THE CRYSTAL STRUCTURE OF GUILLEMINITE, A HYDRATED Ba–U–Se SHEET STRUCTURE

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ABSTRACT

The crystal structure of guilleminite, $Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$, orthorhombic, a 7.084(1), b 7.293(1), c 16.881(4) Å, V 872.1(3) Å^3, $P2_1nm$, $Z = 2$, has been solved by direct methods and refined to an R index of 4.7% based on 975 observed (5σ) reflections measured with MoKα X-radiation on a single-crystal diffractometer. This has resulted in a revision of the chemical formula and space group. There is one unique Ba atom, coordinated by seven oxygen atoms and three H_2O groups in a capped tri-augmented trigonal prismatic arrangement. There is one unique Se atom coordinated by three oxygen atoms, and these four atoms form a triangular pyramid with Se in the apical position, characteristic of stereoactive lone-pair behavior. There are two distinct U atoms: U(1) is coordinated by a hexagonal bipyramidal arrangement of oxygen atoms, and U(2) is coordinated by a pentagonal bipyramidal arrangement of oxygen atoms. In both polyhedra, the apical oxygen atoms constitute the uranyl oxygen atoms, with a U–O distance of ~1.8 Å. The (UO_7) groups form edge-sharing dimers that are linked into chains of the form $[U_3O_{14}]$ by sharing edges with (UO_8) monomers. The chains extend along [100] and are cross-linked in the [001] direction by (SeO_3) groups to form sheets of the form $[U_3(SeO_3)_2O_8]$ parallel to (010). The sheets are linked along [010] by interstitial Ba atoms and by hydrogen bonding involving interstitial (H_2O) groups. The sheets are topologically identical to the sheets in phosphuranylite, $KCa(H_3O)_3[\{(UO_2)_3(PO_4)_2O_2\}_2(UO_2)](H_2O)_8$, except for the fact that (SeO_3) groups proxy for (PO_4) groups in guilleminite.

Keywords: guilleminite, crystal structure, uranium mineral, selenite, barium.

SOMMAIRE

Nous décrivons la structure cristalline de la guilleminite, $Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$, phase orthorhombique, a 7.084(1), b 7.293(1), c 16.881(4) Å, V 872.1(3) Å^3, $P2_1nm$, $Z = 2$; nous en avons affiné la structure par méthodes directes jusqu'à un résidu R de 4.7% en utilisant 975 réflexions observées (5σ), mesurées avec rayonnement MoKα et un diffractomètre à cristal unique. Les données mènent à une révision de la formule chimique et du groupe spatial. Il y a un atome unique de Ba, en coordinence avec sept atomes d'oxygène et trois groupes H_2O, articulés en forme de prisme trigonal chapeauté et avec un complément de trois anions. L'atome de Se, et les trois atomes d'oxygène qui lui sont coordonnés, constituent une pyramide triangulaire ayant l'atome de Se dans la position apicale, ce qui caractérise la présence d'une paire d'électrons isolés stéréoactifs. La structure contient aussi deux atomes distincts d'uranium: U(1) est entouré d'atomes d'oxygène dans un agencement hexagonal bipyramidal, tandis que dans le cas de U(2), les atomes d'oxygène définissent un arrangement en bipyramide pentagonale. Dans les deux cas, les atomes d'oxygène apicaux font partie d'un groupe uranyle, la liaison U–O ayant une longueur d'environ 1.8 Å. Les groupes (UO_7) sont agencés en dimères partageant une arête; ces dimères sont agencés en chaînes $[U_3O_{14}]$ par partage d'arêtes avec des monomères (UO_8). Ces chaînes, allongées selon [100], sont aussi liées dans la direction [001] par des groupes (SeO_3) pour former des feuillets $[U_3(SeO_3)_2O_8]$ parallèles à (010). Ces feuillets sont liés l'un à l'autre dans la direction [010] par des atomes interstitiels de Ba et par des liaisons hydrogène impliquant des groupes (H_2O) interstitiels. Les feuillets seraient topologiquement identiques à ceux de la phosphuranylite, $KCa(H_3O)_3[\{(UO_2)_3(PO_4)_2O_2\}_2(UO_2)](H_2O)_8$, sauf que dans la guilleminite, les groupes (SeO_3) remplacent les groupes (PO_4).

