

The structure of agrinierite: a Sr-containing uranyl oxide hydrate mineral

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ABSTRACT

The structure of agrinierite, $K_2(Ca_{0.65}Sr_{0.35})[(UO_2)_3O_3(OH)_2]_2 \cdot 5H_2O$, orthorhombic, $F2mm$, $Z = 16$, $a = 14.094(2)$, $b = 14.127(2)$, $c = 24.106(4)$ Å, $V = 4799.6(1)$ Å³, was solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor (R) of 6.55% and a goodness-of-fit (S) of 0.851 using 2710 independent observed reflections collected with MoK α X-radiation and a CCD-based detector. This layered material contains four unique U⁶⁺ positions, each of which is part of a nearly linear (UO₂)²⁺ uranyl ion. The U⁶⁺ cations are further coordinated by five anions occupying the equatorial vertices of pentagonal bipyramids that are capped by the uranyl ion O atoms. The uranyl polyhedra are linked by the sharing of equatorial vertices and edges in a fashion topologically identical to the α -U₃O₈ sheet found in billietite, protasite, becquerelite, richetite, compreignacite and masuyite. The arrangement of hydroxyl anions within the sheets varies in these minerals; that of agrinierite is identical to protasite. The cations (Ca, Sr, and K) and H₂O reside in the interlayer region of the structure. The inclusion of Sr in the structure of agrinierite suggests that the release of radioactive ⁹⁰Sr may be impacted by incorporation into this phase if it forms in a geological repository for nuclear waste.

INTRODUCTION

Uranyl (U⁶⁺) oxide hydrate minerals often form as alteration products of uraninite (UO_{2+x}) and commonly occur in the oxidized portions of U deposits, mine tailings piles, and soils contaminated with actinides. In addition, experimental studies have shown that these phases form due to alteration of spent nuclear fuel (mainly UO_{2+x}) and natural and synthetic uraninite when subjected to moist oxidizing conditions similar to those found at the proposed nuclear waste repository at Yucca Mountain, Nevada (Burns et al. 1999; Finch et al. 1999a, 1992; Finn et al. 1996; Pearcy et al. 1994; Wronkiewicz et al. 1992, 1996; Wronkiewicz and Buck 1999). These investigations have also shown that fission products such as ¹³⁷Cs and ⁹⁰Sr and actinides such as ²³⁷Np and ²³⁹Pu are retarded with the alteration products, although the mechanisms are largely unknown (Finn et al. 1996). Thus, the formation of uranyl minerals in a geological repository may impact the release of radionuclides into the surroundings of the storage site.

Agrinierite was described in 1972 by (Cesbron et al. 1972), but was not heretofore characterized structurally. It forms in association with rameauite, becquerelite, billietite, compreignacite and schoepite. As some of these (and other) U-O-H materials are also found in the laboratory studies of spent fuel oxidation, it is possible that agrinierite may also form under similar conditions.

EXPERIMENTAL METHODS

A sample of agrinierite from Mine de Margnac II, France was obtained from the Canadian Museum of Nature (Sample

Number CMNMC 81102). From this, a single crystal was selected and mounted on a glass fiber and diffraction data were collected on a Bruker SMART 1K CCD with a crystal-to-detector distance of 5.0 cm. A hemisphere of three-dimensional data was collected using a frame width of 0.3° and MoK α X-radiation. The unit cell was refined from 794 reflections using least-squares techniques. The data were reduced and corrected for Lorentz, polarization and background effects via the Bruker program SAINT (Bruker-AXS 1998a). An empirical absorption correction (XPREP; Bruker-AXS 1998c) was performed by modeling the crystal as a (010) plate and discarding reflections with a plate-glancing angle of less than 3.0° (12 reflections). This reduced the R_{int} of 369 reflections with $I > 15\sigma$ from 0.24 to 0.079. This procedure has been used extensively in correcting for the effects of highly absorbing species such as U⁶⁺ and has been discussed at length in Finch et al. (1999b) and in the SHELXTL software suite (Bruker-AXS 1998b). Details of the collection and refinement are given in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

