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A Bond Strength Approach to the Structure, Chemistry, and Paragenesis of Hydroxy-Hydrated Oxysalt Minerals*, [1]

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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 by 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: $\{^{[m]}M_a^{+\,[n]}M_b^{2+\,[l]}M_c^{3+}\,(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}$, where $[n]$, $[m]$, and $[l]$ are coordination numbers; a, b, and c are the numbers of monovalent, divalent, and trivalent cations; d is the number of *transformer* (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 uranyl oxide-hydroxy hydrate minerals. There is fairly close agreement between the predicted ranges of interstitial complex and those observed in nature. A connection is established between the crystal structures of uranyl oxide-hydroxy hydrate minerals and the conditions ($\log[M^{2+}]/[H]^2$, $\log[H_2O]$) at which they are stable. Structural units may be formally related by two types of chemical reactions, one of which consumes H and the other of which consumes (H_2O). By combining these equations with the law of mass action, an expression can be formulated that allows arrangement of the structural units in $\log[M^{2+}]/[H]^2 - \log[H_2O]$ space and calculation of the slopes of the associated phase boundaries. The result is an activity–activity diagram with the correct topology and a relative scale along each of the axes. The general classes of polymerization of P, U, and D chains in the structural units change systematically across this activity–activity diagram.

INTRODUCTION

Common rocks are made up of a small number of rock-forming minerals, and we follow petrologic processes through variations in the chemical composition of the constituent phases. The key issue that allows us to do this is the fact that the rock-forming minerals are stable over a wide range of temperature, pressure, and/or chemical composition. The situation is rather different for what we may call "complicated" rocks (e.g., highly fractionated granitic pegmatites) and complex materials of environmental interest (e.g., weathering products of sulfide and uranium mine waste). These materials are made up of a relatively large number of phases, many of which are hydroxy-hydrated oxysalt minerals. These minerals are *not* stable over a wide range of ambient conditions; with small changes in temperature, pressure, or activity of principal components, these minerals do not usually modify their chemical composition while retaining their bond topology; instead, they break down to form new phases. This dif-

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[1] This article was submitted by the author in English.

ference in behavior is compounded by the fact that we know far less about the factors that control their atomic arrangements, chemical compositions, and stabilities than for the (usually) more simple rock-forming minerals. This situation results primarily from the structural complexity of the hydroxy-hydrated oxysalts. Simple oxides (e.g., spinel, $MgAl_2O_4$) and oxysalts (e.g., forsterite, Mg_2SiO_4) are susceptible to standard theoretical approaches of chemistry and physics, such as molecular mechanics, molecular orbital theory, and molecular dynamics. When dealing with hydroxy-hydrated oxysalt minerals [e.g., althupite, $AlTh[(UO_2)\{(UO_2)_3(PO_4)_2(OH)O\}_2](OH)_3(H_2O)_{15}$], structural complexity and the difficulty in dealing with (OH) and (H_2O) groups preclude many of these standard approaches. From a mineralogical perspective, this is a very unsatisfactory situation, as the hydroxy-hydrated oxysalts constitute the bulk of the mineral kingdom, and our inability to deal with them is perhaps the major challenge in mineralogy today. This situation is exacerbated by the fact that many of these minerals are important phases from an environmental perspective, and increased understanding of their behavior is necessary to resolve many environmental problems.

PRELIMINARY CONSIDERATIONS

Detailed paragenetic studies (e.g., Bandy, 1938; Fisher, 1958) have shown that there are well-defined relations between chemical compositions of hydroxy-hydrated minerals and their position in paragenetic sequences. Moore (1965, 1973) showed that this correlation extended to structural arrangements in minerals, leading to the development of structural hierarchies in minerals (Moore, 1975, 1982, 1984; Hawthorne, 1979, 1985, 1986, 1990; Burns, 1999; Hawthorne *et al.*, 1996, 2000; Hawthorne and Huminicki, 2001), with the eventual intention of relating structural change to paragenetic sequence. The uranyl oxide-hydroxy hydrate minerals commonly form by oxidation and alteration/dissolution of uraninite in aqueous solutions (Finch and Murakami, 1999), and play a key role in determining reaction paths of uranyl species in aqueous uranium-rich environments. They are also important corrosion products of UO_2 in spent nuclear fuel (Finch and Ewing, 1992), and their properties may control groundwater concentrations of U in contaminated soils (Buck *et al.*, 1996; Morris *et al.*, 1996). These minerals are difficult to study, as they often hydrate or dehydrate and alter with very minor changes in their ambient environment. Nevertheless, there has been significant progress in the last five years in characterizing many of these minerals (Finch *et al.*, 1996; Burns, 1997, 1998a, 1998b, 1999b; Burns and Hanchar, 1999; Li and Burns, 2000a, 2000b) and related synthetic structures (Cremers *et al.*, 1986; Burns and Hill, 2000a, 2000b; Hill and Burns, 1999; Li and Burns, 2000c).

Here, I will describe some of the progress made toward dealing with the structure, chemical composition, and paragenesis of hydroxy-hydrated oxides and oxysalts, focusing in particular on the uranyl oxide minerals. This work can be found in more detail in Hawthorne (1985, 1986, 1990, 1994, 1997) and Schindler and Hawthorne (2001a, 2001b, 2001c, 2002a, 2002b).

BINARY STRUCTURAL REPRESENTATION

In the hydroxy-hydrated oxysalt minerals, there are many different atom interactions, and their topological and geometrical characteristics are important. This makes these minerals very difficult to deal with from a stereochemical and paragenetic perspective. 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, and electronegativity. Hawthorne (1985) took this approach with a complex crystal structure, dividing it into two components (Fig. 1). The *structural unit* is the strongly bonded part of the structure, and the *interstitial complex* is the assemblage of (usually alkali and alkaline earth) cations, anions, and neutral groups that weakly bind the structural units into a continuous crystal structure. The key issue here 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). Thus, we have developed a *binary representation* that gives a simple quantitative model of even the most complicated structure and allows us insight into the weak bonding that controls the stability of the structure. This being the case, we now need a quantitative way to look at the interaction between the structural unit and the interstitial complex.

BOND-VALENCE THEORY

Initial work in this area was done by Pyatenko (1972) and Brown and Shannon (1973), with additional work in particular by Brown (1981) and Hawthorne (1992, 1994, 1997).

Bond Valence and the Valence-Sum Rule

Over the last 30 years, it has been shown (Pyatenko, 1973; Brown and Shannon, 1973; Ferguson, 1974; Brown, 1981; Brown and Altermatt, 1985; Brese and O'Keeffe, 1991) that the strength of a chemical bond can be expressed as a function of its length. Despite its simple formulation, this type of approach is quite sophisticated. Burdett and Hawthorne (1993) showed that this method of expressing the strength of a chemical bond is actually a form of molecular orbital theory, parameterized on bond length (instead of on, for example, electronegativity). Correlations between bond strength and bond length in crystals have been parameterized for specific cation–anion bonds, in particular by

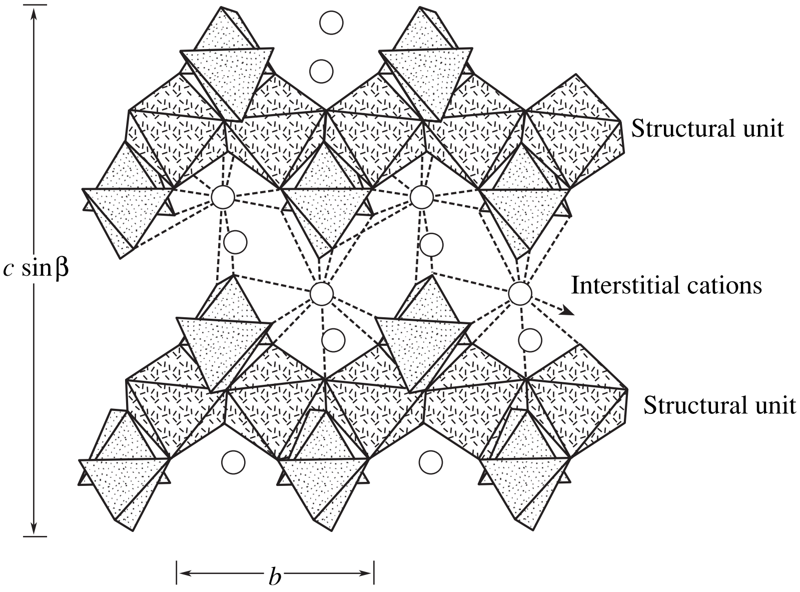

Fig. 1. Partitioning of a complex crystal structure into two units, the strongly bonded *structural unit* (shown as shaded polyhedra) and the weakly bonded *interstitial complex* (shown as individual atoms and chemical bonds).

Brown and Shannon (1973), Brown and Altermatt (1985), and Brese and O'Keeffe (1991):

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

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

Characteristic Bond Strength

Brown (1981) noted that the bond strengths around a specific cation in a wide range of crystal structures lie within ±20% of the mean value; this mean value is thus *characteristic* of that particular cation. If the cation only occurs in one type of coordination, then the mean bond strength for that cation will be equal to the formal charge divided by the coordination number; thus, P (phosphorus) always occurs in tetrahedral coordination to oxygen and will hence have a mean bond strength of 5/4 = 1.25 *vu*. If the cation has more than one coordination number, then the mean bond strength will be equal to the weighted mean of the bond strengths in all the observed structures. Thus, Fe^{2+} occurs in various coordinations from [4] to [8]; the tendency is for [4]- and [5]-coordinations to be more common than [7]- and [8]-coordinations, and the mean bond strength is 0.40 *vu*. The mean bond strength correlates with formal charge and cation size, and values for different cations vary systematically through the periodic table.

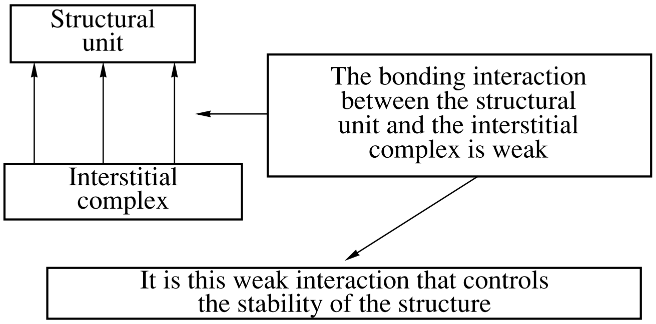

Fig. 2. Representation of the key features of the *binary representation* of a crystal structure.

Lewis Acid and Lewis Base Strengths

The mean bond strength of a cation correlates strongly with its *electronegativity* (Fig. 3). Electronegativity is 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 strength with electronegativity for cations indicates that the characteristic bond strength 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 strength = atomic (formal) valence/(mean coordination number).

The *Lewis base strength* of an anion can be defined in exactly the same way, as the characteristic strength of the bonds formed by the anion. However, bond strength variations around anions are much greater than those around cations; in minerals, the strength of bonds to O_2– can vary between nearly zero and 2.0 *vu*. For example, in apatite, $Ca_5[(PO_4)_3](OH)$, the bond strength to the phosphate O atoms varies between 1.25 *vu* from the [4]-coordinated P atom and 0.25 *vu* from the [8]-coordinated Ca atom. With this range of values, it is obviously not useful to designate a Lewis basicity for oxygen: the range of values is too great for a single predicted value to be useful. However, if we examine the $(PO_4)^{3-}$ group as an oxyanion, each oxygen atom receives 1.25 *vu* from the central P cation and needs an additional 0.75 *vu* from other cations. In apatite, the oxygen atoms of the phosphate group are [4]-coordinated, and hence need an additional three bonds when we consider the phosphate group as an oxyanion; this gives a value for the additional bond strength needed of 0.25 *vu* for each of the oxygen atoms of the $(PO_4)^{3-}$ group. If this process is repeated for all $(PO_4)^{3-}$ groups in minerals, we get a mean value of the characteristic bond strength (and bond valence) required as 0.25 *vu* with a spread of ±0.10 *vu*; this is a useful value for the $(PO_4)^{3-}$ group. In this way, we can define the *Lewis basicity* of an oxyanion. Tables 1 and 2 list Lewis acidities and Lewis basicities for some geochemically common inorganic cations and oxyanions, respectively.

The Principle of Correspondence of Lewis Acidity–Basicity

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*. Here, I will refer to it as the *principle of correspondence of Lewis acidity–basicity*:

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

This is the chemical analogue of the handshaking principle in combinatorial mathematics. As a chemical bond contains two constituents, then the properties of the constituents must match for a stable configuration to form. 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 *vu* (Table 1) and the Lewis basicity of the (SO_4) group is 0.17 *vu* (Table 2). The Lewis basicity of the anion matches the Lewis acidity of the cation, the principle of correspondence of Lewis acidity–basicity is satisfied, and Na_2SO_4 is the mineral thenardite.

Consider next the composition Na_4SiO_4. The Lewis acidity of Na is 0.17 *vu* and the Lewis basicity of the (SiO_4) group is 0.33 *vu* (Table 2). The Lewis basicity of the anion does not match the Lewis acidity of the cation, the principle of correspondence of Lewis acidity–basicity is not satisfied, and Na_2SiO_4 is not a stable mineral.

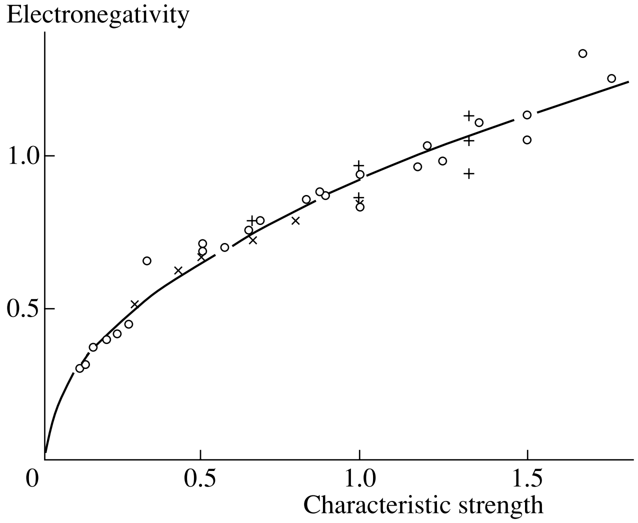

Fig. 3. Variation in electronegativity as a function of the characteristic strength of bonds for common cations (after Brown, 1981).

Table 1. Lewis acid strengths (*vu*) for cations

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

Note: Values taken from Brown (1981), except Pb^{2+}, which was estimated from several oxysalt mineral structures.

Table 2. Lewis basicities (*vu*) for some mineralogically important oxyanions

$(BO_3)^{3-}$	0.33	$(CO_3)^{2-}$	0.25
$(SiO_4)^{4-}$	0.33	$(NO_3)^{3-}$	0.12
$(AlO_4)^{3-}$	0.42	$(VO_4)^{3-}$	0.25
$(PO_4)^{3-}$	0.25	$(SO_4)^{2-}$	0.17
$(AsO_4)^{3-}$	0.25	$(CrO_4)^{2-}$	0.17

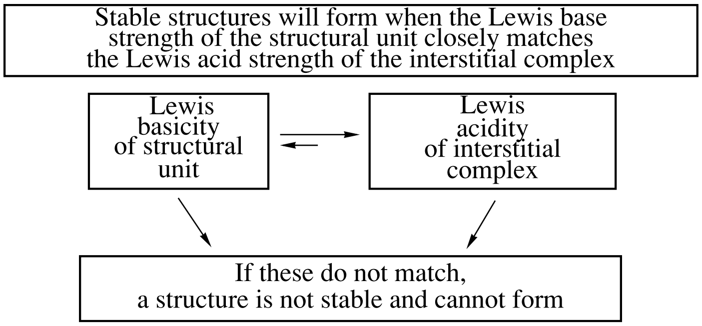

Fig. 4. The principle of correspondence of Lewis acidity–basicity.

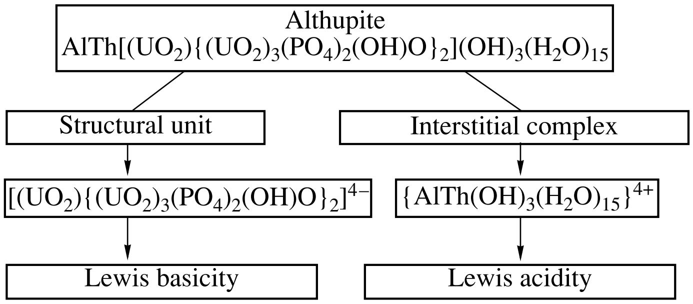

Fig. 5. The structural unit and interstitial complex for the complex uranyl oxide–hydroxy hydrate mineral althupite.

Consider next the hypothetical mineral $NaAlSiO_4$. The Lewis acidity of Na is 0.17 *vu* and the Lewis basicity of the $(AlSiO_4)$ group is 0.13[2] *vu* (Table 2). The Lewis basicity of the anion matches (approximately) the Lewis acidity of the cation, the principle of correspondence of Lewis acidity–basicity is satisfied, and $NaAlSiO_4$ is the mineral nepheline.

