IMPLICATIONS OF THE SYNTHESIS AND STRUCTURE
OF THE Sr ANALOGUE OF CURITE

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ABSTRACT

The structure of the synthetic analogue of curite, $Sr_{2.82}(H_2O)_2[(UO_2)_4O_{3.82}(OH)_{3.18}]_2$, $Z = 2$, orthorhombic, space group *Pnam*, *a* 12.3143(7), *b* 12.9609(8), *c* 8.4053(5) Å, *V* 1341.5(2) Å^3, has been refined to an agreement index (*R*) of 5.30% for 1369 unique observed ($|F_o| \geq 4\sigma_F$) reflections measured using monochromatic Mo*K*α X-radiation and a CCD-based detector. The crystal was synthesized from a mixture of uranyl nitrate and $SrCl_2$ reacted at 185°C for 5 days. The structure determination has demonstrated that the title compound is isostructural with the Pb uranyl oxide hydrate curite. On this basis, a complex series of Sr uranyl oxide hydrates with various Sr:U ratios, analogous to the Pb uranyl oxide hydrate minerals, may exist.

Keywords: Sr uranyl oxide hydrate, uranium, curite, structure refinement.

SOMMAIRE

Nous avons affiné la structure de l'analogue synthétique de la curite, $Sr_{2.82}(H_2O)_2[(UO_2)_4O_{3.82}(OH)_{3.18}]_2$, $Z = 2$, orthorhombique, groupe spatial *Pnam*, *a* 12.3143(7), *b* 12.9609(8), *c* 8.4053(5) Å, *V* 1341.5(2) Å^3, jusqu'à un résidu *R* de 5.30% en utilisant 1369 réflexions uniques observées ($|F_o| \geq 4\sigma_F$) et mesurées avec rayonnement monochromatique Mo*K*α et un détecteur à aire avec couplage de charges. Nous avons synthétisé cette phase à partir d'un mélange de nitrate d'uranyle et de $SrCl_2$ chauffé à 185°C pour cinq jours. L'ébauche de la structure a démontré que ce composé est isostructural avec la curite, oxyde hydraté d'uranyle et de plomb. On peut supposer une série complexe de composés ayant des valeurs variables du rapport Sr:U, tout comme c'est le cas parmi les oxydes hydratés d'uranyle et de plomb.

(Traduit par la Rédaction)

Mots-clés: oxyde hydraté d'uranyle et de plomb, uranium, curite, affinement de la structure.

INTRODUCTION

Uranyl oxide hydrate minerals are common constituents of the oxidized portions of U deposits (Frondel 1958, Finch & Ewing 1992) and are important for understanding water–rock interactions in U deposits and the mine tailings generated by the exploitation of such deposits. In addition, these minerals form in soils contaminated with U, and are likely to form in substantial quantities in geological repositories for spent nuclear fuel (Wronkiewicz *et al.* 1992, 1996, Finn *et al.* 1996). Despite their importance, our knowledge of the crystal chemistry of these minerals lags behind that of many other mineral groups, largely owing to experimental difficulties associated with poor quality of the crystals and the high absorption of X-rays by the crystals.

Uranyl oxide hydrate minerals that contain the divalent cations Ca, Ba and Pb are listed in Table 1. The U^{6+} cations in these structures are strongly bonded to two O atoms, forming nearly linear $(UO_2)^{2+}$ uranyl ions that are further coordinated by four or five anions arranged at the equatorial positions of square and pentagonal bipyramids, respectively. The structure of each of the minerals listed in Table 1 contains sheets formed by the sharing of equatorial edges and corners of uranyl polyhedra, with the uranyl ions oriented roughly perpendicular to the sheets (Fig. 1). The interlayers contain the divalent cations as well as (H_2O) groups. Those minerals that contain Ca and Ba are all based on the α-U_3O_8-type sheet shown in Figure 1a, whereas the Pb uranyl oxide hydrates contain at least six topologically distinct sheets of uranyl polyhedra (Fig. 1). All of the sheets