Structure solution and refinement were carried out with SHELXS and SHELXL respectively within the Bruker suite of programs SHELXTL (Bruker-AXS 1998b). Systematic absences were consistent with space groups $F2mm$, $Fmmm$, and $F222$. Solutions were attempted in all of these space groups, including the different axes choices for $F2mm$. Spacegroup $F2mm$ (number 42) was pursued initially based on the lowest R -factor immediately post solution. Straightforward and successful refinement and subsequent re-investigation of other space group possibilities confirmed this choice. The initial model contained the U positions, while the anions and interlayer cations (Ca, Sr, and K) were located in difference-Fourier maps calculated following later stages of refinement. The occupancies of Ca and Sr were initially assigned to be consistent with

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the chemistry reported by Cesbron et al. (1972) and were subsequently refined with the total occupancy restrained to 1.0. Trials involving refinement of K^+ site occupancy factors revealed no substantial deviation from full occupancy. Refinement of the final model, which included all atomic positional parameters, anisotropic displacement parameters for the cations (excluding H and M^{2+}), and a refined weighting scheme of the structure factors resulted in a final R of 6.55% and an S of 0.851 for the 1453 observed reflections. Atomic parameters (positions and anisotropic displacement) are in Tables 2 and 3, respectively. Table 4 contains selected inter-atomic distances and angles, whereas the observed and calculated structure factors are in Table 5.¹

RESULTS

The structure of agrinierite (Fig. 1, Tables 2 and 3) contains sheets of uranyl polyhedra that share their edges and vertices.

¹For a copy of Table 5, document item AM-00-050, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (<http://www.minsocam.org>).

TABLE 1. Crystal data and structure refinement for agrinierite

Empirical formula*	$K_2(Ca_{0.65}Sr_{0.35})[(UO_2)_2O_3(OH)_2]_2 \cdot 5H_2O$
Formula weight	2008.97
Temperature	294 K
Wavelength	0.71073 Å
Diffractionmeter	Bruker SMART Platform CCD
Crystal system	Orthorhombic
Space group	$F2mm$
Unit cell dimensions	$a = 14.094(2)$ Å $b = 14.127(2)$ Å $c = 24.106(4)$ Å
Volume	$4799.6(1)$ Å ³
Z	8
Density (calculated)	5.562 Mg/m ³
Absorption coefficient	41.74 mm ⁻¹
$F(000)$	6660.4
Crystal size, color, habit	125 × 65 × 40 mm ³ pale yellow, blade
Theta range for data collection	1.69 to 28.37°
Reflections collected	25536
Independent reflections	2710 [$R_{int} = 0.1356$]
Observed reflection	1453 ($E > 4\sigma$)
Completeness to theta = 28.37°	94.7 %
Refinement method	Full-matrix least-squares on F^2
Weighting Scheme	$w = [\sigma^2(F_o^2) + (ap)^2 + bp]^{-1}$, where $p = (F_o^2 + 2F_c^2)/3$, $a = 0.0598$ $b = 0.0$
Data / restraints / parameters	2710 / 1 / 110
Goodness-of-fit on F^2	0.851
Final R indices [$>2\sigma(I)$]	$R1 = 0.0655$, $wR2 = 0.1353$
R indices (all data)	$R1 = 0.1357$, $wR2 = 0.1552$
Largest diff. peak and hole	3.895 and -4.672 e.Å ⁻³

Notes: $R1 = \frac{\sum |F_o^2| - |F_c|}{\sum |F_o|}$
 $S = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)^{1/2}} \right]$
 $wR2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$

