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A BOND-VALENCE APPROACH TO THE URANYL-OXIDE HYDROXY-HYDRATE MINERALS: CHEMICAL COMPOSITION AND OCCURRENCE

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ABSTRACT

The crystal structures, chemical compositions and occurrence of uranyl-oxide hydroxy-hydrate minerals are interpreted in terms of the combined binary-representation – bond-valence approach to oxysalt minerals developed by Schindler & Hawthorne (2001a, b, c). A generalized interstitial complex can be written $[{}^{[m]}M^{+}_{a}\ {}^{[n]}M^{2+}_{b}\ {}^{[l]}M^{3+}_{c}\ (H_2O)_d\ (H_2O)_e\ {}^{[q]}(OH)_f\ (H_2O)_g]^{(a+2b+3c-f)+}$, where *d* is the number of transformer (H_2O) groups, *e* is the number of non-transformer (H_2O) groups, and *g* is the number of interstitial (H_2O) groups not bonded to any interstitial cation. The Lewis acidity of this interstitial complex can be expressed graphically as a function of the amounts and coordination numbers of monovalent, divalent and trivalent interstitial cations and the amount of interstitial transformer (H_2O) groups. The range in Lewis basicity for a specific structural unit may also be expressed graphically. Where there is overlap of the Lewis acidity and Lewis basicity, the valence-matching principle is satisfied, and the details of the possible interstitial complexes can be derived. Detailed predictions of the compositions of other 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 their chemical composition [molar ratio (MO) + (H_2O) : (UO_3)]. The type of interstitial cations and the general classes of polymerization of P-, U- and D-type chains in the structural units change systematically with log $[M^{2+}] / [H^{+}]^2$ and $[(MO)] + H_2O] / [UO_3]$. Structural units may be formally related by a chemical reaction that consumes two H^+ and one M^{2+} cation. Combining this equation with the law of mass action, an expression can be formulated that allows arrangement of the structural units in log $[M^{2+}]$–H 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-type chains in the structural units change systematically across this activity–activity diagram.

Keywords: uranyl-oxide minerals, binary representation, bond-valence theory, activity–activity diagrams.

SOMMAIRE

Nous interprétons les structures cristallines, les compositions chimiques et les modes d'incidence de minéraux à oxyde uranylé hydroxylé-hydraté en termes d'une démarche combinée de représentation binaire et des valences de liaison telle qu'appliquée aux minéraux oxysels par Schindler et Hawthorne (2001a, b, c). On peut écrire la formule d'un complexe interstitiel généralisé sous forme de $[{}^{[m]}M^{+}_{a}\ {}^{[n]}M^{2+}_{b}\ {}^{[l]}M^{3+}_{c}\ (H_2O)_d\ (H_2O)_e\ {}^{[q]}(OH)_f\ (H_2O)_g]^{(a+2b+3c-f)+}$, dans laquelle *d* représente le nombre de groupes (H_2O) transformateurs, *e* est le nombre de groupes (H_2O) non transformateurs, et *g* est le nombre de groupes (H_2O) interstitiels

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non liés à un cation interstitiel. On peut exprimer l'acidité de Lewis de ce complexe interstitiel graphiquement en fonction des quantités de cations monovalent, divalent et trivalent et de leur coordinence, et du nombre de groupes (H_2O) transformateurs interstitiels. On peut aussi exprimer graphiquement l'intervalle de la basicité de Lewis pour une unité structurale en particulier. Où il y a correspondance de l'acidité et de la basicité de Lewis, le principe de correspondance des valences de liaison est satisfait, et on peut ensuite dériver les détails des complexes interstitiels possibles. Nous faisons des prédictions détailées de la composition des autres complexes présents dans les minéraux à oxyde uranylé hydroxylé-hydraté. Nous trouvons une correspondance satisfaisante entre les intervalles prédits pour les complexes interstitiels et ceux que l'on retrouve dans la nature. Nous établissons une connexion entre les structures cristallines des minéraux à oxyde uranylé hydroxylé-hydraté, et leur composition chimique [rapport molaire (MO) + (H_2O) : (UO_3)]. Le type de cation interstitiel et les classes générales de polymérisation des chaînes de type P, U et D des unités structurales changent de façon systématique selon log $[M^{2+}] / [H^+]^2$ et $[(MO) + (H_2O)] / [UO_3]$. Les unités structurales peuvent être formellement liées selon une réaction chimique entre deux H^+ et un cation M^{2+}. La combinaison de cette équation avec la loi de l'action des masses mène à une expression permettant l'arrangement des unités structurales en termes de log $[M^{2+}]$ et H, et un calcul des pentes des limites des champs de stabilité. Il en résulte un diagramme activité–activité ayant une topologie correcte et une échelle relative le long de chaque axe. Les classes générales des chaînes de type P, U et D des unités structurales changent de façon systématique dans ce diagramme activité–activité.

(Traduit par la Rédaction)

Mots-clés: minéraux à oxyde uranylé, représentation binaire, théorie des valences de liaison, diagramme activité–activité.

INTRODUCTION

The uranyl-oxide hydroxy-hydrate minerals commonly form by oxidation and alteration or dissolution of uraninite in aqueous solutions (Protas 1959, Finch & Murakami 1999), and play a key role in determining reaction paths of uranyl species in aqueous uranium-rich environments. As a result, there has been significant progress in the last five years in characterizing many of these minerals (Finch *et al.* 1996, Burns 1997, 1998a, b, 1999b, Burns & Hanchar 1999, Li & Burns 2000a, b) and related synthetic materials (Cremers *et al.* 1986, Burns & Hill 2000a, b, Hill & Burns 1999, Li & Burns 2000c).

Hawthorne (1985, 1990, 1997), Schindler & Hawthorne (2001a, b, c) and Schindler *et al.* (2000) have been developing a new approach to consider the structures, chemical compositions and stabilities of hydroxy-hydrated oxysalt minerals. This approach is based on a combination of a binary representation of structure (Hawthorne 1985, 1990, 1994, 1997) and bond-valence theory (Brown 1981, 2002, Burdett & Hawthorne 1993, Hawthorne 1994); details of the current approach are developed in Schindler & Hawthorne (2001a). Here, we consider the uranyl-oxide hydroxy-hydrate minerals (Table 1). We emphasize that this approach is still under development. At the moment, our principal intention is to try and understand what factors affect the stereochemistry, chemical composition and occurrence of complex oxysalt minerals. Although we attempt to predict certain features of these minerals, the intent of this prediction is to further develop the theory rather than to displace any of the current geochemical and thermodynamic approaches to mineral occurrence.

TABLE 1. MINERALS OF THE URANYL-OXIDE-HYDROXY-HYDRATE GROUP

Mineral	Formula	Ref.
schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	(1)
metaschoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{10}$	(2)
vandendriesscheite	$^{[9]}Pb^{2+}\,^{[8]}Pb^{2-}{}_{0.57}(H_2O)_5[(UO_2)_{10}O_6(OH)_{11}](H_2O)_6$	(3)
becquerelite	$^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2\,(H_2O)_4$	(4)
compreignacite	$^{[7]}K_2(H_2O)_3\,[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$	(5)
fourmarierite	$^{[9]}Pb^{2+}(H_2O)_2[(UO_2)_4O_3(OH)_4](H_2O)_2$	(6)
richetite	$^{[6]}M_x\,^{[8.4]}Pb^{2+}{}_{8.57}(H_2O)_{31}[(UO_2)_{18}O_{18}(OH)_{12}](H_2O)_{10}$	(7)
protasite	$^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$	(8)
masuyite	$^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$	(9)
curite	$^{[9]}Pb^{2+}{}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$	(10)
sayrite*	$^{[9]}Pb^{2+}{}_2(H_2O)_4[(UO_2)_5O_6(OH)_2]$	(11)
wölsendorfite*	$^{[8.15]}(Pb^{2+}{}_{6.2}\,Ba_{0.4})(H_2O)_{10}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$	(12)
billietite	$^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$	(13)
agrinierite	$^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5[(UO_2)_3O_3(OH)_2]_2$	(14)
meta-vandendriesscheite	$Pb^{2+}{}_{1.57}[(UO_2)_{10}O_6(OH)_{11}](H_2O)_{(1-x)}$	(15)
rameauite	$K_2Ca[(UO_2)_6O_4(OH)_6](H_2O)_6$	(15)
calciouranoite	$(Ca,Ba,Pb^{2+},K_2,Na_2)[(UO_2)(O,OH)](H_2O)_5$	(15)
metacalciouranoite	$(Ca,Ba,Pb^{2+},K,Na)[(UO_2)(O,OH)](H_2O)_2$	(15)
clarkeite	$(Na,Ca)[(UO_2)(O,OH)](H_2O)_{0-1}$	(16)
bauranoite	$Ba[(UO_2)(O,OH)](H_2O)_{4-5}$	(15)
uranosphaerite*	$[Bi^{3+}[(UO_2)O_2(OH)]$	(17)
spriggite	$^{[8.4]}Pb^{2-}{}_3[(UO_2)_6O_8(OH)_2](H_2O)_3$	(18)

(1) Finch *et al.* (1996); (2) Finch *et al.* (1998), Weller *et al.* (1999); (3) Burns (1997), (4) Burns & Li (2002); (5) Burns (1998a), (6) Piret (1985), Li & Burns (2000b); (7) Burns (1998b); (8) Pagoaga *et al.* (1987), (9) Burns & Hanchar (1999), (10) Taylor *et al.* (1981), Li & Burns (2000a); (11) Piret *et al.* (1983), (12) Burns (1999b), (13) Finch *et al.* (Unpublished); (14) Cahill & Burns (2000), (15) Finch & Murakami (1999); (16) Finch & Ewing (1997); (17) Hughes *et al.* (2003); (18) Brugger *et al.* (2004)

* The structural unit is modified by strong Pb^{2+}–O or Bi^{3+}–O bonds resulting from stereoactive lone-pair effects.

PRELIMINARY CONSIDERATIONS

As much of the theory used here will not be familiar to many readers, we give a brief introduction to some of the more important ideas. The role of (H_2O) is of particular importance, and the reader is referred to Hawthorne (1992) and Schindler & Hawthorne (2001a, b, c) in this regard.

BINARY REPRESENTATION OF THE STRUCTURE

We can divide any complex structure into two components: (1) the *structural unit*, the strongly bonded part of the structure, and (2) the *interstitial complex*, the assemblage of cations, anions and (H_2O) groups that weakly bind the structural units into a continuous crystal structure. The constituents of the structure can be considered in a simple additive fashion to produce aggregate sets of properties (*e.g.*, charge, Lewis basicity, Lewis acidity) for the structural unit and the interstitial complex. We may then use an extension of the valence-matching principle (Brown 1981, 2002), the principle of correspondence of Lewis acidity–basicity (Hawthorne 1985, 1992, Schindler & Hawthorne 2001a), to examine the interaction of the structural unit with the interstitial complex, and note that it is these weak interstitial bonds that will control the stability of the structure.

THE LEWIS BASICITY OF THE STRUCTURAL UNIT

The Lewis basicity of the structural unit is defined as *the charge on the structural unit divided by the number of bonds to the structural unit* (Schindler & Hawthorne 2001a). To do this calculation, we need to know (1) the charge on the structural unit, and (2) the number of bonds required by the structural unit from the interstitial complex and adjacent structural units. The charge on the structural unit is the formal charge of the constituent ions modified by charge transfer involving hydrogen bonds emanating from the structural unit (see Schindler & Hawthorne 2001a for details) and weak bonds of lone-pair-stereoactive cations; this value is called the *effective charge*. Schindler & Hawthorne (2001a) showed that the prediction of the composition of interstitial complexes is independent of the configuration of the hydrogen bonds emanating from oxygen atoms of the structural unit. This allows us to calculate Lewis basicity and Lewis acidity without knowing the configuration of the hydrogen bonds emanating from oxygen atoms of the structural unit.

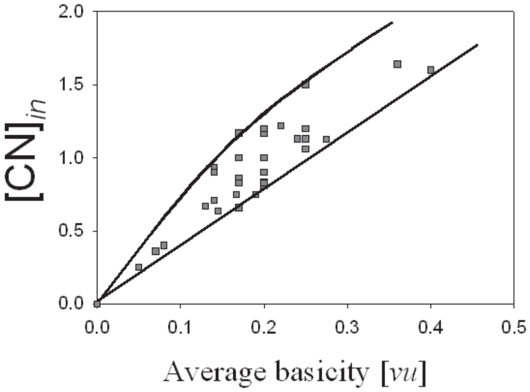


FIG. 1. The average basicity of structural units *versus* the average coordination-number of O referred to interstitial bonds ($[CN]_{in}$) for uranyl-oxide hydroxy-hydrate and uranyl-oxysalt minerals.

Calculation of the number of bonds to the structural unit is trivial if we know the details of the crystal structure. However, we wish to *predict* information *a priori* about the structure, and hence we need to predict this information, which amounts to predicting the anion coordinations in the structural unit. To do this, Schindler & Hawthorne (2001a) introduced a new property, the *average basicity* of the structural unit, which is defined as *the average bond-strength per O atom contributed by the interstitial species and adjacent structural units.* There is a correlation between the average basicity and the average coordination-number of oxygen in borate minerals crystallized from aqueous solution (Schindler & Hawthorne 2001a, b). In uranyl (and sulfate) minerals crystallized from low-temperature aqueous solution, this correlation holds for the average O-coordination number involving bonds solely from the interstitial complex and adjacent structural units, denoted $[CN]_{in}$ (Fig. 1) (Schindler & Hawthorne, in press). Note that in Figure 1, the data define a band rather than a single line. As well as predicting a specific average number of bonds accepted by an O atom of the structural unit, Figure 1 also predicts the *range* in the number of bonds accepted by an O atom of the structural unit. As discussed by Schindler & Hawthorne (2001a, b), this range in bonds per O atom of a structural unit reflects the range in pH over which the mineral is stable, and allows calculation of the range in possible Lewis base-strength for a specific structural unit. A calculation of the Lewis basicity for a specific structural unit is shown in Appendix 1.

THE LEWIS ACIDITY OF INTERSTITIAL COMPLEXES

A general formula for an interstitial complex can be written as follows:

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

where *M* is any type of interstitial cation, *d* and *e* denote the numbers of transformer and non-transformer (H_2O) groups, respectively (Schindler & Hawthorne 2001a), and *g* denotes the number of interstitial (H_2O) groups not bonded to interstitial cations.

The Lewis acidity of the interstitial complex is defined as *its effective charge divided by the number of bonds from the interstitial complex to the structural unit*. The effective charge is as shown above, $(a + 2b + 3c - f)^+$, as modified by any hydrogen bonds emanating from the interstitial complex (Schindler & Hawthorne 2001a). The number of bonds from the interstitial complex to the structural unit may be calculated from the coordination numbers of the cations and hydrogen bonds of the interstitial complex: $m \times a + n \times b + l \times c + d - f \times (q - 1) + s$, where s is the number of hydrogen bonds from the interstitial complex to the structural unit. For simplicity, we set $m \times a + n \times b + l \times c = N$ (the total number of bonds from the interstitial cations) in the following sections. A calculation of the Lewis acidity of a specific interstitial complex is shown in Appendix 1.