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TABLE 1. URANYL OXIDE HYDRATE MINERALS CONTAINING
Ca, Ba AND Pb

	Structure Known	Ref.
Protasite	$Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	1, Fig. 1a
Billietite	$Ba[(UO_2)_3O_3(OH)_2]_2(H_2O)_4$	1, Fig. 1a
Becquerelite	$Ca[(UO_2)_3O_3(OH)_2]_3(H_2O)_8$	1, Fig. 1a
Fourmarierite	$Pb[(UO_2)_4O_3(OH)_4](H_2O)_4$	2, Fig. 1b
Sayrite	$Pb_2[(UO_2)_5O_6(OH)_2](H_2O)_4$	3, Fig. 1c
Curite	$Pb_3[(UO_2)_4O_4(OH)_3]_2(H_2O)_3$	4, Fig. 1d
Richetite	$M_xPb_{8.57}[(UO_2)_{18}O_{18}(OH)_{12}]_2(H_2O)_{41}$	5, Fig. 1a
Vandendriesscheite	$Pb_{1.57}[(UO_2)_{10}O_6(OH)_{11}](H_2O)_{11}$	6, Fig. 1e
Wölsendorfite	$Pb_{6.16}Ba_{0.36}[(UO_2)_{14}O_{19.9}(OH)_4](H_2O)_{12}$	7, Fig. 1f
Masuyite	$Pb[(UO_2)_3O_3(OH)_2](H_2O)_3$	8, Fig. 1a
Agrinierite	$K_2(Ca,Sr)[(UO_2)_3O_3(OH)_2]\cdot 2.5H_2O$	9, Fig. 1a
	Structure Not Yet Known	
Bauranoite	$BaU_2O_7(H_2O)_{4-5}$	
Calciouranoite	$(Ca,Ba,Pb)U_2O_7(H_2O)_{2-5}$	
Rameauite	$K_2CaU_6O_{20}(H_2O)_9$	

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

shown in Figure 1 occur in the structures of Pb uranyl oxide hydrate minerals.

Laboratory tests have shown that various uranyl oxide hydrates are likely to form in the proposed repository at Yucca Mountain, Nevada, as a result of the corrosion of spent nuclear fuel (Wronkiewicz *et al.* 1992, 1996, Finn *et al.* 1996). The hazardous radionuclides contained in the spent fuel may be released to the environment during alteration. However, it is possible that many of the radionuclides will be immobilized by incorporation into the structures of uranyl minerals that form in the repository (Burns *et al.* 1997a, Burns 1998a, b, 1999a, Chen *et al.* 1999). Experiments done using spent fuel indicate that ^{90}Sr is retained to a large extent with the products of alteration of the spent fuel (Finn *et al.* 1996). Sr may be adsorbed onto the alteration phases, it may be incorporated into the structures of minerals such as uranophane or becquerelite by replacing Ca in the interlayer positions of the structures, or discrete Sr-bearing phases may form. To distinguish these possibilities, an understanding of the crystal chemistry of Sr uranyl oxide hydrates is required. As part of a general study of uranyl oxide hydrate structures, we have synthesized crystals of the Sr analogue of curite and refined the structure using X-ray-diffraction data.

EXPERIMENTAL

Synthesis of crystals

Synthesis experiments were done with deionized, distilled ultrapure water with no contaminants present at the ppb level (as verified by ICP–MS analysis), and reagent-grade chemicals. A solution was prepared con-

taining 35 mM $UO_2(NO_3)_2\cdot 6H_2O$ (Alfa ÆSAR) and 335 mM $SrCl_2\cdot 6H_2O$ (Aldrich) dissolved in ultrapure water. The initial pH of the solution was 2.7; a small amount of partially disolved $Sr(OH)_2\cdot 8H_2O$ (Mallinckrodt) was added, raising the pH to 5.2. The solution was reacted in a Teflon-lined Parr bomb at 185°C for 5 days. Yellow, acicular needles up to 0.15 mm in length but only ~0.001 mm in diameter, and small (<0.01 mm diameter) orange, platy crystals were produced by the reaction. The orange crystals could not be positively identified using X-ray powder diffraction.