* Formula obtained by initially setting the occupancies to be consistent with the chemical analysis reported by Cesbron et al. 1972. Subsequent refinements constrained the total occupancy on each site to 1.0.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for agrinierite

	x	y	z	Ueq
U1	3723(2)	2336(2)	5000	15(1)
U2	5803(1)	2710(1)	5903(1)	14(1)
U3	6160(2)	2500	7500	14(1)
U4	3279(1)	2402(1)	3399(1)	14(1)
M1*	6753(8)	0	6584(5)	26(3)
K2	4930(2)	5000	5000	39(7)
K3	6541(2)	5000	6699(1)	41(5)
K4	5629(2)	0	5000	27(5)
O1	2994(2)	3629(2)	3508(1)	7(5)
O2	5579(2)	3972(2)	5847(1)	17(7)
OH4	7434(2)	3036(2)	5646(1)	23(7)
O5	5420(3)	2640(3)	5000	27(1)
O6	4300(2)	2429(2)	4128(1)	25(7)
O7	6700(2)	2025(2)	8338(1)	12(6)
OH8	4817(2)	2908(2)	3095(1)	21(6)
O9	8980(3)	3900(2)	5000	13(9)
O10	6098(2)	1446(2)	5937(1)	19(7)
O11	2810(3)	2500	2500	12(9)
O12	3558(2)	1180(2)	3281(1)	22(7)
O13	6146(2)	1255(2)	7231(1)	20(7)
O14	3400(3)	3590(3)	5000	28(1)
OW1	4640(4)	5000	6860(2)	50(1)
OW2	2950(3)	5000	7400(2)	26(1)
OW3	2390(3)	5000	5628(2)	21(1)
OW4	5020(3)	0	6420(2)	38(1)
OW5	7760(3)	5000	5750(2)	38(1)

Note: $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_i tensor.

* M1 = $Sr_{0.35}Ca_{0.65}$.

TABLE 3. Selected bond lengths (Å) and angles (°) for agrinierite

U1-O9*	1.78(3)	M1-OW4	2.47(5)
U1-O14	1.83(4)	M1-OW3#	2.47(5)
U1-O6 (×2)	2.26(3)	M1-O13 (×2)	2.51(3)
U1-O5	2.43(4)	M1-OW2#	2.59(5)
U1-OH4 (×2)	2.45(3)	M1-O1 (×2)	2.62(2)
U2-O2	1.81(2)	M1-O10 (×2)	2.73(3)
U2-O10	1.84(2)	K2-O2 (×4)	2.67(3)
U2-O6†	2.16(3)	K2-O14 (×2)	2.93(5)
U2-O5	2.244(1)	K2-O5 (×2)	3.41(4)
U2-O7‡	2.25(3)	K3-OW1	2.70(6)
U2-OH4	2.42(3)	K3-OW5	2.86(6)
U2-OH8†	2.80(3)	K3-O2 (×2)	2.86(3)
U3-O13 (×2)	1.87(2)	K3-O7 (×2)	2.87(2)
U3-O7 (×2)	2.26(3)	K3-OW2**	2.94(6)
U3-O11§	2.33(4)	K3-O13 (×2)	3.18(3)
U3-OH8 (×2)	2.44(3)	K3-O12 (×2)	3.30(3)
U4-O12	1.79(3)	K4-O9 (×2)	2.79(4)
U4-O1	1.80(2)	K4-OW3 (×2)	2.90(4)
U4-O11	2.269(1)	K4-O10 (×4)	3.12(3)
U4-O6	2.27(3)	O9*-U1-O14	177.5(2)
U4-O7	2.29(2)	O2-U2-O10	176.6(1)
U4-OH8	2.40(3)	O13-U3-O13‡	178.7(2)
U4-OH4*	2.66(3)	O12-U4-O1	179.3(1)

Notes: Symmetry transformations used to generate equivalent atoms:

* $x - 1/2, -y + 1/2, -z + 1$ † $x, y, -z + 1$
 ‡ $x, -y + 1/2, -z + 3/2$ § $x + 1/2, y, z + 1/2$
 || $x - 1/2, y, z - 1/2$ # $x + 1/2, y - 1/2, z$
 ** $x + 1/2, -y + 1, -z + 3/2$

TABLE 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for agrinierite

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	13(2)	17(1)	14(2)	0	0	0(1)
U2	8(1)	14(1)	19(1)	2(1)	-1(1)	1(1)
U3	11(1)	15(1)	17(2)	4(1)	0	0
U4	8(1)	15(1)	17(1)	-3(1)	2(1)	1(1)
K2	61(2)	43(1)	11(2)	0	0	0
K3	48(1)	21(8)	54(2)	0	9(10)	0
K4	18(1)	42(1)	22(1)	0	0	0

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$.