We may extend this argument in principal to the interaction between the structural unit and the interstitial complex and restate the principle of correspondence of Lewis acidity–basicity in the following way:

Stable structures will form when the Lewis acid strength of the interstitial complex closely matches the Lewis base strength of the structural unit (Fig. 4).

Consider the uranyl mineral althupite, $AlTh[(UO_2)\{(UO_2)_3(PO_4)_2(OH)O\}_2](OH)_3(H_2O)_{15}$, from this perspective (Fig. 5). Although the chemical formula is quite complicated, we may partition it into a structural unit and an interstitial complex. The structural unit is a sheet of uranyl and phosphate polyhedra, and the interstitial complex consists of the Al and Th cations together with their associated (OH) and (H_2O) groups. If we can calculate a Lewis basicity for the structural unit and a Lewis acidity for the interstitial complex, we can examine the interaction of the structural unit and the interstitial complex using the principle of correspondence of Lewis acidity–basicity.

CALCULATION OF THE LEWIS BASICITY OF THE STRUCTURAL UNIT

The Lewis basicity of the structural unit is the average strength of a bond to that structural unit from surrounding interstitial complexes and neighboring 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.* Thus, what we need to know for this calculation is as follows:

(1) What is the charge on the structural unit?

(2) How many bonds does the structural unit need from the interstitial complex and adjacent structural units?

The Charge on the Structural Unit

We obviously cannot use the formal charge of the structural unit here, or structures with formally neutral structural units could not exist. Consider lizardite, $Mg_3Si_2O_5(OH)_4$ (Fig. 6). The structural unit of lizardite is the sheet $[Mg_3Si_2O_5(OH)_4]^0$. Sheets are linked by hydrogen bonds from the (OH) groups of one sheet to the bridging O atoms of the adjacent sheet. From a

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[2] The Lewis basicity of an oxyanion is its effective charge divided by the number of bonds needed from the interstitial cation (see discussion later in this paper). Assuming an anion-coordination number of [4], the Lewis basicity is thus $1/(4 \times 4 - 4 \times 2) = 0.13$ *vu*.

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. 6). Thus we have to factor the transfer of charge into the calculation of the charge of the structural unit. Such transfer of charge can only involve cations which show very asymmetric coordinations (primarily H, with some lone pair–stereoactive cations such as Pb^{2+} and Bi^{3+}). If we take the average strength of a hydrogen bond as ~0.20 *vu* (Brown, 1981), lizardite will have 4 (the number of H atoms per unit) × 0.20 (the strength of those hydrogen bonds) = 0.80 *vu* transferred per unit. In the case of lizardite, the cation side of the structural unit donates 0.80 *vu* and the anion side of the structural unit accepts 0.80 *vu*, and hence, in this particular case, there is no *overall* transfer of charge.

Consider next hydrogen bonds that link to anions of the interstitial complex. Where such linkage occurs, there *is* an overall transfer of charge from the structural unit to the interstitial complex. Hence, we must define the *effective charge* of the structural unit as *the formal charge of the structural unit as modified by the hydrogen bonds to the interstitial complex*, taking the average bond valence of a hydrogen bond as *h vu*. Let there be *t* hydrogen bonds emanating from the structural unit, and let *s* of these hydrogen bonds link to the interstitial complex. In this case, the charge of *s* hydrogen bonds is transferred to the interstitial complex; the effective charge of the interstitial complex becomes $(Z + hs)^+$ and the effective charge of the structural unit is $(Z + hs)^-$. At first sight, the fact that the effective charge is a function of *s* seems to be a problem, as we frequently do not know *s*, whereas we always know *t* (the number of hydrogen bonds emanating from the structural unit). However, Schindler and Hawthorne (2001a) showed that we can set $s = t$ without adversely affecting the operation of the principle of correspondence of Lewis acidity–basicity (i.e., we may set the effective charge equal to the modified charge, as both the Lewis acidity of the interstitial complex and the Lewis basicity of the structural unit are affected in a similar manner).

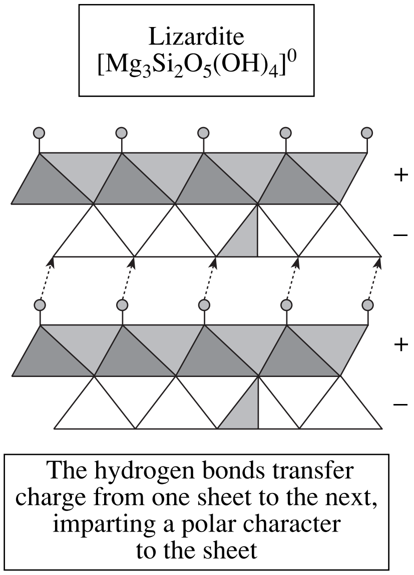

Fig. 6. Representation of the crystal structure of lizardite, showing the polar nature of the structural unit: dark gray, octahedra; unshaded, tetrahedra; dark circles, H atoms; broken lines, hydrogen bonds. The acidic (+) and basic (–) parts of the structural unit are indicated.

The Number of Bonds Needed by the Structural Unit

First of all, 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 the atoms in the structure. However, we want to *predict* information about crystal structures, and in this type of situation, we cannot 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.

In order to predict details of anion coordinations in a structural unit, we introduce a new property, the *average basicity* of a structural unit (Schindler and Hawthorne, 2001a), defined as follows:

The average basicity of a structural unit is defined as the average bond strength sum per O atom contributed by the interstitial species and adjacent structural unit.

This is a very easy quantity to calculate: it is the formal charge of the structural unit modified by any charge transferred by the *t* hydrogen bonds that emanate from the structural unit: $(Z+ ht)^-$, divided by the number of oxygen atoms in the structural unit. For example, consider the structural unit in becquerelite, $[(UO_2)_3O_2(OH)_3]^-$. The modified charge is $(1 + 0.2 \times 3)^- = 1.6^-$, and the number of O atoms in the structural unit is $2 \times 3 + 2 + 1 \times 3 = 11$; the resulting average basicity = 1.6/11 = 0.145 *vu*. As we will see next, there is a close relation between the average basicity of a structural unit and its average oxygen coordination number. 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 by this in that these quantities have such a multiplicity in both the numerator and the denominator of their expressions and, hence, it cancels out in the calculation of these proper-

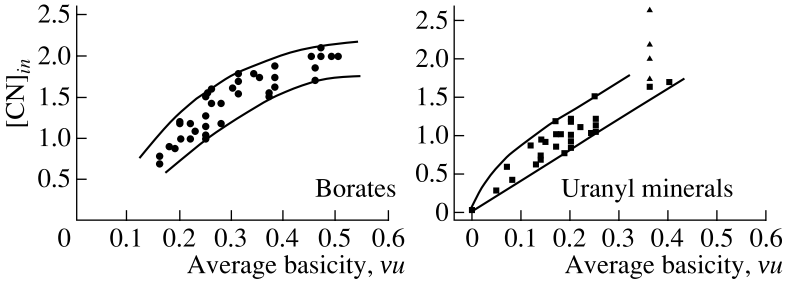

Fig. 7. Correlation between average basicity of structural units and the average coordination numbers of O atoms in the corresponding structural units. The upper and lower border of the distribution are used to define the characteristic range in O-coordination numbers for a specific structural unit.

ties. 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 AVERAGE OXYGEN COORDINATION NUMBER FOR STRUCTURAL UNITS

The bonds of the structural unit contribute most of the bond valence required by the O atoms of the structural unit, and, hence, the average basicity is a measure of the bond valence required by each O atom of the structural unit from the interstitial complex. Thus, the O atoms in a structural unit with a low average basicity require only a small amount of bond valence from the interstitial complex, whereas the O atoms in a structural unit with a high average basicity require more bond valence from the interstitial complex. As the bonds of the structural unit are strong and the bonds of the interstitial complex are weak, differences in average basicity will have a greater effect on the number of interstitial bonds than on the number of bonds within the structural unit; hence, there must be a positive correlation between the average basicity and the mean coordination number of the O atoms in the structural unit.

There is a correlation between the average basicity and the average O-coordination number in borate minerals (Schindler and Hawthorne, 2001a, 2001b). This is an extremely important relation, as it allows us to predict the range in average O-coordination number for a specific structural unit, and, in turn, this allows us to calculate the range in Lewis basicity of that structural unit. However, Schindler *et al.* (2003) showed that the sulfate minerals containing octahedrally coordinated divalent and trivalent cations behave somewhat differently from borate minerals. Structural units involving M^{2+} cations have higher average O-coordination numbers than structural units involving M^{3+} cations, as one would expect from the valence-sum rule (Brown, 1981; Hawthorne, 1994, 1997). We may consider this situation in more detail by factoring the average O-coordination number into two terms:

$$[CN] = [CN]_{su} + [CN]_{in}, \qquad (2)$$

where *su* represents the O-coordination number involving bonds solely from the structural unit and *in* represents the O-coordination number involving bonds from the interstitial complex and from adjacent structural units. The variation of $[CN]_{in}$ as a function of average basicity is shown in Figs. 7a and 7b for borates and uranyl minerals, respectively; it seems apparent that $[CN]_{in}$ is the salient parameter in attempting to establish a relation between O-coordination number and average basicity. If we wish to have any predictive power, we need to be able to derive the average coordination number of such O atoms a priori, without recourse to a known structure. The relation between average basicity and average O-atom coordination number in structural units shown in Fig. 7 allows such prediction.

There is an even more important issue associated with Fig. 7. As well as predicting details of the average coordination for O atoms in a given structural unit, this relation also predicts the *range* of possible average coordination numbers of oxygen in a given structural unit. This range of average coordination numbers for the O atoms of the structural unit reflects the range in pH over which the mineral is stable. Indeed, *it is by varying the coordination numbers of the O atoms in the structural unit that the structural unit maintains its stability as the* pH *of its environment changes.* Moreover, the relations of Fig. 7 allow calculation of the range of possible Lewis base strength for a specific structural unit.

CALCULATION OF THE LEWIS BASICITY OF THE STRUCTURAL UNIT

We define the Lewis basicity of a structural unit as its effective charge divided by the number of bonds required by the structural unit. Above, we showed that each structural unit has a range of average O-coordination numbers and that we can derive this range from the average basicity of the structural unit via Fig. 7. Thus, we can calculate the corresponding range in Lewis basicity for any structural unit.

Example. Consider becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$. 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 *vu*, the average strength of a hydrogen bond (Brown, 1981)). The average basicity of the structural unit is thus $1.6/[2 \times 3 + 2 + 3] = 1.6/11 = 0.145$ *vu*. From Fig. 7, the corresponding range in O-coordination number for this structural unit is [0.65]–[1.05]. Thus, the minimum and maximum possible numbers of bonds from the interstitial complex 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 *vu*.

(H_2O) AS AN INTERSTITIAL SPECIES

Here, we examine the possible stereochemical arrangements adopted by interstitial (H_2O) and consider its effect of 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; (H_2O) also may be occluded in the structure, but this situation is fairly rare]. Where involved in a hydrogen-bond network, the O atom of an (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. 8a), two hydrogen bonds of strength v *vu* 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) *vu*. In order to satisfy the bond strength requirements regarding the H atoms, each H forms a hydrogen bond of strength v *vu* 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. Thus, we designate this type of (H_2O) group as *nontransformer* (H_2O) and denote it by the subscript *g*, $(H_2O)_g$.

Interstitial H_2O *Bonded to One Interstitial Cation*

Let a cation M bond to an anion S (Fig. 8b); the anion S receives a bond strength of v *vu* from the cation M. Consider a cation M that bonds to an (H_2O) group, which, in turn, bonds to an anion S (Fig. 8c). In the second case, the oxygen atom of the (H_2O) group receives a bond strength of v *vu* from the cation M, and its bond strength requirements are satisfied by two short O–H bonds of strength (1 – v/2) *vu*. To satisfy the bond strength requirements around each H atom, each H forms at least one hydrogen bond with its neighboring anions. In Fig. 8c, 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 *vu*) to be split into two weaker bonds (bond strength = v/2 *vu*); we designate this type of (H_2O) as *transformer* (H_2O) and denote it by the subscript *d*, $(H_2O)_d$.

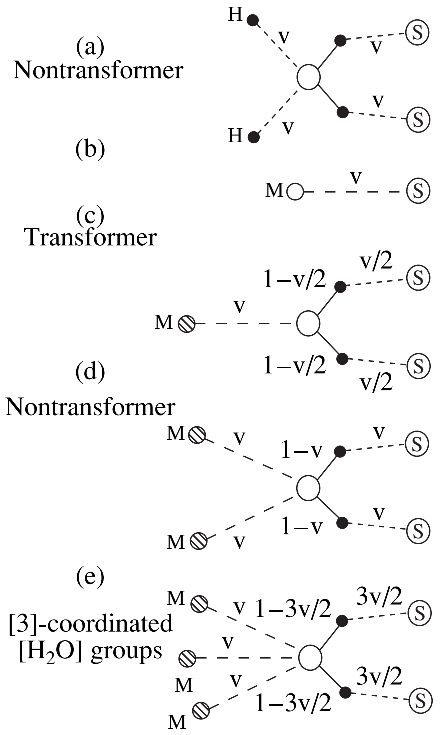

Fig. 8. (a) An (H_2O) group held in a structure solely by hydrogen bonds; the O atom of the (H_2O) group is an acceptor anion for two hydrogen bonds of valence v *vu* and a donor anion for two H atoms; (b) the interstitial cation M bonds to an anion S with bond valence v; (c) bond-valence transformer 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 *vu*) is split into two weaker bonds (bond valence = v/2 *vu*); (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. Cation–oxygen bonds are shown by broken lines, H bonds are shown as dotted lines, and bond valences are in *vu*.

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. 8d). In this case, the O atom receives a bond strength of 2v *vu* from the two cations and its bond strength requirements are satisfied by two short O–H bonds, each of strength (1 – v) *vu*. To satisfy the bond strength requirements of each H atom, each H forms at least one hydrogen bond with its neighboring anions. In Fig. 8d, one of these hydrogen bonds involves the S anion, which thus receives the same bond strength (v *vu*) as where it is bonded directly to one M cation (Fig. 8b). Thus, in this case, the (H_2O) group

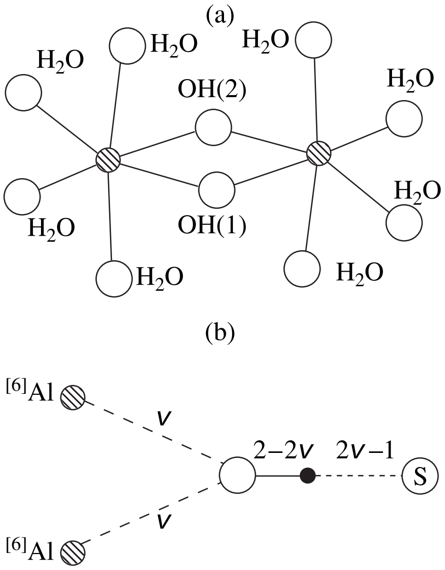

Fig. 9. (a) Two interstitial ($Al\phi_6$) octahedra sharing an edge: $\{Al_2(H_2O)_8(H_2O)_0(OH)_2\}^{4+}$; (b) the arrangement of bond valences around an (OH) group in (a); the large unshaded circle is an O atom of an (OH) group, H atoms are shown as small black circles, and broken lines indicate hydrogen bonds.

does not act as a bond strength transformer; we designate this also as *nontransformer* (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. 8e). In this case, the O atom receives a bond strength of 3v *vu* from the three cations and its bond strength requirements are satisfied by two short O–H bonds, each of strength (1 – 3v/2) *vu*. To satisfy the bond strength requirements of each H atom, each H forms (at least) one hydrogen bond with its neighboring anions. In Fig. 8d, one of these hydrogen bonds involves the S anion, which thus receives 3v/2 *vu* as compared with v *vu* when it is bonded directly to one M cation (Fig. 8b). 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

In most minerals, the interstitial components consist of simple cations and neutral (H_2O) groups. However, some minerals contain interstitial anionic species where the net charge of the interstitial species is negative. Of particular importance in this regard is the monovalent anion $(OH)^-$. 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). When it is an interstitial species, the O anion of the (OH) group receives ≤1.0 *vu* (usually ~0.8 *vu*) from its companion H atom and hence requires ≥1.0 *vu* from the interstitial cations to which it is bonded. By definition, bonds involving interstitial cations are weak, and this feature puts considerable constraints on the occurrence of (OH) as an interstitial species. The average bond valences for octahedrally coordinated monovalent, divalent, and trivalent cations are 0.17, 0.33, and 0.50 *vu*, respectively. For monovalent interstitial cations, this means that interstitial (OH) must bond to (at least) six cations. This arrangement is very crowded and occurs in halite-type structures; in the open arrangements typical of interstitial environments, (OH) cannot occur with [6]- or higher 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 occur as interstitial species where accompanied by divalent cations.