X-ray diffraction

The largest yellow crystal that could be found had approximate dimensions $0.09 \times 0.01 \times 0.005$ mm. The crystal was mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Burns (1998c) discussed the application of CCD detectors to the analysis of mineral structures.

The data were collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.2° in ω, with 180 s used to acquire each frame, resulting in a scan-rate of 0.067° per minute. The slow scan-rate was essential to obtain useful counting statistics owing to the small volume of the crystal. More than a hemisphere of three-dimensional data was collected, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions (Table 2), which were refined with 2445 reflections using least-squares techniques. Data were collected for $3° \leq 2\theta \leq 56.6°$ in approximately 100 hours; comparison of the intensities of equivalent reflections collected at different times during the data collection showed no significant decay. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical absorption-correction was done using the program SADABS (G. Sheldrick, unpublished). A total of 7835 reflections was collected, of which there were 1872 unique reflections (R_{INT} = 6.2%), with 1369 classed as observed ($|F_o| \geq 4\sigma_F$).

TABLE 2. MISCELLANEOUS INFORMATION FOR THE Sr
ANALOGUE OF CURITE

a (Å)	12.3143(7)	Crystal size (mm)	0.09 x 0.01 x 0.005
b (Å)	12.9609(8)	Total reflections	7835
c (Å)	8.4053(5)	Unique reflections	1872
V (Å^3)	1341.5(2)	R_{int}	6.2
Space group	$Pnam$	Unique $|F_o| \geq 4\sigma_F$	1369
$F(000)$	2218	Final R	5.30
μ (mm^{-1})	53.8	S	1.12
D_{calc} (g/cm^3)	6.618		

Unit-cell contents: $2\{Sr_{2.83}[(UO_2)_4O_4(OH)_3]_2(H_2O)_3$

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

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters
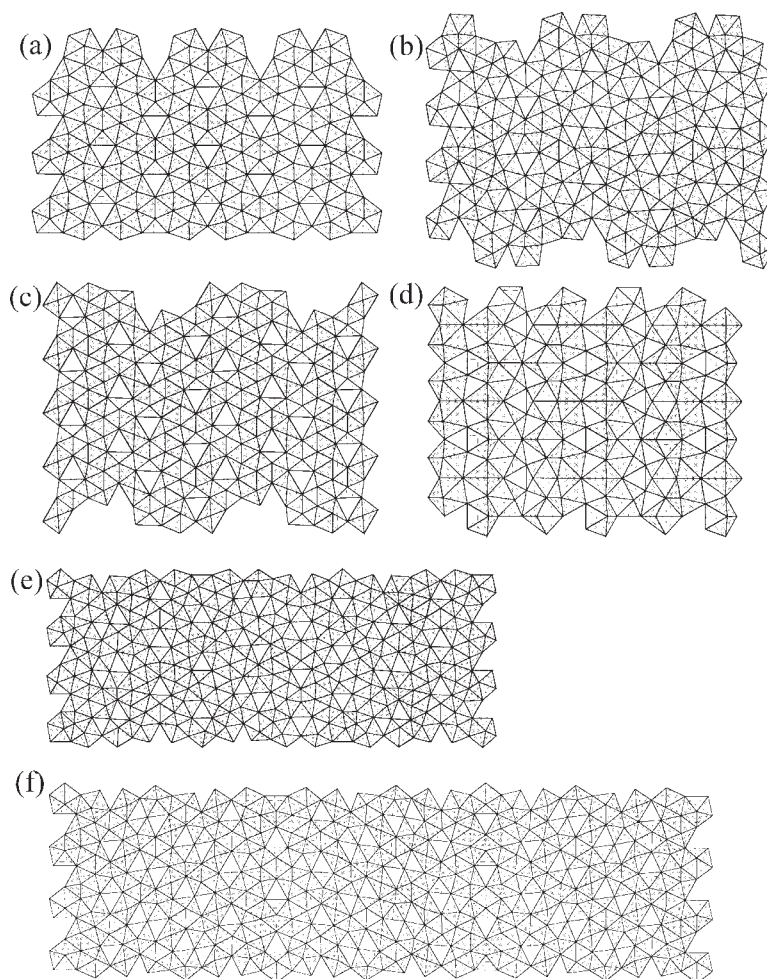
FIG. 1. The sheets of uranyl polyhedra that occur in the structures of uranyl oxide hydrate minerals that contain Ca, Ba and Pb: (a) billietite, becquerelite, protasite, richetite, masuyite and agrinierite, (b) fourmarierite, (c) sayrite, (d) curite, (e) vandendriesscheite, and (f) wölsendorfite.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the refinement of the crystal structure.