(Traduit par la Rédaction)

Mots-clés: guilleminite, structure cristalline, minéral uranifère, sélénite, baryum.

INTRODUCTION

Guilleminite is a hydrated selenite of barium and uranium first described by Pierrot *et al.* (1965) from the oxidized zone of the copper–cobalt deposit of Musonoi, Katanga, Zaire. It occurs as coatings and silky masses, and as small canary-yellow orthorhombic crystals in geodes. As part of a study of uranium oxide and oxysalt crystals, we here report a crystal-structure determination for guilleminite.

EXPERIMENTAL

The crystals used in this study are from the Musonoi

TABLE 1. MISCELLANEOUS INFORMATION FOR GUILLEMINITE

a (Å)	7.084(1)	crystal size (mm)	0.19 x 0.11 x 0.02
b	7.293(1)	Radiation	MoKα/Gr
c	16.881(4)	No. of intensities	1251
V (Å³)	872.1(3)	No. of $|F_o| > 5\sigma(|F_o|)$	975
Sp. Gr.	P2₁nm	R(azimuthal) %	21.9 → 2.3
Z	2	R(obs) %	4.7
		wR(obs) %	5.2

Cell contents $2\{Ba[(UO_2)_3(SeO_3)_2O_2](H_2O)_3\}$

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}, w = 1$

ranges $0 \leq h \leq 9, 0 \leq k \leq 10, 0 \leq l \leq 23$. Two standard reflections were measured every fifty-eight reflections; no significant changes in their intensities occurred during data collection. An empirical absorption-correction, based on 36 psi-scans for each of 11 reflections over the whole 2θ range, was applied, with the crystal modeled as a {001} plate. The absorption-correction reduced R(azimuthal) from 21.9 to 2.3%. Reflections with a plate-glancing angle less than 5° were discarded; the value of 5° was determined by using a range of glancing angles and determining where the effect of varying the glancing angle produced no improvement in the refinement. The remaining data were corrected for Lorentz, polarization and background effects; of the 1251 reflections remaining after the absorption correction, there were 975 unique observed reflections having $|F| \leq 5\sigma|F|$.

mine, Kolwezi, Katanga, Zaire, and were generously donated for this study by Mr. William Pinch. Precession photography confirmed the orthorhombic nature of the crystals but showed violations of the c-glide for the space group Pncm and cell orientation used by Pierrot et al. (1965). A platy crystal (Table 1) was mounted on a Nicolet R3m automated four-circle diffractometer. Thirty-five reflections were centered using graphite-monochromated MoKα X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the thirty-five automatically aligned reflections by least-squares techniques. After solution and refinement of the structure, we reoriented the unit cell and repeated the refinement in this new orientation so that the U–Se–O sheet that constitutes the structural unit in guilleminite would be oriented perpendicular to [010], as is the case with U–Se–O sheets in other U-oxysalt minerals. Data were collected using the θ–2θ scan method; a variable scan-rate proportional to the peak intensity was used, with maximum and minimum scan-rates of 29.3°2θ/min and 3.5°2θ/min, respectively. A total of 1336 reflections was measured over the range $4° \leq 2θ \leq 60°$, with index

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. R indices are of the form given in Table 1 and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study.

Direct methods revealed the heavy-atom positions, and successive cycles of difference-Fourier synthesis and refinement gave the anion positions. Full-matrix least-squares refinement of all variable parameters for a model involving anisotropic displacement of the cations and isotropic displacement of the anions converged to an R index of 4.7%. Final atomic parameters are listed in Table 2, and selected interatomic distances are given in Table 3. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 2. FINAL PARAMETERS FOR GUILLEMINITE

