M^{2+}$ is possible with 2–4 transformer (H_2O) groups, $^{[7]}M^{2+}$ is possible with 1–3 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–2 transformer (H_2O) groups. Trivalent interstitial cations are possible only for coordination numbers of [6] with 5–6 transformer (H_2O) groups, [7] with 4–7 transformer (H_2O) groups, and [8] with 3–7 transformer (H_2O) groups. As indicated in Table 3, all minerals of this group conform to these predictions: both inderite and kurnakovite have interstitial complexes $\{^{[6]}Mg(H_2O)_4\ldots\}^{2+}$, and both inyoite and meyerhofferite have interstitial complexes $\{^{[8]}Ca(H_2O)\ldots\}^{2+}$. Inderborite has interstitial $^{[8]}Ca$ and $^{[6]}Mg$; combining the above predictions results in a possible variation of 0–2 plus 2–4 transformer (H_2O) groups per cation, for a total possible variation of 2–6; the observed value is 2 (H_2O) groups *pfu*.

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

The structural unit $[B_6O_7(OH)_6]^{2-}$ occurs in mcallisterite: $Mg(H_2O)_3[B_6O_7(OH)_6](H_2O)_{1.5}$; admontite: $Mg(H_2O)_3 \cdot [B_6O_7(OH)_6](H_2O)$; aksaite: $Mg(H_2O)_2[B_6O_7(OH)_6](H_2O)$; and rivadavite: $Na_6Mg(H_2O)_{10}[B_6O_7(OH)_6]$; and contains three ($B\varphi_3$) and three ($B\varphi_4$) groups. The effective charge of this structural unit is $(2 + 0.2 \times 6)^- = 3.2^-$, and the number of O atoms in the structural unit is 13; the charge deficiency per anion of the structural unit is $3.2/13 = 0.25$ *v.u.* and the corresponding range in the number of bonds per anion required by the structural unit is 1.0–1.5 (Fig. 9). The corresponding range in Lewis basicity of the $[B_6O_7(OH)_6]^{2-}$ structural unit is 0.16–0.25 *v.u.*.

Using Fig. 13c, we predict the range in chemical composition for possible interstitial complexes. For interstitial monovalent cations, $^{[6]}M^+$ is possible with 0–1 transformer (H_2O) groups, $^{[7]}M^+$ (not shown in Fig. 13c) and $^{[8]}M^+$ are not possible (Table 3). For divalent interstitial cations, $^{[6]}M^{2+}$ is possible with 1–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ (not shown in Fig. 13c) is possible with 0–6 transformer (H_2O) groups, and $^{[8]}M^{2+}$ is possible with 0–5 transformer (H_2O) groups. As indicated in Table 3, all minerals of this group conform to these predictions: mcallisterite and admontite have interstitial complexes $\{^{[6]}Mg(H_2O)_3\ldots\}^{2+}$ and aksaite has an interstitial complex $\{^{[6]}Mg(H_2O)_1\ldots\}^{2+}$.

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

The above calculations for the structural units $[B_3O_3(OH)_5]^{2-}$, $[B_4O_5(OH)_4]^{2-}$ and $[B_6O_7(OH)_6]^{2-}$ illustrate how we can predict aspects of the interstitial complex of a mineral, given its structural unit. This approach is quite successful in predicting the coordination numbers of the interstitial cations. This aspect of the predictions is examined in Fig. 14 where it can be seen that coordination numbers from [4] to [11] are predicted accurately. Five examples lie off the 1:1 line in the central region between [6] and [8], but this amounts to only 9% of the data.

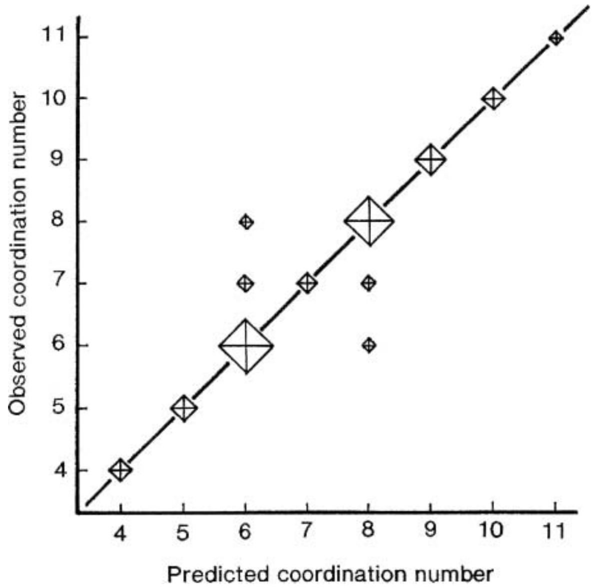

Fig. 14. Comparison of the predicted and observed coordination-numbers of interstitial cations in borate minerals; the areas of the squares are proportional to the number of data defining each point.

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

Aqueous species in concentrated borate solutions

Hawthorne (1979) suggested that structural units in minerals form by condensation of fundamental building blocks that occur as complexes in hydrothermal or surficial aqueous solutions. If this is the case, there should be a connection between some parameter of the structural unit or interstitial complex and the aqueous complexes present in solution.

The pioneering work of Ingri and coworkers (summarized by Ingri, 1963) shows that the following borate species occur in highly concentrated aqueous borate solutions: $[B(OH)_3]^0$, $[B_5O_6(OH)_4]^-$, $[B_3O_3(OH)_4]^-$, $[B_3O_3(OH)_5]^{2-}$, $[B_4O_5(OH)_4]^{2-}$ and $[B(OH)_4]^-$ (Fig. 15a). Raman spectroscopy (Maya, 1976; Janda, Heller, 1979a) and ^{11}B-NMR spectroscopy (Janda, Heller, 1979b; Salentine, 1983; Müller *et al.*, 1993) have confirmed the occurrence and pH ranges for all these aqueous species except $[B_3O_3(OH)_5]^2$. At low pH, the stable aqueous species is $[B(OH)_3]^0$ and the constituent B is [3]-coordinated. At high pH, the stable aqueous phase is $[B(OH)_4]^{1-}$ and the constituent B is [4]-coordinated. Thus the variation in coordination number

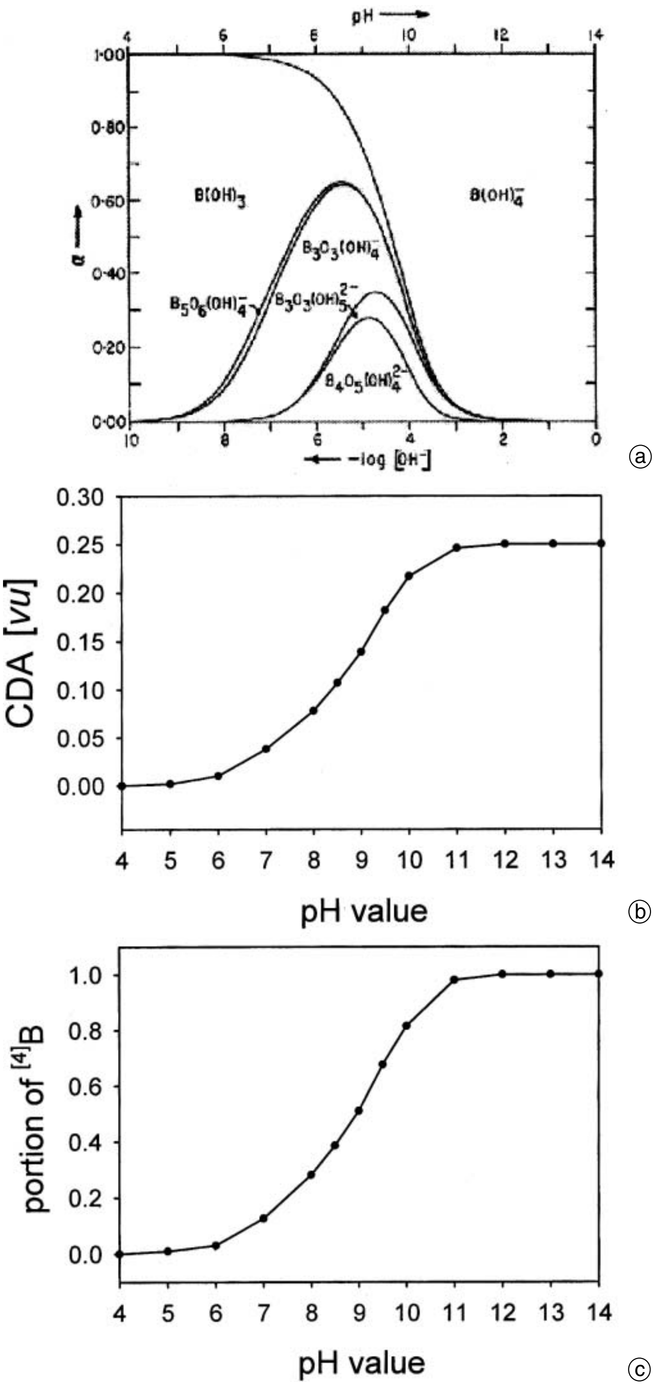

Fig. 15. (**a**) Distribution and occurrence of aqueous borate species in solution after Ingri (1963). At a given pH-value, the vertical distance between successive curves gives the fraction α of the ion present; (**b**) the average basicity of the aqueous species at a specific pH-value; (**c**) the fraction of tetrahedrally coordinated boron ($^{[4]}$B) in the aqueous species at a specific pH-value.

shows a crude correlation with ambient pH. At pH values close to neutrality, more complex aqueous borate species are present (Fig. 15a). These species occur as structural units or fragments of structural units in minerals, and the topologic and geometric details of their structures are well known.

Structure and CDA of aqueous borate complexes

Hawthorne *et al.* (1996) showed that there is a direct correlation between the Lewis basicity of borate complexes (clusters) in solution and the pH of the aqueous solution at the maximum concentration of the complex. However, Hawthorne *et al.* (1996) assumed an average coodination number of [4] for O-atoms. It is preferable not to make such an assumption, and Schindler and Hawthorne (2001c) used the parameter CDA (instead of Lewis basicity), no longer requiring any assumption about coordination number (although see the discussion of Schindler and Hawthorne (2001c) on the calculation of CDA for [B(OH)$_3$]). There is a very well-developed correlation between CDA and pH (Fig. 15b), suggesting that CDA is a relative measure of variation in pH.

The effect of pH on aqueous complexes and crystal structure

We may calculate the percentage of tetrahedrally coordinated B, $^{[4]}$B, in each species; this value decreases from 100% in [B(OH)$_4$] to 66% in [B$_3$O$_3$(OH)$_5$]$^{2-}$ to 50% in [B$_4$O$_5$(OH)$_4$]$^{2-}$ to 33% in [B$_3$O$_3$(OH)$_4$]$^-$ to 20% in [B$_5$O$_6$(OH)$_4$]$^-$ to 0% in [B(OH)$_3$]. From Fig. 15a, we may also calculate the percentage of each species at a specific pH. Combining these two sets of results, we derive the fraction of tetrahedrally coordinated B for each integer pH value between 4 and 14 (Fig. 15c). Below pH 7 and above pH 11, the curve smoothly approaches the limiting values of 0 and 1, respectively. Where pH is in the range 7–11, the proportion of tetrahedrally coordinated B varies rapidly as a function of pH (relative to other ranges of pH). Figure 16 shows that the charge deficiency per anion of the structural unit varies linearly as a function of the fraction of $^{[4]}$B in solution; it seems reasonable to propose that aqueous borate complexes adjust to varying pH by varying the relative amounts of $^{[3]}$B and $^{[4]}$B. Furthermore, if crystal structures crystallize by condensation of aqueous complexes, the atomic arrangements must contain a record of the pH of the solution/environment from which the structure crystallized in the type and relative amounts of fundamental building blocks (aka aqueous complexes) in their structures.