GRAPHICAL REPRESENTATION OF LEWIS ACIDITY IN INTERSTITIAL COMPLEXES

We can represent the variation in Lewis acidity of an interstitial complex graphically with a little judicious simplification. First, we represent a single species of cation; if there are more than one cation species present, we may use the weighted arithmetic average of the salient characteristics (charge and coordination number) of these cations. Second, in cases where $(OH)^-$ is present, we can sum the charges of the cation(s) and the $(OH)^-$, and treat the complex as if it contained a cation of the resulting net charge [*i.e.*, $M^{3+} + (OH)^- \longrightarrow M^{2+}$]. The remaining key variable in the interstitial complex is the number of transformer (H_2O) groups. Hence we may show the variation in Lewis acidity as a function of the number of transformer (H_2O) groups for specific cation charges and cation-coordination numbers (Fig. 2a). 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.

We may now plot the range in Lewis basicity of a specific structural unit on a graph that shows the variation in Lewis acidity of cation complexes (*i.e.*, Fig. 2b). Where the properties of the structural unit and the interstitial complexes intersect, their Lewis acidity and basicity match, and structures of those specific compositions are stable. Where the properties of the structural unit and interstitial complexes do not overlap, the valence-matching principle is not satisfied, and structures of those compositions are not stable.

From Figure 2b, it is apparent that the range in Lewis basicity determines the type of interstitial cation and the number of transformer (H_2O) groups. Let us consider the structural unit of becquerelite, $[(UO_2)_3O_2(OH)_3]^-$, with a formal charge of 1^-, three $(OH)^-$ groups, and a range in Lewis basicity of 0.14 to 0.23 valence units (*vu*). The Lewis acidities of all possible stable interstitial complexes must match this range, and we can formulate the following restrictions for interstitial complexes with only one type of interstitial cation:

$$[^{[m]}M^+ (H_2O)_d (H_2O)_e]^+$$
$$0.14 < (1 + 3h) / (m + d + 3) < 0.23$$

where h is the bond valence of the hydrogen bond, and usually takes the value 0.20 *vu*. For monovalent cations in different coordinations (m), we can predict the possible range in transformer (H_2O) groups and the possible coordination-numbers for the interstitial cations. For cation-coordination numbers m > [8], the above expression does not hold, and hence there can be no minerals with interstitial monovalent cations of coordination number > [8]. Where m = [8], the expression holds only for d = 0.5, and hence there can be no transformer (H_2O) groups for [8]-coordinated monovalent cations. Where m = [6], the expression holds for $0 < d < 2$, and hence there can be 0 to 2 transformer (H_2O) groups for [6]-coordinated monovalent cations.

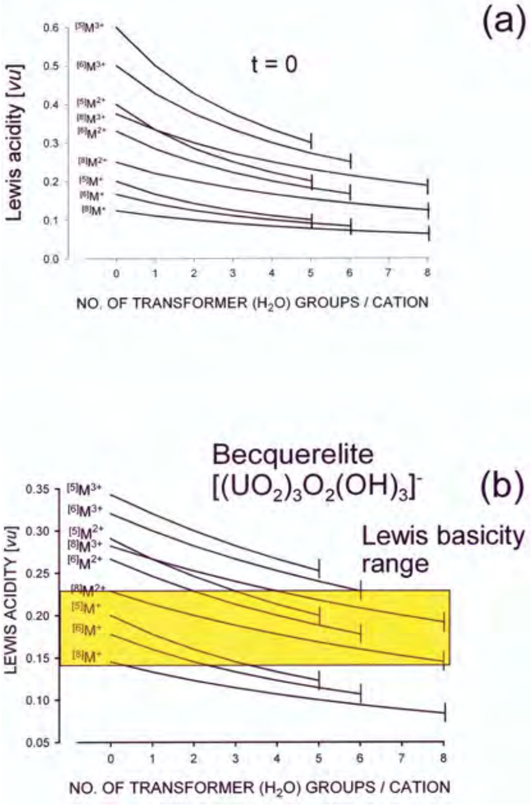


FIG. 2. (a) Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; (b) as (a), with the range in basicity of the $[(UO_2)_3O_2(OH)_3]^-$ structural unit shown by the yellow field.

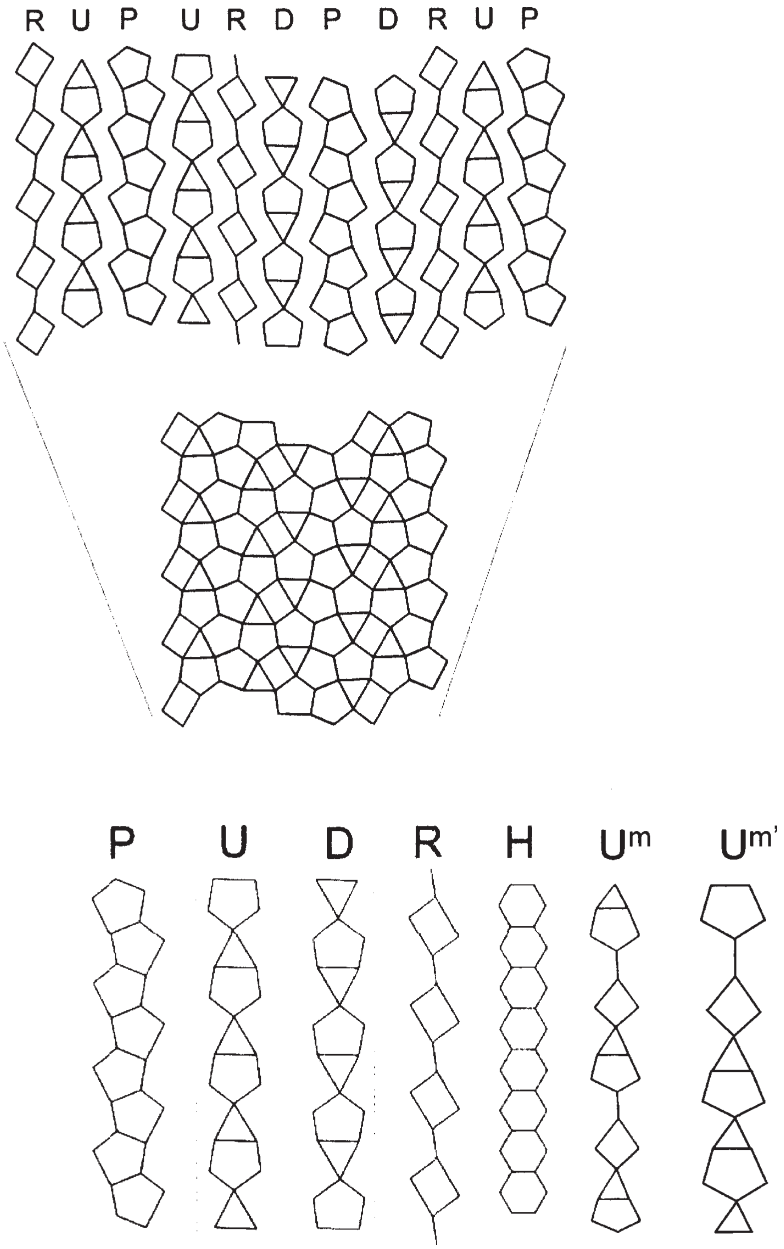


FIG. 3. Top: the anion topology of a sheet structural unit with D-, R-, P- and U-type chains and the topology code $P_3(UD)_5R_3$. Bottom: different types of anion chains that occur in uranyl-oxide hydroxy-hydrate minerals.

Uranyl-Oxide Hydroxy-Hydrate Minerals

Burns *et al.* (1996) subdivided the uranyl-oxide hydroxy-hydrate minerals on the basis of the anion topology of their (sheet) structural unit. Figure 3 shows the anion topology (net) of a sheet structural unit. The net contains triangles, squares and pentagons, and can be constructed by stacking various types of chains together (for details, see Burns *et al.* 1996). Miller *et al.* (1996) gave details of the various types of chains that they la-

TABLE 2. 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
vandenriesscheite	$^{[9]}Pb^{2+}{}_1{}^{[8]}Pb^{2+}{}_{0.57}(H_2O)_5[(UO_2)_{10}O_6(OH)_{11}](H_2O)_6$	$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$	$P_9(UD)_{11}$	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
agrinierite	$^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5[(UO_2)_3O_3(OH)_2]_2$	$[(UO_2)_3O_2(OH)_2]^{1-}$	$P_6(UD)_5$	0.22	0.155–0.23
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	$^{[9]}Pb^{2+}{}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$	$[(UO_2)_8O_8(OH)_6]^{6-}$	$(UD)_6(U^m)_6$	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	$^{[8.15]}(Pb^{2+}{}_{6.2}\ Ba_{0.4})(H_2O)_{10}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$	$^*[(UO_2)_{14}O_{19}(OH)_4]^{14}$	$P_6(UD)_{22}R_9$	0.29	0.175–0.24
spriggite	$^{[8.4]}Pb^{2+}{}_3[(UO_2)_6O_8(OH)_2](H_2O)_3$	$[(UO_2)_6O_8(OH)_2]^{6-}$	$(UD)_3R_3$	0.29	0.176–0.24

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

beled P, U, D, R and H, and Burns (1999a) described a modified version of the U chain in curite, labeling it U^m. Glatz *et al.* (2002) described 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 we label $U^{m'}$. The topology of a sheet structural unit depends on the number, type and sequence of the different chains. The topology of the sheet in Figure 3 can be described by the code RUPURDPDRUP, which contains all information regarding the number, type and sequence of the different chains (Burns *et al.* 1996). However, in wölsendorfite, $Pb^{2+}{}_{6.3}Ba_{0.4}[(UO_2)_{14}O_{19}(OH)_4](H_2O)_{12}$, the topology corresponds to a stacking sequence of 37 chains. Although accurate, the resulting code is complicated, and intuitive comparison with other topology codes is difficult. Here, we introduce a topology code of general form $P_u\ (UD)_v\ R_w\ U^m{}_x\ U^{m'}{}_y\ H$ for uranyl-sheet structural units. The code of the topology in Figure 3 is $P_3(UD)_5R_3$; that of wölsendorfite is $P_6(UD)_{22}R_9$ (Table 2). 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 compare different codes of structural units in minerals formed at different conditions. Future, more detailed work will presumably focus on the more comprehensive representation of Burns *et al.* (1996).

Lone-pair-stereoactive interstitial cations

A common feature of uranyl-oxide hydroxy-hydrate minerals is the presence of interstitial cations that can have stereoactive lone-pairs of electrons, particularly Pb^{2+} and Bi^{3+}. Where such cations are not lone-pair-stereoactive, they show a distribution of individual bond-lengths similar to that exhibited by spherical cations (*e.g.*, Ca^{2+}, Sr^{2+}) of identical formal valence in the same type of environment. Where 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 bonds are always to O atoms of the structural unit, and are *trans* to the stereoactive lone-pair of electrons; longer bonds can be to O atoms of a structural unit or to interstitial (H_2O) groups (or to both). Figure 4 shows the lengths of such bonds in uranyl-oxide and uranyl-oxysalt minerals, taking the maximum bond-length as 3.30 Å (~0.03 *vu*). In Figure 4, we have identified the two different types of bonds described above: (1) those with bond valences in the range 0.45 to 0.65 *vu* (mean value = 0.50 *vu*); these bonds are always approximately *trans* to the inferred position of the lone pair of electrons; (2) those with bond valences in the range 0.03 to 0.45 *vu*. Although there is some overlap between the lengths of very short bonds (*trans* to the lone-pair stereoactive electrons) and the shorter of the remaining bonds in Figure 4, *in any particular* ($Pb^{2+}\varphi_n$) *polyhedron*, there is invariably a distinct gap between these two types of bonds.

According to our initial arguments (Hawthorne 1983, 1985, 1994, 1997, Schindler & Hawthorne 2001a), the short strong Pb^{2+}–O bonds should be considered as part of the structural unit. The question then arises as to how we treat the weak bonds involving these lone-pair-stereoactive cations. By analogy with the H atom, which shows a strong O–H bond involved in the structural unit and a weak hydrogen bond emanating from the structural unit, we consider strong Pb^{2+}–φ bonds (and other lone-pair-stereoactive cations) as belonging to the structural unit, and weak Pb^{2+}–φ bonds are treated in the same way as hydrogen bonds.

As an example, let us 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 (Fig. 5) 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: $[^{[1+7]}Pb^{2+}_2\{(H_2O)_2(H_2O)_2\}(UO_2)_5O_6(OH)_2]$ (Table 2). In order to calculate the effective charge of the structural unit, we need to assign a typical bond-valence to the short bond(s); inspection of Figure 4 shows that the value 0.50 *vu*, equivalent to a bond-length of 2.41 Å, 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

Figure 1 can be used to calculate the range in Lewis basicity of all uranyl-oxide hydroxy-hydrate structural units; from this range in Lewis basicity, we can calculate possible chemical compositions of interstitial complexes. These chemical compositions can be compared with the observed composition of uranyl-oxide hydroxy-hydrate minerals, and also can be used to predict types of anthropogenic radionuclide cations that can be incorporated in the interstices of uranyl-oxide hydroxy-hydrate minerals.

Table 1 lists the chemical compositions of all uranyl-oxide hydroxy-hydrate minerals, and Table 2 lists the corresponding structural units, their average basicity, range in Lewis basicity, and the topology code of their sheet structural unit. Table 3 lists the predicted ranges in coordination number and transformer (H_2O) groups per cation, together with what is observed in minerals. 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 the number of transformer (H_2O) groups. For the first few structural units, we will go through the arguments in detail. For the rest of the structural units, we will just focus on a comparison between the predicted interstitial complexes and 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. 6c) occurs in becquerelite, $^{[7]}Ca(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, compreignacite, $^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$, and billietite, $^{[10]}Ba(H_2O)_4[(UO_2)_3O_2(OH)_3]_2(H_2O)_3$. 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* = 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 1.6 / 11 = 0.145 *vu*. We may use this value of the average basicity, together with Figure 1, to predict the minimum and maximum value of $[CN]_{in}$: 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, *i.e.*, 0.14 to 0.23 *vu*. The valence-matching principle requires that the Lewis acidities of the corresponding interstitial complexes should be in the range 0.14 to 0.23 *vu*; this range is shown in Figure 2b.