For trivalent interstitial cations, (OH) must bond to two octahedrally coordinated cations. Thus, two ($Al\phi_6$) 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 ($Al\phi_6$) octahedra linked through a shared edge (Fig. 9a). Both anions involved in the shared edge are (OH), and their bonding is shown more explicitly in Fig. 9b. The OH anion takes two very strong bonds (≥0.5 *vu*) and transforms them into one weak bond (~0.2 *vu*). Also, it “absorbs” two strong bonds, radically changing the overall Lewis acidity of the interstitial complex. In calculating the aggregate Lewis acidity of interstitial species that include (OH), one can subtract the charge of the (OH) group(s) from the 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

$$\{{}^{[m]}M_a^{+\,[n]}M_b^{2+\,[l]}M_c^{3+}(H_2O)_d(H_2O)_e{}^{[q]}(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}, \qquad (3)$$

where M is any type of interstitial mono-, di-, and trivalent cation; $[m]$, $[n]$, $[l]$, and $[q]$ denote coordination numbers; d denotes the number of transformer (H_2O) groups; e denotes the number of nontransformer (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 nontransformer (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

$$M(H_2O)_{d+e}(OH)_f[\text{structural unit}](H_2O)_g, \qquad (4)$$

where the (H_2O) and (OH) groups before the structural unit bond to an interstitial cation and the (H_2O) group after the structural unit does not bond to an interstitial cation. For example, becquerelite has the composition $Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, and four (H_2O) groups bond to interstitial Ca. The Ca atom is coordinated by four interstitial (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 nontransformer (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., $d = 4$, $e = 0$, 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 nontransformer (H_2O) groups are known.

CALCULATION OF THE LEWIS ACIDITY OF INTERSTITIAL COMPLEXES

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

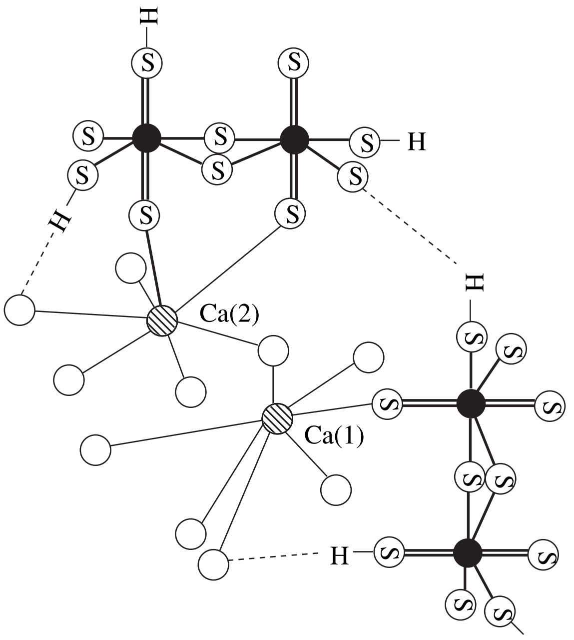

Fig. 10. An example of an interstitial $\{^{[7]}Ca_2(H_2O)_7(H_2O)_3\}^{4+}$ complex. In the structural unit, the central cations are indicated by large black circles and the corresponding anions, by circles marked S; in the interstitial complex, the interstitial (H_2O) groups are shown as large white circles, the hydrogen atoms are shown as H, the Ca atoms are shown as hatched circles, and hydrogen bonds are shown as broken lines.

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. Now, we give a general expression for the calculation of Lewis acidity. The *Lewis acidity* of the interstitial complex $\{^{[m]}M_a^{+[n]}M_b^{2+[l]}M_c^{3+}(H_2O)_d(H_2O)_e(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+}$ can be written as

$$\begin{aligned}(a + 2b + 3c - f + h \times s)/[m \times a \\ + n \times b + l \times c + d - f \times (q-1) + s],\end{aligned} \qquad (5)$$

where h is the average bond valence 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 with three constituent (OH) groups (Fig. 10); we do not know s, but we do not need to know s as we can set $s = t(=3)$. The interstitial complex has seven transformer (H_2O) groups, three nontransformer (H_2O) groups 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

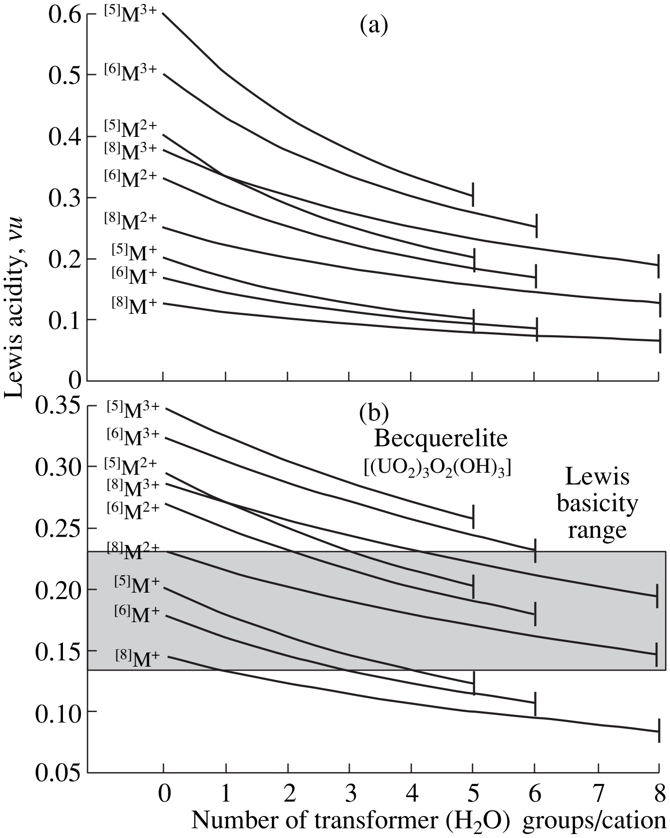

Fig. 11. (a) The Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The lines shown are for interstitial cations with formal charges and coordination numbers shown to the left of the plot. (b) As in (a), with the corresponding range in Lewis basicity of the structural unit $[(UO_2)_3O_2(OH)_3]^-$ marked by the shaded band.

from the hydrogen bonds to the interstitial complex) = 26. Thus, the Lewis acidity of the interstitial complex is 4.6/26 = 0.177 *vu*.

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. 11a). Obviously, the Lewis acidity of the interstitial complex decreases as the number of transformer (H_2O) groups increases, as the cation-coordination numbers increase, and as the cation charge decreases. Figure 11a contains all relevant information concerning variation in Lewis acid strength of interstitial complexes. First, 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., $M^{3+} + (OH)^- \equiv M^{2+}$).

STRUCTURAL UNITS, INTERSTITIAL COMPLEXES, AND THE PRINCIPLE OF CORRESPONDENCE OF LEWIS ACIDITY–BASICITY

The *binary-representation* approach factors a structure into a (usually anionic) *structural unit* and a (usually cationic) *interstitial complex.* We may use the *principle of correspondence of Lewis acidity–basicity* to examine the interaction between these two components. We have shown how each structural unit has a range of Lewis basicity (controlled by variations in coordination numbers of simple anions), and we have seen how we can represent the variation in Lewis acidity of an interstitial complex as a function of the amount of transformer (H_2O), the valence of the 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 cation complexes (i.e., Fig. 11b). 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*

The principle of correspondence of Lewis acidity–basicity requires that the Lewis acidity of the interstitial complex lie within the characteristic range of Lewis basicity for a given structural unit for a stable structure to form. Thus, the range in Lewis basicity determines the type of interstitial cation and the number of transformer (H_2O) groups. We may express the Lewis acidity of a general interstitial complex in terms of the numbers of transformer $(H_2O)_d$ and nontransformer $(H_2O)_e$ groups, in an attempt to understand the mechanism controlling the function and amount of these interstitial components.

Consider a structural unit of formal charge 2^-, four (OH) groups, and a range in Lewis basicity of 0.17–0.22 *vu* (Fig. 11b). The Lewis acidities of all possible stable interstitial complexes must match this range, and, thus, we can formulate the following restrictions for interstitial complexes with only one type of interstitial cation from Eq. (5):

$$\text{(a) } \{^{[m]}M^{+}_{2}(H_2O)_d(H_2O)_e\}^{2+} \quad 0.17 < 2(1 + 2h)/(2m + d + 4) < 0.22, \tag{6}$$

$$\text{(b) } \{^{[n]}M^{2+}(H_2O)_d(H_2O)_e\}^{2+} \quad 0.17 < 2(1 + 2h)/(n + d + 4) < 0.22, \tag{7}$$

$$\text{(c) } \{^{[l]}M^{3+}(H_2O)_d(H_2O)^{[3]}_e(OH)\}^{2+} \quad 0.17 < 2(1 + 2h)/(l + d - 1 \times 2 + 4) < 0.22. \tag{8}$$

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

Consider interstitial complex (a). For cation coordination numbers m > [6], the expression (6) does not hold, and hence there can be no minerals with interstitial monovalent cations of coordination number >[6]. Where m = [6], expression (6) 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 (6) holds for $0 < d < 3$, and hence there can be 0–3 transformer (H_2O) groups for two [5]-coordinated monovalent cations.

Consider interstitial complex (b). For n = [5], expression (7) holds for $4 < d < 7$; as the maximum possible number of (H_2O) groups coordinating a [5]-coordinated cation is 5, 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 0 transformer (H_2O) groups for n = [12].

Consider interstitial complex (c). For l = [6], expression (8) holds for $5 < d < 6$, but 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 6 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 nontransformer (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.

URANYL OXIDE-HYDROXY HYDRATE MINERALS

The uranyl oxide-hydroxy hydrate minerals can be ordered hierarchically based upon the anion topology of their (sheet) structural unit (Burns, 1999; Burns *et al.*, 1996). Figure 12 shows the anion topology (net) of a specific sheet structural unit. The net contains triangles, squares, and pentagons and can be constructed from various types of chains. Miller *et al.* (1996) give details of the various types of chains that they label P, U, D, R, and H, and Burns (1999) describes a modified version of the U chain in curite, labeling it U^m. Glatz *et al.* (2002) describe the structure of synthetic $Ca(H_2O)[(UO_2)_4O_3(OH)_4](H_2O)$, which contains a modified variant of the U^m chain that can be labeled $U^{m'}$. The topology of a sheet structural unit depends on the number, type, and sequence of the different chains. The topology of the sheet in Fig. 12 can be described by the code RUPURDPDRUP, which contains all information regarding the number, type, and sequence of the different chains. However, the resulting code is complicated, and intuitive comparison with other topology codes is difficult. Here, I use a topology code of general form $P_u(UD)_vR_wU^m_xU^{m'}_yH$ for uranyl-sheet structural units. The code of the topology in Fig. 12 is $P_3(UD)_5R_3$. This code contains the number of different chains in the topology of the unit cell, but not the sequence of the chains. However, this formulation makes it easier to

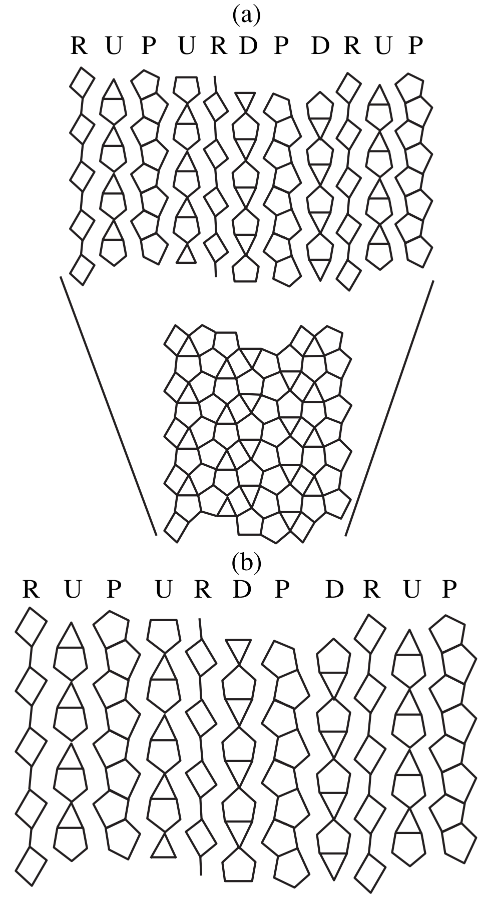

Fig. 12. (a) The anion topology of a sheet structural unit with D-, R-, P-, and U-type chains and the topology code $P_3(UD)_5R_3$; (b) different types of anion chains which occur in uranyl oxide-hydroxy hydrate minerals.

Table 3. Minerals of the uranyl oxide-hydroxy hydrate group

Mineral	Formula	Ref.
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	(1)
Vandenriesscheite	$^{[9]}Pb^{2+[8]}Pb^{2+}_{0.57}(H_2O)_5[(UO_2)_{10}]O_6(OH)_{11}](H_2O)_6$	(2)
Becquerelite	$^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	(3)
Compreignacite	$^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	(4)
Fourmarierite	$^{[7]}Pb^{2+}(H_2O)_2[(UO_2)_4O_2(OH)_4](H_2O)_2$	(5)
Richetite	$^{[6]}M_x{}^{[8.4]}Pb^{2+}_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$	(6)
Protasite	$^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$	(3)
Masuyite	$^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$	(7)
Curite	$^{[9]}Pb^{2+}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$	(8)
Sayrite*	$^{[9]}Pb^{2+}_2(H_2O)_4[(UO_2)_5O_6(OH)_2]$	(9)
Wölsendorfite*	$^{[8.15]}(Pb^{2+}_{6.2}Ba_{0.4})(H_2O)_{10}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$	(10)
Billietite	$^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$	(11)
Agrinierite	$^{[8]}K_2(^{[9]}Ca, Sr)(H_2O)_5[(UO_2)_3O]_2(OH)_3]_2$	(12)
Metavandenriesscheite	$Pb^{2+}_{1.57}[(UO_2)_{10}O_6(OH)_{11}](H_2O)_{(1-x)}$	(13)
Rameauite	$K_2Ca[(UO_2)_6O_4(OH)_6](H_2O)_6$	(13)
Calciouranoite	$(Ca, Ba, Pb^{2+}, K_2, Na_2)[(UO_2)(O, OH)](H_2O)_5$	(13)
Metacalciouranoite	$(Ca, Ba, Pb^{2+}, K, Na)[(UO_2)(O, OH)](H_2O)_2$	(13)
Clarkeite	$(Na, Ca)[(UO_2)(O, OH)](H_2O)_{0-1}$	(13)
Bauranoite	$Ba[(UO_2)(O, OH)](H_2O)_{4-5}$	(13)

Note: (1) Finch *et al*. (1996); (2) Burns (1997); (3) Pagoaga *et al*. (1987); (4) Burns (1998a); (5) Piret (1985); (6) Burns (1998b); (7) Burns and Hanchar (1999); (8) Taylor *et al*. (1981); (9) Piret *et al*. (1983); (10) Burns (1999b); (11) Finch *et al*. (2002); (12) Cahill and Burns (2000); (13) Finch and Murakami (1999).

* The structural unit is modified by strong Pb^{2+}–O bonds resulting from stereoactive lone-pair effects.

compare different codes of structural units in minerals formed under different conditions. Future, more detailed work will presumably focus on the more comprehensive representation of Burns *et al.* (1996).

Lone Pair–Stereoactive Interstitial Cations

Uranyl oxide-hydroxy hydrate minerals often contain interstitial cations that can have stereoactive lone pairs of electrons, particularly Pb^{2+} and Bi^{3+}. When 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, while weak Pb^{2+}–ϕ bonds are treated in the same way as hydrogen bonds.