Site	x	y	z	*U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0	0.0766(4)	0	211(8)	83(11)	173(12)	376(18)	0	0	−5(13)
U(1)	0.8208(7)	0.3912(2)	1/2	108(3)	23(5)	149(6)	151(6)	0	0	4(9)
U(2)	0.3222(6)	0.3942(1)	0.3917(1)	101(2)	24(4)	161(4)	117(4)	7(4)	−9(8)	−2(6)
Se	0.8302(9)	0.3713(4)	0.2959(2)	163(7)	73(12)	255(14)	132(11)	17(10)	14(24)	7(18)
O(1)	0.840(7)	0.146(4)	1/2	171(61)						
O(2)	0.504(6)	0.325(4)	1/2	113(57)						
O(3)	0.140(4)	0.403(4)	1/2	63(51)						
O(4)	0.298(7)	0.363(5)	0	289(98)						
O(5)	0.357(4)	0.636(3)	0.397(1)	161(47)						
O(6)	0.303(5)	0.147(3)	0.385(1)	225(57)						
O(7)	0.994(5)	0.433(4)	0.365(2)	261(52)						
O(8)	0.292(3)	0.428(3)	0.250(1)	169(48)						
O(9)	0.655(5)	0.364(6)	0.362(2)	236(55)						
W(1)	0.617(6)	0.119(5)	0	213(97)						
W(2)	0.154(6)	0.099(5)	0.158(3)	589(101)						

* $U = U$ x 10^4 for U_{eq} and U_{ij}; the anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11}... + 2hka^*b^*U_{12})$.

TABLE 3. BOND DISTANCES (Å) FOR GUILLEMINITE

U(1)–O(1)	1.79(3)		U(2)–O(2)	2.29(2)	
U(1)–O(2)	2.30(4)		U(2)–O(3)	2.24(2)	
U(1)–O(3)b	2.27(3)		U(2)–O(5)	1.78(2)	
U(1)–O(4)c	1.80(4)		U(2)–O(6)	1.81(2)	
U(1)–O(7),h	2.61(3)	x2	U(2)–O(7)g	2.39(4)	
U(1)–O(9),h	2.62(3)	x2	U(2)–O(8)	2.41(2)	
<U(1)–O>	2.33		U(2)–O(9)	2.42(3)	
			<U(2)–O>	2.19	
Ba–O(1)a	2.90(5)				
Ba–O(2)a	2.93(3)		Se–O(7)	1.70(3)	
Ba–O(4)	2.97(4)		Se–O(8)i	1.68(2)	
Ba–O(5)d,e	2.90(2)	x2	Se–O(9)	1.66(3)	
Ba–O(6)a,f	2.90(3)	x2	<Se–O>	1.68	
Ba–W(1)g	2.73(4)				
Ba–W(2),j	2.88(4)	x2			
<Ba–O>	2.89				

Equivalent positions: a: x–½, $\bar{y}$, z–½; b: x+1, y, z; c: x+½, $\bar{y}$+1, z+½; d: x–½, $\bar{y}$+1, $\bar{z}$+½; e: x–½, $\bar{y}$+1, z–½; f: x–½, $\bar{y}$, $\bar{z}$+½; g: x–1, y, z; h: x, y, $\bar{z}$+1; i: x+½, $\bar{y}$+1, $\bar{z}$+½; j: x, y, $\bar{z}$

TABLE 4. BOND-VALENCE ARRANGEMENT* IN GUILLEMINITE

	U(1)	U(2)	Ba	Se	Σ
O(1)	1.83		0.20		2.03
O(2)	0.62	0.63^{x2}→	0.18		2.06
O(3)	0.66	0.70^{x2}→			2.06
O(4)	1.78		0.17		1.95
O(5)		1.87	0.20^{x2}↓		2.07
O(6)		1.74	0.20^{x2}↓		1.94
O(7)	0.36^{x2}↓	0.53		1.25	2.14
O(8)		0.51		1.31	1.82
O(9)	0.35^{x2}↓	0.50		1.37	2.22
W(1)			0.30		0.30
W(2)		0.21^{x2}↓			0.21
Σ	6.31	6.48	2.07	3.93	

* Calculated with the parameters of Brown (1981).

but there are only two additional anions, rather than the four in the original formula. Furthermore, local bond-valence sums (Table 4) indicate that these anions are O^{2-} rather than OH^-, and this satisfies the requirement of overall electroneutrality. Hence the formula of guilleminite is $Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$.