The sheets are identical to those found in the inorganic phase α - U_3O_8 (Loopstra 1977), billietite, protasite, becquerelite (Pagoaga et al. 1987), richetite (Burns 1998b), compreignacite (Burns 1998a), and masuyite (Burns and Hanchar 1999). Each of four symmetrically unique U^{6+} positions are part of a nearly linear $(UO_2)^{2+}$ uranyl ion (designated Ur), with U- O_{Ur} bond lengths of ~ 1.8 Å, as is typically observed for U^{6+} minerals. The presence of $(UO_2)^{2+}$ uranyl ions and the bond-valence sums (Table 6) are consistent with all U in agrinierite being U^{6+} . The uranyl ions are each coordinated by two $(OH)^-$ groups and three O atoms arranged at the equatorial vertices of pentagonal bipyramids that are capped by the O_{Ur} atoms. The location of the hydroxyl groups was determined via bond-valence summation (Bresle and O'Keefe 1991; Burns et al. 1997) at all O positions (Table 6). The mean $\langle U^{6+}-\phi_{eq} \rangle$ bond-lengths (ϕ_{eq} : unspecified equatorial anion, O or OH) for U1, U2, U3, and U4 are 2.37, 2.37, 2.35, and 2.38 Å respectively, and are consistent with the average of 2.37(9) Å for this coordination polyhedron in numerous well-refined structures (Burns et al. 1997). The $Ur\phi_5$ pentagonal bipyramids are linked by sharing equatorial edges and vertices to form α - U_3O_8 type sheets that are stacked along (010), with the uranyl ions directed roughly between, or perpendicular to the sheets.

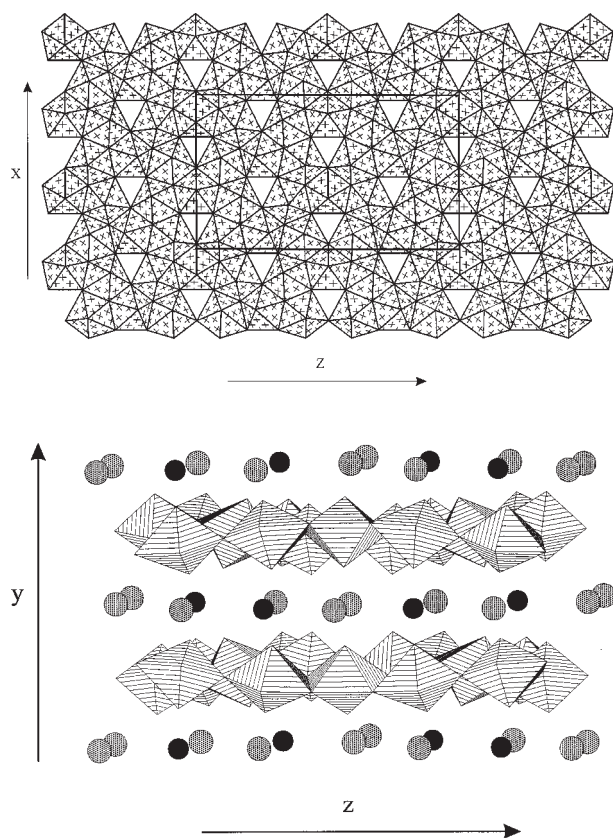


FIGURE 1. Polyhedral representation of the structure of agrinierite. (a) The sheet of uranyl polyhedra projected along [010] with unit cell outlined; (b) The structure projected along [100]. Black and grey circles are K^+ and M^{2+} atoms respectively. H_2O groups are not shown for clarity.