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 to 8.5. This means that interstitial monovalent cations not bonded to transformer (H_2O) groups must have coordination numbers between [4] and [8.5], and those with coordination number lower than [4] [*e.g.*, $(H_3O)^+$] must bond to at least one transformer (H_2O) group. 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]- and [6]-coordination matches the range in Lewis basicity of the structural unit with none, one and two transformer (H_2O) groups, respectively. If all (H_2O) groups were bonded to interstitial cations, a stable mineral with a monovalent [8]-coordinated cation could have a maximum of 11.5 – [8] – 3 = 0.5 transformer (H_2O) groups per cation, and $^{[8]}M^+(H_2O)_{0-0.5}[(UO_2)_3O_2$

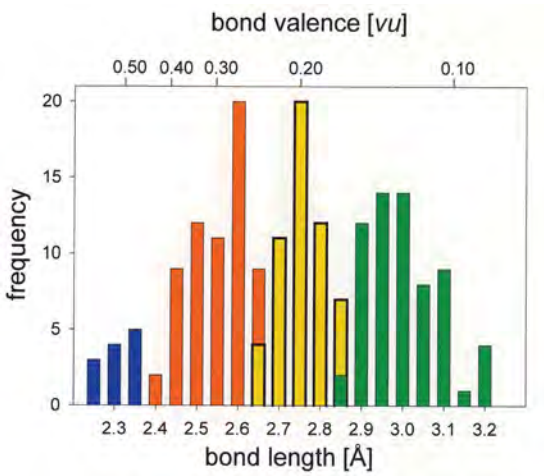


FIG. 4. Frequency of Pb–(O,{OH},{H_2O}) bonds in uranyl-oxide and uranyl-oxysalt minerals. Type (1) bonds (short, bond valence ≤ 0.45 *vu*, *trans* to stereoactive lone-pair of electrons) are shown in blue; type (2) (long, bond valence ≥ 0.45 *vu*, not *trans* to stereoactive lone-pair of electrons) are shown in orange, yellow and green.

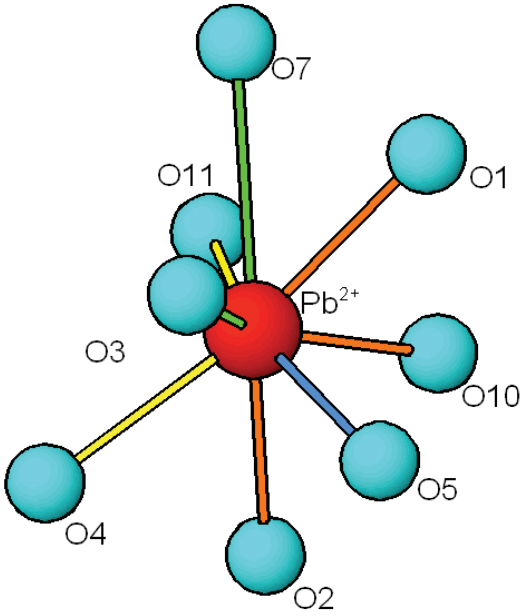


FIG. 5. The *Pb* site in sayrite, showing the coordination and bonds; Pb^{2+}: red circle; O atoms: blue circles; color of bonds denotes their length range: blue: < 2.40 Å; orange: 2.40–2.70 Å; yellow: 2.70–2.85 Å; green: > 2.95 Å.

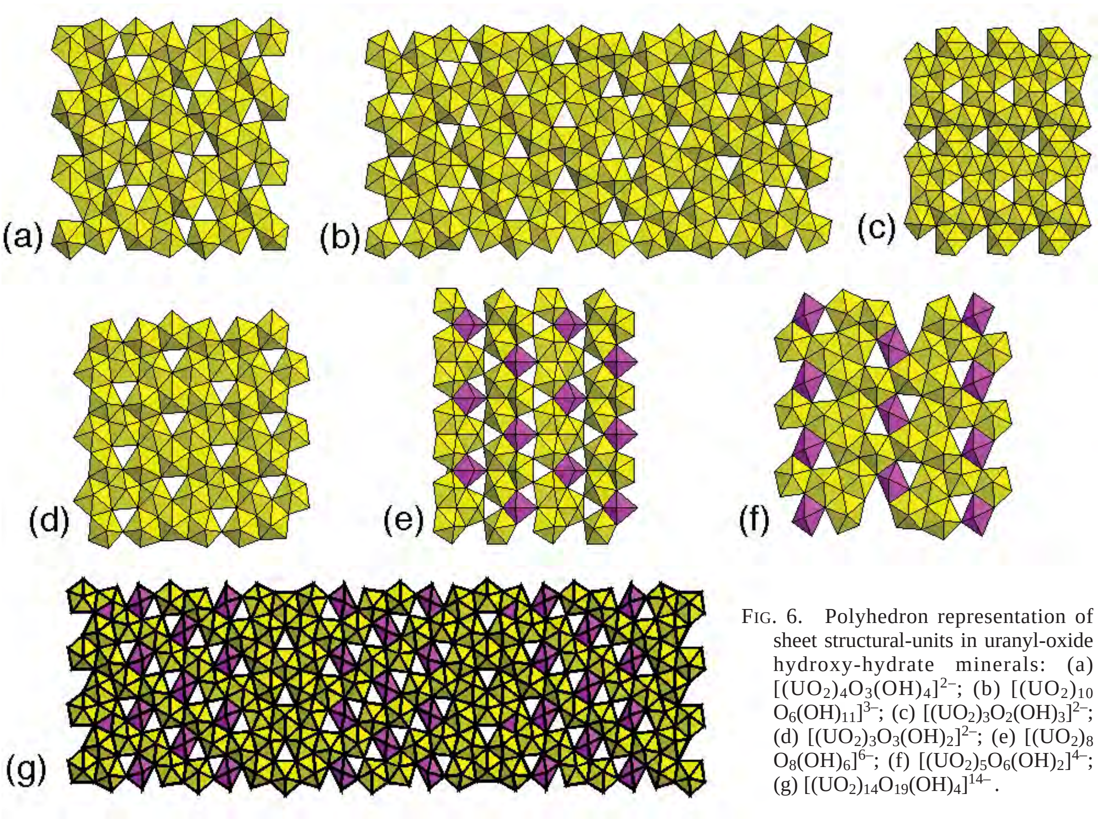


FIG. 6. Polyhedron representation of sheet structural-units in uranyl-oxide hydroxy-hydrate minerals: (a) $[(UO_2)_4O_3(OH)_4]^{2-}$; (b) $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$; (c) $[(UO_2)_3O_2(OH)_3]^{2-}$; (d) $[(UO_2)_3O_3(OH)_2]^{2-}$; (e) $[(UO_2)_8O_8(OH)_6]^{6-}$; (f) $[(UO_2)_5O_6(OH)_2]^{4-}$; (g)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

$(OH)_3]$ is the predicted chemical composition of such minerals. The analogous result for $^{[7]}M^+$ is 0–1.5 transformer (H_2O) groups per cation. There is one mineral containing this structural unit and with monovalent cations in the interstitial complex: compreignacite, $^{[7]}K_2(H_2O)_3[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$; the number of (H_2O) groups bonded to K^+ is in accord with the predicted 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. 2b), 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 in Lewis basicity of the structural unit. Consider the case for [*n*]-coordination and six hydrogen bonds to the interstitial complex. The total number of bonds directly involving the interstitial cations is written as N, where $N = [m]$ (the average coordination number of the divalent cations) $\times\, b$ (the number of divalent cations in the interstitial complex). Where the interstitial divalent cations are bonded to d transformer (H_2O) groups, the corresponding Lewis acidity may be written as $(2 + 6h) / (N + d + 6)$, 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 $3.2 / (N + d + 6)$ must equal 0.23. For $[n] = 6$ and 7, N will be equal to 6 and 7 (as $b = 1$), and d will be equal to 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*), $3.2 / (N + d + 6)$ will be equal to 0.14, from which $d = 11$, 10 or 9. However, six, seven and eight are the maximum possible values of d (Fig. 2b), 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). [Note here that 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.] 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 do not know the number of transformer (H_2O) groups in the two minerals, but we can predict that becquerelite and billietite must contain 1 to 4 and 0 to 7 transformer (H_2O) groups, respectively.

Interstitial complexes with trivalent cations: The trivalent cations possible in this type of environment are octahedrally coordinated small cations (*e.g.*, Al^{3+}, Fe^{3+}) and (usually) [8]- or [9]-coordinated REEs (Y^+ and rare-earth elements). Consider the case for [6]-coordinated Al^{3+} or Fe^{3+}. If the cation is bonded to d transformer (H_2O) groups, its Lewis acidity may be written as $(3 + 9h) / (d + 6 + 9) = 4.8 / (d + 15)$ *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 $4.8 / (d + 15) = 0.23$, from which $d = 6$. For the Lewis acidity to fall at the minimum of the range in Lewis basicity of the structural unit (*i.e.*, 0.14 *vu*), then $4.8 / (d + 15) = 0.14$, from which $d = 19$. This range in d values exceeds the coordination number [6] (the maximum possible for Al^{3+}), and hence only an $\{Al(H_2O)_6(H_2O)_0\}^{3+}$ complex can occur with this structural unit. This result may also be seen directly by inspection of Figure 2b.

Interstitial trivalent cations can also occur if interstitial $(Al\varphi_6)$ octahedra polymerize. Consider two octahedra that link together: the bridging anions will receive an incident bond-valence of $\sim 0.5 \times 2 \leftrightarrow 1.0$ *vu*, and hence these anions will be $(OH)^-$ rather than (H_2O). This being the case, the interstitial complex may be written as $\{Al_2(H_2O)_{12-2f}\,(OH)_f\}^{(6-f)+}$, with $4 \times 3 = 12$ transferred hydrogen bonds. The Lewis acidity is $(6 - f + 12h) / [(12 - 2f) \times 2 + f + 12] = (8.4 - f) / (36 - 3f)$. Where $f = 2$, the Lewis acidity of the complex is 0.21 *vu*; where $f = 4$, 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 $f = 2$ (edge-sharing) or 3 (face-sharing) only are possible. Face-sharing of $(Al\varphi_6)$ octahedra is unlikely in an interstitial environment, and the complex $\{Al_2(H_2O)_{8-10}(OH)_2\}^{4+}$ seems more likely.

For the REE, [7]- and [8]-coordination by (H_2O) will provide Lewis acidities in the range 0.14–0.22 *vu*. Forming a dimer with f (OH) groups linked to two cations, $\{^{[N]}Y^{3+}_2(H_2O)_{2N-2f}\,(OH)_f\}^{(2N-f)+}$, gives the Lewis acidity as $(8.4 - f) / ([2N - 2f] \times 2 + 12 + f) = (6 - f) / (4N - 3f)$. 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 $\{^{[7]}Y_2(H_2O)_{13}(OH)\}^{5+}$, $\{^{[7]}Y_2(H_2O)_{12}(OH)_2\}^{4+}$ and $\{^{[7]}Y_2(H_2O)_{11}(OH)_3\}^{3+}$ are possible interstitial cation complexes with $(OH)^-$ present. However, considering that the charge of the structural unit is 2^-, $\{^{[7]}Y_2(H_2O)_{12}(OH)_2\}^{4+}$ produces a simpler formula.

Note that the graphical approach of Figure 2b can still be used for interstitial complexes with $(OH)^-$. Consider the complex $\{^{[N]}M^{3+}_2(H_2O)_{12-2f}\,(OH)_f\}^{(6-f)+}$. We may rewrite the “cation” as $\{M(OH)_{f/2}\}^{(3-f/2)+}{}_2 = L^{(3-f/2)+}{}_2$. 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 $\{^{[N-f/2]}L^{(3-f/2)+}{}_2(H_2O)_{12-2f}\}^{(6-f)+}$. Consider the case for $f = 2$: the complex reduces to $\{^{[5]}L^{2+}{}_2(H_2O)_8\}^{4+} = \{^{[5]}L^{2+}(H_2O)_4\}^{2+}{}_2$. 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.

For REE interstitial cations in [8]-coordination that do not bond to interstitial $(OH)^-$ groups, Table 2 and Figure 2b summarize the predicted numbers of transformer (H_2O) groups.

The structural unit $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$

The structural unit $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$ (Fig. 6b) is known only in vandendriesscheite, $^{[9]}Pb^{2+}\ ^{[8]}Pb^{2+}{}_{0.57}(H_2O)_5[(UO_2)_{10}O_6(OH)_{11}](H_2O)_6$. Its anion topology can be described as an arrangement of triangles and pentagons (Burns 1999a) with the topology code $P_9(UD)_{11}$. 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 $[CN]_{in}$ is 0.60–1.00 (Fig. 1). 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. 7a). The predicted chemical compositions of all compatible interstitial complexes are summarized in Table 3.

Interstitial complexes with monovalent cations: Inspection of Figure 7a indicates predicted interstitial compositions similar to those for the structural unit $[(UO_2)_3O_2(OH)_3]^{1-}$ (Fig. 2b). This can be seen also if we calculate the required number of bonds per monovalent cation: 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. As for the structural unit $[(UO_2)_3O_2(OH)_3]^{1-}$, we predict a coordination number of [8.5] or lower for monovalent interstitial cations.

Interstitial complexes with divalent and trivalent 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 number of bonds from interstitial complexes with only divalent interstitial cations can be calculated from the expression $5.2 / (d + N + 11) = 0.14$ *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 $N = n + n/2$. Substitution into the above equation gives the expressions $5.2(d + n + n/2 + 11) = 0.14$ and 0.23 *vu*, respectively. These expressions simplify to $2d + 3n = 22.6$ and 52.2, respectively. For possible coordination-numbers [6] to [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): $d = 2$ to 6, 1 to 7, 0 to 8, 0 to 9 and 0 to 10, respectively, for $[n] = 6, 7, 8, 9, 10$. Vandendriesscheite, $^{[9]}Pb^{2+}\ ^{[8]}Pb^{2+}{}_{0.57}(H_2O)_6[(UO_2)_{10}O_6(OH)_{11}](H_2O)_5$, contains the interstitial complex $\{^{[9]}Pb^{2+}\ ^{[8]}Pb^{2+}{}_{0.57}(H_2O)_1(H_2O)_5\}$ 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 (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], [9], the predicted ranges of d are as follows: 6, 5 to 7, 4 to 8, 3 to 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. 6a). 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 to 1.20 (Fig. 1). 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 $2.8 / 12 = 0.155$ to 0.23 *vu* (Fig. 7b). The predicted chemical compositions of all interstitial complexes are summarized in Table 3.