Systematic absences of reflections are consistent with space groups *Pnam* and *Pna*2. The initial structure-model was derived from the structure of curite in space group *Pnam* (Taylor *et al.* 1981), with the Pb sites of curite replaced with Sr. Refinement of the atomic positional and isotropic-displacement parameters and

the site-occupancy factors for the Sr sites within the constraints of space group *Pnam* resulted in an agreement index (R) of 6.65% for the observed reflections. Refinement after conversion of the displacement parameters of the cations to an anisotropic form gave an R of 5.3% for the 1369 observed unique reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (S) of 1.12. A model that included anisotropic-displacement parameters for the anions was tried, but resulted in non-positive-definite parameters for several anions. Difference-Fourier maps calculated with the Sr(2) site empty showed that the site is essentially spherical, unlike the corresponding site in a crystal of synthetic curite, which Mereiter (1979) found to be disordered off the mirror. In the final cycle

of refinement, the mean parameter shift/esd was 0.000. The final atomic-positional parameters are in Table 3, anisotropic-displacement parameters are in Table 4, selected interatomic distances and angles are in Table 5, and a bond-valence analysis is provided in Table 6. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

The structure determination has demonstrated that the Sr uranyl oxide hydrate crystals obtained in our experiments are isostructural with curite. The bond-valence analysis (Table 6) indicates that all U is U^{6+}, and that of the twelve symmetrically distinct anions present in the structure, there are nine O atoms, two $(OH)^-$ groups, and one (H_2O) group, as was also reported for curite (Taylor *et al.* 1981, Li & Burns 2000). The refinement indicates that the Sr(1) and Sr(2) sites are 88(1) and 53(1)% occupied, respectively. Taylor *et al.* (1981) assumed that the Pb(2) site in the curite crystal they studied is occupied by an (H_2O) group if the Pb cation is absent. In contrast, Mereiter (1979) examined a crystal of synthetic curite and indicated that the Pb(2) site is vacant where it is not occupied by a Pb cation. In the Sr analogue of curite, we found no significant residual peaks in the difference-Fourier maps near the Sr(2) site that are attributable to a partially occupied (H_2O) site, so the assumption is made that the Sr(2) site is vacant if there is no Sr cation present.

Compositional variability has been observed in curite (Čejka *et al.* 1998, Li & Burns 2000). Li & Burns (2000) refined the structures of 14 crystals of curite from various localities, and found that the site occupancy of Pb(1) is slightly deficient, ranging from 89 to 100%, whereas the Pb(2) site occupancies range from 57 to 63%. Li & Burns (2000) concluded that the most likely

charge-balancing mechanism that permits the range of Pb is variability of the hydroxyl content of the sheet of uranyl polyhedra, and proposed the formula Pb_{3+x} $(H_2O)_2[(UO_2)_4O_{4+x}(OH)_{3-x}]_2$. The Sr site occupancies in Sr curite [88(1) and 53(1)% for Sr(1) and Sr(2), respectively] are consistent with those found in curite