Consider the structure of sayrite, $Pb^{2+}_2(UO_2)_5O_6(OH)_2(H_2O)_4$. If Pb^{2+} were not lone pair–stereoactive, we would write the formula of sayrite as $Pb^{2+}_2(H_2O)_2(H_2O)_2[(UO_2)_5O_6(OH)_2]$. However, inspection of the stereochemistry of the Pb^{2+} cation in sayrite shows that it is lone pair–stereoactive. We may indicate this behavior by writing the coordination number of Pb^{2+} to indicate the number of short and long bonds: $^{[1+7]}Pb^{2+}$. As with H atoms of the structural unit, we also include the cations as part of the structural unit: $[^{[1-7]}Pb^{2+}_2\{(H_2O)_2(H_2O)_2\}(UO_2)_5O_6(OH)_2]$. In order to

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	Chain sequence	Average basicity, *vu*	Range in Lewis basicity, *vu*
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	$[(UO_2)_{12}O_2(OH)_{12}]^0$	$P_3(UD)_6$	0.08	0.11–0.20
Becquerelite	$^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	$[(UO_2)_3O_2(OH)_3]^{1-}$	$P_6(UD)_5$	0.145	0.14–0.23
Compreignacite	$^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	$[(UO_2)_3O_2(OH)_3]^{1-}$	$P_6(UD)_5$	0.145	0.14–0.23
Billietite	$^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$	$[(UO_2)_3O_2(OH)_3]^{1-}$	$P_6(UD)_5$	0.145	0.14–0.23
Rameauite	$K_2Ca[(UO_2)_6O_4(OH)_6](H_2O)_6$	$[(UO_2)_3O_2(OH)_3]^{1-}$	$P_6(UD)_5$	0.145	0.14–0.23
Agrinierite	$^{[8]}K_2(^{[9]}Ca, Sr)(H_2O)_5[(UO_2)_3O_2(OH)_3]_2$	$[(UO_2)_3O_2(OH)_3]^{1-}$	$P_6(UD)_5$	0.145	0.14–0.23
Vandenriesscheite	$^{[9]}Pb_1^{2+}\,^{[8]}Pb_{0.57}^{2+}(H_2O)_5[(UO_2)_{10}]O_6(OH)_{11}](H_2O)_6$	$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$	$P_9(UD)_{11}$	0.14	0.14–0.23
Fourmarierite	$^{[9]}Pb^{2+}(H_2O)_2[(UO_2)_4O_3(OH)_4](H_2O)_2$	$[(UO_2)_4O_3(OH)_4]^{2-}$	$P_3(UD)_6$	0.19	0.15–0.23
Richetite	$^{[6]}M_x^{[8.4]}Pb_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$	$[(UO_2)_3O_3(OH)_2]^{2-}$	$P_6(UD)_5$	0.22	0.16–0.24
Masuyite	$^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$	$[(UO_2)_3O_3(OH)_2]^{2-}$	$P_6(UD)_5$	0.22	0.16–0.24
Protasite	$^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$	$[(UO_2)_3O_3(OH)_2]^{2-}$	$P_6(UD)_5$	0.22	0.16–0.24
Curite	$^{[9]}Pb_3^{2+}(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$	$[(UO_2)_8O_8(OH)_6]^{6-}$	$(UD)_6(U^m)_6$	0.24	0.17–0.24
Sayrite	$^{[9]}Pb_2^{2+}(H_2O)_4[(UO_2)_5O_6(OH)_2]$	$^*[(UO_2)_5O_6(OH)_2]^{4-}$	$P_4(UD)_8R_5$	0.244	0.17–0.24
Wölsendorfite	$^{[8.15]}(Pb_{6.2}^{2+}Ba_{0.4})(H_2O)_{10}[(UO_2)_{14}]O_{19}(OH)_4](H_2O)_2$	$^*[(UO_2)_{14}O_{19}(OH)_4]^{14-}$	$P_6(UD)_{22}R_9$	0.29	0.175–0.24

* 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 average basicities and ranges of Lewis basicity of 0.189 and 0.15–0.236 and 0.27 and 0.17–0.235 *vu*, respectively.

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 *vu* is appropriate. Thus, the modified 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 average basicity of the structural unit is 3.40/18 = 0.189 *vu*.

Average Basicity versus $[CN]_{in}$ *for Uranyl Oxysalt Minerals*

In Fig. 7b (Schindler and Hawthorne, 2003a), the data for average basicities above 0.33 *vu* are rather scattered for (as yet) unknown reasons. However, the band of data in Fig. 7b gives well-defined maximum and minimum values of $[CN]_{in}$ for structural units with average basicities between 0.00 and 0.33 *vu*. In this range, Fig. 7b can be used to calculate the range in Lewis basicity of all uranyl oxide-hydroxy hydrate structural units. The chemical compositions of all uranyl oxide-hydroxy hydrate minerals are listed in Table 3, and the corresponding structural units, their average basicity, their range in Lewis basicity, and the topology code of their sheet structural unit are listed in Table 4. The predicted ranges in coordination number and transformer (H_2O) groups per cation, together with what is observed in minerals, are given in Table 5. In the following sections, we will examine the interactions between the structural unit and the interstitial complex and predict the possible ranges in cation charge, cation coordination number, and number of transformer (H_2O) groups. For the first structural unit, I will go through the arguments in detail. For the rest of the structural units, I will just compare the predicted interstitial complexes with those observed in minerals.

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

The structural unit $[(UO_2)_3O_2(OH)_3]^{1-}$ (Fig. 13c) occurs in becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$; compreignacite, $^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$; billietite, $^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$; agrinierite, $^{[8]}K_2(^{[9]}Ca, Sr)(H_2O)_5[(UO_2)_3O_2(OH)_3]_2$; and rameauite, $K_2Ca[(UO_2)_6O_4(OH)_6](H_2O)_6$. The sheet (structural unit) can be described as an arrangement of triangles and pentagons (Burns, 1999a) with the topology code $P_6(UD)_5$. The effective and modified charges of the structural unit are both $1 + 3 \times 0.2 = 1.6$ *vu* (h =

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

Structural unit	Predicted transformer (H_2O) groups	Interstitial complex	Mineral
$[(UO_2)_3O_2(OH)_3]^{1-}$	${}^{[6]}M^{+} : d = 0–3$		Compreignacite
	${}^{[7]}M^{+} : d = 0–2.5$	$\{{}^{[7]}K_2(H_2O)_3\}^{2+}$	
	${}^{[8]}M^{+} : d = 0–1$		
	${}^{[8]}M^{+}, {}^{[9]}M^{2+} : d = 0–1$	$\{{}^{[8]}K_2{}^{[9]}Ca(H_2O)_5\}^{4+}$	Agrinierite
	${}^{[6]}M^{2+} : d = 2–6$		
	${}^{[7]}M^{2+} : d = 1–7$	$\{{}^{[7]}Ca(H_2O)_4\}^{2+}$	
	${}^{[10]}M^{2+} : d = 0–7$	$\{{}^{[10]}Ba(H_2O)_4\}^{2+}$	Billietite
	${}^{[6]}M^{3+} : d = 6$		
	${}^{[8]}M^{3+} : d = 4–8$		
$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$	${}^{[6]}M^{+} : d = 0–3$		
	${}^{[8]}M^{+} : d = 0–1$	$\{{}^{[9]}Pb^{2+[8]}Pb^{2+}{}_{0.5}(H_2O)_5\}^{3+}$	Vandenriesscheite
	${}^{[6]}M^{2+} : d = 2–6$		
	${}^{[8]}M^{2+} : d = 0–8$		
	${}^{[6]}M^{3+} : d = 6$		
	${}^{[8]}M^{3+} : d = 4–8$		
$[(UO_2)_4O_3(OH)_4]^{2-}$	${}^{[6]}M^{+} : d = 0–1$		
	${}^{[8]}M^{+}$: not possible		
	${}^{[6]}M^{2+} : d = 2–6$		
	${}^{[8]}M^{2+} : d = 0–6$		
	${}^{[9]}M^{2+} : d = 0–5$	$\{{}^{[9]}Pb(H_2O)_2\}^{2+}$	Fourmarierite
$[(UO_2)_3O_3(OH)_2]^{2-}$	${}^{[6]}M^{+} : d = 0–1$		
	${}^{[8]}M^{+}$: 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
	${}^{[6]}M^{3+} : d = 8, f = 2, d = 6$		
	${}^{[8]}M^{3+} : d = 4–8$		
$[(UO_2)_8O_8(OH)_6]^{6-}$	${}^{[6]}M^{+} : d = 0$		
	${}^{[8]}M^{+}$: not possible		
	${}^{[6]}M^{2+} : d = 2–6$		
	${}^{[8]}M^{2+} : d = 0–3$		
	${}^{[9]}M^{2+} : d = 0–4$	$\{{}^{[9]}Pb_3^{2+}(H_2O)_2\}^{6+}$	Curite
	${}^{[6]}M^{3+} : d = 8, f = 2$		
	${}^{[8]}M^{3+} : d = 5–8$		
$[(UO_2)_5O_6(OH)_2]^{4-}$	${}^{[5]}M^{+} : d = 0–1$		
	${}^{[6]}M^{+} : d = 0$		
	${}^{[6]}M^{2+} : d = 2–6$		
	${}^{[8]}M^{2+} : d = 0–4$		
	${}^{[9]}M^{2+} : d = 0–3$	$[{}^{[1+7]}Pb_2^{2+}]\{(H_2O)_2(H_2O)_2\}$	Sayrite
	${}^{[6]}M^{3+} : d = 8, f = 2$		
	${}^{[8]}M^{3+} : d = 4–8$		
$[(UO_2)_{14}O_{19}(OH)_4]^{14-}$	${}^{[5]}M^{+} : d = 0–1$		
	${}^{[6]}M^{+}$: not possible		
	${}^{[6]}M^{2+} : d = 2–5$		
	${}^{[8]}M^{2+} : d = 0–3$	$[{}^{[2+6]}Pb^{2+}]\{{}^{[8.4]}Pb_{5.2}^{2+}\,{}^{[8]}Ba_{0.4}(H_2O)_{10}\}^{11.2+}$	Wölsendorfite
	${}^{[6]}M^{3+} : d = 8, f = 2$		
	${}^{[8]}M^{3+} : d = 4–8$		

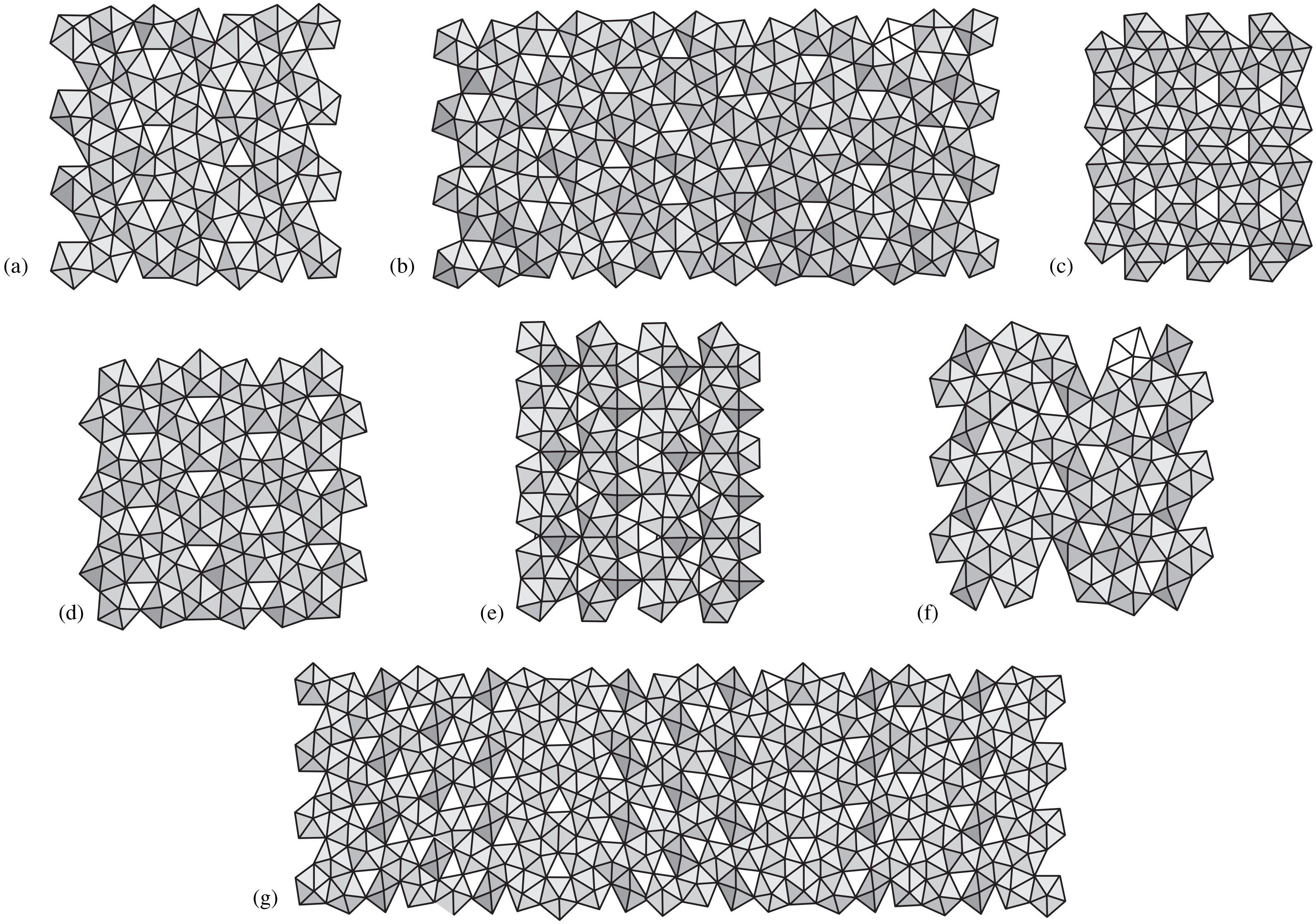

Fig. 13. Polyhedral representation of sheet structural units in uranyl oxide-hydroxy hydrate minerals: (a) $[(UO_2)_3O_2(OH)_3]^{-}$; (b) $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$; (c) $[(UO_2)_4O_3(OH)_4]^{2-}$; (d) $[(UO_2)_3O_3(OH)_2]^{2}$; (e) $[(UO_2)_8O_8(OH)_6]^{6-}$; (f) $[(UO_2)_5O_6(OH)_2]^{4-}$; (g) $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$.

0.20 *vu* and $s = t$) and the number of O atoms in the structural unit is 11. Hence, the structural unit has an average basicity of 0.145 *vu*. We may use this value of the average basicity, together with Fig. 7b, to predict the minimum and maximum values of $[\mathrm{CN}]_{in}$: 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 *vu*. The valence-matching principle requires that the Lewis acidities of the corresponding interstitial complexes should be in the range 0.14–0.23 *vu*; this range is shown in Fig. 11b.

Interstitial complexes with monovalent cations. There are three hydrogen bonds emanating from this structural unit, and, therefore, the range in bonds from interstitial cations and transformer (H_2O) groups to the structural unit is from 7 – 3 to 11.5 – 3 = 4.0–8.5. This means that interstitial monovalent cations not bonded to transformer (H_2O) groups must have coordination numbers between [4] and [8.5]. Considering the variation in coordination numbers of monovalent cations such as K, Rb, Cs, and Tl, we expect to find all types of monovalent cations in minerals with this structural unit.

The Lewis acidity of a monovalent cation in [8]-, [7]-, or [6]-coordination matches the range in Lewis basicity of the structural unit with no, one, or two 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 $^{[8]}M^{+}(H_2O)_{0\text{–}0.5}[(UO_2)_3O_2(OH)_3]$ 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 having 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 values.

Interstitial complexes with divalent cations. The most common coordination numbers for divalent cations are [6], [7], and [8]. Interstitial complexes with divalent cations in [6]-, [7]-, and [8]-coordination and no transformer (H_2O) groups have Lewis acidities of 0.33, 0.285, and 0.25 *vu*, respectively. These values are larger than the range in Lewis basicity of the structural unit (Fig. 11b), and, hence, transformer (H_2O) groups or hydrogen bonds from the structural unit are required to reduce the Lewis acidity such that it falls within the range of Lewis basicity of the structural unit. Consider the case for [N]-coordination and six hydrogen bonds to the interstitial complex. When the interstitial divalent cation is bonded to d transformer (H_2O) groups, the corresponding Lewis acidity may be written as $(2 + 6h)/(2d + N + 6 - d)$, or, for $h = 0.2$ *vu*, $3.2/(N + d + 6)$ *vu*. For the Lewis acidity to fall at the maximum of the range in Lewis basicity of the structural unit (i.e., 0.23 *vu*), then $3.2/(N + d + 6) = 0.23$. For $N = 6$ and 7, $d = 2$ and 1, respectively; thus, a simple [6]-, [7]-, or [8]-coordinated divalent interstitial cation must bond to a *minimum* of two, one, or zero transformer (H_2O) groups, respectively. For the Lewis acidity to fall at the minimum of the range in Lewis basicity of the structural unit (i.e., 0.14 *vu*), $3.2/(N + d + 6) = 0.14$, from which d = 11, 10, or 9. However, six, seven, and eight are the maximum possible values of d (Fig. 3b), and thus a [6]-, [7]-, or [8]-coordinated divalent cation can bond to a *maximum* of six, seven, or eight transformer (H_2O) groups, respectively (Table 2).[3] There are two minerals with only divalent interstitial cations: becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, and billietite, $^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$. We predict that becquerelite and billietite must contain 1–4 and 0–7 transformer (H_2O) groups, respectively.

Interstitial complexes with mixed monovalent and divalent cations. There is one mineral with both monovalent and divalent interstitial cations: rameauite, $K_2Ca[(UO_2)_6O_4(OH)_6](H_2O)_6$. Rameauite contains two $[(UO_2)_3O_2(OH)_3]^{-1}$ structural units; hence, there are a maximum of $2 \times 11.5 = 23$ and a minimum of $2 \times 7 = 14$ bonds from the interstitial complex to the structural unit. There are $2 \times 3 = 6$ hydrogen bonds from the (doubled) structural unit to the interstitial complex, and, thus, the maximum and minimum numbers of bonds from interstitial cations and transformer (H_2O) groups to the structural unit(s) are 23 – 6 = 17 and 14 – 6 = 8 bonds, respectively. For an interstitial complex of the form $\{^{[m]}M_2^{+}\,^{[n]}M^{2+}(H_2O)_d\ldots\}^{4+}$, there are $(2m + n + d)$ bonds to the structural unit, and hence the valence-matching principle requires that $14 < (2m + n + d) < 34$. From this expression, all possible interstitial complexes of this type may be predicted.