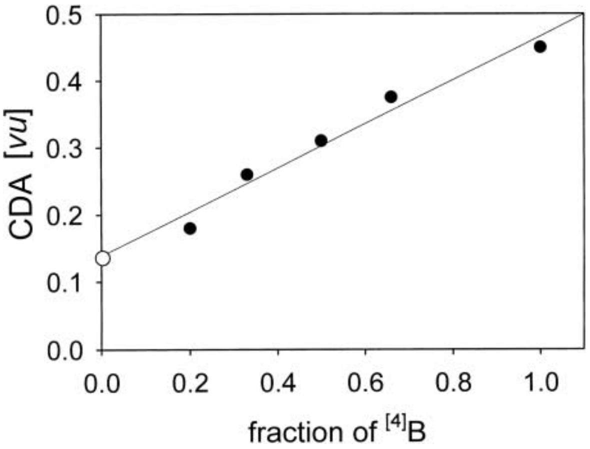

Fig. 16. Correlation between the fraction of tetrahedrally coordinated B, $^{[4]}$B, in the aqueous species and their average basicities (after Hawthorne *et al.*, 1996). The calculated CDA of [B(OH)$_3$] (with zero $^{[4]}$B) was determined by Schindler and Hawthorne (2001c) and its value is marked with a large white circle.

Table 4. Details of the structural units and interstitial complexes in uranyl-oxide-hydroxy-hydrate minerals formed in low-temperature aqueous solution.

Mineral	Formula	Structural unit	CDA (*v.u.*)	Range in Lewis basicity (*v.u.*)	Refs.
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	$[(UO_2)_{12}O_2(OH)_{12}]^0$	0.08	0.11–0.20	(1)
Becquerelite	$^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	$[(UO_2)_3O_2(OH)_3]^{1-}$	0.145	0.14–0.23	(2)
Compreignacite	$^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	$[(UO_2)_3O_2(OH)_3]^{1-}$	0.145	0.14–0.23	(3)
Billietite	$^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$	$[(UO_2)_3O_2(OH)_3]^{1-}$	0.145	0.14–0.23	(2)
Vandenriesscheite	$^{[9]}Pb^{2+}{}_1{}^{[8]}Pb^{2+}{}_{0.57}(H_2O)_5[(UO_2)_{10}O_6(OH)_{11}](H_2O)_6$	$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$	0.14	0.14–0.23	(4)
Fourmarierite	$^{[9]}Pb^{2+}(H_2O)_2[(UO_2)_4O_3(OH)_4](H_2O)_2$	$[(UO_2)_4O_3(OH)_4]^{2-}$	0.19	0.15–0.23	(5)
Agrinierite	$^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5[(UO_2)_3O_3(OH)_2]_2$	$[(UO_2)_3O_2(OH)_2]^{1-}$	0.22	0.155–0.23	(6)
Richetite	$^{[6]}M_x\ ^{[8.4]}Pb_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}\ (OH)_{12}](H_2O)_{10}$	$[(UO_2)_3O_3(OH)_2]^{2-}$	0.22	0.16–0.24	(7)
Masuyite	$^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$	$[(UO_2)_3O_3(OH)_2]^{2-}$	0.22	0.16–0.24	(8)
Protasite	$^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$	$[(UO_2)_3O_3(OH)_2]^{2-}$	0.22	0.16–0.24	(8), (2)
Curite	$^{[9]}Pb^{2+}{}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$	$[(UO_2)_8O_8(OH)_6]^{6-}$	0.24	0.17–0.24	(9)
Sayrite	$^{[9]}Pb^{2+}{}_2(H_2O)_4[(UO_2)_5O_6(OH)_2]$	$[(UO_2)_5O_6(OH)_2]^{4-\ a}$	0.24	0.17–0.24	(10)
Wölsendorfite	$^{[8.15]}(Pb^{2+}{}_{6.2}\ Ba_{0.4})(H_2O)_{10}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$	$[(UO_2)_{14}O_{19}(OH)_4]^{14-\ a}$	0.29	0.175–0.24	(11)

a: The structural unit is modified by stereoactive lone-pair effects of Pb^{2+}: $^{[1+7]}Pb^{2+}{}_2$ and $^{[2+6]}Pb^{2+}$ in sayrite and wölsendorfite, respectively, leading to ranges in Lewis basicity of 0.15–0.236 and 0.17–0.235 *v.u.*, respectively.

References: (1) Finch *et al.*, 1996; (2) Pagoaga *et al.*, 1987; (3) Burns, 1998b; (4) Burns, 1997; (5) Piret, 1985; (6) Cahill, Burns, 2000; (7) Burns, 1998c; (8) Burns, Hanchar, 1999; (9) Taylor *et al.*, 1981; (10) Piret *et al.*, 1983; (11) Burns, 1999b.

Uranyl-oxide-hydroxy-hydrate minerals

The uranyl-oxide-hydroxy-hydrate minerals (Table 4) can be ordered hierarchically based upon the anion topology of their (sheet) structural unit (Burns, 1999a; Burns *et al.*, 1996). Inspection of Table 4 shows that these minerals often contain interstitial cations that can have stereoactive lone-pairs of electrons, particularly Pb^{2+}. Where such cations are not lone-pair stereoactive, they show a distribution of individual bond lengths similar to that exhibited by spherical cations (*e.g.*, Ca, Sr) of identical formal valence in the same type of environment. When lone-pair stereoactive, such cations typically show one to four short bonds to anions arranged to one side of the cation, and several long bonds to anions on the other side of the cation, with room for the lone pair of electrons to project into the space between the long bonds emanating from the central cation. The short strong Pb^{2+}–O bonds should be considered as part of the structural unit; the question then arises as to how we treat the weak bonds involving these lone-pair-stereoactive cations. By analogy with the H atom, which shows a strong O–H bond involved in the structural unit and a weak hydrogen bond emanating from the structural unit, we consider strong Pb^{2+}-φ bonds (and other lone-pair-stereoactive cations) as belonging to the structural unit, and weak Pb^{2+}-φ bonds are treated in the same way as hydrogen bonds.

Example: Consider sayrite, $Pb^{2+}{}_2(UO_2)_5O_6(OH)_2 \cdot (H_2O)_4$. Inspection of the Pb–O distances in sayrite shows that Pb^{2+} is lone-pair stereoactive. We may indicate this behaviour by writing the coordination number of Pb^{2+} to indicate the number of short and long bonds: $^{[1+7]}Pb^{2+}$. We include Pb^{2+} as part of the structural unit: $[^{[1+7]}Pb^{2+}{}_2 \cdot \{(H_2O)_2(H_2O)_2\}(UO_2)_5O_6(OH)_2]$. In order to calculate the effective charge of the structural unit, we need to assign a typical bond-valence to the short bond(s); the value 0.50 *v.u.* is appropriate. Thus the effective charge of the structural unit is $4^- + 0.50^+ \times 2 + 0.20 \times 2 = 3.40^-$. There are eighteen O atoms in the structural unit, and hence the charge deficiency per anion of the structural unit is $3.40/18 = 0.189$ *v.u.*

CDA versus $\langle NB \rangle_{in}$ for uranyl-oxide and oxysalt minerals

As noted above (Fig. 8b), the data for CDA above 0.33 *v.u.* are rather scattered for (as yet) unknown reasons. However, the band of data in Fig. 8b gives well-defined maximum and minimum values of $\langle NB \rangle_{in}$ for structural units with average basicities between 0.00 and 0.33 *v.u.* In this range, Figure 8b can be used to calculate the range in Lewis basicity of the uranyl-oxide-hydroxy-hydrate structural units in Table 4. Below, we examine structural units in selected uranyl-oxide-hydroxy-hydrate minerals with this approach, and see how well we can predict some of their structural and chemical features.

$[(UO_2)_3O_2(OH)_3]^{1-}$

This structural unit occurs in becquerelite, $^{[7]}Ca(H_2O)_4 \cdot [(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, compreignacite, $^{[7]}K_2(H_2O)_3 \cdot [(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, billietite, $^{[10]}Ba(H_2O)_4[(UO_2)_3 \cdot O_2(OH)_3]_2(H_2O)_3$, and agrinierite, $^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5 \cdot [(UO_2)_3O_2(OH)_3]_2$. The effective charge of the structural unit is $1 + 3 \times 0.2 = 1.6^-$ ($h = 0.20$ *v.u.*) and the number of O-atoms in the structural unit is 11. Hence the charge deficiency per anion of the structural unit is 0.145 *v.u.* We may use this value, together with Fig. 8b, to predict the minimum and maximum value of $\langle NB \rangle_{in}$: 0.65 and 1.05, respectively. There are 11 O-atoms in the structural unit; thus there are a minimum of $11 \times 0.65 = 7$ and a maximum of $11 \times 1.05 = 11.5$ bonds from the interstitial complex to the structural unit. This results in a range in Lewis basicity from 1.6/11.5 to 1.6/7 = 0.14–0.23 *v.u.* (Fig. 17a).

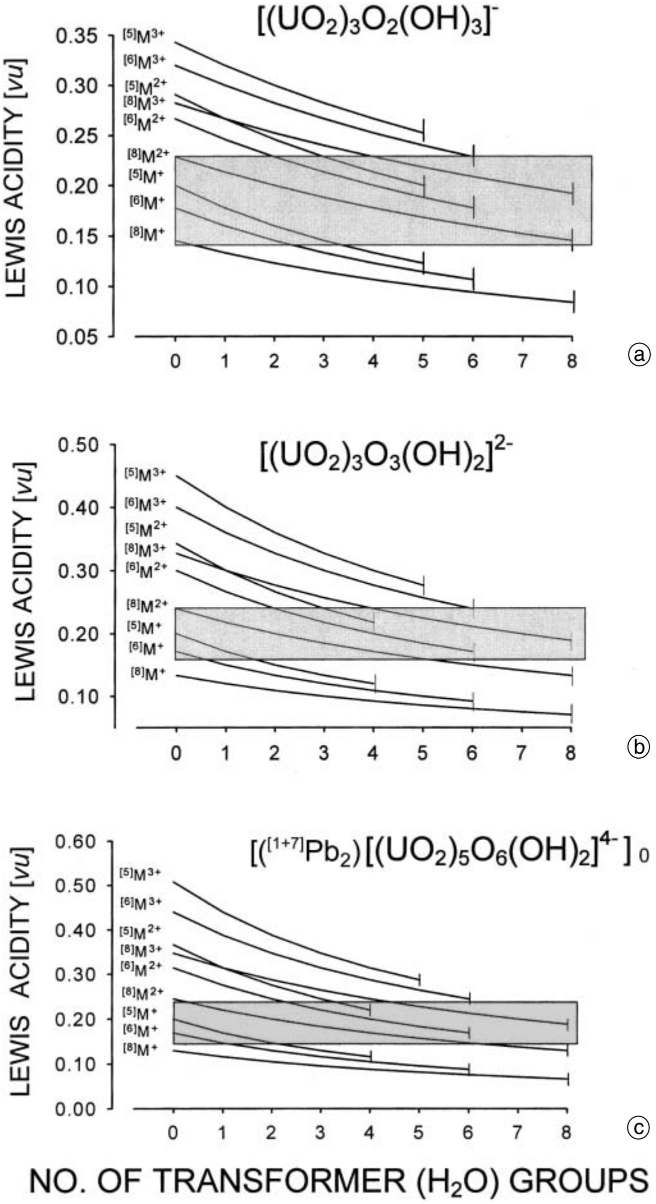

Fig. 17. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in basicity of the structural units of selected uranyl-oxide hydroxy-hydrate minerals are shown by the shaded fields: (**a**) $[(UO_2)_3O_2(OH)_3]^-$; (**b**) $[(UO_2)_3O_3(OH)_2]^{2-}$; (**c**) $[(UO_2)_5O_6(OH)_2]^{4-}$.