The cations K, Ca, and Sr as well as the H_2O groups reside in the interlayer region of the structure of agrinierite. K cations occupy three unique positions (K2, K3, and K4; Table 2) and are coordinated by 8, 11, and 8 ligands respectively. K2 is bound to six O_{Ur} atoms [O14 ($\times 2$) and O2 ($\times 4$)] at a mean distance of 2.76 Å that contribute a total of 1.16 bond-valence units to the K1 cations. A second shell of coordination containing two O5 atoms at 3.41 Å contributes only 0.06 bond-valence units. At distances less than 3.0 Å, K3 is coordinated to three H_2O groups (OW1, OW2, and OW5), two O_{Ur} atoms (O2), and two O_{eq} atoms (O7), giving a bond-valence sum of 1.01. Two additional O_{Ur} atoms (O12 and O13) at 3.30 and 3.18 Å respectively, contribute 0.23 bond-valence units. K4 is bound to six O_{Ur} atoms [O9 ($\times 2$) and O10 ($\times 4$)] and two H_2O groups [OW3 ($\times 2$)] at distances of 2.79, 3.12, and 2.90 Å, respectively for a bond-valence sum of 0.86. Ca and Sr share a single, fully occupied unique site (Table 2) with individual fractions equal to 0.648 and 0.352 respectively. The coordination of this site consists of three interlayer H_2O molecules (OW2, OW3, and OW4) and six O atoms from the U-O sheets [O1 ($\times 2$), O13 ($\times 2$), and O10 ($\times 2$)]. Bond lengths range from 2.47 to 2.73 Å with a mean of 2.58 Å. The bond-valence sum of this site (2.09) was weighted based on the fraction of Ca and Sr (Table 6).

The formula of agrinierite based on the crystal structure analysis is $K_2(Ca_{0.65}, Sr_{0.35})[(UO_2)_3O_3(OH)_2]_2 \cdot 5H_2O$. This can be re-written in the oxide form as $2(K_2O, SrO, CaO) \cdot 6UO_3 \cdot 12H_2O$. This is in agreement with that determined by Cesbron et al. (1972) via microprobe and wet chemical methods with the exception of H_2O ; Cesbron et al. Reported eight H_2O groups.

DISCUSSION

The structure of agrinierite is closely related to minerals that contain of the α - U_3O_8 -type sheet, notably becquerelite, billietite, protasite (Pagoaga et al. 1987), richetite (Burns 1998b), masuyite (Burns and Hanchar 1999), and compreignacite (Burns 1998a). The distribution of hydroxyl groups varies in α - U_3O_8 -type sheets in minerals; that of agrinierite is identical to protasite. The interlayer regions differ considerably, however. Protasite, $Ba[(UO_2)_3O_3(OH)_2] \cdot 3H_2O$, has a single unique cation position and three unique H_2O sites (Pagoaga et al. 1987), whereas agrinierite has four unique cation sites (three monovalent and one divalent) and five unique H_2O group positions. The ratio of the interlayer cation charges to the U charge is identical in

TABLE 6. Bond valence sums* at cation and anion positions in the structure of agrinierite

U1	5.89	O7	2.08
U2	5.93	OH8	1.19
U3	5.62	O9	1.85
U4	5.97	O10	1.56
M1	2.09	O11	1.86
K2	1.22	O12	1.69
K3	1.21	O13	1.47
K4	0.86	O14	1.64
O1	1.82	OW1	0.21
O2	1.96	OW2	0.33
OH4	1.23	OW3	0.43
O5	1.86	OW4	0.30
O6	2.10	OW5	0.14

* Calculated using the parameters of Bresle and O'Keefe (1991) for K^+ and $M^{2+}(Ca, Sr)$ and Burns et al. for U^{6+} (1997).

both minerals; protasite has one M^{2+} cation for three U^{6+} atoms, or 2:18. Agrinierite has one divalent and two monovalent cations for every six U^{6+} atoms, or 4:36. There are six U cations for every five H_2O groups in agrinierite, whereas protasite has a 1:1 ratio.