Interstitial complexes with trivalent cations. The trivalent cations possible in an interstitial complex are octahedrally coordinated small cations (e.g., Al, Fe^{3+}) and (usually) [8]- or [9]-coordinated REEs (Y and rare-earth elements). Consider the case for [6]-coordinated Al or Fe^{3+}. If the cation is bonded to d transformer (H_2O) groups, its Lewis acidity may be written as $(3 + 9h)/(2d + 6 + 9 - d) = 4.8/(6 + d + 9)$ *vu*. For the Lewis acidity to fall at the maximum of the range of Lewis basicity of the structural unit (i.e., 0.23 *vu*), then $4.8/(6 + d + 9) = 0.23$, from which $d = 6$. For the Lewis acidity to fall at the minimum of the range of Lewis basicity of the structural unit (i.e., 0.14 *vu*), then $4.8/(6 + d + 9) =$

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[3] It is possible for the number of transformer (H_2O) groups to exceed the coordination number of the interstitial cation. A hydrogen bond from a transformer (H_2O) group can link to another (H_2O) group not bonded to an interstitial cation; if the latter (H_2O) group accepts only this one hydrogen bond, it is also a transformer (H_2O) group. Thus, the number of transformer (H_2O) groups bonded to an interstitial cation cannot exceed the coordination number of that cation, but the interstitial complex may contain additional transformer (H_2O) groups involved only in hydrogen bonding.

0.14, from which $d = 19$. This range in d values exceeds the coordination number [6] (the maximum possible for Al), and, hence, only an $\{\mathrm{Al(H_2O)_6(H_2O)_0}\}^{3+}$ complex can occur with this structural unit. This result may also be seen directly by inspection of Fig. 11b.

Interstitial trivalent cations can also occur if interstitial $(\mathrm{Al}\phi_6)$ octahedra polymerize. Consider two octahedra that link together: the bridging anions will receive an incident bond valence of $\sim 0.5 \times 2 \approx 1.0$ *vu*, and, hence, these anions will be (OH) rather than $(\mathrm{H_2O})$. This being the case, the interstitial complex may be written as $\{\mathrm{Al_2(H_2O)_{12-2\mathit{f}}(OH)_{\mathit{f}}}\}^{(6-f)^+}$ with $4 \times 3 = 12$ transferred hydrogen bonds. The Lewis acidity is $(6 - f + 12h)/[(12 - 2f) \times 2 + f + 12] = (8.4 - f)/(36 - 3f)$. When $f = 2$, the Lewis acidity of the complex is 0.21 *vu*; when $f = 4$, the Lewis acidity of the complex is 0.18 *vu*. Thus, the complex has the appropriate Lewis acidity for $f = 2$, 3, and 4. However, two octahedra cannot share four anions, and hence only $f = 2$ (edge-sharing) or 3 (face-sharing) are possible. Face-sharing of $(\mathrm{Al}\phi_6)$ octahedra is unlikely in an interstitial environment, and the complex $\{\mathrm{Al_2(H_2O)_{8-10}(OH)_2}\}^{4+}$ seems more likely.

For REEs, [7]- and [8]-coordination by $(\mathrm{H_2O})$ will provide Lewis acidities in the range 0.14–0.22 *vu*. If two polyhedra link to form a dimer with f(OH) groups each linked to two cations, $\{{}^{[N]}M_2^{3+}(\mathrm{H_2O})_{2N-2f}(\mathrm{OH})_f\}^{(2N-f)^+}$, the Lewis acidity is $(8.4 - f)/([2N - 2f] \times 2 + 12 + f) = (6 - f)/(4N - 3f)$. For $N = [7]$, the dimer has the appropriate range in Lewis acidity for $f = 0$, 1, 2, and 3; for $N = [8]$, the dimer has the appropriate range in Lewis acidity for $f = 0$ and 1 (Lewis acidity = 0.15 *vu*). Thus, $\{{}^{[7]}\mathrm{Y_2(H_2O)_{13}(OH)}\}^{5+}$, $\{{}^{[7]}\mathrm{Y_2(H_2O)_{12}(OH_2}\}^{4+}$, and $\{{}^{[7]}\mathrm{Y_2(H_2O)_{11}(OH)_3}\}^{3-}$ are possible interstitial cation complexes with (OH) present. However, considering that the charge of the structural unit is 2^-, $\{{}^{[7]}\mathrm{Y_2IH_2O)_{12}(OH)_2}\}^{4+}$ produces a more stoichiometrically simple formula.

Note that the graphical approach of Fig. 11b can still be used for interstitial complexes with (OH). Consider the complex $\{{}^{[N]}M_2^{3+}(\mathrm{H_2O})_{12-2f}(\mathrm{OH})_f\}^{(6-f)^+}$. We may rewrite the "cation" as $\{M(\mathrm{OH})_{f/2}\}_2^{(3-f/2)^+} = L_2^{(3-f/2)^+}$. This manipulation has also removed (OH) from the coordination polyhedron of the M cation, and thus the coordination number of L has decreased by $d/2$. Hence, we may rewrite the complex as $\{{}^{[N-f/2]}L_2^{(3-f/2)^+}(\mathrm{H_2O})_{12-2f}]^{(6-f)^+}$. Consider the case for $f = 2$: the complex reduces to $\{{}^{[5]}L_2^{2+}(\mathrm{H_2O})_8\}^{4+} = \{{}^{[5]}L^{2+}(\mathrm{H_2O})_4\}_2^{2+}$. From the section on divalent interstitial cations, the Lewis acidity of such a complex is given by $2/(N - f) = 2/(5 + 4) = 0.22$ *vu*, the value calculated above from the composition of the complex.

The Structural Unit $[(\mathrm{UO_2})_{10}\mathrm{O_6(OH)_{11}}]^{3-}$

The structural unit $[(\mathrm{UO_2})_{10}\mathrm{O_6(OH)_{11}}]^{3-}$ (Fig. 13b) occurs only in vandenriesscheite, ${}^{[9]}\mathrm{Pb}^{2+\,[8]}\mathrm{Pb}_{0.57}^{2+}(\mathrm{H_2O})_5[(\mathrm{UO_2})_{10}\mathrm{O_6(OH)_{11}}](\mathrm{H_2O})_6$. Its anion topology can be described as an arrangement of triangles and pentagons (Burns, 1999a) with the topology code $\mathrm{P_9(UD)_{11}}$. The effective and modified charges of the structural unit are $3 + 11 \times 0.2 = 5.2^-$. The average basicity of the structural unit is $5.2/37 = 0.14$ *vu*, and the corresponding predicted range in $[\mathrm{CN}]_{in}$ is 0.60–1.00. This results in a minimum of 22 and a maximum of 37 bonds from the interstitial complex to the structural unit. The corresponding range in Lewis basicity is thus from $5.2/37$ to $5.2/22 = 0.14$ to 0.23 *vu* (Fig. 14a). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. For monovalent cations, there are a minimum of 22 and a maximum of 37 bonds from the interstitial complex to the trivalent structural unit, respectively, and the interstitial complex propagates eleven hydrogen bonds that emanate from the structural unit. Thus, the minimum and maximum number of bonds per monovalent cation are $(22 - 11)/3 = 3.7$ and $(37 - 11)/3 = 8.7$, respectively, resulting in a coordination number of [8.5] or lower for monovalent interstitial cations.

This structural unit has a net charge of 3^- and, hence, requires 1.5 divalent cations or 1 trivalent cation in the interstitial complex. The maximum and minimum numbers of bonds from interstitial complexes with only divalent interstitial cations can be calculated from the expressions $5.2/(d + N + 11) = 0.14$ *vu* and $5.2/(d + N + 11) = 0.23$ *vu*, where N is the sum of the coordination numbers of the 1.5 constituent divalent interstitial cations. Consider first the case for divalent cations of coordination number $[n]$. The aggregate coordination number $[N]$ can be written as $N = n + n/2$. These expressions simplify to $2d + 3n = 22.6$ and 52.2, respectively. For possible coordination numbers [6]–[10], the values of d can be calculated for the minimum and maximum values of the Lewis basicity to give the range in values of d in each case (selected values are shown in Table 2). Vandenriesscheite, ${}^{[9]}\mathrm{Pb}^{2+\,[8]}\mathrm{Pb}_{0.57}^{2+}(\mathrm{H_2O})_6[(\mathrm{UO_2})_{10}\mathrm{O_6(OH)_{11}}](\mathrm{H_2O})_5$, contains the interstitial complex $\{{}^{[9]}\mathrm{Pb}^{2+\,[8]}\mathrm{Pb}_{0.57}^{2+}(\mathrm{H_2O})_1(\mathrm{H_2O})_5\}$ with $N = 13$ and $d = 1$; thus, its Lewis acidity is $5.2/13 + 1 + 11 = 0.21$ *vu*, matching the predicted range in Lewis basicity.

For trivalent cations, the equations predicting the range of d, the amount of transformer $(\mathrm{H_2O})$ groups per cation, are as follows: $5.2/(d + N + 11) = 0.14$ and $5.2/(d + N + 11) = 0.23$ *vu*, where N is the coordination number of the trivalent interstitial cation. These equations reduce to $d + N = 11.6$ and 26.1, respectively. For $N =$

[6], [7], [8], and [9], the predicted ranges of d are as follows: 6, 5–7, 4–8, and 3–9 per interstitial cation.

The Structural Unit $[(UO_2)_4O_3(OH)_4]^{2-}$

The structural unit $[(UO_2)_4O_3(OH)_4]^{2-}$ occurs in fourmarierite, $^{[9]}Pb^{2+}(H_2O)_2[(UO_2)_4O_3(OH)_4](H_2O)_2$ (Fig. 13c). Its anion topology is identical to the anion topology of the neutral structural unit in schoepite, $[(UO_2)_8O_2(OH)_{12}]^0$, and can be described as an arrangement of triangles and pentagons (Burns, 1999a) with the topology code $P_3(UD)_6$. The effective and modified charges of the structural unit are $2 + 4 \times 0.2 = 2.8^-$. The average basicity of the structural unit is $2.8/15 = 0.19$ *vu*, and the corresponding predicted range in $[CN]_{in}$ is 0.80–1.20. This results in a minimum of 12 and a maximum of 18 bonds from the interstitial complex to the structural unit. The corresponding range in Lewis basicity is from 2.8/18 to 2.8/12 = 0.155–0.23 *vu* (Fig. 14b). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. The maximum and minimum numbers of bonds from an interstitial complex can be calculated from the relations $2.8/(d + N + 4) = 0.155$ and $2.8/(d + N + 4) = 0.23$ *vu*, where N is either the sum of coordination numbers of two monovalent cations or the coordination number of a divalent cation. The maximum value of $(N + d)$ is 14, and, hence, the average coordination number of two monovalent interstitial cations cannot exceed [7]. The minimum value of $(N + d)$ is eight, and, thus, [6]-coordinated divalent cations ($N = 6$) must bond to a minimum of two transformer (H_2O) groups ($d = 2$) and [7]- to [9]-coordinated divalent cations can bond to a minimum of one and a maximum of 5–7 transformer (H_2O) groups, respectively.

In fourmarierite, $^{[9]}Pb^{2+}(H_2O)_2[(UO_2)_4O_3(OH)_4](H_2O)_2$, the [9]-coordinated Pb^{2+} cation bonds to two (H_2O) groups. We do not know if these (H_2O) groups are transformer or nontransformer; however, the range in $(N + d)$ values allows both possibilities. For trivalent cations, $(N + d)$ must be between 12 and 21, and hence [6]- and [8]-coordinated cations must occur with minima of 6 and 4 transformer (H_2O) groups, respectively.

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

The structural unit $[(UO_2)_3O_3(OH)_2]^{2-}$ (Fig. 14d) occurs in richetite, $^{[6]}M_x\,^{[8.4]}Pb^{2+}_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$; protasite, $^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$; and masuyite, $^{[10]}Pb^{2+}(H_2O)_3[(UO)_2)_3O_3(OH)_2]$. Its anion topology can be described as an arrangement of triangles and pentagons (Burns, 1999a) with the topology code $P_6(UD)_5$, and its effective and modified charges are $2 + 2 \times 0.2 = 2.4^-$. The average basicity of the structural unit is $2.4/11 = 0.22$ *vu*, and the corresponding predicted range in $[CN]_{in}$ 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 *vu* (Fig. 14c). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. The maximum and minimum numbers of bonds from an interstitial complex to the structural unit can be calculated from the expressions $2.4/(d + N + 2) = 0.24$ *vu* and $2.4/(d + N + 2) = 0.16$ *vu*, where N is the sum of the coordination numbers of two monovalent cations or the coordination number of a divalent cation. The resulting range in $(N + d)$ bonds is 8–13, from which we can directly predict the possible interstitial cations and the corresponding number, d, of transformer (H_2O) groups. The average coordination number of two monovalent cations cannot exceed [6], a divalent octahedrally coordinated cation must bond to one transformer (H_2O) group, and higher coordinated divalent cations ([7]–[12]) cannot bond to transformer (H_2O) groups. In richetite, $^{[6]}M_x\,^{[8.4]}Pb^{2+}_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$; protasite, $^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$; 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 0–3 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 $^{[6]}(Mg + Fe^{2+})$.

The range in $(N + d)$ bonds for a trivalent cation is 12–20; thus [6]- and [8]-coordinated cations must bond to a minimum of 6 or 4 transformer (H_2O) groups, respectively.

The Structural Unit $[(UO_2)_8O_8(OH)_6]^{6-}$

The structural unit $[(UO_2)_8O_8(OH)_6]^{6-}$ (Fig. 13e) occurs in curite, $^{[9]}Pb^{2+}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$, and its anion topology can be described as an arrangement of triangles, squares and pentagons with the topology code $(UD)_6(U^m)_6$. The structural unit has effective and modified charges of $6 + 6 \times 0.2 = 7.2^-$, an average basicity of $7.2/30 = 0.24$ *vu*, and a range of $[CN]_{in}$ of 1.00–1.45. The minimum and maximum numbers of bonds are 25.5 and 43.5, respectively, and this corresponds to a range in Lewis basicity of 0.17–

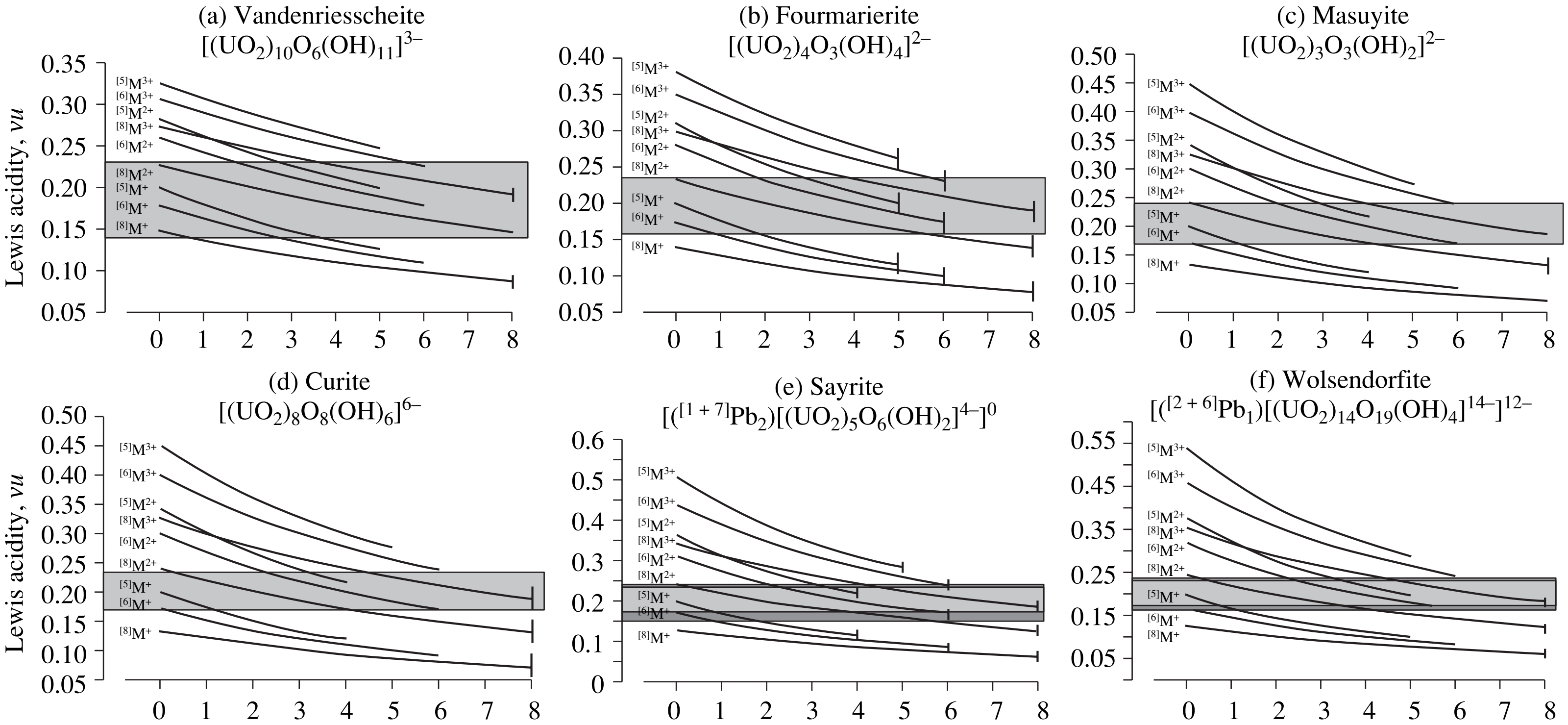

Fig. 14. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the ranges in basicity of the different structural units are shown by the shaded fields: (a) $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$; (b) $[(UO_2)_4O_3(OH)_4]^{2-}$, (c) $[(UO_2)_3O_3(OH)_2]^{2-}$; (d) $[(UO_2)_8O_8(OH)_6]^{6-}$; (e) $[(UO_2)_5O_6(OH)_2]^{4-}$; (f) $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$.