The Lewis acidity of a monovalent cation in [8]-, [7]- and [6]-coordination matches the range in Lewis basicity of the structural unit with 0, 1 and 2 transformer (H_2O) groups, respectively. Thus, if all (H_2O) groups are bonded to interstitial cations, a stable mineral with a monovalent [8]-coordinated cation would have a maximum of $11.5 - [8] - 3 = 0.5$ transformer (H_2O) groups per cation, and $^{[8]}M^+(H_2O)_{0-0.5}[(UO_2)_3O_2(OH)_3]$ is the predicted chemical composition of such minerals. The analogous result for $^{[7]}M^+$ is 0–1.5 transformer (H_2O) groups per cation. There is one mineral containing this structural unit and with monovalent cations in the interstitial complex: compreignacite, $^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$; the number of ($H_2O$) groups bonded to K is in accord with the predicted value. A [6]-, [7]- or [8]-coordinated divalent interstitial cation must bond to a minimum of two, one or zero transformer (H_2O) groups, respectively, and a maximum of six, seven or eight transformer (H_2O) groups, respectively (Table 5). There are two minerals with only divalent interstitial cations: becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3 \cdot O_2(OH)_3]_2\ (H_2O)_4$, and billietite, $^{[10]}Ba(H_2O)_4[(UO_2)_3O_2 \cdot (OH)_3]_2(H_2O)_3$, which are predicted to contain 1–4 and 0–7 transformer (H_2O) groups, respectively.

$[(UO_2)_3O_3(OH)_2]^{2-}$

This structural unit occurs in richetite, $^{[6]}M_x{}^{[8.4]}Pb^{2+}{}_{8.57} \cdot (H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$, protastite, $^{[10]}Ba \cdot (H_2O)_3[(UO_2)_3O_3(OH)_2]$, and masuyite, $^{[10]}Pb^{2+}(H_2O)_3 \cdot [(UO_2)_3O_3(OH)_2]$. Its effective charge is $2 + 2 \times 0.2 = 2.4^-$, the charge deficiency per anion of the structural unit is $2.4/11 = 0.22$ *v.u.*, and the corresponding range in $\langle NB \rangle_{in}$ is 0.90–1.35. The minimum and maximum numbers of bonds from the interstitial complex to the structural unit are 10 and 15, respectively. The corresponding range in Lewis basicity is from 2.4/15 to 2.4/10 = 0.16–0.24 *v.u.* (Fig. 17b). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

The coordination number of monovalent cations cannot exceed [6], a divalent octahedrally coordinated cation must bond to 2–6 transformer (H_2O) groups and a divalent [8]-coordinated cation bonds to 0–5 transformer (H_2O) groups. In richetite, $^{[6]}M_x{}^{[8.4]}Pb^{2+}{}_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18} \cdot (OH)_{12}](H_2O)_{10}$, protastite, $^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$, and masuyite, $^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$, we do not know the exact number of transformer (H_2O) groups in the interstitial complexes. However, based on the predicted range of $(N + d)$ bonds, the interstitial cations $^{[10]}Ba^{2+}$ and $^{[10]}Pb^{2+}$ can bond to 0–1 transformer (H_2O) groups. For richetite, the situation is complicated by the fact that the current formula bears a positive charge of 6.4^+. However, considering the presence of $^{[6]}(Mg + Fe^{2+})$ and $^{[8]}Pb$, the former should bond to 2–6 transformer (H_2O) groups and the latter should bond to 0–5 transformer (H_2O) groups; the former value is in accord with the observed number (4) of (H_2O) groups bonded to $^{[6]}(Mg + Fe^{2+})$.

$[(UO_2)_5O_6(OH)_2]^{4-}$

This structural unit occurs in sayrite, $^{[9]}Pb^{2+}{}_2(H_2O)_4 \cdot [(UO_2)_5O_6(OH)_2]$ (ignoring stereoactive lone-pair effects). The structural unit has an effective charge of 4.4^-, a charge deficiency per anion of $4.4/18 = 0.244$ *v.u.*, and the predicted range in $\langle NB \rangle_{in}$ is 1.0–1.45. The minimum and maximum numbers of bonds from the interstitial complex to the structural unit are 18 and 26, respectively, corresponding to a range in Lewis basicity from 4.4/24 to 4.4/18 = 0.17–0.24 *v.u.* (Fig. 17c). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

As noted above, sayrite has lone-pair stereoactive Pb^{2+} as its 'interstitial cation', and the strong Pb^{2+}—O bonds must be included as part of the structural unit: $[^{[1+7]}Pb^{2+}{}_2(UO_2)_5O_6(OH)_2]^0$. As shown above, the charge deficiency per anion of this modified structural unit is

Table 5. Predicted and observed transformer (H_2O) groups in interstitial complexes of selected uranyl-oxide-hydroxy-hydrate minerals.

Structural unit	Predicted transformer (H_2O) groups	Interstitial complex	Mineral
$[(UO_2)_3O_2(OH)_3]^{1-}$	$^{[6]}M^+$: $d = 0–3$		
	$^{[7]}M^+$: $d = 0–2.5$	$\{^{[7]}K_2(H_2O)_3\}^{2+}$	compreignacite
	$^{[8]}M^+$: $d = 0–1$		
	$^{[6]}M^{2+}$: $d = 2–6$		
	$^{[7]}M^{2+}$: $d = 1–7$	$\{^{[7]}Ca(H_2O)_4\}^{2+}$	becquerelite
	$^{[10]}M^{2+}$: $d = 0–7$	$\{^{[10]}Ba(H_2O)_4\}^{2+}$	billietite
$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$	$^{[6]}M^+$: $d = 0–3$		
	$^{[8]}M^+$: $d = 0–1$		
	$^{[6]}M^{2+}$: $d = 2–6$		
	$^{[8]}M^{2+}$: $d = 0–8$	$\{^{[9]}Pb^{2+\,[8]}Pb^{2+}{}_{0.5}(H_2O)_5\}^{3+}$	vandenriesscheite
$[(UO_2)_3O_3(OH)_2]^{2-}$	$^{[6]}M^+$: $d = 0–1$		
	$^{[8]}M^+$: not possible		
	$^{[6]}M^{2+}$: $d = 2–6$		
	$^{[8]}M^{2+}$: $d = 0–5$		
	$^{[10]}M^{2+}$: $d = 0–3$	$\{^{[10]}Pb^{2+}(H_2O)_3\}$	masuyite
		$\{^{[10]}Ba(H_2O)_2\}$	protasite
	$^{[8]}M^+$, $^{[9]}M^{2+}$: $d = 0–1$	$\{^{[8]}K_2{}^{[9]}Ca(H_2O)_5\}^{4+}$	agrinierite
$[(UO_2)_5O_6(OH)_2]^{4-}$	$^{[6]}M^+$: $d = 0$		
	$^{[6]}M^{2+}$: $d = 2–6$		
	$^{[8]}M^{2+}$: $d = 0–4$		
	$^{[9]}M^{2+}$: $d = 0–3$	$[^{[1+7]}Pb^{2+}{}_2]\{(H_2O)_2(H_2O)_2\}$	sayrite

0.189 *v.u.*, and hence the minimum and maximum values of $\langle NB\rangle_{in}$ are 0.80 and 1.25, respectively. The number of O atoms in the structural unit is 18, and hence the minimum and maximum number of bonds to the structural unit are $18/1.25–18/0.80 = 14.4–22.5$, respectively. The effective charge of the modified structural unit is 0 (the formal charge) $+ 0.2 \times 2$ (due to hydrogen bonds) $+ (2–0.5) \times 2 = 3.4^-$. Hence the range in Lewis basicity is $3.4/22.5–3.4/14.4 = 0.15–0.236$ *v.u.*, respectively (shown in darker shading on Fig. 17c). The predicted range of transformer (H_2O) groups is 0–6 per structural unit, and the observed value of 2 transformer (H_2O) groups (Table 5) lies within this range).

Hydroxy-hydrated sulfate minerals

Hawthorne *et al.* (2000) described the structural hierarchy developed in sulfate minerals, and Schindler *et al.* (2006) examined sulfate structures within the framework of bond-valence theory, and showed how many crystal-chemical features of sulfate minerals may be understood in terms of the valence-matching principle and the principle of correspondence of Lewis-acidity – Lewis-basicity. Schindler *et al.* (2006) went further, examining the polar nature of structural units in sulfate minerals. Specifically, the sulfate minerals differ from borates and uranyl-oxide hydroxy-hydrates in that their structural units can have two distinct components: (1) sulfate tetrahedra, and (2) di- and tri-valent-metal octahedra. The anions of the sulfate component accept weak bonds from the interstitial complex and form a basic component of the structural unit, whereas the anions bonded only to di- and tri-valent metals [usually (OH) and (H_2O)] donate hydrogen bonds to the interstitial complex or to adjacent structural units, and form an acidic component of the structural unit. Initial considerations suggest that such polarized behaviour can affect the relative positioning and interaction of adjacent structural units

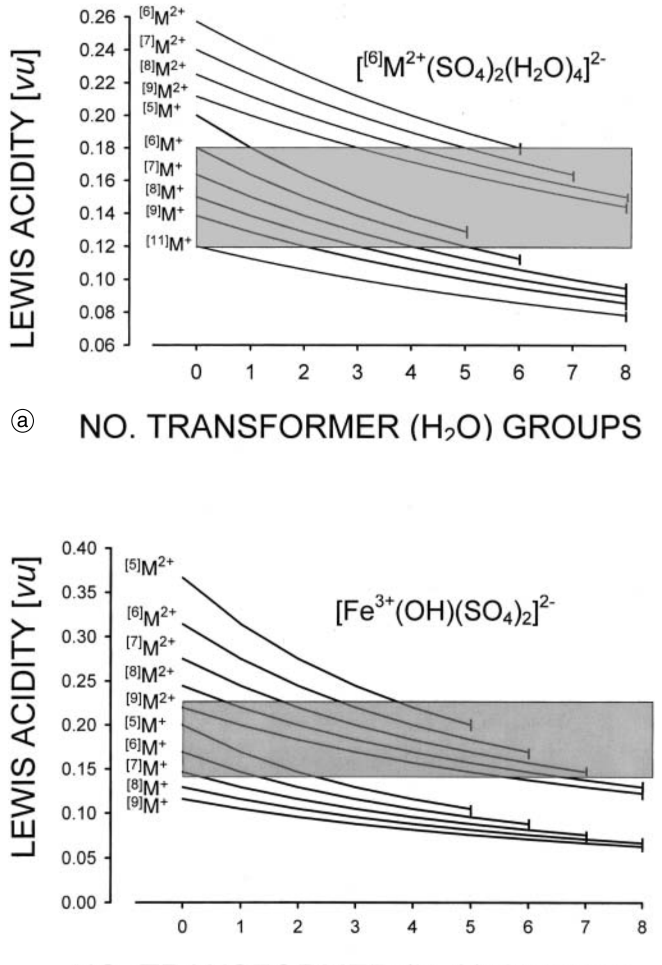

Fig. 18. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in basicity of the structural units of selected sulfate minerals are shown by the shaded fields: (**a**) $[^{[6]}M^{2+}(SO_4)_2(H_2O)_4]^{2-}$; (**b**) $[Fe^{3+}(OH)(SO_4)_2]^{2-}$.

(Schindler *et al.*, 2006). However, the role of this spatial difference between basicity and acidity in the structural unit is still not well-understood in terms of affecting the range in Lewis basicity of the structural unit. As this aspect of Lewis acidity-basicity relations has not been examined for any other group of oxysalts besides the sulfates, we will forgo discussion of this issue at the moment and use the Lewis basicity and acidity expressions described above and used for borates and uranyl minerals. Below, we examine selected structural units in sulfate minerals with this approach.