TABLE 4. ANISOTROPIC-DISPLACEMENT PARAMETERS FOR THE Sr ANALOGUE OF CURITE

	*U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	150(4)	82(4)	74(4)	18(3)	0	0
U(2)	138(4)	64(4)	53(4)	3(3)	0	0
U(3)	117(3)	76(3)	62(3)	-2(2)	-8(2)	-12(2)
Sr(1)	169(15)	157(15)	129(14)	-50(12)	0	0
Sr(2)	125(23)	165(24)	124(23)	-19(16)	0	0

*$U_{ij} = U_{ij}$ Å^2 x 10^4

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR THE Sr ANALOGUE OF CURITE

U(1)-O(7)	1.83(2)	Sr(1)-O(8)	2.54(2)
U(1)-O(5)	1.85(2)	Sr(1)-O(4)g,h	2.58(1) x2
U(1)-O(1),a	2.16(1) x2	Sr(1)-O(6)	2.74(2)
U(1)-O(6)	2.32(2)	Sr(1)-O(2),a	2.77(1) x2
U(1)-OH(10)b	2.33(2)	Sr(1)-O(5)	2.78(2)
<U(1)-O$_{Ur}$>	1.84	Sr(1)-O(7)i	2.93(2)
<U(1)-ϕ$_{eq}$>	2.24	Sr(1)-H$_2$O(3),h	3.060(2) x2
O(7)-U(1)-O(5)	180.0(4)	<Sr(1)-ϕ>	2.78
U(2)-O(11)c	1.81(2)	Sr(2)-O(2)d,a	2.64(1) x2
U(2)-O(8)c	1.84(2)	Sr(2)-O(4)h,j	2.74(1) x2
U(2)-O(9)c	2.27(2)	Sr(2)-H$_2$O(3)d,h	2.743(3) x2
U(2)-O(1)a,d	2.30(1) x2	Sr(2)-O(7)k	2.76(2)
U(2)-OH(12)c,e	2.38(1) x2	Sr(2)-O(9)j	2.81(2)
<U(2)-O$_{Ur}$>	1.82	Sr(2)-O(8)j	2.94(2)
<U(2)-ϕ$_{eq}$>	2.33	Sr(2)-O(11)c	3.02(2)
O(11)c-U(2)-O(8)c	178.7(9)	<Sr(2)-ϕ>	2.78
U(3)-O(2)	1.82(1)		
U(3)-O(4)f	1.83(1)	a = x, y, ½-z; b = x, y-1, z; c = ½-x,
U(3)-O(9)f	2.227(8)	y-½, 1-z; d = x, y, z+1; e ·· ½-x, y-½,
U(3)-O(1)	2.29(1)	z+½; f = ½-x, y-½, -z; g = -x, 1-y, -z;
U(3)-OH(12)	2.30(1)	h = -x, 1-y, z+½; i ·· x-½, ½-y, z; j =
U(3)-O(6)	2.319(5)	x, 1-y, 1-z; k = ½-x, y+½, 1-z
U(3)-OH(10)f	2.60(1)	
<U(3)-O$_{Ur}$>	1.82	
<U(3)-ϕ$_{eq}$>	2.35	
O(2)-U(3)-O(4)f	177.9(5)	