0.24 *vu* (Fig. 14d). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. For the Lewis acidity of the interstitial complex to fall within the range of Lewis basicity of the structural unit, $7.2/(N + d + 6) = 0.17$–0.24. The resulting range in possible values of $(N + d)$ is 24–38, where N is the sum of the coordination numbers of six monovalent cations or three divalent cations. First, let us consider the case for monovalent interstitial cations. For monovalent cations not bonded to any transformer (H_2O) groups, the average coordination number must fall within the range (24–38)/6 = [4]–[6.3]. The presence of transformer (H_2O) groups decreases these coordination numbers (by [1] per transformer (H_2O) group per cation). Hence, only low coordination numbers (i.e., ~[6] or less) are possible for monovalent interstitial cations. Now, let us consider the case for divalent interstitial cations. The average coordination number must fall within the range (24–38)/3 = [8]–[12.7], and the presence of transformer (H_2O) groups decreases these values; thus, divalent interstitial cations with coordination numbers [6], [7], [8], [9], and [10] have 2–6, 1–6, 0–5, 0–4, and 0–3 transformer (H_2O) groups, respectively. Following the same argument for trivalent interstitial cations gives the following result: [6]-, [7]-, [8]-, and [9]-coordinated cations have 6, 5–7, 4–8, and 3–9 transformer (H_2O) groups, respectively.

Curite has the interstitial complex $\{{}^{[9]}Pb_3^{2+}(H_2O)_0(H_2O)_2\}^{6+}$. Our prediction above suggests 0–4 transformer (H_2O) groups per ${}^{[9]}Pb^{2+}$ cation, for a total predicted range of 0–12 transformer (H_2O) groups; the observed value of 0 transformer groups is within the predicted range.

The Structural Unit $[(UO_2)_5O_6(OH_2)]^{4-}$

The structural unit $[(UO_2)_5O_6(OH)_2]^{4-}$ (Fig. 13f) occurs in sayrite, ${}^{[9]}Pb_2^{2+}(H_2O)_4[(UO_2)_5O_6(OH)_2]$ (ignoring stereoactive lone-pair effects), and its anion topology can be described as an arrangement of triangles, squares, and pentagons (Burns, 1999a) with the topology code $P_4(UD)_8R_5$. The structural unit has effective and modified charges of 4.4^-, its average basicity is 4.4/18 = 0.244 *vu*, and the predicted range of $[CN]_{in}$ 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 *vu* (Fig. 14e). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. The maximum and minimum numbers of bonds from the interstitial complex can be calculated from the relations $2.4/(N + d + 2) = 0.24$ and $2.4/(N + d + 2) = 0.17$ *vu*, where N is the average coordination number of four monovalent or two divalent interstitial cations, respectively. The range in $(N + d)$ is thus 16–24. As a result, the average coordination number of four monovalent cations can vary between (16–24)/6 = [4] and [6]. The presence of transformer (H_2O) groups will decrease these values accordingly. Thus, [6]-coordination with no transformer (H_2O) groups is the most likely option for monovalent interstitial cations. For interstitial cations, the average coordination number is in the range [8]–[12] for no transformer (H_2O) groups. The following coordination numbers can occur with the associated ranges of transformer (H_2O) groups per cation: [6], [7], [8], [9], and [10] with 2–6, 1–5, 0–4, 0–3, and 0–2, respectively.

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 average basicity of this modified structural unit is 0.189 *vu*, and, hence, the minimum and maximum values of $[CN]_{in}$ are 0.80 and 1.25, respectively. The number of O atoms in the structural unit is 18, and thus 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 *vu*, respectively (shown in darker shading in Fig. 14e). There are 2 (hydrogen bonds) + 7 × 2 (weak Pb^{2+}–O bonds) between structural units, with a mean Lewis acidity of 0.21 *vu*; this falls within the Lewis basicity range for this structural unit and, thus, the lower limit for transformer (H_2O) groups is zero. For the Lewis acidity to fall above the lower range of Lewis basicity (i.e., 0.15 *vu*), $0.21 \times 16/(16 + d) \geq 0.15$, from which $d \leq 6.4$. Thus, the allowed 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.

The Structural Unit $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$

The structural unit $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$ (Fig. 13g) occurs in wölsendorfite, ${}^{[8.4]}Pb_{6.2}^{2+}\,{}^{[8]}Ba_{0.4}(H_2O)_{10}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$ (ignoring stereoactive lone-pair effects), and its anion topology can be described as an arrangement of triangles, squares, and pentagons (Burns, 1999a) with the topology code $P_6(UD)_{22}R_9$. The structural unit has effective and modified charges of $14 + 4 \times 0.2 = 14.8^-$ (ignoring stereoactive lone-pair effects for Pb^{2+}), an average basicity of 14.8/51 = 0.29 *vu*, and a range of $[CN]_{in}$ of 1.20–1.65. This results in a minimum of 61 and a maximum of 84 bonds to the interstitial complex, and the range in Lewis basicity is thus 0.175–0.24 *vu* (Fig. 14f). The predicted chemical compositions of all interstitial complexes are summarized in Table 5.

Restrictions on the chemical composition of possible interstitial complexes. For the Lewis acidity to fall within the range of Lewis basicity of the structural unit, then $14.8/(N + d + 4) = 0.175–0.24$. The possible range in $(N + d)$ is 54–80, where N is the sum of the coordination numbers of 14 monovalent cations or seven divalent cations. For the case where there are no transformer (H_2O) groups, the average coordination number of 14 monovalent cations must be between [4.0] and [5.7] and that of seven divalent cations between [8.1] and [11.4]. It is apparent that possible interstitial complexes cannot contain just monovalent cations, irrespective of the presence or absence of transformer (H_2O) groups (except perhaps for [6]-coordinated cations with no transformer (H_2O) groups). For divalent cations, a wide range of coordination numbers are possible.

Wölsendorfite has one Pb^{2+} cation that is lone pair–stereoactive, and other Pb^{2+} cations that are not lone pair–stereoactive. The lone pair–stereoactive Pb^{2+} has two short bonds to the structural unit, which must thus be written as $[^{[2+6]}Pb^{2+}(UO_2)_{14}O_{19}(OH)_4]^{12-}$; the resulting interstitial complex is $\{^{[8.15]}(Pb^{2+}_{5.2}Ba_{0.4})(H_2O)_{0–2})(H_2O)_{10–8}\}^{11.6+}$, where d- and e-type (H_2O) groups are considered together; i.e., $d + e = 0–2$, $g = 10–8$. The modified charge of the structural unit $14^- + 0.5^+ \times 2 + 0.2^- \times 4 = 13.8^-$ and the number of O atoms in the structural unit is 51; hence, the average basicity is $13.8/51 = 0.27$ *vu*. The resulting range in $[CN]_{in}$ is 1.15–1.60, and thus the minimum and maximum numbers of bonds to the structural unit are 58.7 and 81.6, respectively. The effective charge of the structural unit is 13.8^-, and hence the range in Lewis basicity of the structural unit is 0.17–0.235 *vu* (shown in darker shading in Fig. 14f). For an [8]-coordinated divalent cation, Fig. 14f predicts 0–4 transformer (H_2O) groups per interstitial cation, and the interstitial complex in wölsendorfite lies within this range.

POSSIBLE OCCURRENCE OF RADIONUCLIDES IN URANYL OXIDE-HYDROXY HYDRATE MINERALS

We are now in the position to predict the occurrence of radionuclide isotopes in interstitial complexes of uranyl oxide-hydroxy hydrate minerals. These cations are most likely monovalent, divalent and, trivalent cations such as Cs, K, Sr and actinides such as Ac, Am, Cm, Bk, Cf, Es, Fm, and Lr. On the basis of the above arguments, we expect that monovalent cations such as Cs and K will most likely occur with structural units of low average basicity (i.e., <0.22 *vu*). This is the case in synthetic $K_5[(UO_2)_{10}O_8(OH)_9]$ (Burns and Hill, 2000a) and $Cs_3[(UO_2)_{12}O_7(OH)_{13}](H_2O)_3$ (Hill and Burns, 1999) in which the corresponding structural units have average basicities of 6.8/37 = 0.18 *vu* and 5.6/44 = 0.13 *vu*, respectively.

Interstitial complexes with divalent radionuclides such as Sr should occur with all structural units, and they do not require any transformer (H_2O) groups. For example, Burns and Hill (2000b) synthesized the Sr analogue of curite, $Sr_{2.84}(H_2O)_2[(UO_2)_4O_4(OH)_3]_2(H_2O)_2$, in which the interstitial complex $\{^{[10]}Sr_{2.84}(H_2O)_0(H_2O)_2\}$ does not contain any transformer (H_2O) groups. Trivalent actinides occur generally in [6]- to [10]-coordination. This means that they can occur in interstitial complexes of all uranyl oxide-hydroxy hydrate minerals, but, depending on their coordination number, they must bond to additional transformer (H_2O) groups (Table 5).

AN ACTIVITY–ACTIVITY DIAGRAM FOR URANYL OXIDE-HYDROXY HYDRATE MINERALS

We can calculate an activity–activity diagram for $\log[M^{2+}]/[H]^2$ (M = Ca, Ba, Pb^{2+}, K_2, Na_2) versus $\log[H_2O]$ for all structural units in uranyl oxide-hydroxy hydrate minerals and synthetic compounds (Figs. 15a, 15b). The construction of such diagrams has been described in detail by Schindler and Hawthorne (2001c). All minerals in this diagram are related via combinations of the general equations:

$$\{M^{2+}_n \text{ interstitial complex}\}^{z+}[(UO_2)_kO_l(OH)_m]^{z-} + a(H_2O) + a\{M^{2+}\}$$

$$\longleftrightarrow \{M^{2+}_{n+a} \text{ interstitial complex}\}^{(z+2a)+}[(UO_2)_kO_{l+a}(OH)_m]^{(z+2a)-} + 2aH^+, \quad [1]$$

$$\{M^{2+}_n \text{ interstitial complex}\}^{z+}[(UO_2)_kO_l(OH)_m]^{z-} + a(H_2O) + b\{M^{2+}\}$$

$$\longleftrightarrow \{M^{2+}_{n+b} \text{ interstitial complex}\}^{(z+2b)+}[(UO_2)_kO_{l-a+b}(OH)_{m+2a-2b}]^{(z+2b)-} + 2bH^+, \quad [2]$$

$$\{M^{2+}_n \text{ interstitial complex}\}^{z+}[(UO_2)_kO_l(OH)_m]^{z-} + aM^{2+}$$

$$\longleftrightarrow \{M^{2+}_{n+a} \text{ interstitial complex}\}^{(z+2a)+}[(UO_2)_kO_{l+a}(OH)_{m-2a}]^{(z+2a)-} + 2aH^+, \quad [3]$$

$$\{M^{2+}_n \text{ interstitial complex}\}^{z+}[(UO_2)_kO_l(OH)_m]^{z-} + a(H_2O)$$

$$\longleftrightarrow \{M^{2+}_n \text{ interstitial complex}\}^{z+}[(UO_2)_kO_{l-a}(OH)_{m+2a}]^{a-}. \quad [4]$$

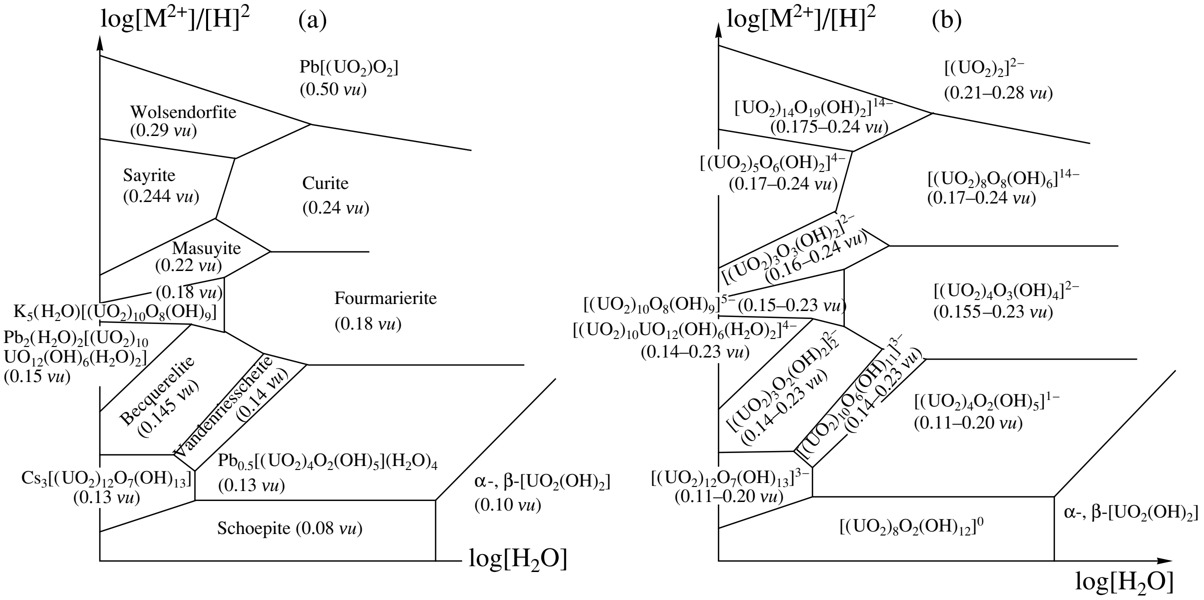

Fig. 15. (a) An activity–activity diagram: $\log[M^{2+}]/[H]$ versus $\log[H_2O]$ for selected uranyl oxide-hydroxy hydrate minerals. The diagram has been calculated without considering different types of interstitial cations (e.g., Pb^{2+}, Ca) or the possible influence of Eh, and stereoactive lone-pair effects are not considered. The corresponding average basicity of the structural unit is given in parentheses. (b) The general occurrence of the structural units in the activity–activity diagram with the corresponding ranges in Lewis basicity.

These general equations do not consider the number of interstitial (H_2O) groups because their number varies with the type of M cation(s) in the interstitial complex or with slightly different temperatures during crystallization. For example, the structural units in schoepite, metaschoepite, and dehydrated schoepite have the composition $[(UO_2)_8O_2(OH)_{12}]$ (Finch *et al.*, 1996; Weller *et al.*, 1999; Finch *et al.*, 1998). All three minerals can be synthesized in aqueous solution at similar values of $\log[M^{2+}]/[H]^2$ but at slightly different temperatures. Hence, they have overlapping stability fields, despite their different numbers of interstitial (H_2O) groups.

From the law of mass action, we may then write the following relations for all equations:

$$\log[M^{2+}]/[H]^2 = a/b\log[H_2O] + \log K, \quad [1]$$

$$\log[M^{2+}]/[H]^2 = \log K, \quad [2]$$

$$a\log[H_2O] = \log K. \quad [3]$$

We do not know $\log K$, and hence our calculated values are only on a relative basis. However, the slope of the boundary between stability fields is given by either a/b, 0, or $a\log[H_2O]$ (which we do know), and, hence, we can construct an activity–activity diagram with the correct topology. The activity of $[H_2O]$ is 1 in water and, therefore, does not affect the stability of minerals grown in aqueous solution. However, we can use the activity of $\log[H_2O]$ in order to understand how the degree of polymerization of the structural unit and the chemical composition of the interstitial complex change with the amount of (H_2O) in the structural unit (see below). Figures 15a and 15b show the stability fields of the structural units and indicate the corresponding minerals and compounds, the average basicity and chemical composition of the structural units, and the corresponding range in Lewis basicity.