$[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ (M = Mg, Ni, Zn, Fe^{2+})

This structural unit occurs in blödite, $\{Na_2\} \cdot [Mg(SO_4)_2(H_2O)_4]$, nickelblödite, $\{Na_2\}[Ni(SO_4)_2(H_2O)_4]$, changoite, $\{Na_2\}[Zn(SO_4)_2(H_2O)_4]$, leonite, $\{K_2\} \cdot [Mg(SO_4)_2(H_2O)_4]$, mereiterite, $\{K_2\}[Fe(SO_4)_2(H_2O)_4]$, and roemerite, $\{Fe^{2+}(H_2O)_6\}[Fe^{2+}(SO_4)_2(H_2O)_4]$. The effective charge of the structural unit is $(2 + 0.2 \times 8)^- = 3.6^-$, and the number of O-atoms in the structural unit is 12; hence the charge deficiency per anion of the structural unit is 3.6/12 = 0.30 *v.u.* (based on a hydrogen bond-valence of 0.20 *v.u.*). Inspection of Fig. 8c shows that the corresponding range in $\langle NB \rangle_{in}$ for this structural unit is 1.65–2.50. Thus, there are a maximum of $12 \times 2.50 = 30$ and a minimum of $12 \times 1.65 = 20$ bonds. This results in a maximum Lewis basicity of $(8 \times 0.20 + 2)/20 = 0.18$ *v.u.* and a minimum Lewis basicity of $(8 \times 0.20 + 2)/30 = 0.12$ *v.u.* (Fig. 18a).

First, consider interstitial monovalent cations. For coordination numbers [12] and above, the curves do not intersect the range of Lewis basicity of the structural unit (Fig. 18a), and monovalent cations cannot occur. For coordination numbers [11] to [5], a monovalent cation can occur with 0 down to 1–4 transformer (H_2O) groups present, respectively (Table 6). For divalent interstitial cations, $^{[6]}M^{2+}$ is possible as $^{[6]}M^{2+}(H_2O)_6$ groups, $^{[7]}M^{2+}$ is possible with 5–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ is possible with 4–8 transformer (H_2O) groups, and $^{[9]}M^{2+}$ is possible with 3–9 transformer (H_2O) groups (Table 5).

$[Fe^{3+}(SO_4)_2(OH)]^{2-}$

This structural unit occurs in sideronatrite, $\{Na_2(H_2O)_3\} \cdot [Fe^{3+}(SO_4)_2(OH)]$, metasideronatrite, $\{Na_4(H_2O)_3\} \cdot [Fe^{3+}(SO_4)_2(OH)]_2(H_2O)_3$, guildite, $\{^{[4+2]}Cu^{2+}(H_2O)_4\} \cdot [Fe^{3+}(SO_4)_2(OH)]$, and chaidamuite, $\{^{[6]}Zn(H_2O)_4\} \cdot [Fe^{3+}(SO_4)_2(OH)]$. The effective charge of this structural unit is $(2 + 0.2 \times 1)^- = 2.2^-$, and the number of O atoms in the structural unit is 9; hence the charge deficiency per anion of the structural unit is 2.2/9 = 0.24 *v.u.*. Using this value in combination with Fig. 8c, we may derive the minimum and maximum possible values of $\langle NB \rangle_{in}$: 1.10–1.75. which results in a range in Lewis basicity of 0.14–0.22 *v.u.* for this structural unit. Using Fig. 18b, we can predict the range in chemical composition for possible interstitial complexes.

Interstitial monovalent cations are possible for coordination numbers [5] to [7] with 0–2, 0–1 and 0 transformer (H_2O) groups per cation, respectively (Table 6). For divalent interstitial cations, $^{[6]}M^{2+}$ is possible with 3–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ is possible with 2–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ is possible with 1–6 transformer (H_2O) groups, and $^{[9]}M^{2+}$ is possible with 0–6 transformer (H_2O) groups. As indicated in Table 6, all minerals of this group conform to these predictions: both sideronatrite and metasideronatrite have an interstitial complex $\{^{[6]}Na_2(H_2O)_0 \ldots\}$, guildite has an interstitial complex $\{^{[6]}Cu^{2+}(H_2O)_4\}$, and chaidamuite has an interstitial complex $\{^{[6]}Zn(H_2O)_4\}$.

The generalized structural unit $[^{[m]}M_a(SO_4)_b(OH)_c(H_2O)_d]$

The calculations discussed above illustrate how we can predict aspects of the interstitial complex of a mineral, given its structural unit. Similar calculations for all sulfate minerals with structural units $[^{[m]}M_a(SO_4)_b(OH)_c(H_2O)_d]^{z-}$ are shown in Table 7, where they are compared with the observed interstitial complexes. The agreement between the observed and predicted values is quite close. For some structural units, the predicted interstitial complexes vary

Table 6. Range in Lewis basicity and predicted and most probable interstitial complexes with transformer H_2O groups for the structural units $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ and $[M^{3+}(SO_4)_2(OH)]^{2-}$.

Structural unit	CDA [*v.u.*]	$\langle NB \rangle_{in}$	Lewis basicity [*v.u.*]	Predicted interstitial complex	Most probable interstitial complex	Observed interstitial complex	Mineral
$[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$	0.30	1.65–2.50	0.12–0.18	$\{^{[6]}M^+{}_2(H_2O)_{0-10}\}^{2+}$	$\{^{[6]}M^+{}_2(H_2O)_0\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$	blödite nickelblödite changoite
				$\{^{[8]}M^+{}_2(H_2O)_{0-6}\}^{2+}$	$\{^{[8]}M^+{}_2(H_2O)_2\}^{2+}$	$\{^{[11]}K_2\}^{2+}$	leonite mereiterite
				$\{^{[11]}M^+{}_2(H_2O)_0\}^{2+}$	$\{^{[11]}M^+{}_2(H_2O)_0\}$		
				$\{^{[6]}M^{2+}(H_2O)_6\}^{2+}$	$\{^{[6]}M^{2+}(H_2O)_6\}^{2+}$		
				$\{^{[8]}M^{2+}(H_2O)_{4-8}\}^{2+}$	$\{^{[8]}M^{2+}(H_2O)_4\}^{2+}$		
$[M^{3+}(SO_4)_2(OH)]^{2-}$	0.24	1.10–1.75	0.14–0.22	$\{^{[6]}M^+{}_2(H_2O)_{0-1}\}^{2+}$	$\{^{[6]}M^+{}_2(H_2O)_0\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$	sideronatrite metasideronatrite
				$\{^{[8]}M^+{}_2\}^{2+}$: not possible			
				$\{^{[9]}M^+{}_2\}^{2+}$: not possible			
				$\{^{[6]}M^{2+}(H_2O)_{3-6}\}^{2+}$	$\{^{[6]}M^{2+}(H_2O)_{4-6}\}^{2+}$	$\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$ $\{^{[6]}Zn(H_2O)_4\}^{2+}$	guildite chaidamuite
				$\{^{[8]}M^{2+}(H_2O)_{1-7}\}^{2+}$	$\{^{[8]}M^{2+}(H_2O)_{2-4}\}^{2+}$		

Table 7. Predicted and observed interstitial complexes in selected sulfate minerals.

Structural unit	CDA (*v.u.*)	Predicted $\langle \mathrm{NB} \rangle_{in}$	Range in Lewis basicity (*v.u.*)	Predicted interstitial complex	Observed interstitial complex	Mineral
$[M^{3+}{}_3(SO_4)_6(H_2O)_6]^{3-}$	0.18	0.80–1.45	0.14–0.25	$\{M^{3+}(H_2O)_6\}^{3+}$	$\{^{[6]}Fe^{3+}(H_2O)_6\}^{3+}$ $\{^{[6]}Al(H_2O)\}^{3+}$	paracoquimbite coquimbite
$[M^{3+}{}_3O(SO_4)_6(H_2O)_3]^{5-}$	0.22	0.90–1.55	0.15–0.26	$\{^{[9]}M^{+}{}_5\}^{5+}$: not possible $\{^{[6]}M^{+}(H_2O)_{0-8}\}^{5+}$ $\{^{[6]}M^{2+}{}_{2.5}(H_2O)_{4-15}\}^{5+}$	$\{^{[9]}K_2{}^{[6]}Na_6Fe^{2+}(H_2O)_6\}^{10+}$	metavoltine
$[^{\{4+2]}Cu^{2+}(SO_4)_2(H_2O)_2]^{2-}$	0.28	1.45–1.90	0.16–0.20	$\{^{[7]}M^{+}{}_2(H_2O)_{0-1}\}^{2+}$	$\{^{[7]}Na_2\}^{2+}$	
$[M^{3+}(SO_4)_2(H_2O)_2]^{-}$	0.18	0.80–1.45	0.14–0.25	$\{^{[10]}M^{+}(H_2O)_0\}^{+}$ $\{^{[6]}M^{2+}(H_2O)_{2-6}\}^{2+}$	$\{^{[10]}K\}^{+}$ $\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	krausite
$[M^{3+}(SO_4)_2(OH)]^{2-}$	0.24	1.10–1.75	0.14–0.22	$\{^{[6]}M^{+}(H_2O)_{0-3}\}^{+}$ $\{^{[6]}M^{2+}(H_2O)_{3-6}\}^{2+}$	$\{^{[6]}Na_2\}^{2+}$ $\{^{[4+2]}Cu^{2+}(H_2O)_4\}^{2+}$	sideronatrite guildite
$[M^{3+}(SO_4)_3]^{3-}$	0.25	1.15–1.80	0.14–0.22	$\{^{[7]}M^{+}{}_3(H_2O)_0\}^{3+}$	$\{^{[7]}Na_3\}^{3+}$	
$[M^{3+}{}_2(SO_4)_3(OH)(H_2O)_4]_2{}^{2-}$	0.16	0.70–1.30	0.15–0.27	$\{^{[6]}M^{2+}(H_2O)_{0-6}\}^{2+}$	$\{Fe^{2+}(H_2O)_6\}^{2+}$ $\{Mg(H_2O)_6\}^{2+}$ $\{Ca(H_2O)_6\}^{2+}$ $\{Cu^{2+}(H_2O)_6\}^{2+}$ $\{Zn(H_2O)_6\}^{2+}$	copiapite magnesiocopiapite calciocopiapite cuprocopiapite zincocopiapite
$[M^{3+}(SO_4)_2(OH)(H_2O)]^{2-}$	0.26	1.20–1.80	0.15–0.23	$\{^{[6]}M^{2+}(H_2O)_{3-6}\}^{2+}$	$\{Mg(H_2O)_4(H_2O)_1\}^{2+}$ $\{Zn(H_2O)_4(H_2O)_1\}^{2+}$	botryogen zincobotryogen
$[^{[4+2]}Cu^{2+}{}_2(SO_4)_2(OH)(H_2O)]^{-}$	0.16	0.70–1.30	0.13–0.24	$\{^{[8]}M^{+}(H_2O)_{0-2}\}^{+}$	$\{^{[8]}Na\}^{+}$	natrochalcite
$[M^{2+}{}_5Fe^{3+}{}_3(SO_4)_{12}(H_2O)_{12}]^{5-}$	0.16	0.70–1.30	0.13–0.23	$\{^{[12]}M^{+}{}_5\}^{5+}$: not possible $\{^{[6]}M^{3+}(H_2O)_6\}_{1.67}$	$\{^{[12]}K_2{}^{[6]}Al(H_2O)_6\}^{5+}$	voltaite zincvoltaite
$[^{[4+2]}Cu^{[4+1]}Cu_2O(SO_4)_3]^{2-}$	0.15	0.65–1.20	0.13–0.24	$\{^{[7]}M^{+}{}_2(H_2O)_{0-1}\}^{2+}$	$\{^{[7]}Na^{[7]}K\}^{2+}$	euchlorine
$[^{[4+1]}Cu_3O(SO_4)_3]^{2-}$	0.17	0.75–1.40	0.11–0.21	$\{^{[7]}M^{+}{}_2(H_2O)_{0-4}\}^{2+}$	$\{^{[7]}K_2\}^{2+}$	fedotovite
$[^{[4+1]}Cu_3M^{3+}O_2(SO_4)_4]^{3-}$	0.17	0.75–1.40	0.12–0.22	$\{^{[8]}M^{+}{}_3(H_2O)_{0-1}\}^{3+}$ $\{^{[7]}M^{+}{}_3(H_2O)_{0-4}\}^{3+}$	$\{^{[8]}K_2{}^{[7]}K\}^{3+}$	klyuchevskite

over a wide range of cations or transformer (H_2O) groups, which in terms of prediction, is not satisfactory. However, as we emphasize above, we are involved in trying to understand the factors affecting the chemistry of the weakly bonded constituents in oxysalts. The idea of "prediction" is to evaluate how well we understand the causal factors: lack of agreement between predicted and observed values points to a lack in the theory and serves to guide further development. If we examine why the predicted values span such a wide range for some structural units, it is apparent that this is caused by the structural unit having a wide range in Lewis basicity. Further work will examine the possible role of polarization (spatial variation in Lewis basicity and Lewis acidity) within a structural unit.