TABLE 3. FINAL ATOMIC PARAMETERS FOR THE Sr ANALOGUE OF CURITE

	x	y	z	*U_{eq}
U(1)	0.21316(7)	0.08052(6)	¼	102(2)
U(2)	0.19875(7)	0.06928(6)	¾	85(2)
U(3)	0.30511(5)	0.28911(4)	-0.01208(6)	85(2)
Sr(1)	0.0544(2)	0.3363(2)	¼	152(9)
Sr(2)	0.0161(3)	0.3649(3)	¾	138(14)
O(1)	0.2318(9)	0.1266(9)	0.004(1)	151(24)
O(2)	0.170(1)	0.3445(9)	-0.032(1)	178(26)
H$_2$O(3)	0	½	0	269(43)
O(4)	0.059(1)	0.7351(9)	-0.016(1)	175(26)
O(5)	0.070(1)	0.122(1)	¼	167(38)
O(6)	0.259(1)	0.254(1)	¼	145(35)
O(7)	0.355(2)	0.039(1)	¼	203(41)
O(8)	0.173(2)	0.497(2)	¼	333(49)
O(9)	0.196(1)	0.713(1)	¼	203(39)
OH(10)	0.150(1)	0.911(1)	¼	170(38)
O(11)	0.429(1)	0.638(1)	¼	137(35)
OH(12)	0.378(1)	0.4418(9)	0.079(2)	201(28)

*$U_{eq} = U_{eq}$ Å^2 x 10^4

TABLE 6. BOND-VALENCE* ANALYSIS (*vu*) FOR THE Sr ANALOGUE OF CURITE

	U(1)	U(2)	U(3)	Sr(1)	Sr(2)	**Σ
O(1)	0.86 x2↓	0.61 x2↓	0.62			2.09
O(2)		1.55		0.17 x2↓	0.24 x3↓	1.83
H$_2$O(3)				0.08 x2↓ x2→	0.18 x3↓ x2→	0.33
O(4)			1.52	0.29 x2↓	0.19 x3↓	1.88
O(5)	1.50			0.17		1.65
O(6)	0.64		0.58 x2→	0.19		1.97
O(7)	1.55			0.11	0.18	1.74
O(8)		1.49		0.32	0.11	1.83
O(9)		0.64	0.70 x3→		0.15	2.12
OH(10)	0.63		0.34 x2→			1.31
O(11)		1.59			0.09	1.64
OH(12)		0.52 x2↓	0.61			1.13
	6.04	5.98	5.92	1.87	1.75	

*Bond-valence parameters for U^{6+} from Burns *et al.* (1997b) and for Sr from Brese & O'Keeffe (1991)

**Bond-valence contributions into anion sums scaled by the Sr(1) and Sr(2) site occupancies

by Li & Burns (2000), and the formula for the crystal of Sr-substituted curite is $Sr_{2.82}(H_2O)_2[(UO_2)_4O_{3.82}(OH)_{3.18}]_2$, $Z = 2$, where the sheet constituents are enclosed in square braces.

Sheets of uranyl polyhedra

The structure contains three symmetrically distinct U positions. All of the U^{6+} cations are part of approximately linear $(UO_2)^{2+}$ uranyl ions (designated *Ur*) with $U^{6+}-O_{Ur}$ bond-lengths of ~1.8 Å, as is almost invariably found for U^{6+} in minerals and inorganic crystals (Burns *et al.* 1997b). The U(1) uranyl ion is coordinated by three O atoms and one $(OH)^-$ group, arranged at the equatorial corners of a square bipyramid, with the O_{Ur} atoms forming the apices of the bipyramid. The U(2) and U(3) uranyl ions are each coordinated by three O atoms and two $(OH)^-$ groups, forming pentagonal bipyramids with the O_{Ur} atoms at the apices. The $<U^{6+}-\phi_{eq}>$ (ϕ: unspecified ligand; ϕ_{eq}: equatorial ϕ) bond-length for the $Ur\phi_4$ square bipyramid about the U(1) position is 2.24 Å, and the $<U^{6+}-\phi_{eq}>$ bond-lengths in the $Ur\phi_5$ polyhedra about U(2) and U(3) are 2.33 and 2.35 Å, respectively. These values are in good agreement with the average $^{[6]}U^{6+}-\phi_{eq}$ of 2.28(5) Å and $^{[7]}U^{6+}-\phi_{eq}$ of 2.37(9) Å for well-refined structures (Burns *et al.* 1997b).