Average Basicity and pH

Schindler *et al.* (2000b) and Schindler and Hawthorne (2001c) showed that, in reactions of the type

$$[B_kO_n(OH)_m]^{a-} + xH^+ \longleftrightarrow [B_kO_{n-x}(OH)_{m+x}]^{(a-x)-} \quad [5]$$

and

$$[V_kO_n]^{a-} + 2xH^+ \longleftrightarrow [V_kO_{n-2x}]^{(a-2x)-} + xH_2O \quad [6]$$

the average basicity decreases in the forward reaction; i.e., an increase in pH favors formation of the structural unit with a higher average basicity. Because reactions [5] and [6] also apply to the formation of aqueous species in solution, the average basicities of structural units and aqueous species correlate with the pH of the solution. This emphasizes that the pH controls the crystallization of minerals via condensation of the principal species in solution.

Equations [1]–[3] are similar to Eqs. [5] and [6], and thus we expect that formation of structural units with higher average basicity is favored by an increase in pH. This indeed the case: the average basicity of structural units increases with increasing $\log[M^{2+}]/[H]^2$ (i.e., with increasing pH or increasing activity of [M^{2+}]; Fig. 15a). Hence, average basicity correlates with increasing Pb^{2+}/U^{6+} in uranyl oxide-hydroxy hydrate minerals, and thus can be used as an indicator of the degree of weathering of primary uraninite.

Schindler and Hawthorne (2001c) showed that borate structural units related via

$$[B_kO_{n-y}(OH)_{m+2y}]^{a-} \longleftrightarrow [B_kO_n(OH)_m]^{a-} + y(H_2O), \quad [7]$$

have similar average basicities. Moreover, they observed that changes in average basicity are much smaller relative to changes involving structural units related via equations [5] and [6]. Equation [4] is similar to equation [7], and so we expect similar average basicities in the corresponding structural units. This is again the case: the structural units $[(UO_2)_4O_2(OH)_5]^{1-}$ and $[(UO_2)_{12}O_7(OH)_{13}]^{3-}$ have average basicities 0.133 and 0.127 *vu*; the structural units $[(UO_2)_4O_3(OH)_4]^{2-}$ and $[(UO_2)_{10}O_8(OH)_9]^{5-}$ have average basicities 0.183 and 0.186 *vu;* and the structural units of schoepite, α-$[(UO_2)(OH)_2]$, and β-$[(UO_2)(OH)_2]$ have average basicities 0.08, 0.10 and 0.10 *vu*, respectively (Figs. 15a, 15b).

Lewis Basicity, Average Basicity, and pH

For uranyl oxide-hydroxy hydrate minerals (Table 4), the minimum and maximum Lewis basicities of a structural unit increase with increasing average basicity. The minimum and maximum Lewis basicities increase from 0.14–0.23 *vu* for the structural unit $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$ (with an average basicity of 0.14 *vu*) to 0.20–0.29 *vu* for the structural unit $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$ (with an average basicity of 0.29 *vu*). Hence, minimum and maximum Lewis basicities of a uranyl oxide-hydroxy hydrate structural unit correlate with pH and $\log[M^{2+}]$ (Fig. 15b).

Change in Topology of the Structural Unit with Increasing $\log[M^{2+}]/[H]^2$ *and* $\log[H_2O]$

Figure 16 shows the activity–activity diagram with the codes of the anion topology of the corresponding structural units. The structural units in α-$[(UO_2)(OH)_2]$, β-$[(UO_2)(OH)_2]$, and $Pb[(UO_2)O_2]$ are the only structural units which contain only H and R chains. These chains contain U^{6+} in [8]-coordination or in [6]-coordination. All other structural units contain a combination of P, U, D, R, U^m, and $U^{m'}$ chains, and the corresponding average coordination numbers of U^{6+} are between [6] and [7] (Fig. 16). In this group, structural units with a high amount of [H_2O] and at low $\log[M^{2+}]/[H]^2$ have $P_3(UD)_6$ topology, structural units at moderate values of $\log[M^{2+}]/[H]^2$ have either $U^{m'}$ or $P_3(UD)_6$ topology, and structural units at high values of $\log[M^{2+}]/[H]^2$ have $(UD)_6(U^m)_6$ topology. The situation is different in structural units with less [H_2O]: at low values of $\log[M^{2+}]/[H]^2$, they contain a high ratio of P to (UD) chains, whereas at high values of $\log[M^{2+}]/[H]^2$, they contain low ratios of R to (UD) chains. The explanation for this is straightforward: U, D, U^m, and $U^{m'}$ chains contain triangles, which are not occupied by U^{6+} cations. Hence, the corresponding structural units have lower packing densities of uranyl polyhedra (i.e., a lower degree of polymerization). Transformation of a structural unit with a high degree of polymerization to a structural unit with a low degree of polymerization is always favored by increasing activity of [H_2O]. Furthermore, the arrangement of chains with triangles in the layer structural units results in [2]-coordinated O atoms that link two $(U\phi_7)$ polyhedra. These O atoms receive (on average) $2 \times 0.54 = 1.08$ *vu* from the two $^{[7]}U^{6+}$–O bonds and require an additional 0.92 *vu*; this bond valence can be only contributed by an O–H bond, which means that [2]-coordinated O atoms almost always involve an (OH) group. Thus, structural units with a high ratio of (UD), U^m, or $U^{m'}$ chains to P and R chains have a lower degree of polymerization and a higher number of (OH) groups; their formation is favored by an increase in the activity of [H_2O], and their stability fields occur at higher activities of $\log[H_2O]$ on an activity–activity diagram (Fig. 16).

The increase in R, U^m, or $U^{m'}$ chains with increasing $\log[M^{2+}]/[H]^2$ results in a decrease in the average coordination number of U^{6+} from [7] to [6] (Fig. 16). Burns *et al.* (1997) showed that $\{(UO_2)\phi_4\}$ polyhedra more commonly share corners than edges with other uranyl polyhedra. This means that increasing $^{[6]}U^{6+}$ reduces the number of edge-shared polyhedra and slightly reduces the degree of polymerization of the structural unit. In turn, this depolymerization reduces the sum of bond valences from the U^{6+} cations to O atoms in the structural unit and increases the average basicity of the structural unit. Furthermore, the ratio of $(UO_2)^{2+}$ to (OH) groups in structural units decreases with increasing $\log[M^{2+}]/[H]^2$ (Fig. 15b). This reduces the sum of bond valences from U^{6+} cations incident at O atoms, again resulting in an increase in average basicity.

We can summarize structural changes in the activity–activity diagram as follows:

(1) Depolymerization through change from P to (UD) or R to U^m or $U^{m'}$ correlates with a decrease in the $(UO_2)^{2+}/(OH)$ ratio and is favored by increase in [H_2O] activity. This process changes only slightly the average basicity (and hence the range of Lewis basicity).

(2) Depolymerization through decrease in the coordination number of U^{6+} and increase in the $(UO_2)^{2+}/(OH)$ ratio is favored by increase in

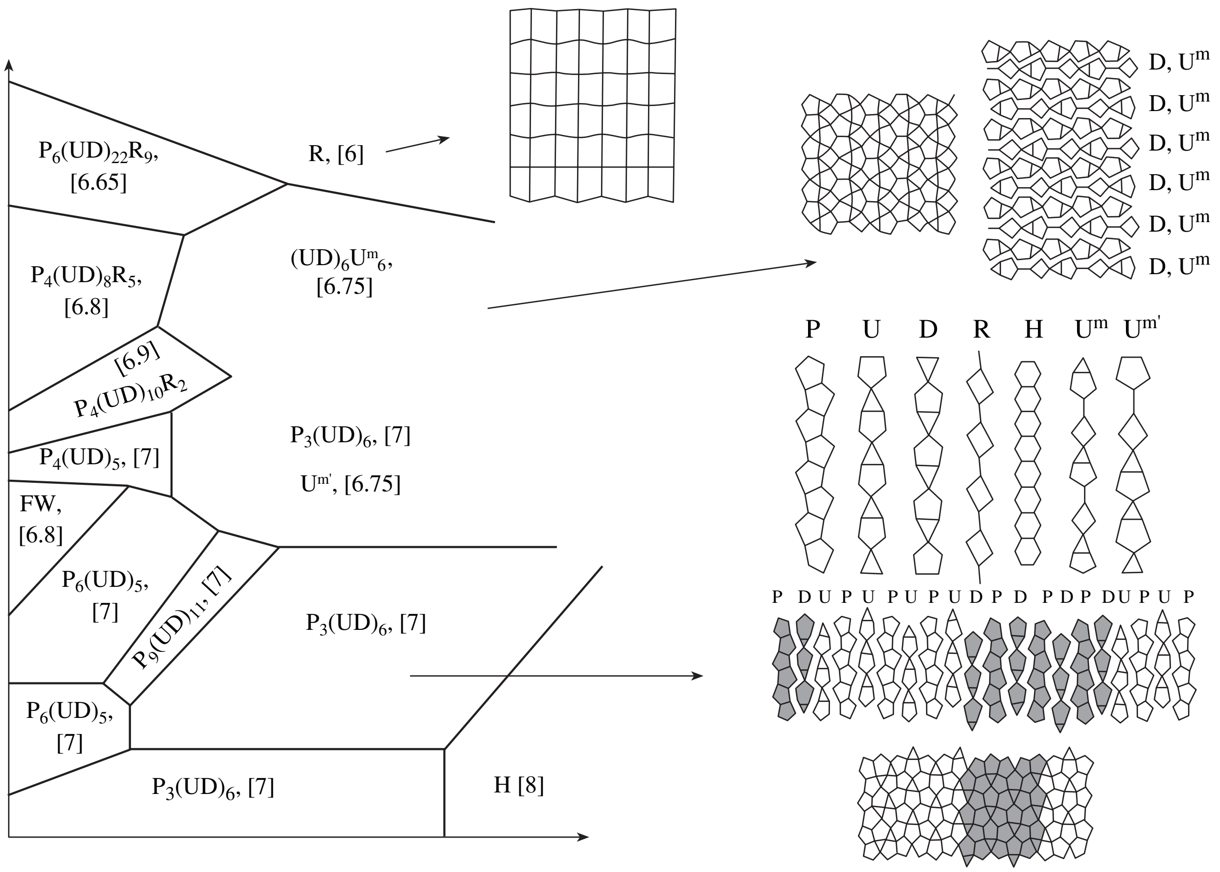

Fig. 16. The chain-stacking sequences of the corresponding anion topologies in the activity–activity diagram. FW indicates framework. Three examples are shown to the right: the anion topology in synthetic $Pb^{2+}[(UO_2)O_2]$ (top), curite (center), and schoepite (bottom). The average coordination number of U is shown in square brackets.

$\log[M^{2+}]/[H]^2$, and results in an increase in average basicity and in the range of Lewis basicity.

Chemical Composition of Interstitial Complexes and the Topology of the Structural Unit

The occurrence of interstitial cations in minerals depends on the range of Lewis basicity of the structural unit and on the mole proportion of (H_2O) in the structural unit (Figs. 15a, 15b). We also know that the mole proportion of (H_2O) in the structural unit is related to whether the structural unit has $P_6(UD)_5$–$P_3(UD)_6$ or $P_4(UD)_8R_5$–$(UD)_6U^m_6$ topology (Fig. 16). Figure 17 summarizes this information and also indicates the corresponding ratios of the number of uranyl groups and (OH) groups in the structural unit. It is apparent that Pb^{2+} cations only occur with structural units of topology $P_6(UD)_5$ and with $(UO_2)/(OH) > 1$. There are three notable differences between the occurrence of Pb^{2+} cations with the more highly polymerized structural units $P_6(UD)_5$, $P_4(UD)_8R_5$, and $P_6(UD)_{22}R_9$ (Fig. 17, left side) and with the less highly polymerized structural units $P_3(UD)_6$ and $(UD)_6U^m_6$:

(1) Pb^{2+} is disordered over more than one site in the interstices of the more highly polymerized structural units (masuyite, richetite, wölsendorfite).

(2) As a result of stereoactive lone-pair behavior, Pb^{2+} occurs in more distorted environments in the interstices of the more highly polymerized structural units (sayrite, wölsendorfite).

(3) None of the minerals with more highly polymerized structural units have yet been synthesized.

These three points suggest that the geometrical features of structural units with $P_3(UD)_6$ topology may better match the size and coordination number of $(Pb^{2+}\phi_n)$ polyhedra and therefore such compositions are more easily synthesized.

Figure 17 shows that alkali and alkaline-earth cations occur only in minerals with structural units of $P_6(UD)_5$ and $P_4(UD)_8R_5$ topology. They only occur with less highly polymerized structural units of $U^{m'}$ and $(UD)_6U^m_6$ topology in synthetic compounds (Table 5). However, more highly coordinated monovalent cations occur with structural units of $P_6(UD)_5$ and $P_4(UD)_8R_5$ topology in minerals and synthetic compounds. The reason for this becomes apparent when we consider that the corresponding interstitial complexes have more cations than interstitial complexes with divalent cations only and the corresponding structural units have a higher density of bond-valence acceptors than structural units with $P_3(UD)_6$ or $(UD)_6U_6^m$ topology. Hence, interstitial complexes with alkali and alkaline-earth isotopes as products of nuclear fission will occur with structural units of $P_6(UD)_5$ topology rather than with structural units of $P_3(UD)_6$ topology.

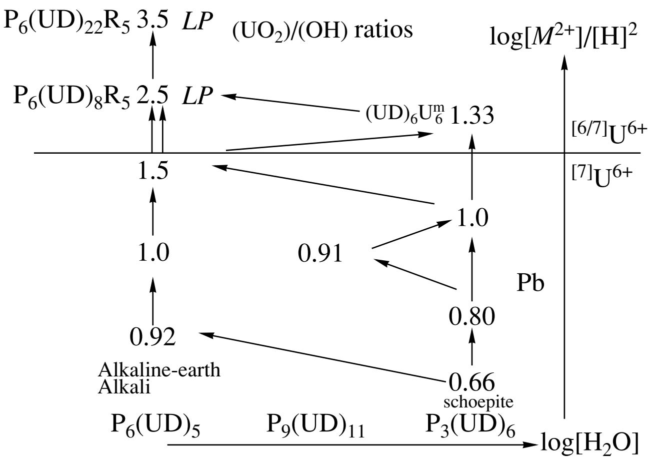

Fig. 17. Schematic of the general occurrence of Pb^{2+} and alkali and alkaline-earth cations in structural units of minerals with different layer topologies and different ratios of $(UO_2)/(OH)$. The arrows indicate the possible sequence of change in structural units during weathering processes with increase in $\log[M^{2+}]/[H]^2$; $(UO_2)/(OH)$ ratios are shown. The horizontal line indicates a change in the coordination number of U^{6+} from exclusively [7]-coordinated in $P_6(UD)_5$, $P_9(UD)_{11}$, and $P_3(UD)_6$ to [7]–[6]-coordinated in $(UD)_6U_6^m$, $P_4(UD)_8R_5$, and $P_6(UD)_{22}R_5$. The occurrence of stereoactive lone-pair electrons in Pb^{2+} is indicated by *LP*.

SUMMARY

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

(2) The interstitial complex is an array of large low-valence cations, usually monovalent anions and (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

$$\{^{[m]}M_a^{+}\,^{[n]}M_b^{2+}\,^{[l]}M_c^{3+}(H_2O)_d(H_2O)_e\,^{[q]}(OH)_f(H_2O)_g\}^{(a+2b+3c-f)+},$$

where [*n*], [*m*], [*l*], and [*q*] are coordination numbers; *a*, *b*, and *c* are the numbers of monovalent, divalent, and trivalent cations; *d* is the number of *transformer* (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 *average basicity* of a structural unit is defined as the effective charge divided by the number of O atoms in the structural unit.

(10) The average basicity 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 of the average O atom coordination number (by which the structural unit responds to small changes in pH 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. The maximum and minimum coordination numbers are multiplied by the number of O atoms in the structural unit to give the minimum and maximum numbers of bonds required from the interstitial complex by the O atoms of the structural unit. The minimum and maximum numbers of bonds required by the structural unit from the interstitial complex are the min-

imum and maximum total numbers of bonds minus the number of bonds within the structural unit. The range in Lewis basicity of the structural unit is its effective charge divided by the maximum and minimum numbers of bonds required by the structural unit from the interstitial complex.

(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 uranyl oxide-hydroxy hydrate minerals shows that there are 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 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 all cases, they are accurate.

(16) Structural units of uranyl oxide-hydroxy hydrate minerals may be formally related by two types of chemical reactions, one of which consumes H and the other of which consumes (H_2O).

(17) Combining these equations with the law of mass action leads to an expression that allows arrangement of structural units in $\log[M^{2+}]/[H]^2 – \log[H_2O]$ space and calculation of the slopes of the associated phase boundaries. The result is an activity–activity diagram with the correct topology and a relative scale along each axis.