Uranyl-oxysalt minerals

Schindler and Hawthorne (2007) have examined the stability of uranyl-oxysalt structures within the framework of bond-valence theory, and showed how many crystal-chemical features of their minerals may be understood in terms of the principle of correspondence of Lewis acidity-basicity. Below, we discuss the understanding and prediction of interstitial (H_2O) contents in these minerals, and examine structural units in selected uranyl-oxysalt minerals to see how well we can predict the structural and chemical features of their interstitial complexes.

Transformer and non-transformer (H_2O)

In an interstitial complex, (H_2O) groups have two distinct roles: (1) as transformer or inverse-transformer (H_2O) groups that affect the Lewis acidity of the interstitial complex (Figs. 9c, e); (2) as non-transformer (H_2O) groups whose role is to propagate bonds from cations to anions that are too distant to bond directly to the cation (Figs. 9a, d). Of course, transformer and inverse-transformer (H_2O) groups also propagate bonds in the same way as non-transformer (H_2O) groups, but they have the additional transformer role. The Lewis acidity-basicity interaction between the structural unit and the interstitial complex controls the amount of transformer (or inverse transformer) (H_2O) in the interstitial complex, but does not affect the amount of non-transformer (H_2O). So what does control the amount of non-transformer (H_2O)? Schindler and Hawthorne (2007) examine this question for sheet-structure uranyl-oxysalts and show that the key controls involve (1) the ratio between the number of anions in the structural unit and the number of bonds emanating from interstitial cations and (OH) groups of the structural unit, and (2) the number of (OH) groups of the structural unit. The ratio in (1) is designated the *bond-valence distribution factor*, *D*, because it controls the number of (H_2O) groups (in the interstitial complex) which distribute bond-valence to the anions of the structural unit. It is defined as follows:

$$D = (N^{A}{}_{SU})/[(N^{-}{}_{IC}) + (N^{(OH)}{}_{SU})] \tag{4}$$

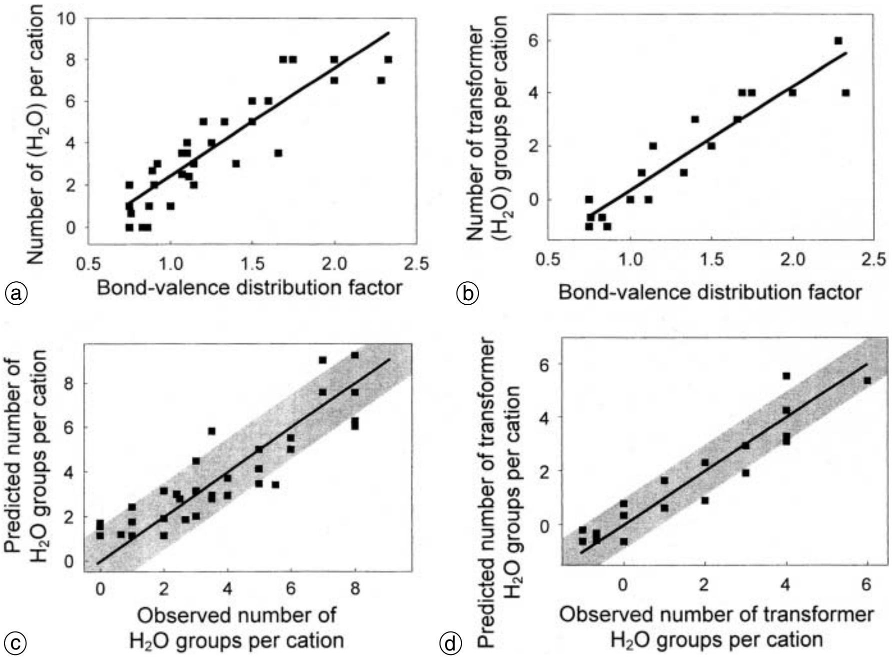

Fig. 19. Variation in the (**a**) total number of (H_2O) groups per cation, and (**b**) number of transformer (H_2O) groups per cation as a function of the bond-valence distribution factor for uranyl-oxysalt minerals with sheet structural-units; comparison of predicted and observed (**c**) total number of (H_2O) groups per cation, and (**d**) number of transformer (H_2O) groups per cation in uranyl-oxysalt minerals with sheet structural-units. The shaded bands in (c) and (d) denote ±1 (H_2O) group from the 1 : 1 relation.

where $N^{A}{}_{SU}$ is the number of anions (A) in the structural unit (SU), $N^{-}{}_{IC}$ is the number of bonds emanating from the interstitial complex (IC), and $N^{(OH)}{}_{SU}$ is the number of (OH) groups in the structural unit.

The number of (H_2O) groups and the *D* factor for sheet structural-units

For the correlation between number of transformer or total number of H_2O groups and *D*, Schindler and Hawthorne (2007) did not consider any structural data from highly hydrated minerals of the autunite, carnotite and zippeite groups (*e.g.*, autunite, torbernite, zeunerite, marecottite). In the interlayer of these minerals, there are additional layers of (H_2O) groups that do not bond to any interstitial cation (Locock, Burns, 2003a, b; Locock *et al.*, 2004a, 2005; Brugger *et al.*, 2003). Many of these minerals are not stable in air and dehydrate to phases with a lower degree of hydration. For example, Locock and Burns (2003b) and Locock *et al.* (2004a) reported the occurrence of two or three possible hydration states for phases with the structural unit of the autunite group $[(UO_2)(TO_4)]^-$ ($T = $ P, As) and octahedrally coordinated divalent cations ($^{[6]}M^{2+} = Cu^{2+}$, Mg, Mn^{2+}, and Fe^{2+}) in the interstitial complex: octahydrates, decahydrates and dodecahydrates. Schindler and Hawthorne (2007) considered only structural data for the octahydrates, which Gaines *et al.* (1997) and Finch and Murakami (1999) listed as members of the meta-autunite group.

The total number of (H_2O) groups per cation versus *D* and (OH) content

Figure 19 shows that the variation in the total number of (H_2O) groups per cation (Fig. 19a) and the variation in the number of transformer (H_2O) groups per cation (Fig. 19b) for minerals containing sheet structural-units are linear functions of *D*, the bond-valence distribution factor, and the linear trends are described by the following regression equations:

$$\text{Total number of } (H_2O) \text{ groups per cation} = 5.1D - 2.17 \quad R^2 = 0.83, \ \sigma = 1.1 \tag{5}$$

$$\text{Number of transformer } (H_2O) \text{ groups per cation} = 3.9D - 3.60 \quad R^2 = 0.89, \ \sigma = 0.7 \tag{6}$$

suggesting that the arguments behind the development of the parameter *D* correctly reflect the role of (H_2O) groups in sheet-structure uranyl-oxysalt minerals.

The correlations between [1] the total number of (H_2O) groups per interstitial cation and *D* (Fig. 19a), and [2] the number of transformer (H_2O) groups per interstitial cation and *D* (Fig. 19b), allow us now to predict more accurately the number of (H_2O) groups for a specific cation (Figs. 19c, d). In the following sections, we compare predicted and observed chemical compositions for minerals of the uranophane, phosphuranylite, carnotite and zippeite groups; Table 8 shows similar comparison for some additional groups, and Table 9 shows predictions of transformer, non-transformer and inverse-transformer (H_2O) groups.

$[UO_2)SiO_3(OH)]^-$

The minerals of the uranophane group are based on $[(UO_2)SiO_3(OH)]^-$ sheets that contain $(U^{6+}\varphi_7)$ pentagonal bipyramids and acid $[(SiO_3(OH)]$ groups [except kasolite, which contains $(SiO_4$ groups]. The pentagonal bipyramids form edge-sharing chains that are connected by $(Si\varphi_4)$ tetrahedra. The $(OH)^-$ groups are located at the free apices of the $(Si\varphi_4)$ tetrahedra and form hydrogen bonds to interstitial (H_2O) groups.

The charge deficiency per anion of the structural unit $[(UO_2)SiO_3(OH)]^-$ is $(1 + h)/6 = 1.2/6 = 0.20$ *v.u.* (using $h = 0.20$ *v.u.*). Using Fig. 8b, we may derive the corresponding minimum and maximum values of $\langle NB \rangle_{in}$: 0.80 and 1.33, respectively. We may now use these values to

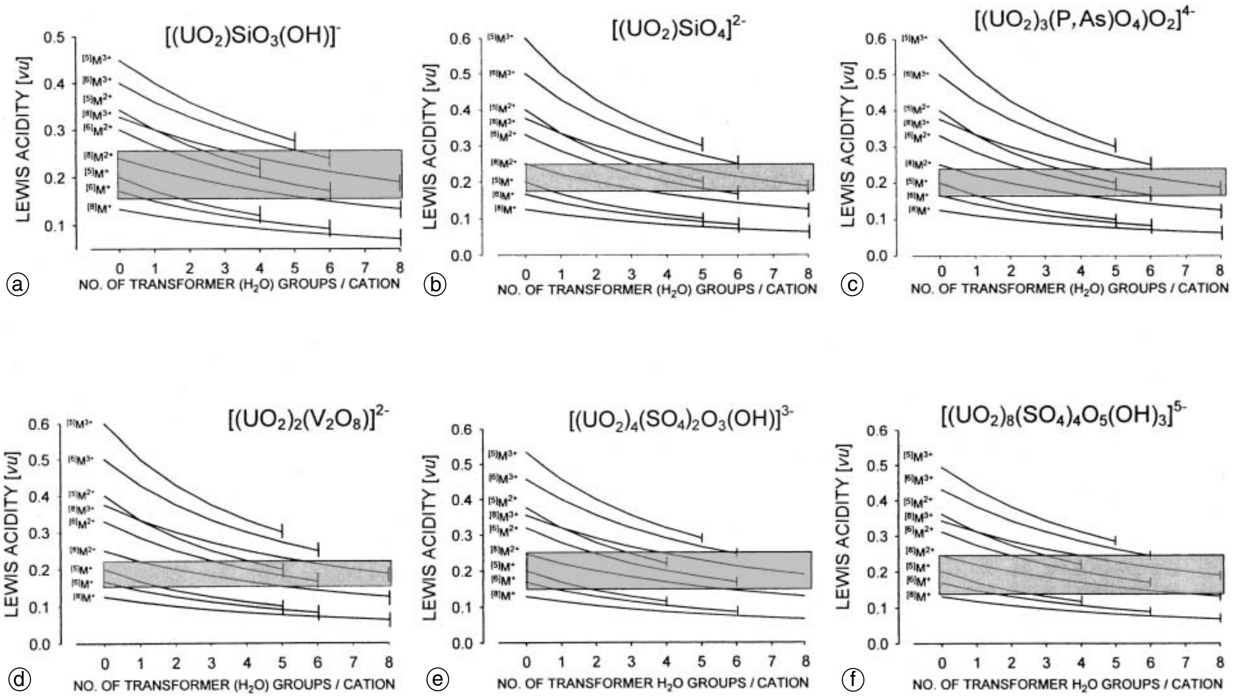

Fig. 20. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in basicity of the structural units of selected uranyl-oxysalt minerals are shown by the shaded fields: (**a**) $[(UO_2)SiO_3(OH)]^{-}$; (**b**) $[(UO_2)SiO_4]^{2-}$; (**c**) $[(UO_2)_3(P(As)O_4)_2O_2]^{4-}$; (**d**) $[(UO_2)_2(V_2O_8)]^{2-}$, (**e**) $[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$; (**f**) $[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$.

calculate the range in Lewis basicity. The minimum and maximum numbers of bonds from the interstitial complex to the structural unit are 4.8 and 8.0. The corresponding minimum and maximum values of the Lewis basicity of the $[(UO_2)SiO_3(OH)]^{-}$ structural unit are $1.2/4.5 = 0.15$ and $1.2/4.8 = 0.25$ *v.u.*, respectively; this range of Lewis basicity is marked on Fig. 20a.

