

A new uranyl carbonate sheet in the crystal structure of fontanite, $\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2](\text{H}_2\text{O})_6$

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ABSTRACT

The structure of fontanite, $\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2](\text{H}_2\text{O})_6$, is monoclinic, space group $P2_1/n$, $a = 6.968(3)$, $b = 17.276(7)$, $c = 15.377(6)$ Å, $\beta = 90.064(6)^\circ$, $V = 1851(1)$ Å³, $Z = 4$. The structure was solved by direct methods and refined on the basis of F^2 for all unique reflections using least-squares techniques to an agreement index ($R1$) of 9.9%. The structure contains two symmetrically distinct uranyl pentagonal bipyramids, one uranyl hexagonal bipyramid, and two CO_3 triangles. The uranyl polyhedra form chains by sharing equatorial edges, and CO_3 groups occur on either side of the chains, where they share equatorial edges of the uranyl hexagonal bipyramids. The CO_3 groups share their third ligand with a uranyl pentagonal bipyramid of an adjacent chain, resulting in uranyl carbonate sheets of composition $[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2]^{2-}$. The single symmetrically unique Ca^{2+} cation is located between the sheets, and is coordinated by two O atoms of uranyl ions of adjacent sheets, and six H_2O groups. The uranyl carbonate sheet in fontanite is novel, but is based upon the phosphuranylite anion topology that is the basis of uranyl phosphate, uranyl selenite, and uranyl sulfate sheets in a variety of minerals.

INTRODUCTION

Twenty-six uranyl carbonate minerals have been described, but owing to a lack of material suitable for crystallographic study, structures have only been reported for eleven of these. We are interested in the structures of uranyl carbonates because they impact the mobility of actinides in the environment, are essential to an understanding of the genesis of uranium deposits, and are important for the long-term performance of geological repositories for nuclear waste (Burns and Finch 1999; Li and Burns 2001a, 2001b; Li et al. 2001; Li and Burns 2002).

The crystal structure of fontanite, $\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2](\text{H}_2\text{O})_6$, has been determined using single-crystal diffraction techniques and a CCD-based detector. Fontanite was originally described by Deliens and Piret (1992), with the formula $\text{Ca}(\text{UO}_2)_3(\text{CO}_3)_4(\text{H}_2\text{O})_3$ and orthorhombic symmetry (space groups $Pnmm$, $Pmn2_1$, or $P2_1nm$).

EXPERIMENTAL METHODS

Specimen locality

Specimens labeled RC 4216 and RX 9450 were inspected during a recent visit to l'Institut Royal des Sciences Naturelles in Brussels, Belgium. Specimen RC 4216 is the holotype for fontanite. Both specimens are from the Rabejec deposit located seven km southeast of Lodève, Hérault, France, where fontanite occurs in alteration zones in association with billietite and uranophane (Deliens and Piret 1992).

Collection of X-ray data

Various crystals of fontanite from both samples were studied, and most were found to be inappropriate for single crystal analysis, either because the crystals were too small, or their diffraction patterns contained streaking and other deleterious effects. Only one crystal, taken from RC 4216, yielded diffraction data of sufficient quality for structure analysis. The crystal was mounted on a tapered glass

fiber on a Bruker PLATFORM 3-circle goniometer equipped with an APEX 4 K SMART CCD detector with a crystal-to-detector distance of 4.67 cm. A sphere of three-dimensional data was collected to $60^\circ 2\theta$ using graphite-monochromated $\text{MoK}\alpha$ X-radiation and frame widths of 0.6° in ω , with 30 seconds spent counting per frame. Unit-cell parameters (Table 1) were refined using 3140 reflections and least-squares techniques. Data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical correction for adsorption was applied by modeling the crystal as an ellipsoid, which reduced R_{int} of 393 reflections from 10.8% to 5.9%. A total of 34,675 reflections were collected, of which 5223 were unique, and 3140 were classed as observed ($|F_o| \geq 4\sigma F$).