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 hence [6]-coordinated divalent cations ($N = 6$) must bond to a minimum of two transformer (H_2O) group ($d = 2$) 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

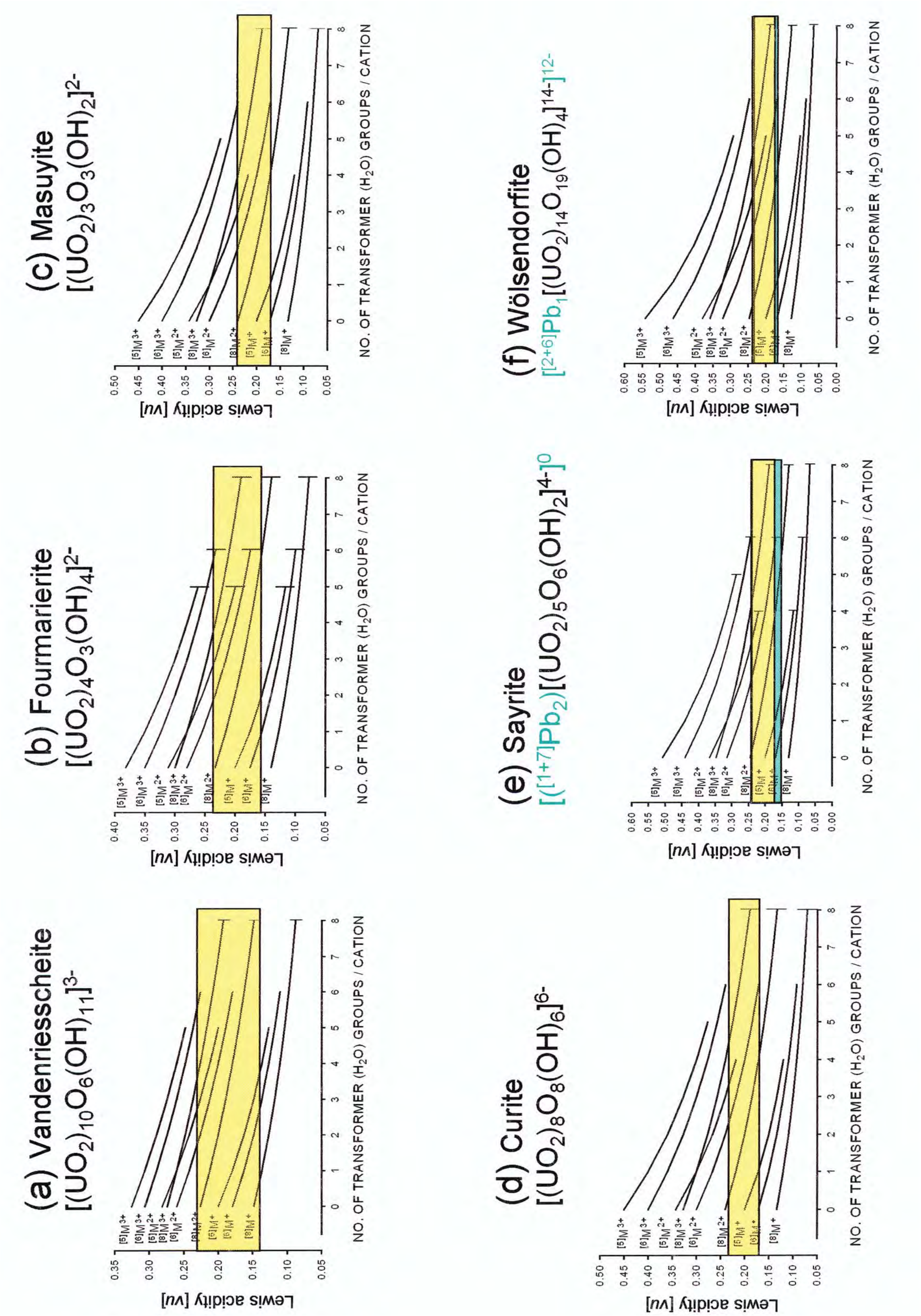
(H_2O) groups. We do not know if these (H_2O) groups are transformer or non-transformer; however, the range in ($N + d$) values allows both possibilities. For trivalent cations, ($N + d$) must be between 12 and 21, and hence [6]- and [8]-coordinated cations must occur with minima of 6 and 4 transformer (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. 6d) 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, $^{[10]}Ba(H_2O)_3[(UO_2)_3O_3(OH)_2]$, masuyite, $^{[10]}Pb^{2+}(H_2O)_3[(UO_2)_3O_3(OH)_2]$, and

TABLE 3. 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		
	$^{[7]}M^+$: d = 0–2.5	$\{^{[7]}K_2(H_2O)_3\}^{2+}$	compreignacite
	$^{[8]}M^+$: d = 0–1		
	$^{[6]}M^{2+}$: d = 2–6		
	$^{[7]}M^{2+}$: d = 1–7	$\{^{[7]}Ca(H_2O)_4\}^{2+}$	becquerelite
	$^{[10]}M^{2+}$: d = 0–7	$\{^{[10]}Ba(H_2O)_4\}^{2+}$	billietite
	$^{[6]}M^{3+}$: 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		
	$^{[6]}M^{2+}$: d = 2–6		
	$^{[8]}M^{2+}$: d = 0–8	$\{^{[9]}Pb^{2+}\ ^{[8]}Pb^{2+}_{0.5}(H_2O)_5\}^{3+}$	vandenriesscheite
	$^{[6]}M^{3+}$: 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
	$^{[8]}M^+$, $^{[9]}M^{2+}$: d = 0–1	$\{^{[8]}K_2\ ^{[9]}Ca(H_2O)_5\}^{4+}$	agrinierite
	$^{[6]}M^{3+}$: 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	$\{^{[9]}Pb^{2+}_3(H_2O)_2\}^{6+}$	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		
$[(UO_2)_{14}O_{19}(OH)_4]^{14-}$ $[(UO_2)_6O_8(OH)_2]^{6-}$	$^{[5]}M^+$: d = 0		
	$^{[6]}M^+$: not possible		
	$^{[6]}M^{2+}$: d = 2–5		
	$^{[8]}M^{2+}$: d = 0–3	$[^{[2+6]}Pb^{2+}]\{^{[8.4]}Pb^{2+}_{5.2}\ ^{[8]}Ba_{0.4}(H_2O)_{10}\}^{11.2+}$	wölsendorfite
		$\{^{[8.4]}Pb^{2+}_3(H_2O)_3\}^{6+}$	spriggite
	$^{[6]}M^{3+}$: d = 8, f = 2		
	$^{[8]}M^{3+}$: d = 4–8		


(a) Vandenriesscheite
$[(UO_2)_{10}O_6(OH)_{11}]^{3-}$
(b) Fourmarierite
$[(UO_2)_4O_3(OH)_4]^{2-}$
(c) Masuyite
$[(UO_2)_3O_3(OH)_2]^{2-}$
(d) Curite
$(UO_2)_8O_8(OH)_6]^{6-}$
(e) Sayrite
$[(^{[1+7]}Pb_2)[(UO_2)_5O_6(OH)_2]^{4-}]^0$
(f) Wölsendorfite
$[^{[2+6]}Pb_1[(UO_2)_{14}O_{19}(OH)_4]^{14-}]^{12-}$
Lewis acidity [vu]
NO. OF TRANSFORMER (H$_2$O) GROUPS / CATION
$^{[5]}M^{3+}$
$^{[6]}M^{3+}$
$^{[5]}M^{2+}$
$^{[8]}M^{3+}$
$^{[6]}M^{2+}$
$^{[8]}M^{2+}$
$^{[5]}M^{+}$
$^{[6]}M^{+}$
$^{[8]}M^{+}$
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
7
8

agrinierite, $^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5[(UO_2)_3O_3(OH)_2]_2$. 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 to 1.35 (Fig. 1). 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, *i.e.*, 0.16–0.24 *vu* (Fig. 7c). The predicted chemical compositions of all interstitial complexes are summarized in Table 3.

Restrictions on the chemical composition of possible interstitial complexes: The maximum and minimum number of bonds from an interstitial complex to the structural unit can be calculated from the expression $2.4 / (d + N + 2) = 0.24$ *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 to 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 divalent cations of higher coordination ([7] to [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, on the basis of the predicted range of $(N + d)$ bonds, the interstitial cations $^{[10]}Ba^{2+}$ and $^{[10]}Pb^{2+}$ can bond to 0 to 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 $^{[6]}(Mg^{2+} + Fe^{2+})$ and $^{[8]}Pb^{2+}$, the former should bond to 2 to 6 transformer (H_2O) groups, and the latter should bond to 0 to 5 transformer (H_2O) groups; the former value is in accord with the observed number (4) of (H_2O) groups bonded to $^{[6]}(Mg^{2+} + Fe^{2+})$. In agrinierite, $^{[8]}K_2(^{[5]}Ca,Sr)(H_2O)_5[(UO_2)_3O_3(OH)_2]_2$, there are 25 bonds emanating from the interstitial complex, and thus 12.5 of these bonds are accepted by each $[(UO_2)_3O_3(OH)_2]^{6-}$ structural unit. As the maximum number of bonds to the structural unit cannot exceed 13, the interstitial complex should not contain more than one transformer (H_2O) group.

FIG. 7. Variation in Lewis acidity with the number of transformer (H_2O) groups for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in basicity of the different structural units are shown by the yellow fields, and by the blue fields where short Pb^{2+} bonds are included in the structural unit: (a) $[(UO_2)_3O_2(OH)_3]^{1-}$; (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) $[(UO_2)_{14}O_{19}(OH)_4]^{14-}$.

The range in $(N + d)$ bonds for a trivalent cation is 12 to 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. 6e) 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 in $[CN]_{in}$ of 1.00 to 1.45. The minimum and maximum number of bonds are 25.5 and 43.5, respectively, and this corresponds to a range in Lewis basicity of 0.17 to 0.24 *vu* (Fig. 7d). The predicted chemical compositions of all interstitial complexes are summarized in Table 3.

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, $7.2 / (N + d + 6)$ must be in the range 0.17 to 0.24. The resulting range in possible values of $(N + d)$ is 24 to 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 to 38) / 6 = [4] to [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 to 38) / 3 = [8] to [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 to 6, 1 to 6, 0 to 5, 0 to 4 and 0 to 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 to 7, 4 to 8 and 3 to 9 transformer (H_2O) groups, respectively.

Curite has the interstitial complex $\{^{[9]}Pb^{2+}_3(H_2O)_0(H_2O)_2\}^{6+}$. Our above prediction suggests 0 to 4 transformer (H_2O) groups per $^{[9]}Pb^{2+}$ cation for a total predicted range of 0 to 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. 6f) 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 in $[CN]_{in}$ is 1.0 to 1.45. The minimum and maximum numbers of bonds from the interstitial complex to the structural unit are 18 and 26, respectively, which corresponds to a range in Lewis basicity from 4.4 / 24 to 4.4 / 18 = 0.17 to 0.24 *vu* (Fig. 7e). The predicted chemical compositions of all interstitial complexes are summarized in Table 3.

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 to 24. As a result, the average coordination-number of four monovalent cations can vary between (16 and 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] to [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], [10] with 2 to 6, 1 to 5, 0 to 4, 0 to 3, and 0 to 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 $[CN]_{in}$ (Fig. 1) are 0.80 and 1.25, respectively. The number of O atoms in the structural unit is 18, and hence the minimum and maximum number of bonds to the structural unit are 18/1.25 to 18/0.80 = 14.4 to 22.5, respectively. The effective charge of the modified structural unit is 0 (the formal charge) + 0.2 × 2 (due to hydrogen bonds) + (2 – 0.5) × 2 = $3.4^–$. Hence the range in Lewis basicity is 3.4/22.5 to 3.4/14.4 = 0.15 to 0.236 *vu*, respectively (shown in blue on Fig. 7e). 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 hence 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 × 16 / (16 + d) ≥ 0.15, from which $d \leq 6.4$. Thus the allowed range of transformer (H_2O) groups is 0 to 6 per structural unit, and the observed value of 2 transformer (H_2O) groups (Table 3) 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. 6g) occurs in wölsendorfite, $^{[8.4]}Pb^{2+}{}_{6.2}\ ^{[8]}Ba_{0.4}\ (H_2O)_{10}\ [(UO_2)_{14}O_{19}(OH)_4](H_2O)_2$ (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 × 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 in $[CN]_{in}$ of 1.20 to 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 to 0.24 *vu* (Fig. 7f). The predicted chemical compositions of all interstitial complexes are summarized in Table 3.

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 to 0.24. The possible range in (N + d) is 54 to 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 only 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 is possible. The structural unit $[(UO_2)_6O_8(OH)_2]^{6–}$ has similar average and Lewis basicities (Table 2). The predicted chemical compositions of the interstitial complex are identical to those of the structural unit $[(UO_2)_{14}O_{19}(OH)_4]^{14–}$ (Table 3), and are not discussed any further here.

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 to 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 $[CN]_{in}$ (Fig. 1) is 1.15 to 1.60, and hence 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 to 0.235 *vu* (shown in blue in Fig. 7f). For an [8]-coordinated divalent cation, Figure 7f predicts 0 to 4 transformer (H_2O) groups per interstitial cation, and the interstitial complex in wölsendorfite lies within this range.

GENERAL COMPOSITION OF INTERSTITIAL COMPLEXES IN URANYL-OXIDE HYDROXY-HYDRATE MINERALS

Figure 8 shows the correlation between the average basicity and the minimum and maximum Lewis basicities in uranyl-oxide hydroxy-hydrate minerals, together with the average Lewis acidity of interstitial complexes containing only K^+, Ba^{2+}, Pb^{2+}, Ca^{2+}, Cu^{2+} and Al^{3+}. Each diagram also indicates the average Lewis acidity of each interstitial cation in uranyl-oxysalt minerals.

Interstitial complexes with only K^+ as an interstitial cation have Lewis acidities from 0.14 to 0.17 *vu* in uranyl-oxysalt minerals (Schindler & Hawthorne, in press). The maximum Lewis acidity occurs only if K^+ bonds to one reverse bond-valence-transformer (H_2O) group. In this way, interstitial complexes with K^+ and without reverse bond-valence transformer have a range in Lewis acidity from 0.14 to 0.16 *vu*; thus, these interstitial complexes occur most likely with structural units that have average basicity less than 0.22 *vu*. This observation for all types of uranyl-oxysalt structures closely matches our predictions for uranyl-oxide hydroxy-hydrate minerals (Table 2). Moreover, K^+ should be able to be an interstitial cation for any structural unit with an average basicity of less than or equal to 0.22 *vu*.

The above predictions for uranyl-oxide hydroxy-hydrate structural units indicate that interstitial complexes with only [8]- to [10]-coordinated divalent cations do not require any transformer (H_2O) groups (Table 2). However, inspection of Figure 8 shows that the average Lewis acidity of $^{[8.3]}Pb^{2+}$ and $^{[7.5]}Ca^{2+}$ are higher than the range in Lewis basicities for all structural units with average basicities smaller than 0.29 *vu*, respectively. How is this possible? Schindler & Hawthorne (2001a) showed that the Lewis acidity of an interstitial complex can be reduced by the transferred bond-valence of hydrogen bonds emanating from the structural unit. Because uranyl-oxide hydroxy-hydrate structural units of low average basicity involve a large number of hydrogen bonds, the corresponding interstitial complexes (with $^{[8.3]}Pb^{2+}$ and $^{[7.5]}Ca^{2+}$) do not require additional transformer (H_2O) groups.

This is not the case for interstitial complexes with [6]-coordinated divalent and trivalent cations such as Cu^{2+} and Al^{3+} (Fig. 8). To match the ranges in Lewis basicity of the corresponding uranyl-oxide hydroxy-hydrate structural units, interstitial complexes with Cu^{2+} must contain one to two additional transformer (H_2O) groups, and interstitial complexes with Al must contain four to six transformer (H_2O) groups per interstitial cation.