For monovalent interstitial cations, [6] and [7]-coordinations are predicted to be possible (Fig. 20a). Using equation [5], the predicted numbers of transformer (H_2O) groups are −0.3, −0.7 and −1, respectively, which means that [7] and [8]-coordinated monovalent cations must bond to more inverse-transformer (H_2O) groups than transformer (H_2O) groups. Considering also the predicted total number of (H_2O) groups, possible compositions of minerals are $^{[6]}M^{+}[(UO_2)SiO_3(OH)](H_2O)_2$, $^{[7]}M^{+}(H_2{}^{[5]}O)_1[(UO_2)SiO_3 \cdot (OH)](H_2O)_1$ and $^{[8]}M^{+}(H_2{}^{[5]}O)_1[(UO_2)SiO_3(OH)]$. These predictions are in good agreement with the observed chemical compositions of boltwoodite, $^{[7]}K(H_2{}^{[5]}O)[(UO_2)(SiO_3OH)]$, Na-substituted boltwoodite, $^{[6]}Na(H_2{}^{[5]}O)[(UO_2)(SiO_3OH)]$, and synthetic Cs-substituted boltwoodite, $^{[7.5]}Cs[(UO_2)(SiO_3OH)]$ (Tables 7, 8).

For divalent cations, [6]-, [7]- and [8]-coordinations are possible, and the predicted compositions of the interstitial

Table 8. Observed and predicted chemical composition of selected uranyl-oxysalt minerals with sheet-structural units.

Mineral	Observed chemical composition	Predicted chemical composition	Ref.
Meta-autunite group			
Meta-ankoleite (LT)	$^{[8]}K[(UO_2)(PO_4)](D_2O)_3$	$^{[8]}M[(UO_2)(PO_4)](H_2O)_{2.0}$	[1]
Metazeunerite	$^{[6]}Cu[(UO_2)(AsO_4)]_2(H_2O)_8$	$^{[6]}Cu[(UO_2)(AsO_4)]_2(H_2O)_8$	[2]
Metatorbernite	$^{[6]}Cu[(UO_2)(PO_4)]_2(H_2O)_8$	$^{[6]}Cu[(UO_2)(PO_4)]_2(H_2O)_8$	[2]
Threadgoldite^{a}	$^{[6]}Al(OH)[(UO_2)(PO_4)]_2(H_2O)_8$	$Al(^{[3]}OH)[(UO_2)(PO_4)]_2(H_2O)_9$	[3]
Metakahlerite^{a}	$^{[6]}Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	$^{[6]}Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	[4]
Metakirchheimerite^{a}	$^{[6]}Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	$^{[6]}Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8$	[4]
Meta-uranocircite (II,I)	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_{6-7}$	$^{[9]}Ba[(UO_2)(PO_4)_2](H_2O)_5$	[5]
Uranophane group			
Uranophane	$^{[7]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	$^{[7]}Ca[(UO_2)SiO_3(OH)]_2(H_2O)_4$	[6]
Uranophane-beta^{a}	$^{[8]}Ca\ [(UO_2)(SiO_3OH)]_2(H_2O)_5$	$^{[8]}Ca[(UO_2)SiO_3(OH)]_2(H_2O)_{3.5}$	[7]
Boltwoodite	$^{[7]}K[(UO_2)(SiO_3OH)](H_2O)_1$	$^{[7]}K[(UO_2)SiO_3(OH)](H_2O)_2$	[8]
Sodium boltwoodite	$^{[6]}Na[(UO_2)(SiO_3OH)](H_2O)_1$	$^{[6]}Na[(UO_2)SiO_3(OH)](H_2O)_{2.5}$	[8]
Sklodowskite^{a}	$^{[6]}Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$^{[6]}Mg[(UO_2)SiO_3(OH)]_2(H_2O)_5$	[9]
Cupro-sklodowskite	$^{[6]}Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$^{[6]}Cu[(UO_2)SiO_3(OH)]_2(H_2O)_5$	[10]
Kasolite	$^{[2+6]}Pb[(UO_2)(SiO_4)](H_2O)_1$	$^{[2+6]}Pb^{2+}[(UO_2)(SiO_4)](H_2O)_2$	[11]

Table 8. Continued.

Mineral	Observed chemical composition	Predicted chemical composition	Ref.
Phosphuranylite group			
Phuralumite^a	$^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$	$^{[6]}Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}$	[12]
Dewindtite^a	$^{[8]}Pb_2{}^{[11]}Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_{12}$	$^{[8]}Pb_2{}^{[11]}Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_9$	[13]
Upalite	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_7$	$^{[6]}Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_9$	[14]
Francoisite(-Nd) ^{a}	$^{[9]}Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6$	$^{[9]}Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6$	[15]
Dumonite	$^{[7,8]}Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_5$	$^{[8]}Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_6$	[16]
Hügelite^a	$^{[7,8]}Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_5$	$^{[7]}Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_7$	[17]
Phurcalite	$^{[8]}Ca^{[7]}Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_7$	$^{[8]}Ca^{[7]}Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_6$	[18]
Bergenite^a	$^{[8]}Ca_2{}^{[9.5]}Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{16}$	$^{[8]}Ca_2{}^{[9.5]}Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{13}$	[19]
Carnotite group			
Francevillite^a	$^{[9]}Ba\ [(UO_2)_2(V_2O_8)](H_2O)_5$	$^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$	[20]
Curienite^a	$^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	$^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	[21]
Sengierite	$^{[6]}Cu_2(OH)_2[(UO_2)_2(V_2O_8)](H_2O)_6$	$^{[6]}Cu_2(^{[4]}OH)_2[(UO_2)_2(V_2O_8)](H_2O)_9$	[22]
Zippeite group			
Zippeite^a	$^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_3$	$^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5$	[23]
Sodium-zippeite	$^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$	$^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{15}$	[23]
Marecottite^a	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{23}$	[24]
Magnesium-zippeite	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_6$	[23]
Zinc-zippeite	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_6$	[23]
Cobalt-zippeite	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_6$	[23]
Uranyl-hydroxy-hydrates			
Becquerelite	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_6$	[25]
Compreignacite^a	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_6$	[26]
Fourmarierite^a	$^{[8]}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	$^{[8]}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	[27]
Protastite^a	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_2$	[28]
Masuyite^a	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_2$	[29]
Curite	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_2$	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_5$	[30]
Sayrite^a	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	[31]
Agrinierite	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_3$	[32]
Miscellaneous			
Guilleminite	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_3$	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_{4.5}$	[33]
Marthozite	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_9$	[34]
Roubaultite	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_5$	[35]
Johannite	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_8$	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_6$	[36]

a: H positions not determined.

[1] Cole *et al.*, 1993; [2] Locock, Burns, 2003b; [3] Khosrawan-Sazedj, 1982; [4] Locock *et al.*, 2004b; [5] Locock *et al.*, 2005; [6] Ginderow, 1988; [7] Viswanathan, Harneit, 1986; [8] Burns, 1998a; [9] Ryan, Rosenzweig, 1977; [10] Rosenzweig, Ryan, 1975; [11] Rosenzweig, Ryan, 1977; [12] Piret *et al.*, 1979; [13] Piret *et al.*, 1990; [14] Piret, Declercq, 1983; [15] Piret *et al.*, 1988; [16] Piret, Piret-Meunier, 1988; [17] Locock, Burns, 2003d; [18] Atencio *et al.*, 1991; [19] Locock, Burns, 2003c; [20] Mereiter, 1986; [21] Borene, Cesbron, 1971; [22] Piret *et al.*, 1980; [23] Burns *et al.*, 2003; [24] Brugger *et al.*, 2003; [25] Burns, Li, 2002; [26] Burns, 1998b; [27] Piret, 1985; Li, Burns, 2000; [28] Pagoaga *et al.*, 1987; [29] Burns, Hanchar, 1999; [30] Taylor *et al.*, 1981; [31] Piret *et al.*, 1983; [32] Cahill, Burns, 2000; [33] Cooper, Hawthorne, 1995; [34] Cooper, Hawthorne, 2001; [35] Ginderow, Cesbron, 1985; [36] Mereiter, 1982.

complexes are $^{[6]}M^{2+}(H_2O)_2[(UO_2)SiO_3(OH)]_2(H_2O)_3$, $^{[7]}M^{2+}(H_2O)_{1.5}[(UO_2)SiO_3(OH)]_2(H_2O)_{2.5}$, and $^{[8]}M^{2+} \cdot (H_2O)_1[(UO_2)SiO_3(OH)]_2(H_2O)_{2.5}$. Minerals with divalent cations are cupro-sklodowskite, $^{[6]}Cu^{2+}(H_2O)_2[(UO_2) \cdot (SiO_3OH)]_2(H_2O)_4$, sklodowskite, $^{[6]}Mg[(UO_2)(SiO_3OH)]_2 \cdot (H_2O)_6$, uranophane $^{[7]}Ca(H_2O)_1[(UO_2)(SiO_3OH)]_2(H_2O)_4$, and uranophane-beta, $^{[8]}Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$; the number of transformer (H_2O) groups was not determined for sklodowskite and uranophane-beta. Except for uranophane-beta, the differences between the predicted and observed values of the total number of (H_2O) groups do not exceed one (H_2O) group per cation (Table 8).

The structural unit $[(UO_2)(SiO_4)]^{2-}$ has a charge deficiency per anion of the structural unit of $2/6 = 0.33$ *v.u.* The corresponding minimum and maximum values of $\langle NB \rangle_{in}$ are 1.35 and 1.8 (Fig. 8b), and the minimum and maximum numbers of bonds to the structural unit are 8.4 and 11.1, respectively. The resulting range in Lewis basicity is 0.18–0.25 *v.u.*, and this is shown for $[(UO_2)(SiO_4)]$ on Fig. 20b. The predicted composition of a mineral containing a [8]-coordinated divalent cation is $^{[8]}Pb(H_2{}^{[5]}O)_1 \cdot [(UO_2)(SiO_4)](H_2O)_1$, in good agreement with the observed composition of kasolite, $^{[2+6]}Pb(H_2{}^{[5]}O)_0[(UO_2) \cdot (SiO_4)](H_2O)_1$.

We are now able to answer the question why uranophane-beta, $^{[8]}\mathrm{Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5}$, has more $(\mathrm{H_2O})$ groups than kasolite, $^{[8]}\mathrm{Pb[(UO_2)(SiO_4)](H_2O)}$. The values of D in uranophane-beta is 1.2, whereas it is only 0.75 in kasolite. In order to transfer the bond valence from the interstitial cation to the anions, uranophane-beta must contain more non-transformer $(\mathrm{H_2O})$ groups than kasolite.