CHEMICAL FORMULA

Pierrot *et al.* (1965) reported the formula of guilleminite as $Ba(UO_2)_3(SeO_3)_2(OH)_4 \cdot 3H_2O$. As is apparent from Table 2, the anion part of the chemical formula must be revised. The Ba, uranyl, selenite and H_2O components of the previous formula are correct,

COORDINATION OF THE CATIONS

The coordination polyhedra around the cations in guilleminite are illustrated in Figure 1. Ba is surrounded by seven oxygen atoms and three H_2O
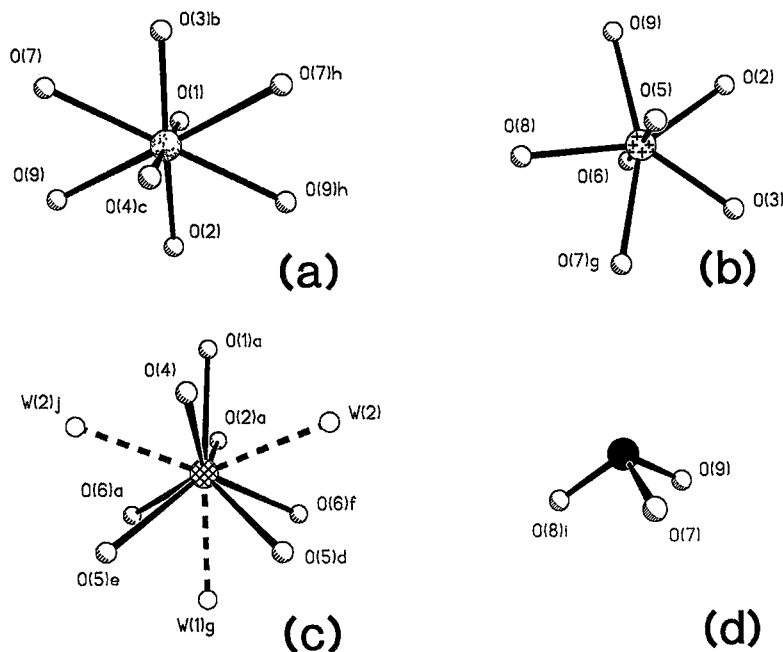
(a)

(b)

(c)

(d)

Fig. 1. The cation coordination polyhedra in guilleminite: (a) the $U(1)O_8$ polyhedron, (b) the $U(2)O_7$ polyhedron, (c) the $BaO_7(H_2O)_3$ polyhedron, (d) the SeO_3 polyhedron. $Ba-(H_2O)$ bonds are shown by broken lines.

groups at distances from 2.73 to 2.97 Å, with a mean distance of 2.89 Å; this is a very restricted range of distances for such a large coordination polyhedron, and hence there is not the usual problem of determining whether the longest distances represent significant bonds. The oxygen atoms form a capped trigonal prism (Fig. 1c), augmented by three H_2O groups in a triangular arrangement.

Selenium is coordinated to three oxygen atoms arranged in a triangle, with the central cation significantly displaced from the plane of the oxygen atoms (Fig. 1d). This triangular pyramidal coordination is typical for Se^{4+} and is indicative of stereoactive lone-pair behavior. The observed <Se–O> distance, 1.68 Å, is within the range of <Se–O> distances observed in inorganic structures (Hawthorne et al. 1987).

The U(1) cation is surrounded by six equatorial oxygen atoms with U(1)–O distances in the range 2.27–2.62 Å and by two "uranyl" (apical) oxygen atoms 1.79 and 1.80 Å from the central cation, the anions forming a hexagonal bipyramid around the central U(1) atom; the <U(1)–O> distance is 2.33 Å. The U(2) cation is surrounded by five equatorial oxygen atoms with U(2)–O distances in the range 2.24–2.42 Å and by two apical oxygen atoms at 1.78 and 1.81 Å from the central cation, the anions forming a pentagonal bipyramid around the central U(2) atom;

the <U(2)–O> distance is 2.19 Å. The larger <U–O> distance for the U(1) cation is in accord with the higher coordination number for U(1) relative to U(2). The bond-valence sums around the U cations (Table 4) are significantly larger than their ideal values of 6.0 vu (valence units), a fairly typical situation for U^{6+} that suggests that the bond-valence curve for U^{6+}–O is somewhat inaccurate.