OCCURRENCE AND SOLUBILITY

Uranyl-oxide hydroxy-hydrate minerals are the most important products of corrosion of UO_2 in spent nuclear fuel (Finch & Ewing 1992), and their properties may control groundwater concentrations of U in contaminated soils (Buck *et al.* 1996, Morris *et al.* 1996). The occurrence and paragenesis of these minerals are affected strongly by the chemical composition and pH of the groundwater. Hexavalent uranium bonds strongly to two O atoms, forming the linear $(UO_2)^{2+}$ uranyl cation (Burns *et al.* 1997). In the absence of F, the uranyl ion is the dominant U species in groundwater at pH values below 5. Frondel (1958) gave the first comprehensive summary of their paragenesis, and Garrels & Christ (1959), Finch & Ewing (1992) and Janeczek & Ewing (1992) characterized the role of these minerals as alteration products of uraninite. Reviews of the crystal structures of uranyl-oxide hydroxy-hydrate minerals were given by Smith (1984) and Burns (1999a), and details of their paragenesis were given by Finch & Murakami (1999). Table 4 lists structural units, average basicities, and the topology-codes of the (sheet) structural-units for related synthetic compounds.

Occurrence

Frondel (1956, 1958), Finch & Ewing (1992) and Finch & Murakami (1999) showed that vandendriesscheite, $Pb^{2+}_{1.5}[(UO_2)_{10}O_6(OH)_{11}](H_2O)_{11}$, and fourmarierite, $Pb^{2+}[(UO_2)_4O_3(OH)_4]\,(H_2O)_4$, form at the earliest stage of alteration of Pb-bearing uraninite. With increasing alteration, the following Pb^{2+}-minerals form in the outer rim of altered material: richetite, $M_x\,Pb^{2+}_{8.57}[(UO_2)_{18}O_{18}(OH)_{12}]_2(H_2O)_{41}$; masuyite, $Pb^{2+}[(UO_2)_3O_3(OH)_2](H_2O)_3$; sayrite, $Pb^{2+}_2[(UO_2)_5O_6(OH)_2]\,(H_2O)_4$; curite, $Pb^{2+}_3[(UO_2)_8O_8(OH)_6]\,(H_2O)_3$; and wölsendorfite, $Pb^{2+}_{6.2}Ba_{0.4}[(UO_2)_{14}O_{19}(OH)_4]\,(H_2O)_{12}$. Frondel (1956) suggested that this sequence of alteration is due to preferential loss of U to groundwater and enrichment of radiogenic Pb. Finch & Murakami (1999) argued that this alteration does not necessarily require a high concentration of Pb in solution.

Solubility

Solubility measurements on uranyl-oxide hydroxy-hydrate minerals (*e.g.*, Casas *et al.* 1994, 1997, Vochten & van Haverbeke 1990, Sandino & Grambow 1995) show maximum stability of uranyl-oxide hydroxy-hydrate minerals to be in the pH range 5.5 to 8, in accord with the conclusion of Langmuir (1978) that uranyl minerals have maximum stabilities between pH 5 and 8.5. Finch & Ewing (1992) and Casas *et al.* (1997) stated that the stability of uranyl-oxide hydroxy-hydrate minerals increases from schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, to becquerelite, $Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$, and to the Pb^{2+}-uranyl-oxide hydroxy-hydrate minerals.

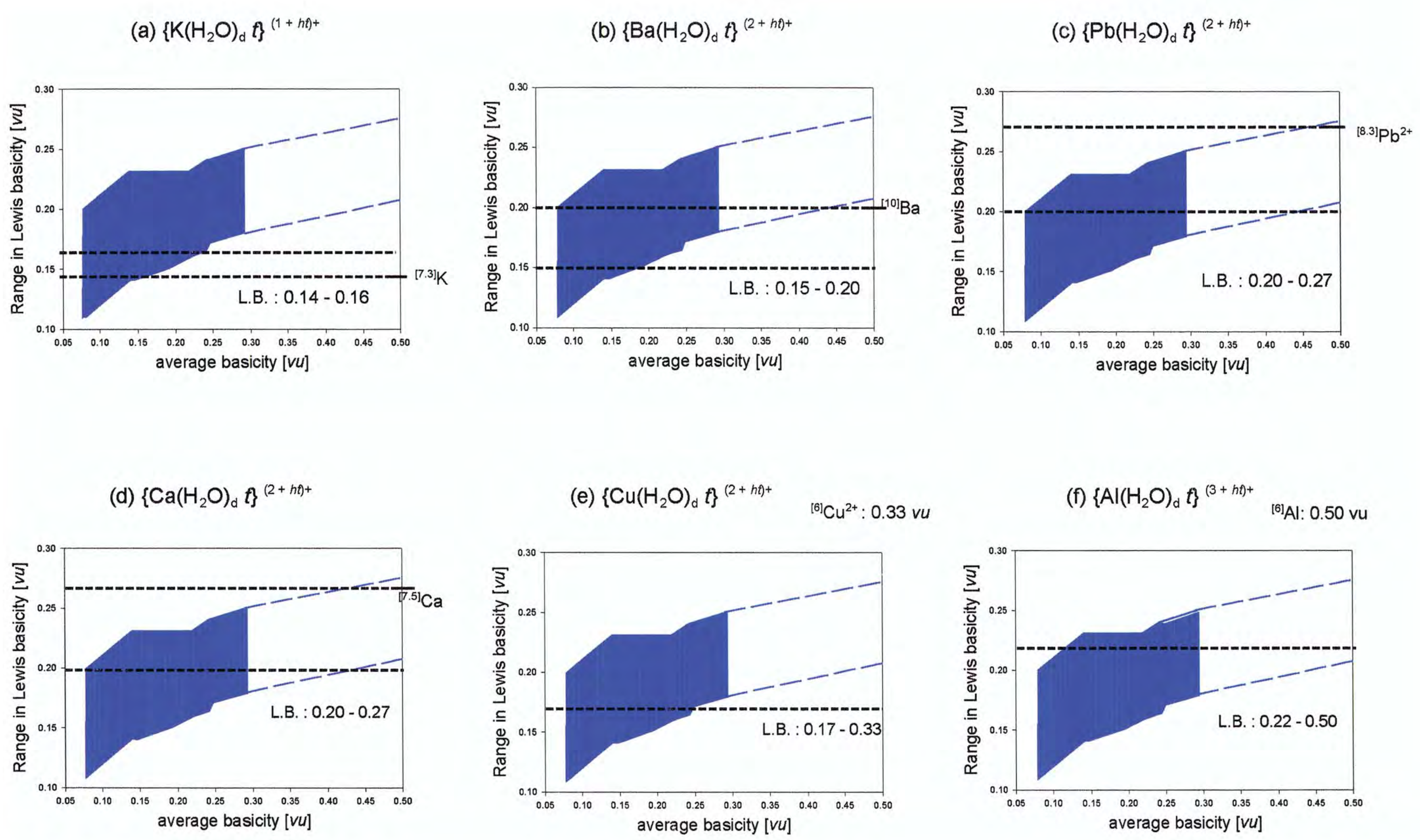


FIG. 8. The variation in the average basicity as a function of range in Lewis basicity for all uranyl-oxide hydroxy-hydrate minerals, with the corresponding ranges in Lewis acidity of interstitial complexes with only (a) K, (b) Ba, (c) Pb^{2+}, (d) Ca, (e) Cu^{2+} and (f) Al indicated by broken lines. The average Lewis acidities of the isolated cations are indicated beside each diagram.

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

In order to visualize the occurrence of different uranyl-oxide hydroxy-hydrate phases in the U^{6+}-bearing aqueous system, one can calculate an activity–activity diagram for log $[M^{2+}]$ ($M^{2+} = Ca^{2+}, Ba^{2+}, Pb^{2+}, K^{+}_{2}, Na^{+}_{2}$) *versus* pH value for all structural units in uranyl-oxide hydroxy-hydrate minerals and synthetic compounds (Figs. 9a, c). The construction of such diagrams has been described in detail by Schindler & Hawthorne (2001c). All minerals in this diagram are related by the general reaction:

$$\{M^{2+}_{n} \text{ interstitial complex}\}^{z+} [(UO_2)_k O_l (OH)_m]^{z-} + a(H_2O) + b\{M^{2+}\} \leftrightarrow \{M^{2+}_{n+b} \text{ interstitial complex}\}^{(z+2b)+} [(UO_2)_k O_{l-a+b} (OH)_{m+2a-2b}]^{(z+2b)-} + 2bH^{+} \qquad [1]$$

in which a and b can be any integer.

This general reaction does 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 of crystallization.

From the law of mass action, we may write the following relation for reaction [1]:

$$pH = -a/2b \log [H_2O] + -\tfrac{1}{2}\, b \log K - \tfrac{1}{2} \log [M^{2+}] \qquad (1)$$

Uranyl-oxide hydroxy-hydrate minerals generally form in dilute aqueous solutions in which the activity of $[H_2O]$ is very close to one. In this case, the law of mass action simplifies to

$$pH = \tfrac{1}{2} \log K - \tfrac{1}{2} \log [M^{2+}] \qquad (2)$$

We do not know $-\tfrac{1}{2}$ log K, and hence our calculated values are on a relative basis only. However, the slope of the boundary between all stability fields is $-\tfrac{1}{2}$ (which we do know), and hence we can construct an activity–activity diagram having the correct topology. If b is equal to zero in reaction [1], the two minerals are related *via* the reaction

$$\{M^{2+}_{n} \text{ interstitial complex}\}^{z+} [(UO_2)_k O (OH)_m]^{z-} + a(H_2O) \leftrightarrow \{M^{2+}_{n} \text{ interstitial complex}\}^{z+} [(UO_2) O_{l-a} (OH)_{m+2a}]^{z-} \qquad [2]$$

The corresponding law of mass action becomes

$$\log K = a \log [H_2O] \qquad (3)$$

and both structural units occur in the same field of stability in an activity–activity diagram with log $[M^{2+}]$ *versus* pH. Figures 10a and c show the stability fields of the structural units and indicate the corresponding minerals and compounds, the average basicities and chemical compositions of the structural units, and the corresponding ranges in Lewis basicity.

Average basicity and pH

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

$$[B_k O_n (OH)_m]^{a-} + xH^{+} \leftrightarrow [B_k O_{n-x} (OH)_{m+x}]^{(a-x)-} \qquad [3]$$

and

$$[V_k O_n]^{a-} + 2xH^{+} \leftrightarrow [V_k O_{n-2x}]^{(a-2x)-} + xH_2O \qquad [4]$$

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 [3] and [4] 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. The pH thus clearly controls the crystallization of minerals *via* condensation of the principal species in solution.

TABLE 4. SELECTED STRUCTURAL UNITS OF SYNTHETIC URANYL-OXIDE HYDRATES: AVERAGE BASICITY, LEWIS BASICITY AND THE CHAIN SEQUENCE

Structural unit	chemical composition	average basicity [*vu*]	range in Lewis basicity [*vu*]	chain sequence	Ref.
$[(UO_2)_4O_3(OH)_4]^{1-}$	$^{[8]}Pb^{2+}_{0.5}(H_2O)_4[(UO_2)_4O_2(OH)_5](H_2O)_4$	0.13	0.11-0.20	$P_3(UD)_6$	(1)
$[(UO_2)_{12}O_7(OH)_{13}]^{3-}$	$Cs_3(H_2O)_3[(UO_2)_{12}O_7(OH)_{13}]$	0.13	0.11-0.20	$P_6(UD)_5$	(2)
$[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]^{4-}$	$Pb^{2+}_2(H_2O)_2[(UO_2)_{10}UO_{12}(OH)_6(H_2O)_2]$	0.15	0.14-0.23	Framework	(3)
$[(UO_2)_4O_3(OH)_4]^{2-}$	$Ca(H_2O)[(UO_2)_4O_3(OH)_4](H_2O)$	0.19	0.15–0.23	$U^{m'}$	(4)
$[(UO_2)_{10}O_8(OH)_9]^{5-}$	$K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$	0.18	0.15–0.23	$P_4(UD)_{10}R_2$	(5)
$[(UO_2)_4O_4(OH)_3]^{3-}$	$Sr_{2.84}(H_2O)_2[(UO_2)_4O_4(OH)_3]_2(H_2O)_2$	0.24	0.175–0.24	$(UD)_6(U^m)_6$	(6)
$[(UO_2)O_2]^{2-}$	$^{[9]}Pb^{2-}[(UO_2)O_2]$	0.5	0.21-0.28	R	(7)

(1) Li & Burns (2000a); (2) Hill & Burns (1999), (3) Li & Burns (2000c); (4) Glatz *et al.* (2002); (5) Burns & Hill (2000a), (6) Burns & Hill (2000b), (7) Cremers *et al.* (1986).

Reaction [1] is similar to reactions [3] and [4], and so we expect that formation of structural units with higher average basicity is favored by an increase in pH. This indeed is the case: the average basicity of structural units increases with increases with pH as well as with log [M^{2+}] (Fig. 9a). Hence, average basicity correlates with increasing Pb^{2+}/U^{6+} in uranyl-oxide hydroxy-hydrate minerals, and also can be used as an indicator of the degree of weathering of primary uraninite.

Schindler & Hawthorne (2001c) showed that borate structural units related *by the reaction*

$$[B_k\,O_{n-y}\,(OH)_{m+2y}]^{a-} \leftrightarrow [B_k\,O_n\,(OH)_m]^{a-} + y(H_2O) \qquad [5]$$

have similar average basicities. Moreover, they observed that changes in average basicity are much smaller relative to changes involving structural units related by reactions [3] and [4]. Reaction [2] is similar to reaction [5], and so we expect similar average basicities in the corresponding structural units. This is again the case: the structural units $[(UO_2)_{14}O_{19}(OH)_2]^{14-}$ and $[(UO_2)_6O_8(OH)_2]^{6-}$ have the same average basicity, 0.29 *vu*, 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.