$[(\mathrm{UO_2})_3(\mathrm{PO_4})_2(\mathrm{O,OH})_2]^{n-}$

The structural unit of minerals of the phosphuranylite group is the sheet $[(\mathrm{UO_2})_3(\mathrm{PO_4})_2(\mathrm{O,OH})_2]^{n-}$ that contains $(\mathrm{P}\varphi_4)$ tetrahedra, and $(\mathrm{U}\varphi_7)$ pentagonal bipyramids and $(\mathrm{U}\varphi_8)$ hexagonal bipyramids in the ratio 2 : 1. There are three different compositions of sheet structural-units with slightly different ranges in Lewis basicity:

$[(\mathrm{UO_2})_3(\mathrm{PO_4})_2(\mathrm{OH})_2]^{2-}$	(0.14–0.21 *v.u.*)
$[(\mathrm{UO_2})_3(\mathrm{PO_4})_2(\mathrm{O})(\mathrm{OH})]^{3-}$	(0.15–0.25 *v.u.*)
$[(\mathrm{UO_2})_3(T\mathrm{O_4})_2\mathrm{O_2}]^{4-}$, $T = \mathrm{P}, \mathrm{A}^{5+}{}_3$	(0.17–0.24 *v.u.*)

The structural unit $[(\mathrm{UO_2})_3(\mathrm{PO_4})_2(\mathrm{OH})_2]^{2-}$ occurs in phuralumite, the structural unit $[(\mathrm{UO_2})_3(\mathrm{PO_4})_2\mathrm{O(OH)}]^{2-}$ occurs in dewindtite, upalite and francoisite-(Nd), and the structural unit $[(\mathrm{UO_2})_3(T\mathrm{O_4})_2\mathrm{O_2}]^{4-}$ occurs in dumontite, phurcalite, bergenite and hügelite. The range in Lewis basicity of the $[(\mathrm{UO_2})_3(\mathrm{P(As)O_4})_2\mathrm{O_2}]^{4-}$ structural unit is shown in Fig. 20c, which indicates that the cations $^{[4]-[6]}M^{+}$, $^{[5]-[10]}M^{2+}$, $^{[7]-[10]}M^{3+}$ and $\{^{[6]}M^{3+}(\mathrm{OH})\}^{2+}$ can be compatible with the structural unit if they bond to a specific number of transformer $(\mathrm{H_2O})$ groups. Monovalent cations with coordination numbers higher than [6] can also occur if they bond to a specific number of inverse-transformer $(\mathrm{H_2O})$ groups.

Tables 8 and 9 show that differences between total numbers of $(\mathrm{H_2O})$ groups per cation observed and predicted from equation [5] do not exceed one $(\mathrm{H_2O})$ group per cation. In the case of phuralumite, $^{[6]}\mathrm{Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}}$, the predicted total number of $(\mathrm{H_2O})$ groups is identical with the observed number of $(\mathrm{H_2O})$ groups. In the structure of dumontite and hügelite, the coordination number of the Pb^{2+} cations can be assigned as either [7] or [8], depending on the definition of the coordination sphere of the cation. However,

Table 9. Observed and predicted number of transformer (TR), inverse-transformer (INV) and non-transformer (NTR) $(\mathrm{H_2O})$-groups in uranyl-oxysalt minerals with sheet-structural units.

Mineral	Chemical composition	Observed			Predicted			Ref.
		TR	INV	NTR	TR	INV	NTR	
Meta-autunite group								
Meta-ankoleite (LT)	$^{[8]}\mathrm{K[(UO_2)(PO_4)](D_2O)_3}$	0	1	2	0	1	1	[1]
Metazeunerite	$^{[6]}\mathrm{Cu[(UO_2)(AsO_4)]_2(H_2O)_8}$	4	0	4	4	0	4	[2]
Metatorbernite	$^{[6]}\mathrm{Cu[(UO_2)(PO_4)]_2(H_2O)_8}$	4	0	4	4	0	4	[2]
Threadgoldite[a]	$^{[6]}\mathrm{Al(OH)[(UO_2)(PO_4)]_2(H_2O)_8}$	n.d.	n.d.	n.d.	5	0	4	[3]
Metakahlerite[a]	$^{[6]}\mathrm{Fe^{2+}[(UO_2)AsO_4]_2(H_2O)_8}$	n.d.	n.d.	n.d.	4	0	4	[4]
Metakirchheimerite[a]	$^{[6]}\mathrm{Co^{2+}[(UO_2)AsO_4]_2(H_2O)_8}$	n.d.	n.d.	n.d.	4	0	4	[4]
Meta-uranocircite (II,I)	$^{[9]}\mathrm{Ba[(UO_2)(PO_4)_2](H_2O)_5}$	n.d.	n.d.	n.d.	2	0	3	[5]
Uranophane group								
Uranophane	$^{[7]}\mathrm{Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5}$	1	0	4	1.5	0	2.5	[6]
Uranophane-beta[a]	$^{[8]}\mathrm{Ca\ [(UO_2)(SiO_3OH)]_2(H_2O)_5}$	n.d.	n.d.	n.d.	1	0	2.5	[7]
Boltwoodite	$^{[7]}\mathrm{K[(UO_2)(SiO_3OH)](H_2O)_1}$	0	1	0	0	1	1	[8]
Sodium boltwoodite	$^{[6]}\mathrm{Na[(UO_2)(SiO_3OH)](H_2O)_1}$	0	1	0	0	0.5	2	[8]
Sklodowskite[a]	$^{[6]}\mathrm{Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6}$	n.d.	n.d.	n.d.	2	0	3	[9]
Cupro-sklodowskite	$^{[6]}\mathrm{Cu[(UO_2)(SiO_3OH)]_2(H_2O)_6}$	2	0	4	2	0	3	[10]
Kasolite	$^{[2+6]}\mathrm{Pb[(UO_2)(SiO_4)](H_2O)_1}$	0	0	1	0	1	1	[11]
Phosphuranylite group								
Phuralumite[a]	$^{[6]}\mathrm{Al_2(OH)_4[(UO_2)_3(PO_4)_2(OH)_2](H_2O)_{10}}$	n.d.	n.d.	n.d.	6	0	4	[12]
Dewindtite[a]	$^{[8]}\mathrm{Pb_2}{}^{[11]}\mathrm{Pb[(UO_2)_3(PO_4)_2(OH)O]_2(H_2O)_{12}}$	n.d.	n.d.	n.d.	2	0	7	[13]
Upalite	$^{[6]}\mathrm{Al[(UO_2)_3(PO_4)_2(OH)O](H_2O)_7}$	6	0	1	5	0	4	[14]
Francoisite(-Nd) [a]	$^{[9]}\mathrm{Nd[(UO_2)_3(PO_4)_2(OH)O](H_2O)_6}$	n.d.	n.d.	n.d.	3	0	3	[15]
Dumonite	$^{[7/8]}\mathrm{Pb_2[(UO_2)_3(PO_4)_2O_2](H_2O)_5}$	2	0	3	2	0	4	[16]
Hügelite[a]	$^{[7/8]}\mathrm{Pb_2[(UO_2)_3(AsO_4)_2O_2](H_2O)_5}$	n.d.	n.d.	n.d.	2	0	5	[17]
Phurcalite	$^{[8]}\mathrm{Ca}{}^{[7]}\mathrm{Ca[(UO_2)_3(PO_4)_2O_2](H_2O)_7}$	2	0	5	1	0	5	[18]
Bergenite[a]	$^{[8]}\mathrm{Ca_2}{}^{[9.5]}\mathrm{Ba_4[(UO_2)_3(PO_4)_2O_2]_3(H_2O)_{16}}$	n.d.	n.d.	n.d.	0	1	12	[19]
Carnotite group								
Francevillite[a]	$^{[9]}\mathrm{Ba[(UO_2)_2(V_2O_8)](H_2O)_5}$	n.d.	n.d.	n.d.	2	0	3	[20]
Curienite[a]	$^{[8]}\mathrm{Pb[(UO_2)_2(V_2O_8)](H_2O)_5}$	n.d.	n.d.	n.d.	2	0	3	[21]
Sengierite	$^{[6]}\mathrm{Cu_2(OH)_2[(UO_2)_2(V_2O_8)](H_2O)_6}$	4	0	2	4	0	5	[22]

Table 9. Continued.

Mineral	Chemical composition	Observed			Predicted			Ref.
		TR	INV	NTR	TR	INV	NTR	
Zippeite group								
Zippeite^a	$^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_3$	n.d.	n.d.	n.d.	0	0	5	[23]
Sodium-zippeite	$^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$	0	0	12	3	0	12	[23]
Marecottite^a	$^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$	n.d.	n.d.	n.d.	12	0	11	[24]
Magnesium-zippeite	$^{[6]}Mg[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	[23]
Zinc-zippeite	$^{[6]}Zn[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	[23]
Cobalt-zippeite	$^{[6]}Co[(UO_2)_2(SO_4)O_2](H_2O)_{3.5}$	3	0	0.5	3	0	3	[23]
Becquerelite	$^{[7]}Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	4	0	4	3	0	3	[25]
Compreignacite^a	$^{[7]}K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	n.d.	n.d.	n.d.	1	0	5	[26]
Fourmarierite^a	$^{<[8]>}Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	n.d.	n.d.	n.d.	1	0	3	[27]
Protastite^a	$^{[10]}Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	n.d.	n.d.	n.d.	0	0	2	[28]
Masuyite^a	$^{[10]}Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	n.d.	n.d.	n.d.	0	0	2	[29]
Curite	$^{[10]}Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_2$	0	2	0	0	1	4	[30]
Sayrite^a	$^{[9]}Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	n.d.	n.d.	n.d	0	0	4	[31]
Agrinierite	$^{[7]}K^{[9]}K(^{[9]}Ca,Sr)[(UO_2)_3O_3(OH)_2]_2(H_2O)_5$	1	3	1	0	2	1	[32]
Miscellaneous								
Guilleminite	$^{[10]}Ba[(UO_2)_3O_2(SeO_3)_2](H_2O)_3$	3	0	0	1.5	0	3	[33]
Marthozite	$^{[6]}Cu[(UO_2)_3O_2(SeO_3)_2](H_2O)_8$	4	0	4	5	0	4	[34]
Roubaultite	$^{[6]}Cu_2[(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$	4	0	0	2	0	4	[35]
Johannite	$^{[6]}Cu[UO_2)_2(OH)_2(SO_4)_2](H_2O)_8$	4	0	4	3	0	3	[36]

a: H positions not determined.

[1] Cole *et al.*, 1993; [2] Locock, Burns, 2003b; [3] Khosrawan-Sazedj, 1982; [4] Locock *et al.*, 2004b; [5] Locock *et al.*, 2005; [6] Ginderow, 1988; [7] Viswanathan, Harneit, 1986; [8] Burns, 1998a; [9] Ryan, Rosenzweig, 1977; [10] Rosenzweig, Ryan, 1975; [11] Rosenzweig, Ryan, 1977; [12] Piret *et al.*, 1979; [13] Piret *et al.*, 1990; [14] Piret, Declercq, 1983; [15] Piret *et al.*, 1988; [16] Piret, Piret-Meunier, 1988; [17] Locock, Burns, 2003d; [18] Atencio *et al.*, 1991; [19] Locock, Burns, 2003c; [20] Mereiter, 1986; [21] Borene, Cesbron, 1971; [22] Piret *et al.*, 1980; [23] Burns *et al.*, 2003; [24] Brugger *et al.*, 2003; [25] Burns, Li, 2002; [26] Burns, 1998b; [27] Piret, 1985; Li, Burns, 2000; [28] Pagoaga *et al.*, 1987; [29] Burns, Hanchar, 1999; [30] Taylor *et al.*, 1981; [31] Piret *et al.*, 1983; [32] Cahill, Burns, 2000; [33] Cooper, Hawthorne, 1995; [34] Cooper, Hawthorne, 2001; [35] Ginderow, Cesbron, 1985; [36] Mereiter, 1982.

the observed total number of (H_2O) groups per cation is 2.5, and agrees well with the predicted numbers of either 3.50 and 3.0 for a cation in [7]- or [8]-coordination, respectively (Table 8). For upalite and phurcalite, the predicted numbers of transformer (H_2O) groups per cation are smaller than the observed values, but the differences do not exceed two (H_2O) groups per cation (Table 9).

$[(UO_2)_2(V_2O_8)]^{2-}$

The minerals of the carnotite group contain the structural unit $[(UO_2)_2(V_2O_8)]^{2-}$, an anion sheet with (UO_7) pentagonal bipyramids and $(V^{5+}O_5)$ square pyramids. The $(V^{5+}O_5)$ square-pyramids share common edges and form a $[V_2O_8]$ dimer that shares corners with dimers of edge-sharing (UO_7) pentagonal bipyramids. The $[(UO_2)_2(V_2O_8)]^{2-}$ structural unit has a charge deficiency per anion of the structural unit of $2/12 = 0.17$ *v.u.*, which results in a range in Lewis basicity of 0.14–0.22 *v.u.*.