The $Ur\phi_4$ square bipyramids and $Ur\phi_5$ pentagonal bipyramids link by sharing equatorial edges and corners to form sheets at $x \approx \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 2). This sheet is known to occur only in the structure of curite. The uranyl ions are each oriented roughly perpendicular to the sheet of polyhedra, in opposition to the statement of Taylor *et al.* (1981) that the U(1) uranyl ion lies within the plane of the sheet in the structure of curite. We have inspected the structure reported by Taylor *et al.* (1981), and conclude that the U(1) uranyl ion is in fact roughly perpendicular to the sheet of polyhedra, contrary to their interpretation.

Interlayer constituents

The interlayer occurs at $x \approx 0$ and $\frac{1}{2}$ and contains both Sr cations and H_2O groups. The distribution of these constituents is shown, in relation to the sheet of uranyl polyhedra, in Figure 2. Both symmetrically distinct Sr positions are coordinated by ten anions, with $<Sr-\phi>$ distances of 2.78 Å. The polyhedra contain two (H_2O) groups and eight O atoms. Each polyhedron contains seven O_{Ur} atoms, and each cation is bonded to one O atom that is an equatorial ligand of three uranyl polyhedra within the sheet.

Additional linkages between the sheets of uranyl polyhedra are provided by H bonds, but the X-ray data did not provide the H atom positions. Two H bonds probably bridge between adjacent sheets of uranyl polyhedra, with $(OH)^-$ groups at equatorial positions of uranyl polyhedra donating the bonds that are accepted by
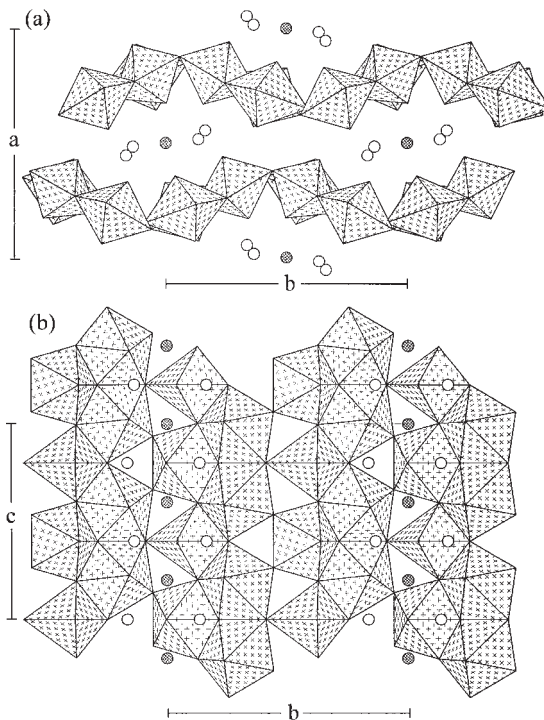

Fig. 2. Structure of the Sr analogue of curite. (a) Structure projected onto (001). (b) Structure projected onto (100). The uranyl polyhedra are shaded with crosses, Sr atoms are shown as open circles, and (H_2O) groups are illustrated with cross-hatched circles.

O_{Ur} atoms. The probable H bonds are OH(10)...O(11) and OH(12)...O(5), with donor–acceptor separations of 2.79 and 2.89 Å, respectively. These H bonds probably also occur in the structure of curite (Taylor *et al.* 1981). There are several possible acceptors for the H bonds donated by the $H_2O(3)$ group, with donor–acceptor distances less than 3.0 Å, suggesting that these bonds may be disordered.