Lewis basicity, average basicity and pH

For the uranyl-oxide minerals, the minimum and maximum Lewis basicities of a structural unit increase

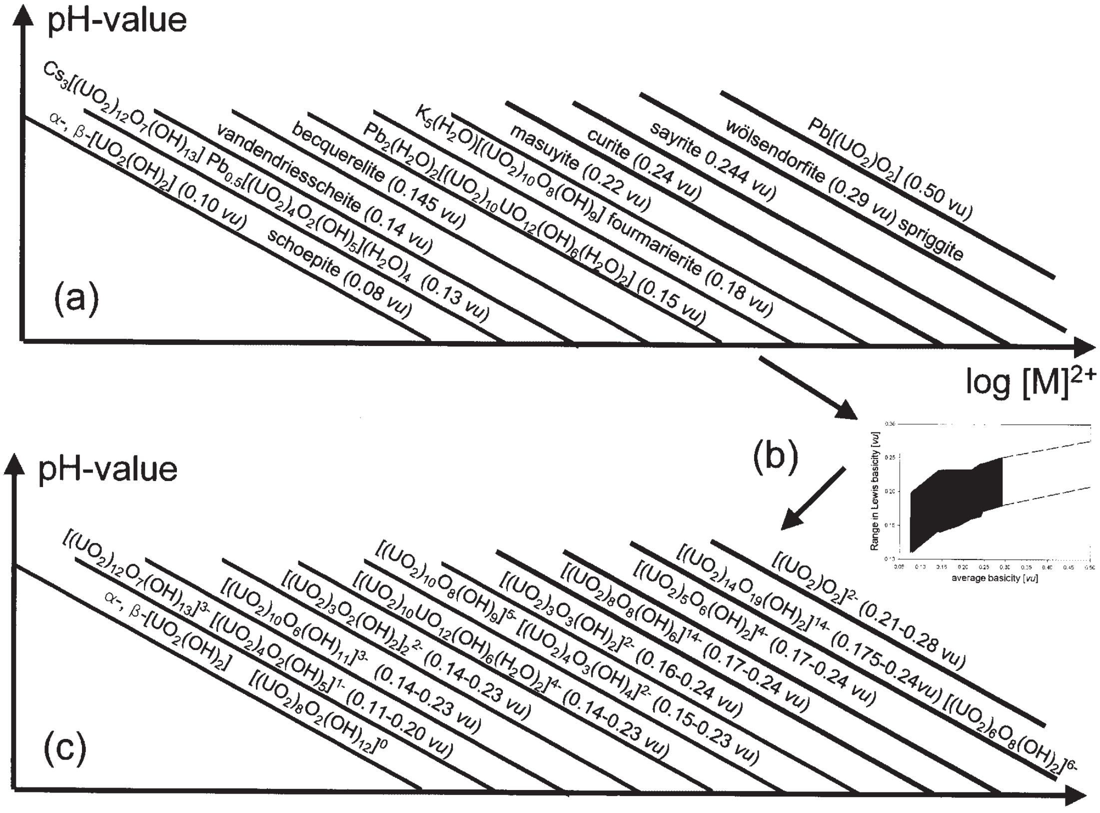


FIG. 9. (a) An activity–activity diagram: pH *versus* log [M^{2+}] for selected uranyl-oxide hydroxy-hydrate minerals. The diagram has been calculated without considering different types of interstitial cations (*e.g.*, Pb^{2+}, Ca) or the possible influence of Eh, and stereoactive lone-pair effects are not considered. The corresponding average basicity of the structural unit is given in brackets; (b) the correlation between average basicity and the range in Lewis basicity for all uranyl minerals; (c) the general occurrence of the structural units in the activity–activity diagram with the corresponding ranges in Lewis basicity from Figure 9b.

with increasing average basicity (Table 2): the minimum and maximum Lewis basicities increase from 0.14 to 0.23 *vu* for the structural unit $[(UO_2)_{10}O_6(OH)_{11}]^{3-}$ (with an average basicity of 0.14 *vu*) to 0.175 to 0.24 *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 an uranyl-oxide hydroxy-hydrate structural unit correlate with pH and log $[M^{2+}]$ (Fig. 9c).

Chemical composition of interstitial complexes as a function of log $[M^{2+}]$ and pH

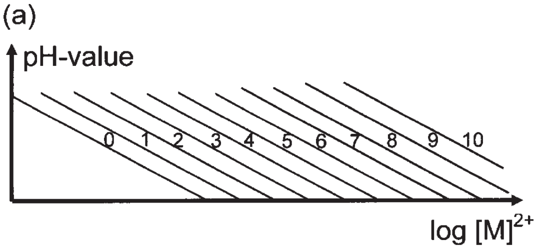
Figure 10 shows the activity–activity diagram with the composition of the corresponding interstitial cations in uranyl-oxide hydroxy-hydrate minerals. We know that the minimum and maximum Lewis basicities increase with increasing pH and log $[M^{2+}]$, and therefore we expect that interstitial complexes containing only more highly coordinated monovalent cations (*e.g.*, $^{[7-10]}K^+$) would occur (in the activity–activity diagram) at lower pH and lower log $[M^{2+}]$. This is indeed the case: the only interstitial complex with exclusively monovalent cations occurs with the structural unit $[(UO_2)_3O_2(OH)_3]^-$ (in compreignacite), which occurs at low log $[M^{2+}]$ and low pH (Figs. 10c, 11). Interstitial complexes containing more highly coordinated monovalent cations, *e.g.*, $\{^{[8]}K_2{}^{[9]}(Ca,Sr)_1(H_2O)_{0.5}\}$ (agrinierite) occur at moderate log $[M^{2+}]$ and moderate pH, and there are no interstitial complexes with monovalent cations at high log $[M^{2+}]$ and high pH.

Chemical composition of synthetic compounds

Synthetic compounds crystallize in a chemically restricted system, and the resultant arrangements of atoms are restricted by what chemical species are available during crystallization. In some cases, the arrangements that result may be relatively unstable; they may show exotic coordination-numbers or large deviations from the valence-matching principle. For this reason, the arguments developed here are likely to work better for minerals than for synthetic compounds, as natural systems are more likely to have the optimum interstitial cations available for uptake. Nevertheless, examination of synthetic compounds from this perspective, and comparison with analogous natural systems, may give significant insight into less stable arrangements of atoms.

Consider synthetic $Pb^{2+}[(UO_2)O_2]$ (Cremers *et al.* 1986); the predicted range in Lewis basicity for the structural unit is 0.21 to 0.28 *vu*. The valence-matching principle requires that the Lewis acidity of the interstitial complex matches the range in Lewis basicity. The Lewis acidity of the interstitial complex $\{^{[9]}Pb^{2+}\}^{2+}$ is 0.22 *vu*; this value matches the range in Lewis basicity, and thus $Pb[(UO_2)O_2]$ is a stable compound.

Next, consider synthetic $Ca(H_2O)[(UO_2)_4O_3(OH)_4](H_2O)_2$ (Glatz *et al.* 2002). Its structural unit has a range in Lewis basicity of 0.15 to 0.23 *vu*, and the Lewis acidity of Ca^{2+} is 0.275 *vu* (Brown 1981). The interstitial complex may be written as $\{^{[8]}Ca(H_2O)_0(H_2O)_1(H_2O)_1\}$, and there are thus eight bonds from the interstitial complex to the structural unit. There are also four hydrogen bonds emanating from the structural unit, and hence there are twelve bonds accepted by the structural unit from the interstitial complex and adjacent structural units. The effective charge of the interstitial complex is 2.8^+, and the resulting Lewis acidity is 2.8 /12 = 0.23 *vu*. The Lewis acidity overlaps the range of Lewis basicity of the structural unit (at its maximum value), and hence $Ca(H_2O)[(UO_2)_4O_3(OH)_4](H_2O)$ is a stable compound.



(b)

Field	Interstitial complex composition
0	**$\{(H_2O)_{12}\}$** **$\{(H_2O)_{10}\}$**
1.	$\{^{[8]}Cs_3(H_2O)_3\}^{3+}$ $\{^{<[8]>}Pb_{0.5}(H_2O)_4(H_2O)_4\}^{2+}$
2.	**$\{^{[9]}Pb_1{}^{[8]}Pb_{0.57}(H_2O)_5(H_2O)_6\}^{2+}$**
3.	**$\{^{[7]}Ca(H_2O)_4(H_2O)_4\}^{2+}$,** **$\{^{[7]}K_2(H_2O)_3(H_2O)_4\}^{2+}$** **$\{^{[10]}Ba(H_2O)_4\}^{2+}$** **$\{K_2Ca(H_2O)_6\}^{4+}$**
4.	$\{^{[10]}Pb_2(H_2O)_2\}^{2+}$
5.	$\{^{[6+x]}K_5(H_2O)\}^{5+}$ **$\{^{[9]}Pb(H_2O)_2(H_2O)_2\}^{2+}$** $\{^{[8]}Ca(H_2O)_2\}^{2+}$
6.	**$\{^{[6]}M_{3.5}{}^{<[8.4]>}Pb_{8.57}(H_2O)_{24}(H_2O)_{17}\}^{24+}$** **$\{^{[8]}K_2(^{[9]}Ca,Sr)(H_2O)_5\}^{4+}$** **$\{^{[10]}Pb(H_2O)_3\}^{2+}$** **$\{^{[10]}Ba(H_2O)_3\}^{2+}$**
7.	$\{^{[10]}Sr_{2.84}(H_2O)_2(H_2O)_2\}^{2+}$ **$\{^{[9]}Pb_3(H_2O)_2(H_2O)_1\}^{2+}$**
8.	**$\{^{[9]}Pb_2(H_2O)_4\}$** **$\{Na_2\}^{2+}$**
9.	**$\{^{<[8.4]>}Pb_{6.2}{}^{[8]}Ba_{0.4}(H_2O)_{10}(H_2O)_2\}^{2+}$** **$\{^{[8.44]}Pb_3(H_2O)_3\}^{3+}$**

FIG. 10. (a) The activity–activity diagram pH *versus* log $[M^{2+}]$; the numbers denote the interstitial complexes occurring under these conditions and are identified in (b); (b) the composition of the interstitial complexes; minerals are indicated in bold, synthetic compounds are indicated in normal font. The numbers increase with increasing pH and log $[M^{2+}]$. The interstitial complexes are written in the form $\{^{[m]}M_a(H_2O)_{d+e}(H_2O)_g\}$ as *d* and *e* are not known individually for most minerals.

Change in topology of the structural unit with increasing log [M^{2+}] / [H^+]^2 and molar proportion of (MO) + (H_2O) / (UO_3)

The stability of phases as a function of pH and log [M^{2+}] can be also represented in a one-dimensional activity diagram with log [M^{2+}] / [H^+]^2 as the only parameter (Fig. 12). The structural units occur in the same sequence along the axis log [M^{2+}] / [H^+]^2 as in the activity–activity diagram of pH *versus* log [M^{2+}] (Figs. 10, 11).

The one-dimensional activity diagram gives us now the opportunity to introduce a compositional parameter in the second dimension. This parameter is the ratio between the molar proportion of (MO) and (H_2O) of the structural unit and the molar proportion of (UO_3), *i.e.*, the molar ratio [(MO)+(H_2O)] : (UO_3). We can understand this relation if we consider that the degree of polymerization of a structural unit depends on the charge per polyhedron [*i.e.*, the molar ratio (MO) : (UO_3)], and the number of (H_2O) and (OH) groups per polyhedron [*i.e.*, the molar ratio (H_2O) : (UO_3)].

Figure 11 shows this activity–composition 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 that contain only H and R chains. These chains contain U^{6+} in [6]- or [8]-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. 11). In this group, structural units with a high molar ratio [(MO) + (H_2O)] / (UO_3) and at low values of 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 a low molar ratio [(MO) + (H_2O)] / (UO_3) and at low values of log [M^{2+}] / [H^+]^2; they contain a high ratio of P to (UD)

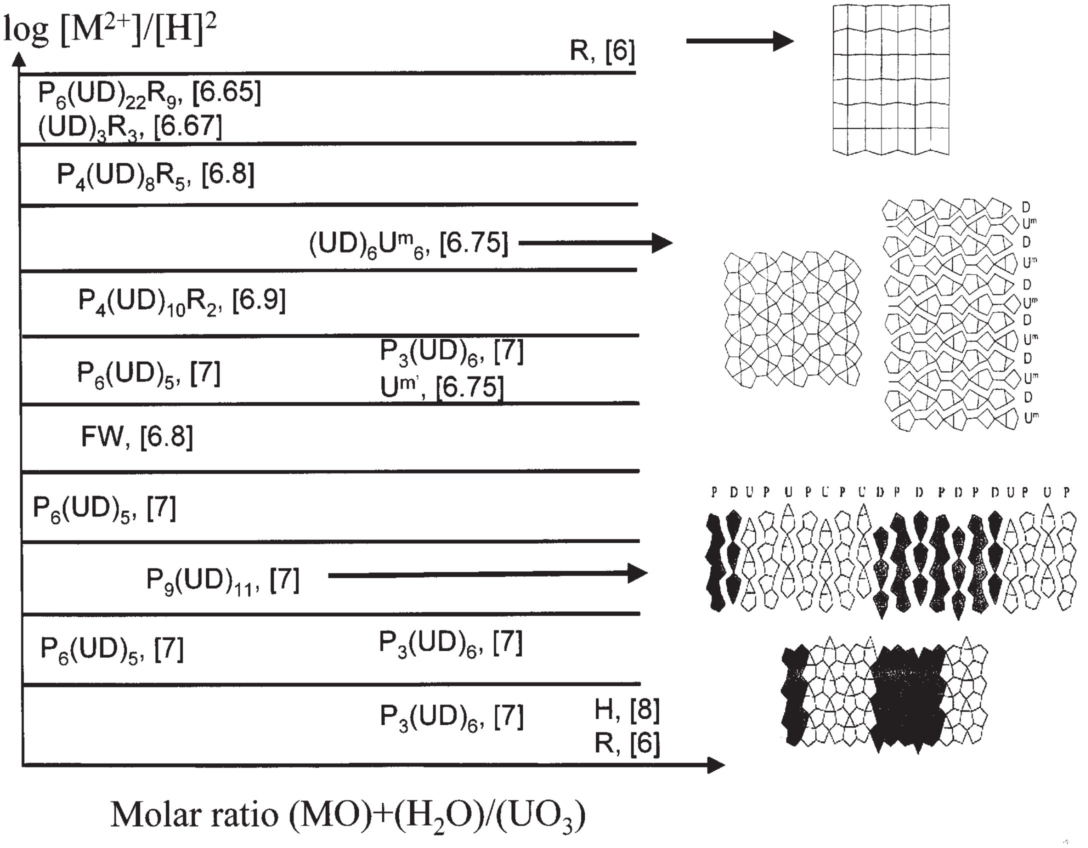


FIG. 11. The activity–composition diagram log [M^{2+}] / [H^+]^2 *versus* the molar ratio [(MO) + (H_2O)] / (UO_3). The chain-stacking sequences of the corresponding anion topologies; FW indicates framework; three examples are shown to the right: the anion topology in synthetic Pb^{2+}[(UO_2)O_2] (top), curite (center) and vandendriesscheite (bottom). The average coordination number of U is shown in square brackets.

chains, whereas at high values of log $[M^{2+}] / [H^+]^2$, they contain a low ratio 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-bearing polyhedra (*i.e.*, a lower degree of polymerization); a structural unit with a high degree of polymerization has a smaller molar ratio $[(MO) + (H_2O)] / (UO_3)$ than a structural unit with a low degree of polymerization. Furthermore, the arrangement of chains with triangles in the layer structural units results in [2]-coordinated O-atoms that link two $(U\varphi_7)$ 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, *i.e.*, a higher molar ratio of $(H_2O) / (UO_3)$ (Fig. 11).