The range in Lewis basicity for the structural unit $[(UO_2)_2(V_2O_8)]^{2-}$ requires that monovalent cations with coordination numbers higher than [7] must bond to inverse-transformer (H_2O) groups, whereas lower-coordination interstitial cations will occur with no transformer (H_2O) groups (Fig. 20d). This may be the case in carnotite, $K_2[(UO_2)_2(V_2O_8)](H_2O)_3$, and margaritasite, $(Cs,K)_2[(UO_2)_2(V_2O_8)](H_2O)_n$ $(n = 1–3)$, in which the large cations K and Cs normally occur in coordination numbers higher than [7]. The predicted composition for monovalent cations with coordination numbers [8], [10] and [12] are $^{[8]}M(H_2{}^{[5]}O)_1[(UO_2)_2(V_2O_8)](H_2O)_1$, $^{[10]}M(H_2{}^{[5]}O)_1[(UO_2)_2(V_2O_8)](H_2O)_0$ and $^{[12]}M(H_2{}^{[5]}O)_2 \cdot [(UO_2)_2(V_2O_8)](H_2O)_0$, respectively.

The compositions of only three minerals of the carnotite group have been determined on the basis of structural data: francevillite, $^{[9]}Ba[(UO_2)_2(V_2O_8)](H_2O)_5$, curienite, $^{[8]}Pb[(UO_2)_2(V_2O_8)](H_2O)_5$, and sengierite, $^{[6]}Cu_2(OH)_2 \cdot (H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_2$. For francevillite and curienite, the predicted compositions of the interstitial complex, $^{[9]}Ba(H_2O)_2[(UO_2)_2(V_2O_8)](H_2O)_3$ and $^{[8]}Pb(H_2O)_2 \cdot [(UO_2)_2(V_2O_8)](H_2O)_3$, are in good agreement with the observed compositions (Table 8). For a [6]-coordinated cation such as $^{[6]}Cu^{2+}$ in sengierite, the possible interstitial complex can be calculated without or with $(^{[4]}OH)$ groups. In the first case, the predicted composition is $^{[6]}Cu(H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_3$. In the second case, four transformer (H_2O) groups are required by the interstitial complex because each $(^{[4]}OH)^-$ group reduces by two the number of bonds from $^{[6]}Cu^{2+}$ to the structural unit. Hence, the predicted chemical composition is $^{[6]}Cu_2(^{[4]}OH)_2(H_2O)_4[(UO_2)_2(V_2O_8)](H_2O)_5$, in reasonable accord with the observed composition.

The zippeite group

The structures of the zippeite-group minerals contain topologically identical sheets in which uranyl pentagonal bipyramids link together by sharing edges and vertices to form chains that are cross-linked by sulfate tetrahedra. There are three different sheet structural-units (Burns *et al.*, 2003) with similar ranges in Lewis basicity:

$[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$ (0.15–0.25 *v.u.*)

$[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$ (0.15–0.24 *v.u.*)

$[(UO_2)_2(SO_4)O_2]^{2-}$ (0.16–0.25 *v.u.*)

The structural unit $[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$ occurs in zippeite, $^{[7.33]}K_3[(UO_2)_4(SO_4)_2O_3(OH)]\ (H_2O)_3$, and marecottite, $^{[6]}Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$. The calculated range in Lewis basicity indicates that [7]-coordinated monovalent cations are possible if they do not bond to any transformer (H_2O) groups (Fig. 20e), whereas three [6]-coordinated divalent cations must bond to at least eight transformer (H_2O) groups. The predicted chemical compositions are as follows: zippeite $^{[7.33]}K_3(H_2{}^{[5]}O) \cdot [(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5$; marecottite, $^{[6]}Mg_3(H_2O)_{12} \cdot [(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{11}$.

The structural unit $[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$ occurs in sodium-zippeite, $^{[6.6]}Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$, and its Lewis basicity indicates that cations in [6]- and [7]-coordination can occur in the interstitial complex without bonding to any transformer (H_2O) groups (Fig. 20f). The predicted chemical composition on the basis of the average coordination number of Na is $^{[6.6]}Na_5(H_2O)_3 \cdot [(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$, in reasonable agreement with the observed composition.

The structural unit $[(UO_2)_2(SO_4)O_2]^{2-}$ occurs in synthetic magnesium-, zinc- and cobalt-zippeite, $^{[6]}M(H_2O)_3 \cdot [(UO_2)_2(SO_4)O_2](H_2O)_{0.5}$ with M = Mg, Zn and Co^{2+}. The predicted chemical composition for a [6]-coordinated divalent cation is $^{[6]}M(H_2O)_3[(UO_2)_2(SO_4)O_2](H_2O)_3$, which shows a good agreement between the predicted and observed numbers of transformer (H_2O) groups (Tables 8, 9).

Summary

Here, we have presented a summary of the current status of some of our ideas on what controls the chemical composition and structure of oxysalt minerals that have crystallized from aqueous solutions. We emphasize that this is a work in progress. Apart from what we have presented here, the only known constraints on chemical composition of complex inorganic crystals are (1) the electroneutrality principle, (2) simple aspects of the valence-matching principle (Dent Glasser, 1979; Brown, 1981; see discussions by Hawthorne, 2007), and (3) simple applications of the handshaking dilemma (Wilson, 1979; Hawthorne, 2007). Our approach incorporates these three factors and is attempting to develop a quantitative understanding of the controls on the composition and structure of oxysalt minerals. Below, we give a summary of the key aspects of this approach.

(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 (H_2O) 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 *principle of correspondence of Lewis acidity-basicity*: for a structural arrangement to be stable, the Lewis acidity and Lewis 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 $\{^{[m]}M^{+}_{a}{}^{[n]}M^{2+}_{b}{}^{[l]}M^{3+}_{c}(H_2O)_d(H_2O)_e{}^{[q]}(OH)_f \cdot (H_2O)_g\}^{(a+2b+3c-f)+}$, 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* (H_2O) groups, e is the number of (H_2O) 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 (H_2O) groups not bonded to any cation.

(6) A *transformer* (H_2O) 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 (H_2O) 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 (H_2O) groups in the complex.

(8) The *effective 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 *charge deficiency per anion, CDA,* of a structural unit is defined as the effective charge divided by the number of O atoms in the structural unit.

(10) The charge deficiency per anion of a structural unit correlates with the mean number of bonds from the interstitial complex to the O atoms of the structural unit. This correlation defines a band that allows prediction of the range in the average number of bonds to O atoms of the structural unit. Variation in the number of these bonds is the mechanism by which the structural unit responds to small changes in the pH of its environment while remaining stable.

(11) The range in Lewis basicity of the structural unit may be calculated from the maximum and minimum values of the mean number of bonds from the interstitial complex to the O atoms of the structural unit, and is its effective charge divided by the maximum and minimum numbers of bonds required by the structural unit from the interstitial complex.

(12) Where the Lewis acidity of a generalized interstitial complex overlaps the range of Lewis basicity of a specific structural unit, the principle of correspondence of Lewis acidity-basicity is satisfied and a stable structural arrangement is possible.

(13) Application of this approach to the hydroxyl-hydrated borate, uranyl-oxide, sulfate and uranyl-oxysalt minerals shows that the principle of correspondence of Lewis acidity-basicity exerts significant restrictions on the chemical and structural details of the interstitial complexes.

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

(15) The overlap of Lewis basicity and acidity required for structural stability by the principle of correspondence of Lewis acidity-basicity leads to an explanation for and prediction of the number of transformer (H_2O) groups in the interstitial complexes of these minerals. These predictions can be precise or imprecise, but in nearly all cases, they are accurate.

Appendix

Bond valence: a measure of the strength of a bond which varies with the corresponding bond length. The bond valence, s, may be expressed as a function of bond length, R, in the following way: $s = \exp\{(R_0 - R)/b\}$, where R_0 and b are constant characteristic of cation-anion pairs (Brown, 1981, 2002).

Characteristic bond-valence: the formal valence of a cation or an anion divided by its mean coordination-number. The characteristic bond-valence of an oxyanion is its formal charge divided by the mean number of bonds to the oxyanion. For example, an O-atom of an (SO_4) group is, on average, [4]-coordinated, which means it receives three bonds in addition to that from the central S atom; thus, there are, on average, twelve bonds to the oxyanion, and its characteristic bond-valence is $2/12 = 0.17$ *v.u.*

Lewis acid strength (Lewis acidity): the characteristic bond-valence of a cation or complex cation; the Lewis acidity of a cation correlates with its electronegativity.

Lewis base strength (Lewis basicity): the characteristic bond-valence of an anion or an oxyanion.

Valence-matching principle: The most stable structures will form when the Lewis acidity of the cation closely matches the Lewis basicity of the anion or oxyanion.

Structural unit: the strongly bonded part of the structure; it is usually anionic, but can be neutral or cationic.

Interstitial complex: the weakly bonded part of the structure, consisting of large low-valence alkali and alkaline-earth cations, (H_2O) groups and monovalent anions such as $(OH)^-$ and Cl^-.

Binary structural representation: Interstitial complex and structural unit are each considered as single components whose interaction can be examined using the valence-matching principle.

Transformer (H_2O) groups: (H_2O) groups in which the O-atoms accept only one bond from a cation (inclusive of hydrogen bonds). Hence, they receive only one bond but propagate two hydrogen bonds, *i.e.*, they split one bond into two bonds. This effect transforms the higher bond-valence of one cation-(H_2O) bond into the lower bond-valences of two hydrogen bonds.

Non-transformer (H_2O) groups: (H_2O) groups in which the O-atoms accept two additional bonds from cations (inclusive of hydrogen bonds). Hence, they receive two bonds and also propagate two bonds (*i.e.*, they do not transform bonds). Non-transformer (H_2O) groups propagate bond-valence to acceptor O-atoms of the structural unit.

Inverse-transformer (H_2O) groups: (H_2O) groups in which the O-atoms accept three additional bonds from cations (inclusive of hydrogen bonds). Hence, they receive three bonds and propagate two bonds (*i.e.*, they transform bonds from stronger to weaker).

General formula of a mineral: this indicates the *interstitial complex* and the *structural unit*, and is written as follows:

$$\{{}^{[m]}M^{+}{}_{a}{}^{[n]}M^{2+}{}_{b}{}^{[l]}M^{3+}{}_{c}(H_2O)_d(H_2O)_e{}^{[q]}(OH)_f\}^{(a+2b+3c-f)+}$$

$$[M^{z+}(H_2O)_i(OH)_j(SO_4)_k]^{(a+2b+3c-f)-}(H_2O)_g$$

where d is the number of interstitial transformer (H_2O) groups, e is the number of interstitial non-transformer (H_2O) groups, f is the number of interstitial (OH) groups, and g is the number of interstitial (H_2O) groups which do not bond to interstitial cations.

Effective charge of a structural unit: the formal charge plus the amount of bond-valence transferred to the interstitial complex or adjacent structural units by hydrogen bonds of (H_2O) and (OH) groups in the structural unit. For example, the formal charge of the structural unit $[Fe^{2+}(H_2O)_4(SO_4)_2]^{2-}$ is 2^- and there are eight hydrogen bonds emanating from the structural unit; thus, the effective charge of the structural unit is $(2 + 8h)^-$, where h is the bond valence of the hydrogen bond. The corresponding interstitial complex must have the same effective charge with an opposite sign.

Charge deficiency per anion of the structural unit, CDA: the effective charge of the structural unit divided by the number of O-atoms in the structural unit.

Lewis basicity of the structural unit: the effective charge of the structural unit divided by the number of bonds from the structural unit.

Lewis acidity of an interstitial complex: the effective charge of the interstitial complex divided by the number of bonds emanating from the interstitial complex.

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