DISCUSSION

The structural diversity of the Pb uranyl oxide hydrate minerals, as compared to other uranyl oxide hydrate minerals containing divalent cations, remains an enigma. In many low-temperature minerals, the Pb^{2+} cation contains a stereoactive lone pair of electrons, resulting in strongly asymmetric coordination polyhedra about the Pb^{2+} cation. The Sr polyhedra in the Sr analogue of curite are compared to the Pb polyhedra in curite, as reported by Taylor *et al.* (1981), in Figure 3. The mean bond-lengths of the Pb polyhedron are longer than those of the Sr polyhedra, as expected on the basis of cation size. The bond-lengths of the Pb polyhedron
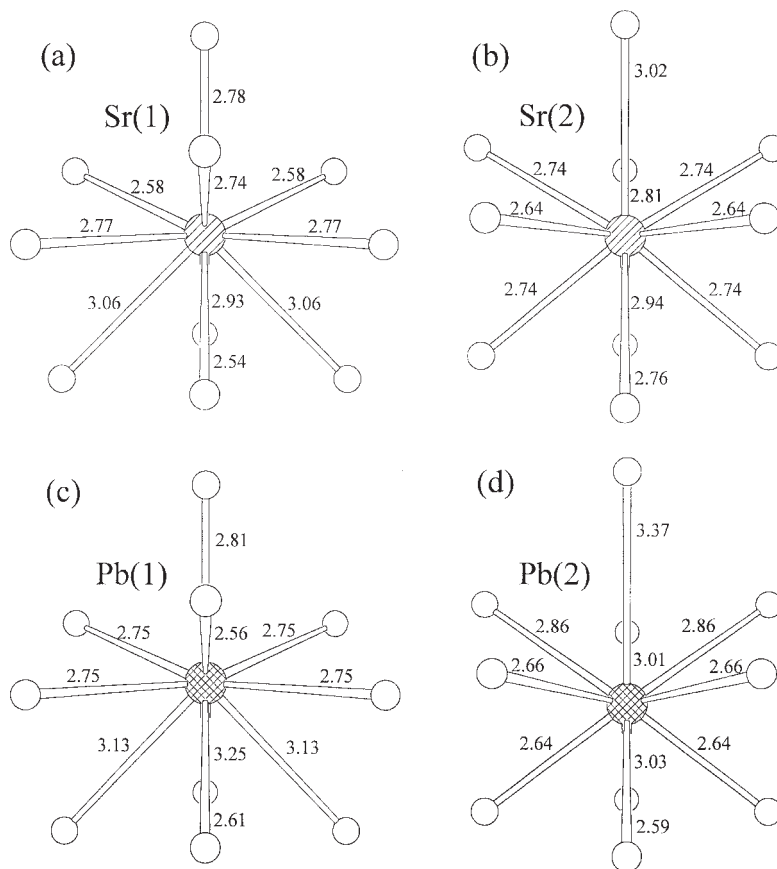
FIG. 3.   Comparison of the Srφ₁₀ and Pbφ₁₀ polyhedron geometries in the Sr analogue of
curite and curite (Taylor *et al.* 1981). (a) Sr(1) in the Sr analogue of curite, (b) Sr(2) in
the Sr analogue of curite, (c) Pb(1) in curite, (d) Pb(2) in curite.

are also more distorted from ideal than in the Sr polyhedra, which suggests that electron lone-pair stereoactivity on the Pb cations may be a factor, although it is not as pronounced as in some structures that contain Pb. However, the existence of the Sr analogue of curite demonstrates that electron lone-pair stereoactivity of the interlayer cation is not essential to the connectivity of the structure.

The effective ionic radius of $^{[10]}Pb^{2+}$ (1.40 Å) is intermediate between that of $^{[10]}Ca^{2+}$ (1.23 Å) and $^{[10]}Ba^{2+}$ (1.52 Å), and is similar to that of $^{[10]}Sr^{2+}$ (1.36 Å) (Shannon 1976). Our demonstration of the existence of the Sr analogue of curite supports the hypothesis that the curite sheet is compatible with interlayer cations that are similar in size to Pb, but not with cations that are significantly larger or smaller. Sr uranyl oxide hydrates may be complex from the crystal chemistry point of view, analogous to Pb uranyl oxide hydrates, and a

series of phases likely exists with a range of Sr:U ratios. This fact may have important implications for the disposal of spent nuclear fuel in a geological repository.

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