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. 11). Burns *et al.* (1997) showed that $\{(U^{6+}O_2)\varphi_4\}$ polyhedra more commonly share corners than edges with other uranyl polyhedra. Increasing $^{[6]}U^{6+}$ thus reduces the number of edge-sharing 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 the 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. 9c). This decrease reduces the sum of bond valences from U^{6+} cations incident at O atoms, again resulting in an increase in average basicity. The mechanism of incorporation of $^{[6]}U^{6+}$ polyhedra was also recently discussed by Brugger *et al.* (2004).

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

(1) Depolymerization through change from P to (UD) or R to U^m or $U^{m\cdot}$ correlates with an increase in the molar ratio $[(MO) + (H_2O)] / (UO_3)$. This process changes only slightly the average basicity (and hence the range in Lewis basicity).

(2) Depolymerization through decreasing coordination-number of U^{6+} and increase in the $(UO_2)^{2+} / (OH)$ ratio is favored by increase in log $[M^{2+}] / [H^+]^2$, and results in a significant increase in average basicity and in the range in Lewis basicity.

Chemical composition of interstitial complexes and the topology of the structural unit

In Figure 12, we show a sketch of the activity–composition diagram with log$[M^{2+}] / [H^+]^2$ *versus* the molar ratio $[(MO) + (H_2O)] / (UO_3)$, which indicates the type of interstitial cation in the interstitial complexes, the type of topology of the structural unit, and the corresponding ratios of the number of uranyl groups and (OH) groups in the structural unit. What is illuminating in Figure 12 is that structural units with a higher value of the molar ratio $[(MO) + (H_2O)] / (UO_3)$ occur only with interstitial Pb^{2+} cations, whereas structural units with a lower value of the molar ratio $[(MO) + (H_2O)] / (UO_3)$ and at low log $[M^{2+}] / [H^+]^2$ occur generally with interstitial alkali and alkaline-earth cations. In particular, interstitial complexes with monovalent cations in synthetic compounds and minerals occur only with structural units with a low molar ratio $[(MO) + (H_2O)] / (UO_3)$.

It is apparent that Pb^{2+} cations occur only with structural units of topology $P_6(UD)_5$ and with $(UO_2)^{2+}/(OH)^- > 1$. There are two 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. 12, 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, spriggite); (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, spriggite). These two points suggest that the geometrical features of structural units with $P_3(UD)_6$ topology may better match the size and coordination number of $(Pb^{2+}\varphi_n)$ polyhedra than do other topologies.

Figure 12 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, and only occur in synthetic compounds with less highly polymerized structural units of $U^{m\cdot}$ and $(UD)_6U^m{}_6$ topology (Table 3). 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 finding 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 $(UD)_6U^m{}_6$ topology. Hence, interstitial complexes with alkali and alkaline-earth interstitials 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.

Molar proportion of (H_2O) in the structural unit as a fraction of log $[M^{2+}] / [H^+]^2$

Finch & Ewing (1992) recognized that in secondary uranyl-oxide hydroxy-hydrate minerals, the molar proportion of [*M*O] (*M* = divalent cation) increases and the molar proportion of (H_2O) decreases with increasing degree of weathering of uraninite (Fig. 13a). In a uranyl-oxide hydroxy-hydrate structure, the molar proportion of *M*O is related to the molar proportion of (H_2O) by the general equation

$$M^{2+}_{a}[(^{[7]}UO_2)_nO_m(OH)_k] + M^{2+} \rightarrow M^{2+}_{a+1}[(^{[7]}UO_2)_nO_{m+2}(OH)_{k-2}] + 2H^+ \qquad [6]$$

in which the coordination number of U^{6+} does not change, and the molar proportion of (H_2O) decreases *via* replacement of two $(OH)^-$ groups by two O^{2-} anions. From this equation, the molar proportion of *M*O (M = K^+_2, Cs^+_2, Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Pb^{2+}) should correlate inversely with the molar proportion of (H_2O) in the structural unit. This is indeed the case: the molar proportion of (H_2O) decreases with increasing molar proportion of (*M*O) (Fig. 13b). The data show an inverse linear correlation at lower molar proportion of *MO*:

$$\text{molar proportion of } MO = -0.87(4) \times \text{molar proportion of } (H_2O) + 0.37(1),\ R^2 = 0.98 \qquad (4).$$

The data for synthetic $Pb[(UO_2)O_2]$ do not follow this linear correlation, which might indicate an exponential correlation:

$$\text{molar proportion } MO = 0.94(6) \exp[-8.8(8) \times \text{molar proportion of } (H_2O)],\ R^2 = 0.94 \qquad [5].$$

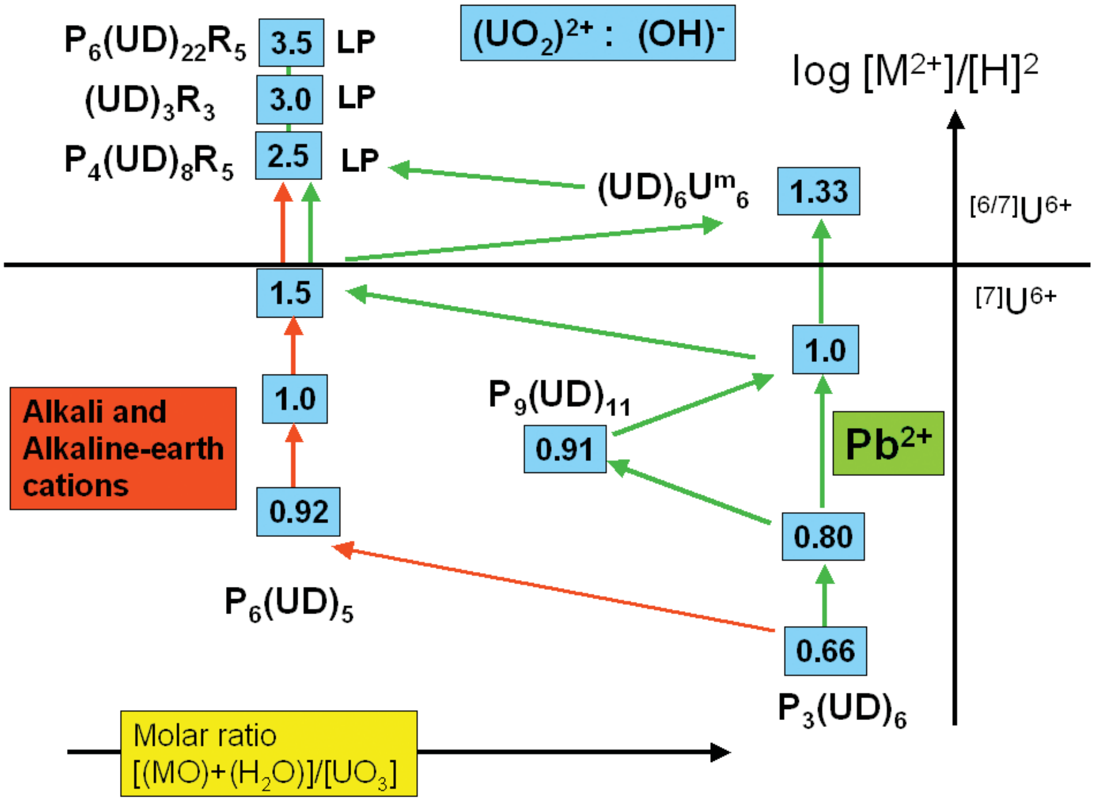


FIG. 12. Schematic of the general occurrence of Pb^{2+} and alkali and alkaline-earth cations with structural units of minerals [with different layer-topologies and different values of the ratio $(UO_2)/(OH)$] as a function of log $[M^{2+}] / [H^+]^2$ and the molar ratio $[(MO) + (H_2O)] / (UO_3)$. The arrows indicate possible sequences of change in structural units during weathering processes, with increase in log $[M^{2+}] / [H^+]^2$; Pb^{2+}-bearing minerals are indicated by green lines, alkali and alkaline-earth minerals are indicated by orange lines; $(UO_2) / (OH)$ values are shown in blue. The horizontal line in the center of the figure 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 $(UD)_6U^m_6$, $P_4(UD)_8R_5$ and $P_6(UD)_{22}R_5$. The occurrence of stereoactive lone-pair electrons in Pb^{2+} is indicated by the letters LP.

The exponential decrease in the molar proportion of (H_2O) at higher molar proportions of MO is a result of depolymerization of the structural units through decrease in the average coordination-number of U^{6+} from [7] to [6]: the average coordination-numbers of U^{6+} are ~[7] in minerals with lower molar proportion of MO, but exponentially decrease from [6.67] in spriggite, [6.65] in wölsendorfite and [6.75] in curite to [6] in $Pb[(UO_2)O_2]$. This exponential correlation between the molar proportions of MO and (H_2O) suggests the following relation:

$$M^{2+}[(^{[7]}UO_2)_nO_m(OH)_k] + aM^{2+} \longrightarrow M^{2+}_{a+1}[(^{[6]}(UO_2)_nO_l] + m + k - l\ (H_2O) + 2l - 2m - kH^+ \qquad [6].$$

Variation in interstitial (H_2O) with the topology of the structural unit

The number of interstitial (H_2O) groups varies with the type of interstitial cation, with the type of structural unit, and with the Lewis basicity of the structural unit. In order to see the influence of the type of structural unit on the number of interstitial (H_2O) groups, we restrict our consideration to cations of similar Lewis acidity. For the uranyl-oxide hydroxy-hydrate minerals, the important interstitial divalent cations are Ca^{2+}, Pb^{2+}, Ba^{2+} and Sr^{2+} (Table 1). The topology of the structural unit is related strongly to the molar proportion of (H_2O) in the structural unit, and hence we might expect a correlation between this value and M^{2+} / (H_2O), the ratio of the (Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}) cations to the number of (H_2O) groups in the interstitial complex (Fig. 13c). The corresponding plot shows two different inverse linear correlations: the more highly polymerized structural units with a higher number of either P or R chains occur with interstitial complexes of lower M^{2+} : (H_2O) ratio than the corresponding structural units with a higher

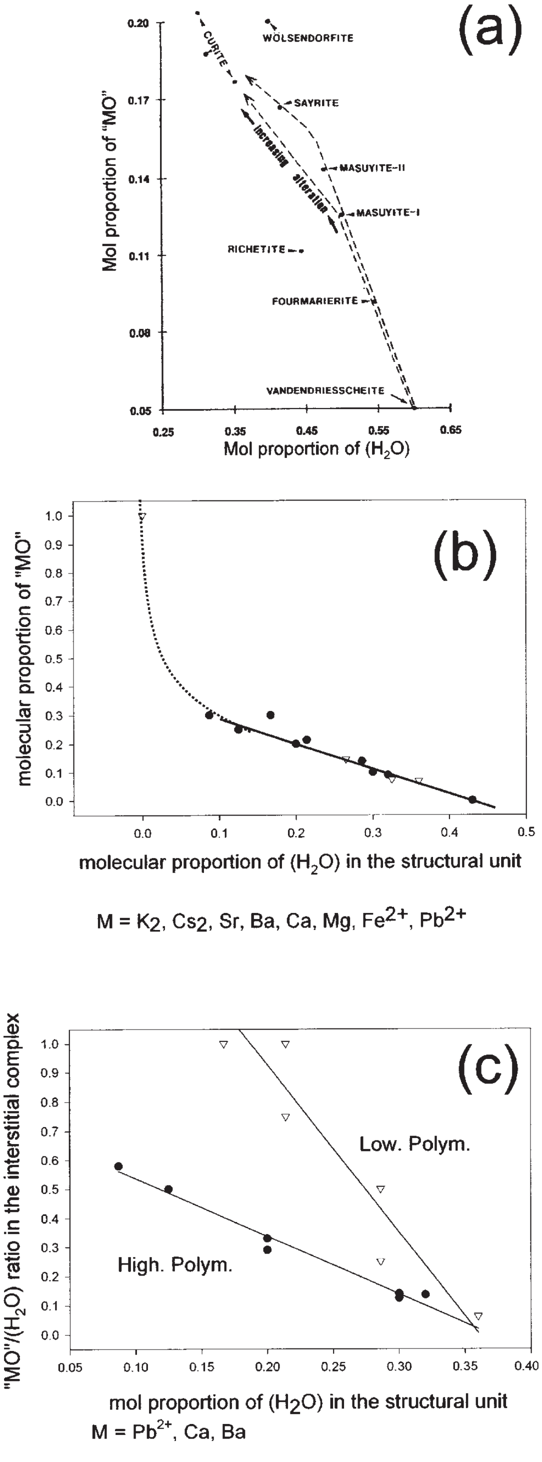


FIG. 13. (a) Compositions of Pb^{2+}-uranyl-oxide hydroxy-hydrate minerals as a function of molecular proportions of H_2O and MO ($M = Pb^{2+}$) (after Finch & Ewing 1992); (b) the variation in the molar proportion of (H_2O) in the structural unit and the molar proportion of MO. The latter value was calculated without considering the molar proportion of (H_2O) in the interstitial complex. Data for minerals are shown as filled circles, data for synthetic phases are shown as white triangles; (c) the variation in molar proportion of (H_2O) in the structural unit and the MO/(H_2O) ratio in the interstitial complex. The less highly polymerized structural units with more U, D or U^m chains than O and R chains are shown as white circles, and the more highly polymerized structural units with more P and R chains than U, D, and U^m chains are shown as filled circles.

number of U, D, U^m and $U^{m'}$ chains. The reason for this is the same as that for the occurrence of monovalent cations: more highly polymerized structural units contain a higher density of bond-valence acceptors (mainly uranyl–oxygen atoms), and therefore the corresponding interstitial complexes require a higher number of (H_2O) groups in order to distribute the bond valence emanating from H atoms of the structural unit.

We may summarize the following points regarding the relation between the topology of the structural unit and the composition of interstitial complexes:

(a) Structural units in synthetic phases and minerals with more P or R chains than (UD) or U^m chains have more (*i.e.*, a higher density of) bond-valence acceptors. Thus, they occur with interstitial complexes that contain monovalent cations and that have a low value of the $[M^{2+} / (H_2O)]$ ratio ($M^{2+} = Ca^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}$).

(b) Structural units with R and U^m chains have higher ranges in Lewis basicity than structural units containing only P and (UD) chains. Hence, the Lewis acidities of the corresponding interstitial complexes must match the higher Lewis basicities of these structural units, and hence the interstitial complexes cannot contain monovalent cations only.

SUMMARY

(1) The ideas developed by Hawthorne (1985, 1990, 1997) and Schindler & Hawthorne (2001a, b, c) are fairly successful in understanding aspects of the stereochemistry and chemical composition of the interstitial complexes of uranyl-oxide hydroxy-hydrate minerals.

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

(3) Combining these equations with the law of mass action leads to an expression that allows arrangement of structural units in pH – log $[M^{2+}]$ 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.