Structure solution and refinement

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

Data were collected for the best available crystal of fontanite, but overall data quality was lower than ideal and many reflections exhibited broad profiles. Analysis of the data gave an orthorhombic unit cell, which is consistent with the earlier work of Deliens and Piret (1992), who suggested space groups $Pnmm$, $Pmn2_1$, or $P2_1nm$. Reflection statistics were consistent with $Pmn2_1$, or $P2_1nm$, but attempts to solve the structure in these and a variety of other orthorhombic space groups consistently failed to give reasonable solutions. Eventually, it was concluded that the structure was probably monoclinic with $\beta \approx 90^\circ$. The structure was solved in space group $P2_1/n$, and refinement of a model that contained only the U atoms gave an agreement factor ($R1$) of 26.9%. Twinning with twin operator 100, 010, 001 was accounted for using the method of Jameson (1982) and Herbst-Irmer and Sheldrick (1998), which reduced $R1$ of the model containing only the U atoms to 15.6%. Additional atoms were located on difference-Fourier maps and were inserted into the model, which refined to an $R1$ value of 11.0%. We noted that the calculated and observed structure factors that were most disparate corresponded to those with $F_{observed}$ much greater than $F_{calculated}$. This probably indicates that the diffraction pattern contains interference from another crystal orientation, due either to a split crystal or perhaps additional twinning. The 172 reflections that were most impacted by this overlap, which corresponded to 3.2% of the unique reflections, were removed from the data. The final model contained all atomic positional parameters, anisotropic displacement parameters for U and Ca, isotropic displacement parameters for C and O, and a weighting scheme of the structure factors. A model that

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TABLE 1. Crystallographic data and details of the structure refinements of fontanite

Formula	Ca[(UO ₂) ₃ (CO ₃) ₂ O ₂](H ₂ O) ₆
Formula weight	1078.27
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	6.968(3)
<i>b</i> (Å)	17.276(7)
<i>c</i> (Å)	15.377(6)
β (°)	90.064(6)
<i>V</i>	1851.0(13) Å ³
<i>Z</i>	4
ρ _{calculated} (g/cm ³)	3.984
μ (mm ⁻¹)	26.552
<i>F</i> (000)	1920
Crystal size (mm ³)	0.04 x 0.04 x 0.14
Radiation	MoK α
Reflections collected	34,675
Independent reflections	5223
Unique <i>F</i> _o $\geq 4\sigma F$	3140
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters varied	127
<i>R</i> 1 (%)	9.95
<i>wR</i> 2 (%)	23.01
<i>S</i>	1.036
Largest diff. peak (e/Å ³)	11.48 and -6.66

included anisotropic displacement parameters for C and O resulted in some physically unrealistic displacement parameters, as is often the case when refining the structures of uranyl minerals. The model was refined on the basis of *F*² for all unique reflections, and converged to a final *R*1 of 9.9%, which was calculated for the 3140 observed reflections ($|F_o| \geq 4\sigma F$). Final atomic positional and displacement parameters are given in Table 2. Selected interatomic distances and angles are in Table 3. Calculated and observed structure factors are provided in Table 4¹. A bond-valence analysis is presented in Table 5.

The overall quality of the refined structure is not as high as is desirable, as reflected by bond-length errors that are higher than normal for uranyl minerals. However, the best available crystal of fontanite was used for data collection. The diminished quality of the refined structure is due to the relatively poor crystal quality and the presence of twinning. Although the precision of the refined structure is not ideal, the cation coordination polyhedra and connectivity of the structure are not in question.

RESULTS

Projection of the structure of fontanite along [100] reveals that it contains sheets of uranyl polyhedra and carbonate triangles, with Ca atoms and H₂O groups located in the interlayer between the sheets (Fig. 1). Thus, the structure is generally consistent with the bulk of uranyl minerals, which most commonly contain sheets of polyhedra of higher bond-valence (Burns 1999).

Cation polyhedra

The structure of fontanite contains three symmetrically unique U⁶⁺ cations, each of which is part of an approximately linear uranyl ion [(UO₂)²⁺, designated Ur], with $\langle U-O_{Ur} \rangle$ bond lengths of ~ 1.8 Å. The uranyl ions are coordinated by additional O atoms arranged at the equatorial vertices of bipyramids that are capped by the O_{Ur} atoms. The U1 uranyl ion is coordinated by six O atoms, giving a hexagonal bipyramid, with an $\langle U-O_{eq} \rangle$ (O_{eq}: equatorial O) bond length

of 2.44 Å. This compares favorably with the average $\langle [^{16}U-O_{eq}] \rangle$ of 2.47(12) Å derived from numerous well-refined structures (Burns et al. 1997). The U2 and U3 uranyl ions are each coordinated by five O atoms, giving uranyl pentagonal bipyramids with $\langle U2-O_{eq} \rangle$ and $\langle U3-O_{eq} \rangle$ bond lengths of 2.33 and 2.38 Å, respectively. These are consistent with the average $\langle [^{15}U2-O_{eq}] \rangle$ bond length of 2.37(9) Å derived from many well-refined structures (Burns et al. 1997).