(18) Structural units of similar topology occur in contiguous fields of the activity–activity diagram, and the general classes of polymerization of P, U, and D chains in the structural units change systematically across this activity–activity diagram. Depolymerization through change from P to (UD) or R to U^m or $U^{m'}$ chains correlates with decreasing $(UO_2)^{2+}/(OH)$ ratio and increasing $[H_2O]$ activity. Depolymerization through decreasing coordination number of U^{6+} and increasing $(UO_2)^{2+}/(OH)$ ratio is favored by increasing $\log[M^{2+}]/[H]^2$, and results in an increase in average basicity and in the range of Lewis basicity.

(19) In accord with the principle of correspondence of Lewis acidity–basicity, the details of the interstitial complexes show systematic variation across the activity–activity diagram. In highly polymerized structural units, interstitial Pb^{2+} tends to be disordered over more than one site. Moreover, Pb^{2+} tends to exhibit stereoactive lone-pair behavior in more highly polymerized structural units.

(20) The average basicity of structural units in uranyl oxide-hydroxy hydrate minerals varies only in the range 0.08–0.29 *vu*, in accord with the small range of pH (5–8) over which almost all of these minerals have their maximum stability. The details of the interstitial complexes in these minerals are in accord with this observation: monovalent cations are favored by moderate pH, divalent cations are favored by higher pH, and trivalent cations do not occur under any conditions.

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REFERENCES

Bandy, M.C., Mineralogy of Three Sulfate Deposits of Northern Chile, *Am. Mineral.*, 1938, vol. 23, pp. 669–760.

Brese, N.E. and O'Keeffe, M., Bond-Valence Parameters for Solids, *Acta Crystallogr.*, 1991, vol. B47, pp. 192–197.

Brown, I.D., The Bond-Valence Method: An Empirical Approach to Chemical Structure and Bonding, in *Structure and Bonding in Crystals II*, O'Keeffe, M. and Navrotsky, A., Eds., New York: Academic Press, 1981, pp. 1–30.

Brown, I.D. and Altermatt, D., Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database, *Acta Crystallogr.*, 1985, vol. B41, pp. 244–247.

Brown, I.D. and Shannon, R.D., Empirical Bond-Strength–Bond-Length Curves for Oxides, *Acta Crystallogr.*, 1973, vol. A29, pp. 266–282.

Buck, E.C., Brown, N.R., and Dietz, N.L., Contaminant Uranium Phases and Leaching at the Fernald Site in Ohio, *Environ. Sci. Technol.*, 1996, vol. 30, pp. 81–88.

Burdett, J.K. and Hawthorne, F.C., An Orbital Approach to the Theory of Bond Valence, *Am. Mineral.*, 1993, vol. 78, pp. 884–892.

Burns, P.C., A New Uranyl Oxide Hydrate Sheet in Vandenriesscheite: Implications for Mineral Paragenesis and the Corrosion of Spent Nuclear Fuel, *Am. Mineral.*, 1997, vol. 82, pp. 1176–1186.

Burns, P.C., The Structure of Compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$, *Can. Mineral.*, 1998a, vol. 36, pp. 1061–1067.

Burns, P.C., The Structure of Richetite, a Rare Lead Uranyl Oxide Hydrate, *Can. Mineral.*, 1998b, vol. 36, pp. 187–199.

Burns, P.C., The Crystal Chemistry of Uranium, *Rev. Mineral.*, 1999a, vol. 38, pp. 23–90.

Burns, P.C., A New Complex Sheet of Uranyl Polyhedra in the Structure of Wölsendorfite, *Am. Mineral.*, 1999b, vol. 84, pp. 1661–1673.

Burns, P.C. and Hanchar, J.M., The Structure of Masuyite, $Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$, and Its Relationship to Protasite, *Can. Mineral.*, 1999, vol. 37, pp. 1483–1492.

Burns, P.C. and Hill, F.C., A New Uranyl Sheet in $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$: New Insight into Sheet Anion-Topologies, *Can. Mineral.*, 2000a, vol. 38, pp. 163–173.

Burns, P.C. and Hill, F.C., Implications of the Synthesis and Structure of the Sr Analogue of Curite, *Can. Mineral.*, 2000b, vol. 38, pp. 175–181.

Burns, P.C., Miller, M.L., and Ewing, R.C., U^{6+} Minerals and Inorganic Phases: A Comparison and Hierarchy of Structures, *Can. Mineral.*, 1996, vol. 34, pp. 845–880.

Burns, P.C., Ewing, R.C., and Hawthorne, F.C., The Crystal Chemistry of Hexavalent Uranium: Polyhedral Geometries, Bond-Valence Parameter, and Polymerization of Polyhedra, *Can. Mineral.*, 1997, vol. 35, pp. 1551–1570.

Cahill, C.L. and Burns, P.C., The Structure of Agrinierite: A Sr-containing Uranyl Oxide Hydrate Mineral, *Am. Mineral.*, 2000, vol. 85, pp. 1294–1297.

Casas, I., Bruno, J., Cera, E., Finch, R.J., and Ewing, R.C., Kinetic and Thermodynamic Studies of Uranium Minerals. Assessment of the Long-Term Evolution of Spent Nuclear Fuel, *SKB Technical Report 94–16*, Stockholm, 1994.

Casas, I., Bruno, J., Cera, E., Finch, R.J., and Ewing, R.C., Characterization and Dissolution Behavior of a Becquerelite from Shinkolobwe, Zaire, *Geochim. Cosmochim. Acta*, 1997, vol. 61, pp. 3879–3884.

Cremers, T.L., Eller, P.G., Larson, E.M., and Rosenzweig, A., Single-Crystal Structure of Lead Uranate(VI), *Acta Crystallogr.*, 1986, vol. C42, pp. 1684–1685.

Ferguson, R.B., A Cation–Anion Distance-Dependent Method for Evaluating Valence-Bond Distributions in Ionic Structures and Results for Some Olivines and Pyroxenes, *Acta Crystallogr.*, 1974, vol. B30, pp. 2527–2542.

Finch, R.J. and Ewing, R.C., The Corrosion of Uraninite under Oxidizing Conditions, *J. Nucl. Mater.*, 1992, vol. 190, pp. 133–156.

Finch, R.J. and Murakami, T., *Rev. Mineral.*, 1999, vol. 38, pp. 91–180.

Finch, R.J., Cooper, M.A., Hawthorne, F.C., and Ewing, R.C., The Crystal Structure of Schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, *Can. Mineral.*, 1996, vol. 34, pp. 1071–1088.

Finch, R.J., Hawthorne, F.C., and Ewing, R.C., Structural Relations among Schoepite, Metaschoepite, and “Dehydrated Schoepite,” *Can. Mineral.*, 1998, vol. 36, pp. 831–845.

Finch, R.J., Burns, P.C., Cooper, M.A., Hawthorne, F.C., and Ewing, R.C., Refinement of the Crystal-Structure of Billietite, $Ba[(UO_2)_6O_4(OH)_6](H_2O)_7$, *Can. Mineral.*, 2002 (submitted).

Fisher, D.J., Pegmatite Phosphates and Their Problems, *Am. Mineral.*, 1958, vol. 43, pp. 181–207.

Frondel, C., Systematic Mineralogy of Uranium and Thorium, *US Geol. Surv. Bull.*, 1958, vol. 1064.

Frondel, C. and Barnes, I., Structural Relations of UO_2, Isometric $PbUO_4$, and Orthorhombic $PbUO_4$, *Acta Crystallogr.*, 1958, vol. 11, pp. 562–563.

Garrels, R.M. and Christ, C.L., Behavior of Uranium Minerals during Oxidation, *US Geol. Surv. Prof. Pap.*, 1959, vol. 320, pp. 81–89.

Glatz, R.E., Li, Y., Hughes, K.A., Cahill, C.L., and Burns, P., Synthesis and Structure of a New Ca Uranyl Oxide Hydrate, $Ca[(UO_2)_4O_3(OH)_4](H_2O)_2$, and Its Relationship to Becquerelite, *Can. Mineral.*, 2002, vol. 40, pp. 217–224.

Hawthorne, F.C., The Crystal Structure of Morinite, *Can. Mineral.*, 1979, vol. 17, pp. 93–102.

Hawthorne, F.C., Graphical Enumeration of Polyhedral Clusters, *Acta Crystallogr.*, 1983, vol. A39, pp. 724–736.

Hawthorne, F.C., Towards a Structural Classification of Minerals: the $^{vi}M^{iv}T_2O_n$ Minerals, *Am. Mineral.*, 1985, vol. 70, pp. 455–473.

Hawthorne, F.C., Structural Hierarchy in $^{VI}M_x{}^{III}T_y\phi_z$ Minerals, *Can. Mineral.*, 1986, vol. 24, pp. 625–642.

Hawthorne, F.C., Structural Hierarchy in $M(T(\phi_4))$ Minerals, *Z. Kristallogr.*, 1990, vol. 192, pp. 1–52.

Hawthorne, F.C., The Role of OH and H_2O in Oxide and Oxysalt Crystals, *Z. Kristallogr.*, 1992, vol. 201, pp. 183–206.

Hawthorne, F.C., Structural Aspects of Oxide and Oxysalt Crystals, *Acta Crystallogr.*, 1994, vol. B50, pp. 481–510.

Hawthorne, F.C., Structural Aspects of Oxide and Oxysalt Minerals, *EMU Notes Mineral.*, 1997, vol. 1, pp. 373–429.

Hawthorne, F.C., Burns, P.C., and Grice, J.D., The Crystal Chemistry of Boron, *Rev. Mineral.*, 1996, vol. 33, pp. 41–110.

Hawthorne, F.C., Krivovichev, S.V., and Burns, P.C., The Crystal Chemistry of Sulfate Minerals, *Rev. Mineral.*, 2000, vol. 40, pp. 1–112.

Hill, F.C. and Burns, P.C., The Structure of a Synthetic Cs Uranyl Oxide Hydrate and Its Relationship to Compreignacite, *Can. Mineral.*, 1999, vol. 37, pp. 1283–1288.

Janeczek, J. and Ewing, R.C., Dissolution and Alteration of Uraninite under Reducing Conditions, *J. Nucl. Mater.*, 1992, vol. 190, pp. 157–173.

Langmuir, D., Uranium Solution-Minerals Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits, *Geochim. Cosmochim. Acta*, 1978, vol. 42, pp. 547–569.

Li, Y. and Burns, P.C., Investigations of Crystal-Chemical Variability in Lead Uranyl Oxide Hydrates: I. Curite, *Can. Mineral.*, 2000a, vol. 38, pp. 727–735.

Li, Y. and Burns, P.C., Investigations of Crystal-Chemical Variability in Lead Uranyl Oxide Hydrates: II. Fourmarierite, *Can. Mineral.*, 2000b, vol. 38, pp. 737–749.

Li, Y. and Burns, P.C., Synthesis and Crystal Structure of a New Pb Uranyl Oxide Hydrate with a Framework Structure That Contains Channels, *Can. Mineral.*, 2000c, vol. 38, pp. 1433–1441.

Miller, M.L., Finch, R.J., Burns, P.C., and Ewing, R.C., Descriptions and Classification of Uranium Oxide Hydrate Sheet Topologies, *J. Mater. Res.*, 1996, vol. 11, pp. 3048–3056.

Moore, P.B., A Structural Classification of Fe–Mn Orthophosphate Hydrates, *Am. Mineral.*, 1965, vol. 50, pp. 2052–2062.

Moore, P.B., Bracelets and Pinwheels: A Topological–Geometrical Approach to the Calcium Orthosilicate and Alkali Sulfate Structures, *Am. Mineral.*, 1973, vol. 58, pp. 32–42.

Moore, P.B., Laueite, Pseudolaueite, Stewartite, and Metavauxite: A Study in Combinatorial Polymorphism, *Neues Jahrb. Mineral. Abh.*, 1975, vol. 123, pp. 148–159.

Moore, P.B., Pegmatite Minerals of P(V) and B(III), *Mineral. Assoc. Can. Short Course*, 1982, vol. 8, pp. 267–291.

Moore, P.B., Crystallochemical Aspects of the Phosphate Minerals, in *Phosphate Minerals*, Niagru, J.O. and Moore, P.B., Eds., Berlin: Springer-Verlag, 1984, pp. 155–170.

Morris, D.E., Allen, P.G., Berg, J.M., Chisolm-Brause, C.J., Conradson, S.D., Hess, N.J., Musgrave, J.A., and Tait, C.D., Speciation of Uranium in Fernald Soils by Molecular Spectroscopic Methods: Characterization of Untreated Soils, *Environ. Sci. Technol.*, 1996, vol. 30, pp. 2322–2331.

Pagoaga, M.K., Appleman, D.E., and Stewart, J.M., Crystal Structures and Crystal Chemistry of the Uranyl Oxide Hydrates Becquerelite, Billietite, and Protasite, *Am. Mineral.*, 1987, vol. 72, pp. 1230–1238.

Piret, P., Structure cristalline de la fourmariérite, $Pb(UO_2)_4O_3(OH)_4 \cdot 4H_2O$, *Bull. Minéral.*, 1985, vol. 108, pp. 659–665.

Piret, P., Deliens, M., Piret-Meunier, J., and Germain, G., La Sayrite, $Pb_2[(UO_2)_5O_6(OH)_2] \cdot 4H_2O$, nouveau minéral; propriétés et structure cristalline, *Bull. Minéral.*, 1983, vol. 106, pp. 299–304.

Protas, J., Contribution à l'étude des oxydes d'uranium hydratés, *Bull. Minéral.*, 1959, vol. 82, pp. 239–272.

Pyatenko, Yu.A., Unified Approach to Analysis of the Local Balance of Valences in Inorganic Structures, *Sov. Phys. Crystallogr.*, 1973, vol. 17, pp. 677–682.

Sandino, M.C.A. and Grambow, B., Solubility Equilibria in the U(VI)–Ca–K–Cl–H_2O-System: Transformation of Schoepite into Becquerelite and Compreignacite, *Radiochim. Acta*, 1995, vol. 66/67, pp. 37–43.

Schindler, M. and Hawthorne, F.C., A Bond-Valence Approach to the Structure, Chemistry, and Paragenesis of Hydroxy-Hydrated Oxysalt Minerals: I. Theory, *Can. Mineral.*, 2001a, vol. 39, pp. 1225–1242.

Schindler, M. and Hawthorne, F.C., A Bond-Valence Approach to the Structure, Chemistry, and Paragenesis of Hydroxy-Hydrated Oxysalt Minerals: II. Crystal Structure and Chemical Composition of Borate Minerals, *Can. Mineral.*, 2001b, vol. 39, pp. 1243–1256.

Schindler, M. and Hawthorne, F.C., A Bond-Valence Approach to the Structure, Chemistry, and Paragenesis of Hydroxy-Hydrated Oxysalt Minerals: III. Paragenesis of Borate Minerals, *Can. Mineral.*, 2001c, vol. 39, pp. 1257–1274.

Schindler, M. and Hawthorne, F.C., A Bond-Valence Approach to Uranyl–Oxysalt Minerals: I. Chemical Composition, *Can. Mineral.* (submitted).

Schindler, M. and Hawthorne, F.C., A Bond-Valence Approach to Uranium Minerals: II. Paragenesis, *Can. Mineral.* (submitted).

Schindler, M., Hawthorne, F.C., and Baur, W.H., Crystal Chemical Aspects of Vanadium: Polyhedral Geometries, Characteristic Bond Valences, and Polymerization of (VO_n) Polyhedra, *Chem. Mater.*, 2000a, vol. 12, pp. 1248–1259.

Schindler, M., Hawthorne, F.C., and Baur, W.H., A Crystal-Chemical Approach to the Composition and Occurrence of Vanadium Minerals, *Can. Mineral.*, 2000b, vol. 38, pp. 1443–1456.

Schindler, M., Huminicki, D.C., and Hawthorne, F.C., A Bond-Valence Approach to the Chemical Composition and Occurrence of Sulfate Minerals, *Chem. Geol.* (accepted).

Smith, D.K., Uranium Mineralogy, in *Uranium Geochemistry, Mineralogy, Geology, Exploration, and Resources*, DeVivo, B., Ippolito, F., Capaldi, G., and Simpson, P.R., Eds., London: Institute of Mining and Metallurgy, 1984, pp. 43–88.

Taylor, J.C., Stuart, W.I., and Mumme, I.A., The Crystal Structure of Curite, *J. Inorg. Nucl. Chem.*, 1981, vol. 43, pp. 2419–2423.

Vochten, R. and van Haverbeke, L., Transformation of Schoepite into the Uranyl Oxide Hydrates: Becquerelite, Billietite, and Wölsendorfite, *Mineral. Petrol.*, 1990, vol. 43, pp. 65–72.

Weller, M.T., Light, M.E., and Gelbrich, T., Structure of Uranium(VI) Oxide Dihydrate, $UO_3 \cdot 2H_2O$; Synthetic Metaschoepite $(UO_2)_4O(OH)_5 \cdot 5H_2O$, *Acta Crystallogr.*, 1999, vol. B56, pp. 577–583.