The structures of several U-O-H minerals are known: richetite (Burns 1998b), billietite, becquerelite, protasite (Pagoaga et al. 1987), compreignacite (Burns 1998a), masuyite (Burns and Hanchar 1999), agrinierite, fourmarierite (Piret 1985), schoepite (Finch et al. 1996), wölsendorfite (Burns 1999), vandendriesschite (Burns 1997), vandenbrandeite (Rosenzweig and Ryan 1977), curite (Taylor et al. 1981), and sayrite (Piret et al. 1983). In this listing, richetite through agrinierite all contain the α - U_3O_8 sheet type; each differing only in $(OH)^-$ distributions (Fig. 2). Thus it is apparent that the α - U_3O_8 sheet type is compliant not only to a range of anion arrangements, but also to a variety of interlayer species. The other minerals listed (except for schoepite and fourmarierite) each have a unique sheet topology. As the structures of more U-O-H minerals are determined however, additional representatives of each structure type may be found.

Agrinierite is the first reported U-O-H mineral to contain Sr. Further, radionuclide release fractions as determined from drip tests on spent nuclear fuel indicate that ^{90}Sr is either incorporated into or adsorbed onto alteration products (Finn et al. 1996). Thus it is conceivable that agrinierite could impact the release of ^{90}Sr if it forms under repository conditions.

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REFERENCES CITED

- Breese, N.E. and O'Keefe, M. (1991) Bond-Valence Parameters for Solids. *Acta Crystallographica*, B47, 192–197.
- Bruker-AXS (1998a) SAINT, V 5.01 program for reduction of data collected on Bruker AXS CCD area detector systems. Bruker Analytical X-ray Systems, Madison, Wisconsin.
- (1998b) SHELXTL NT, V5.1 program suite for solution and refinement of crystal structures. Bruker Analytical X-ray Systems, Madison, Wisconsin.
- (1998c) XPREP V5.0 program for Data Preparation & Reciprocal Space Exploration. Bruker Analytical X-ray Systems, Madison, Wisconsin.
- Burns, P.C. (1997) A new uranyl oxide hydrate sheet in vandendriesschite: Implications for mineral paragenesis and the corrosion of spent nuclear fuel. *American Mineralogist*, 82, 1176–1186.
- (1998a) The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. *Canadian Mineralogist*, 36, 1061–1067.
- (1998b) The structure of richetite, a rare lead uranyl oxide hydrate. *Canadian Mineralogist*, 36, 187–199.
- (1999) A new sheet complex of uranyl polyhedra in the structure of wölsendorfite. *American Mineralogist*, 84, 1661–1673.
- Burns, P.C. and Hanchar, J.M. (1999) The structure of masuyite, $Pb[(UO_2)_3O_2(OH)_2](H_2O)_3$, and its relationship to protasite. *Canadian Mineralogist*, 37, 1483–1491.
- Burns, P.C., Ewing, R.C., and Hawthorne, F.C. (1997) The crystal chemistry of hexavalent uranium: Polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Canadian Mineralogist*, 35, 1551–1570.
- Burns, P.C., Olson, R.A., Finch, R.J., Hanchar, J.M., and Thibault, Y. (2000) $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$: a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass. *Journal of Nuclear Materials*, 278, 290–300.
- Cesbron, F., Brown, W.L., and Bariand, P. (1972) Rameauite and agrinierite, two new hydrated complex uranyl oxides from Margnac, France. *Mineralogical Magazine*, 38, 781–789.

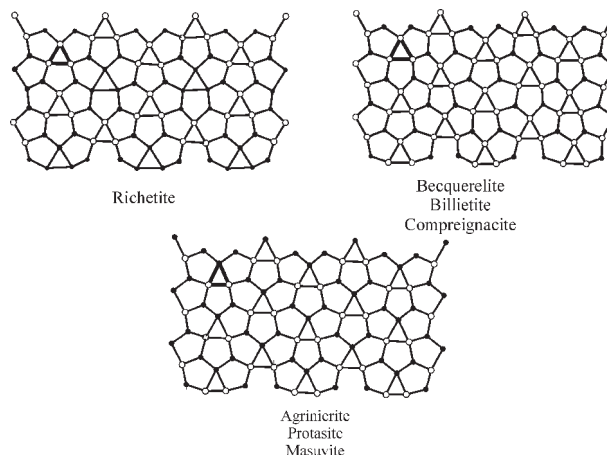


FIGURE 2. Sheet anion topology of U-O-H minerals containing the α - U_3O_8 sheet type. Small black circles = O atoms; open circle = OH groups. The single bold triangle in each structure is to aid in visualizing the hydroxyl distribution.