STRUCTURAL CONNECTIVITY

The $U\phi_n$ (ϕ: unspecified anion) polyhedra polymerize to form an important chain component of the guilleminite structure. Two $U\phi_7$ pentagonal bipyramids share an edge to form a $[U_2\phi_{12}]$ dimer. These dimers link to form a chain of the type $[U_3\phi_{14}]$ by sharing edges with $U\phi_8$ hexagonal bipyramids (Fig. 2). These chains extend along [100] and are cross-linked in the [001] direction by SeO_3 groups, with adjacent $[U_3\phi_{14}]$ chains staggered such that they pack as densely as possible in the (010) plane (Fig. 2). This strongly bonded sheet is the structural unit of guilleminite, with Ba and H_2O as the interstitial species. The $[U_3(SeO_3)_2\phi_8]$ sheets are linked in the [010] direction by Ba atoms and by hydrogen bonds. As is apparent in Figure 3, the sheets are modulated in the [001] direction, and the modulations of adjacent sheets intermesh. The fact that the structural unit is a sheet parallel to
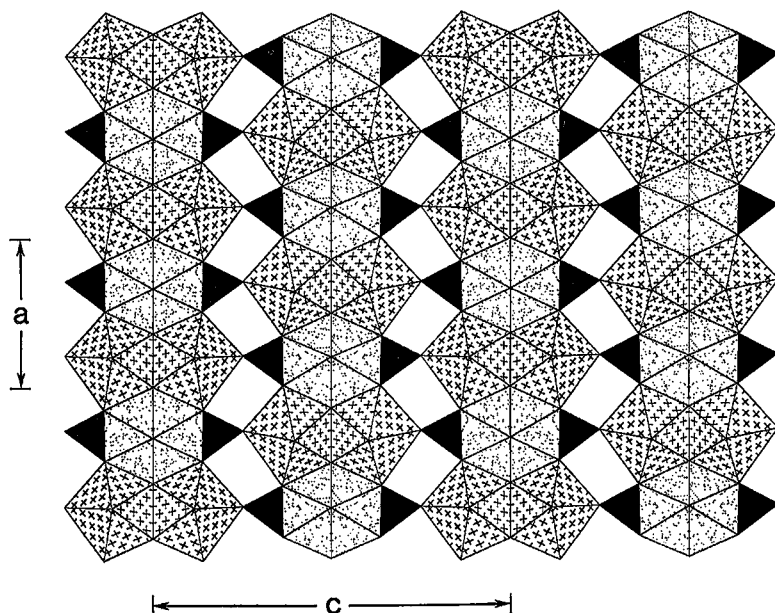