(4) The change in the topology of the structural units can be indicated in an activity–composition diagram with log $[M^{2+}] / [H^+]^2$ *versus* the molar ratio $[(MO) + (H_2O)] / (UO_3)$. Structural units of similar topology occur in contiguous fields of the activity–composition diagram, and the general classes of polymerization of P, U and D chains in the structural units change systematically across this diagram. Depolymerization through change from P to (UD) or R to U^m or $U^{m'}$ chains correlates with increasing molar ratio $[(MO) + (H_2O)] / (UO_3)$. 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 in Lewis basicity.

(5) In accord with the valence-matching principle, the details of the interstitial complexes show systematic variation across the activity–activity diagram with pH *versus* log $[M^{2+}]$. In highly polymerized structural units, interstitial Pb^{2+} tends to be disordered over more than one site, and tends to exhibit stereoactive lone-pair behavior.

(6) The average basicity of structural units in uranyl-oxide hydroxy-hydrate minerals varies only over the range 0.08 to 0.29 *vu*, in accord with the small range of pH (5 to 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

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

________ (2002): *The Chemical Bond in Inorganic Chemistry. The Bond-Valence Model*. Oxford University Press, Oxford, U.K.

BRUGGER, J., KRIVOVICHEV, S.V., BERLEPSCH, P., MEISSER, N., ANSERMET, S. & ARMBRUSTER, T. (2004): Spriggite, $Pb_3[(UO_2)_6O_8(OH)_2](H_2O)_3$, a new mineral with β-U_3O_8-type sheets: description and crystal structure. *Am. Mineral.* **89**, 339-347.

BUCK, E.C., BROWN, N.R. & DIETZ, N.L. (1996): Contaminant uranium phases and leaching at the Fernald site in Ohio. *Environ. Sci. Technol.* **30**, 81-88.

BURDETT, J.K. & HAWTHORNE, F.C. (1993): An orbital approach to the theory of bond valence. *Am. Mineral.* **78**, 884-892.

BURNS, P.C. (1997): A new uranyl oxide hydrate sheet in vandendriesscheite: implications for mineral paragenesis and the corrosion of spent nuclear fuel. *Am. Mineral*. **82**, 1176-1186.

________ (1998a): The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. *Can. Mineral.* **36**, 1061-1067.

________ (1998b): The structure of richetite, a rare lead uranyl oxide hydrate. *Can. Mineral*. **36**, 187-199.

_______ (1999a): The crystal chemistry of uranium. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 23-90.

________ (1999b): A new complex sheet of uranyl polyhedra in the structure of wölsendorfite. *Am. Mineral*. **84**, 1661-1673.

________, Ewing, R.C. & Hawthorne, F.C. (1997): The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Can. Mineral.* **35**, 1551-1570.

________ & Hanchar, J.M. (1999): The structure of masuyite, $Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$, and its relationship to protasite. *Can. Mineral*. **37**, 1483-1491.

________ & Hill, F.C. (2000a): A new uranyl sheet in $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$: new insight into sheet anion-topologies. *Can. Mineral.* **38**, 163-173.

________ & ________ (2000b): Implications of the synthesis and structure of the Sr analogue of curite. *Can. Mineral.* **38**, 175-181.

________ & Li, Yaping (2002): The structures of becquerelite and Sr-exchanged becquerelite. *Am. Mineral.* **87**, 550-557.

________, Miller, M.L. & Ewing, R.C. (1996): U^{6+} minerals and inorganic phases: a comparison and hierarchy of structures. *Can. Mineral.* **34**, 845-880.

Cahill, C.L. & Burns, P.C. (2000): The structure of agrinierite: a Sr-containing uranyl oxide hydrate mineral. *Am. Mineral.* **85**, 1294-1297.

Casas, I., Bruno, J., Cera, E., Finch, R.J. & Ewing, R.C. (1994): Kinetic and thermodynamic studies of uranium minerals. Assessment of the long-term evolution of spent nuclear fuel. *SKB Tech. Rep.* (*Stockholm*) **94-16**.

________, ________, ________, ________ & ________ (1997): Characterization and dissolution behavior of a becquerelite from Shinkolobwe, Zaire. *Geochim. Cosmochim. Acta* **61**, 3879-3884.

Cremers, T.L., Eller, P.G., Larson, E.M. & Rosenzweig, A. (1986): Single-crystal structure of lead uranate (VI). *Acta Crystallogr.* **C42**, 1684-1685.

Finch, R.J., Cooper, M.A., Hawthorne, F.C. & Ewing, R.C. (1996): The crystal structure of schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$. *Can. Mineral*. **34**, 1071-1088.

________ & Ewing, R.C. (1992): The corrosion of uraninite under oxidizing conditions. *J. Nucl. Mater.* **190**, 133-156.

________ & ________ (1997): Clarkeite: new chemical and structural data. *Am. Mineral.* **82**, 607-619.

________, Hawthorne, F.C. & Ewing, R.C. (1998): Structural relations among schoepite, metaschoepite and "dehydrated schoepite". *Can. Mineral.* **36**, 831-845.

________ & Murakami, T. (1999): Systematics and paragenesis of uranium minerals. *In* Uranium: Mineralogy, Geochemistry and the Environment (P.C. Burns & R.J. Finch, eds.). *Rev. Mineral.* **38**, 91-179.

Frondel, C. (1956): Mineral composition of gummite. *Am. Mineral.* **41**, 539-568.

________ (1958): Systematic mineralogy of uranium and thorium. *U.S. Geol. Surv., Bull.* **1064**.

Garrels, R.M. & Christ, C.L. (1959): Behavior of uranium minerals during oxidation. *U.S. Geol. Surv., Prof. Pap.* **320**, 81-89.

Glatz, R.E., Li, Yaping, Hughes, K.-A. Cahill, C.L. & Burns, P.C. (2002): 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.* **40**, 217-224.

Hawthorne, F.C. (1983): Graphical enumeration of polyhedral clusters. *Acta Crystallogr*. **A39**, 724-736.

________ (1985): Towards a structural classification of minerals: the $^{vi}M^{iv}T_2O_n$ minerals. *Am. Mineral.* **70**, 455-473.

________ (1990): Structural hierarchy in $M^{[6]}T^{[4]}\phi_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

________ (1992): The role of OH and H_2O in oxide and oxysalt minerals. *Z. Kristallogr.* **201**, 183-206.

________ (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.

________ (1997): Structural aspects of oxide and oxysalt minerals. *EMU Notes in Mineralogy* **1**, 373-429.

Hill, F.C. & Burns, P.C. (1999): The structure of a synthetic Cs uranyl oxide hydrate and its relationship to compreignacite. *Can. Mineral.* **37**, 1283-1288.

Hughes, K.-A., Burns, P.C. & Kolitsch, U. (2003): The crystal structure and crystal chemistry of uranosphaerite, $Bi(UO_2)O_2OH$. *Can. Mineral.* **41**, 677-685.

Janeczek, J. & Ewing, R.C. (1992): Dissolution and alteration of uraninite under reducing conditions. *J. Nucl. Mater.* **190**, 157-173.

Langmuir, D. (1978): Uranium solution – mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* **42**, 547-569.

Li, Yaping & Burns, P.C. (2000a): Investigations of crystal-chemical variability in lead uranyl oxide hydrates. I. Curite. *Can. Mineral.* **38**, 727-735.

________ & ________ (2000b): Investigations of crystal-chemical variability in lead uranyl oxide hydrates. II. Fourmarierite. *Can. Mineral.* **38**, 737-749.

________ & ________ (2000c): Synthesis and crystal structure of a new Pb uranyl oxide hydrate with a framework structure that contains channels. *Can. Mineral.* **38**, 1433-1441.

Miller, M.L., Finch, R.J., Burns, P.C. & Ewing, R.C. (1996): Descriptions and classification of uranium oxide hydrate sheet topologies. *J. Mater. Res.* **11**, 3048-3056.

Morris, D.E., Allen, P.G., Berg, J.M., Chisolm-Brause, C.J., Conradson, S.D., Hess, N.J., Musgrave, J.A. & Tait, C.D. (1996): Speciation of uranium in Fernald soils by molecular spectroscopic methods: characterization of untreated soils. *Environ. Sci. Technol*. **30**, 2322-2331.

Pagoaga, M.K., Appleman, D.E. & Stewart, J.M. (1987): Crystal structures and crystal chemistry of the uranyl oxide hydrates becquerelite, billietite, and protasite. *Am. Mineral.* **72**, 1230-1238.

Piret, P. (1985): Structure cristalline de la fourmariérite, $Pb(UO_2)_4O_3(OH)_4•4H_2O$. *Bull. Minéral.* **108**, 659-665.

________, Deliens, M., Piret-Meunier, J. & Germain, G. (1983): La sayrite, $Pb_2[(UO_2)_5O_6(OH)_2]•4H_2O$, nouveau minéral; propriétés et structure cristalline. *Bull. Minéral.* **106**, 299-304.

Protas, J. (1959): Contribution à l'étude des oxydes d'uranium hydratés. *Bull. Minéral.* **82**, 239-272.

Sandino, M.C.A. & Grambow, B. (1995): Solubility equilibria in the U(VI)–Ca–K–Cl–H_2O system: transformation of schoepite into becquerelite and compreignacite. *Radiochim. Acta* **66/67**, 37-43.

Schindler, M. & Hawthorne, F.C. (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.* **39**, 1225-1242.

________ & ________ (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.* **39**, 1243-1256.

________ & ________ (2001c): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. III. Paragenesis of borate minerals. *Can. Mineral.* **39**, 1257-1274.

________, ________ & Baur, W.H. (2000): A crystal chemical approach to the composition and occurrence of vanadium minerals. *Can. Mineral*. **38**, 1443-1456.

Smith, D.K., Jr. (1984): Uranium mineralogy. *In* Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources (B. DeVivo, F. Ippolito, G. Capaldi & P.R. Simpson, eds.). Institute of Mining and Metallurgy, London, U.K. (43-88).

Taylor, J.C., Stuart, W.I. & Mumme, I.A. (1981): The crystal structure of curite. *J. Inorg. Nucl. Chem*. **43**, 2419-2423.

Vochten, R. & van Haverbeke, L. (1990): Transformation of schoepite into the uranyl oxide hydrates: becquerelite, billietite and wölsendorfite. *Mineral. Petrol.* **43**, 65-72.

Weller, M.T., Light, M.E. & Gelbrich, T. (1999): Structure of uranium(VI) oxide dihydrate, $UO_3•2H_2O$; synthetic meta-schoepite $(UO_2)_4O(OH)_6•5H_2O$. *Acta Crystallogr.* **B56**, 577-583.

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APPENDIX 1: CALCULATION OF THE LEWIS BASICITY OF THE STRUCTURAL UNIT

The structural unit of curite, $^{[9]}Pb^{2+}_3(H_2O)_2[(UO_2)_8O_8(OH)_6](H_2O)_1$, is $[(UO_2)_8O_8(OH)_6]^{6-}$.

The charge of the structural unit = 6^-.

The number of hydrogen bonds emanating from the structural unit = 6.

The average bond-valence of a hydrogen bond, *h*, is 0.20 *vu*.

The bond valence emanating from the structural unit as hydrogen bonds = 6×0.2 *vu*.

The effective charge is equal to the bond valence required for charge balance: $-6 + 6 \times -0.2 = -7.2$ *vu*.

The number of oxygen atoms in the structural unit = 30.

The average basicity is the effective charge per O atom in the structural unit = 7.2 / 30 = 0.24 *vu*.

$[CN]_{in}$ is the range in number of bonds per O atom accepted by the structural unit, 1.00–1.45.

The range of number of bonds accepted by *all* O atoms in the structural unit: $30 \times 1.0 - 30 \times 1.45$, *i.e.*, 30 – 43.5.

The range in Lewis basicity is the effective charge divided by minimum and maximum numbers of bonds to the structural unit = (43.5–7.2/30) = 0.17–0.24 *vu*.

The Lewis acidity is the effective charge / number of bonds emanating from the interstitial complex.

The valence-matching principle states that the Lewis acidity must closely match the Lewis basicity, *i.e.*, the Lewis acidity must be in range calculated above for the Lewis basicity: $0.17 \leq$ Lewis acidity ≤ 0.24 *vu*.

The number of possible bonds emanating from the interstitial complex is the number of bonds involving the interstitial cations (N) plus the number of transformer (H_2O) groups (d) plus the number of hydrogen bonds from the structural unit to the interstitial complex (and back to the structural unit) ($t = 6$) = $N + d + 6$.

Thus the Lewis acidity can be expressed as $7.2 / (N + d + 6)$.

As the Lewis acidity must obey the valence-matching principle, $0.17 \leq 7.2 / (N + d + 6) \leq 0.24$ *vu*.

Three (of many) possible examples of interstitial cation species are given below:

Example 1: Six $^{[6]}M^+$

The number of bonds involving the interstitial cations = N = 6 (the number of interstitial cations) $\times$ 6 (the average coordination-number of those cations) = 36.

From the arguments developed above, the range in Lewis basicity constrains the range in Lewis acidity *via* the valence-matching principle:

$0.17 \leq 7.2 / (36 + d + 6) \leq 0.24 = 0.17$
$\leq 7.2 / (42 + d) \leq 0.24$ *vu*.

The maximum value of d, the number of transformer (H_2O) groups, is given by the minimum bound on the Lewis acidity: $0.17 \leq 7.2 / (42 + d)$. Hence $d \leq 0.35$, and thus *the maximum value of* $d = 0$ (as d cannot be negative).

Thus an interstitial complex of six $^{[6]}M^+$ cations will contain no interstitial transformer (H_2O) groups.

Example 2: Three $^{[8]}M^{2+}$

The number of bonds involving the interstitial cations = $N = 3 \times 8 = 24$.

The range in Lewis basicity constrains the range in Lewis acidity:

$0.17 \leq 7.2 / (24 + d + 6) \leq 0.24 = 0.17$
$\leq 7.2 / (30 + d) \leq 0.24$ *vu*.

The maximum value of d is given by $0.17 = 7.2 / (30 + d)$. Hence $d_{max} = 12$.

The minimum value of d is given by $0.24 = 7.2 / (30 + d)$. Hence $d_{min} = 0$.

Thus an interstitial complex of three $^{[8]}M^{2+}$ cations will contain 0–12 interstitial transformer (H_2O) groups.

Example 3: Two $^{[6]}M^{3+}$

The number of bonds involving the interstitial cations = $N = 2 \times 6 = 12$.

The range in Lewis basicity constrains the range in Lewis acidity:

$0.17 \leq 7.2 / (12 + d + 6) \leq 0.24 = 0.17$
$\leq 7.2 / (18 + d) \leq 0.24$ *vu*.

The maximum value of d is given by $0.17 = 7.2 / (18 + d)$. Hence $d_{max} = 24$; however, two [6]-coordinated cations can only link to 12 (H_2O) groups, and thus the practical value of d_{max} is 12.

The minimum value of d is given by $0.24 = 7.2 / (18 + d)$. Hence $d_{min} = 12$.

Thus an interstitial complex of three $^{[8]}M^{2+}$ cations will contain 12 interstitial transformer (H_2O) groups.