- Finch, R.J., Miller, M.L., and Ewing, R.C. (1992) Weathering of Natural Uranyl Oxide Hydrates—Schoepite Polytypes and Dehydration Effects. *Radiochimica Acta*, 58–9, 433–443.
- Finch, R.J., Cooper, M.A., Hawthorne, F.C., and Ewing, R.C. (1996) The crystal structure of schoepite, $[(UO_2)_3O_2(OH)_2](H_2O)_{12}$. *Canadian Mineralogist*, 34, 1071–1088.
- Finch, R.J., Buck, E.C., Finn, P.A., and Bates, J.K. (1999a) Oxidative corrosion of spent UO_2 fuel in vapor and dripping groundwater at 90 °C. In *Scientific Basis for Nuclear Waste Management XXII*, Materials Research Society Symposium Proceedings, 556, 431–438.
- Finch, R.J., Cooper, M.A., and Hawthorne, F.C. (1999b) Refinement of the crystal structure of Rutherfordine. *Canadian Mineralogist*, 37, 929–938.
- Finn, P.A., Hoh, J.C., Wolf, S.F., Slater, S.A., and Bates, J.K. (1996) The release of uranium, plutonium, cesium, strontium, technetium and iodine from spent fuel under unsaturated conditions. *Radiochimica Acta*, 74, 65–71.
- Loopstra, B.O. (1977) On the crystal structure of α - U_3O_8 . *Journal of Inorganic and Nuclear Chemistry*, 39, 1713–1714.
- Pagoaga, M.K., Applemal, D.E., and Stewart, J.M. (1987) Crystal structures and crystal chemistry of the uranyl oxide hydrates becquerelite, billietite and protasite. *American Mineralogist*, 72, 1230–1238.
- Pearcy, E.C., Prikryl, J.D., Murphy, W.M., and Leslie, B.W. (1994) Alteration of Uraninite From the Nopal-I Deposit, Pena-Blanca District, Chihuahua, Mexico, Compared to Degradation of Spent Nuclear-Fuel in the Proposed United-States High-Level Nuclear Waste Repository At Yucca Mountain, Nevada. *Applied Geochemistry*, 9, 713–732.
- Piret, P. (1985) Structure cristalline de la fourmarierite. *Bulletin de Minéralogie*, 108, 659–665.
- Piret, P., Deliens, M., Piret-Meunier, J., and Germain, G. (1983) La sayrite, $Pb_2[(UO_2)_3O_2(OH)_2]_4H_2O$, nouveau minéral; propriétés et structure cristalline. *Bulletin de Minéralogie*, 106, 299–304.
- Rosenzweig, A. and Ryan, R.R. (1977) Vandendriesschite $CuUO_2(OH)_4$. *Crystal Structure Communications*, 6, 53–56.
- Taylor, J.C., Stuart, W.I., and Mumme, I.A. (1981) The crystal structure of curite. *Journal of Inorganic and Nuclear Chemistry*, 43(10), 2419–2423.
- Wronkiewicz, D.J. and Buck, E.C. (1999) Uranium mineralogy and the geologic disposal of spent nuclear fuel. In *Mineralogical Society of America Reviews in Mineralogy*, 38, 475–498.
- Wronkiewicz, D.J., Bates, J.K., Gerding, T.J., Veleckis, E., and Tani, B.S. (1992) Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90°C. *Journal of Nuclear Materials*, 190, 107–127.
- Wronkiewicz, D.J., Bates, J.K., Wolf, S.F., and Buck, E.C. (1996) Ten-year results from unsaturated drip tests with UO_2 at 90°C: Implications for the corrosion of spent nuclear fuel. *Journal of Nuclear Materials*, 238, 78–95.

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