FIG. 2. The $(U\phi_n)(SeO_3)$ sheet in guilleminite projected down [010]; the polyhedra are shaded as follows: $U(1)O_8$ by irregular dots; $U(2)O_7$ by crosses; SeO_3 by solid black.
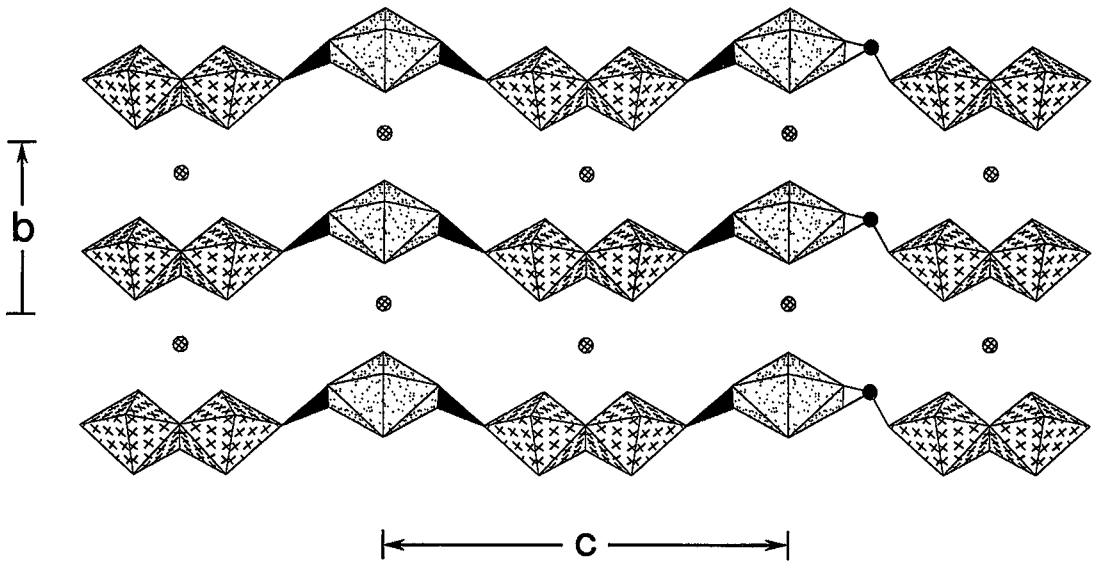
FIG. 3. The crystal structure of guilleminite projected down an axis 10° away from [100]; the polyhedra are shaded as in Figure 2, SeO₃ groups are shaded black, as are Se atoms on the right side of the diagram; Ba atoms are shown as latticed circles.
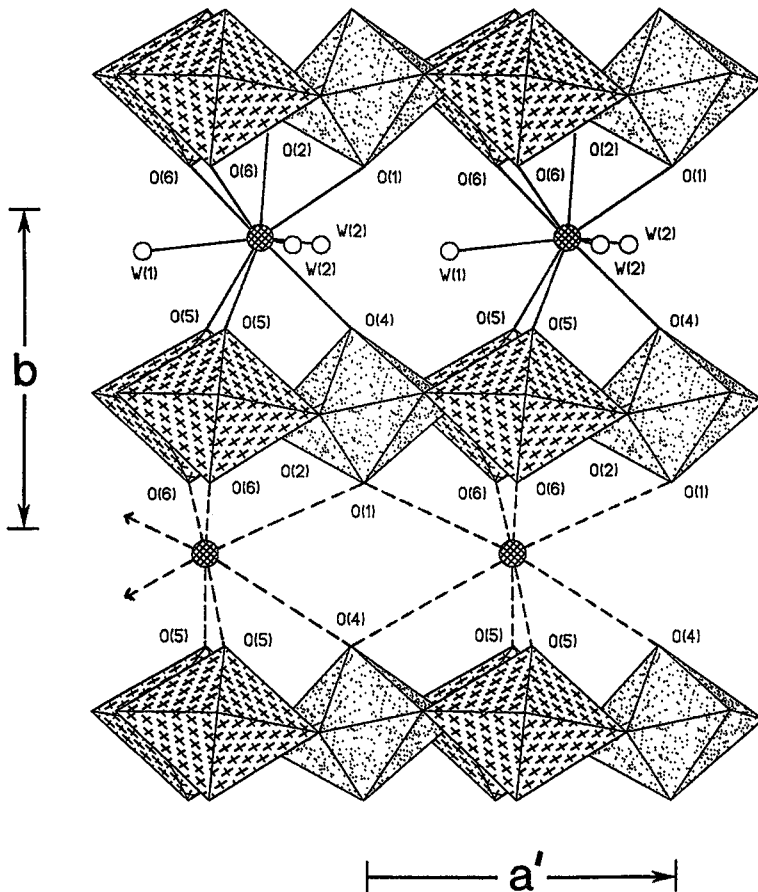

FIG. 4. Part of the crystal structure of guilleminite projected down an axis 7° away from [001]; the polyhedra are shaded as in Figure 3. The upper part of the diagram shows the actual position of Ba and its coordination; the lower part of the diagram shows Ba at the position it would occupy if guilleminite were centrosymmetric.

(010) accounts for the perfect {010} cleavage in guilleminite.

The guilleminite structure has marked *Pmnm* pseudosymmetry. The aspect of the structure that breaks *Pmnm* symmetry is the position of Ba and the positions of the three equatorial H_2O groups. The Ba atom is displaced ~1.2 Å from the pseudo-(100)-mirror plane at $x = \pm\frac{1}{2}$, and the three H_2O groups are slightly displaced from positions required by true mirror symmetry; Figure 4 shows both these aspects of the structure in the upper interstitial layer. In the lower interstitial layer, the Ba atom is shown on the pseudo-mirror plane; note that the coordination of the Ba atom changes quite markedly. In the real structure (upper layer), the Ba coordination is a tri-augmented mono-capped triangular prism, whereas in the idealized *Pmnm* structure (lower layer) the Ba coordination is a gable disphenoid (Johnson 1966). This displacement is due possibly to the bond-valence requirements of the O(1) and O(4) anions. In the real structure, the Ba–O(1) and Ba–O(4) distances are 2.90 and 2.97 Å, respectively. If Ba were to occur on the mirror plane, these Ba–O(1) and Ba–O(4) distances would lengthen to ~3.9 Å, well beyond any significant bonding interaction; this would result in a drastic incident bond-valence deficiency at the Ba atom (with a sum of ~1.63 *vu*, Table 4) and less pronounced deficiencies at O(1) and O(4). Thus the incident bond-valence requirements of the interstitial Ba atom seem reasonable for the $P2_1nm$ (rather than *Pmnm*) symmetry of guilleminite. However, it is possible that guilleminite might transform to this symmetry at higher temperature, provided dehydration were suppressed.

RELATION TO OTHER STRUCTURES

The structural unit in guilleminite is topologically identical to the sheet in phosphuranylite, $KCa(H_3O)_3$ $[\{(UO_2)_3(PO_4)_2O_2\}_2(UO_2)](H_2O)_8$ (Demartin *et al.* 1991), except that in the latter structure, the cross-linkage between the $[U_3\phi_{14}]$ chains occurs *via* (PO_4) groups rather than (SeO_3) groups (Fig. 5), and the sheets in phosphuranylite are cross-linked into a framework by $U\phi_6$ octahedra. The similarity of the sheets in each mineral is directly apparent from their cell dimensions: $a_g \times 2 \approx b_p$ and $c_g \approx c_p$. In guilleminite, the SeO_3 groups flanking the $[U_3\phi_{14}]$ chain are identical as a result of translational symmetry (Fig. 2), whereas in phosphuranylite, the corresponding tetrahedra alternately point up and down the *a* axis (Fig. 5).
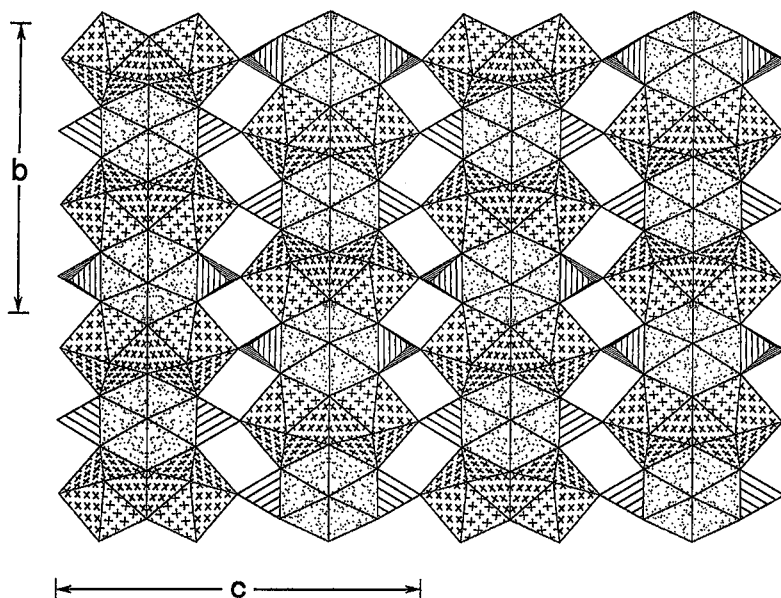

FIG. 5. The structural unit in phosphuranylite projected down [100]; the shading corresponds to that used in Fig. 2, except that (PO_4) tetrahedra are shaded by parallel lines.

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).

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

_____ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

DEMARTIN, F., DIELLA, V., DONZELLI, S., GRAMACCIOLI, C.M. & PILATI, T. (1991): The importance of accurate crystal structure determination of uranium minerals. I. Phosphuranylite $KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 8H_2O$. *Acta Crystallogr.* **B47**, 439-446.

HAWTHORNE, F.C., GROAT, L.A. & ERCIT, T.S. (1987): Structure of cobalt diselenite. *Acta Crystallogr.* **C43**, 2042-2044.

JOHNSON, N.W. (1966): Convex polyhedra with regular faces. *Can. J. Math.* **18**, 169-200.

PIERROT, R., TOUSSAINT, J. & VERBEER, T. (1965): La guilleminite, une nouvelle espèce minérale. *Soc. Franç. Minéral. Cristallogr., Bull.* **88**, 132-135.