The single unique Ca atom is coordinated by two O_{Ur} atoms and six H₂O groups, with a $\langle Ca-\phi \rangle$ bond length of 2.50 Å (ϕ : O²⁻ or H₂O). The structure contains two unique C atoms, each of which is coordinated by three atoms of O in a triangular arrangement, with $\langle C1-O \rangle$ and $\langle C2-O \rangle$ bond lengths of 1.29 and 1.28 Å, respectively.

Structural connectivity

The uranyl pentagonal bipyramids share an equatorial edge, with the resulting dimers sharing two equatorial edges with uranyl hexagonal bipyramids on either side, giving chains of uranyl polyhedra that extend along [100]. Two equatorial edges of each hexagonal bipyramid are shared with CO₃ groups, one on either side of the chain. The third vertex of each CO₃ group is shared with a uranyl pentagonal bipyramid of an adjacent chain, resulting in novel uranyl carbonate sheets of composition [(UO₂)₃(CO₃)₂O₂]²⁻ that are parallel to (100) (Fig. 2). The Ca²⁺ cations located in the interlayer are bonded to one uranyl ion from each of the two adjacent sheets, and thus provide direct linkage of the uranyl carbonate sheets into a three-dimensional structure (Fig. 1). Six ligands of the Ca²⁺ polyhedra are H₂O groups, and additional linkages between the sheets is undoubtedly provided by H bonding, although the positions of the H atoms were not revealed by the X-ray data.

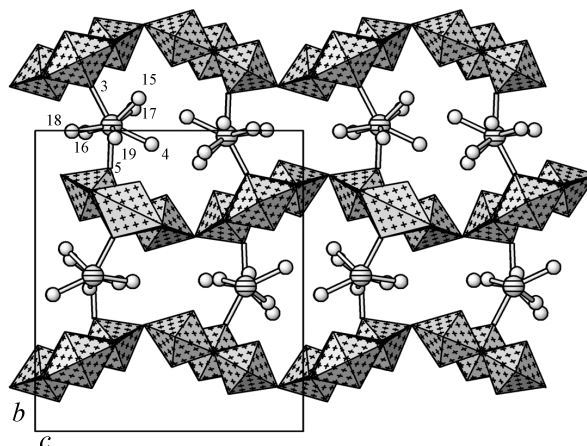


FIGURE 1. Polyhedral representation of the structure of fontanite projected along [100]. The uranyl polyhedra are shaded with crosses, the carbonate triangles are colored black, Ca atoms are shaded with parallel lines, and O atoms are shown as open circles. Numbers refer to atom labels in Table 2.

¹For a copy of Table 4, document item AM-03-033, 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 at <http://www.minsocam.org>.

TABLE 2. Atomic coordinates and equivalent displacement parameters for fontanite

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U1	0.5267(2)	0.2371(1)	0.8372(1)	0.025(1)	0.011(1)	0.044(1)	0.020(1)	0.002(1)	-0.003(1)	-0.002(1)
U2	1.0267(2)	0.2843(1)	0.7301(1)	0.024(1)	0.011(1)	0.036(1)	0.024(1)	0.002(1)	-0.002(1)	-0.001(1)
U3	0.0257(2)	0.1952(1)	0.9483(1)	0.024(1)	0.010(1)	0.043(1)	0.019(1)	0.002(1)	-0.003(1)	-0.001(1)
Ca1	0.941(1)	0.5174(6)	0.7848(6)	0.043(2)	0.037(5)	0.052(6)	0.039(5)	0.003(4)	0.000(4)	-0.001(4)
C1	1.532(4)	0.317(1)	0.666(1)	0.001(4)						
C2	0.527(4)	0.169(2)	1.015(1)	0.006(5)						
O1	0.023(5)	0.288(2)	0.990(2)	0.049(7)						
O2	1.040(3)	0.351(1)	0.597(1)	0.015(4)						
O3	0.513(5)	0.144(2)	0.790(2)	0.049(8)						
O4*	-0.088(5)	0.455(2)	0.935(2)	0.059(9)						
O5	1.013(5)	0.375(2)	0.778(2)	0.054(8)						
O6	-0.316(4)	0.176(2)	0.969(2)	0.036(7)						
O7	0.844(4)	0.234(2)	0.833(2)	0.037(8)						
O8	0.028(4)	0.145(2)	1.094(2)	0.035(6)						
O9	0.684(4)	0.292(2)	0.700(2)	0.030(6)						
O10	1.370(4)	0.302(2)	0.707(2)	0.032(7)						
O11	0.207(4)	0.238(2)	0.835(2)	0.029(6)						
O12	0.541(4)	0.331(2)	0.890(2)	0.036(6)						
O13	0.371(3)	0.187(1)	0.978(2)	0.021(5)						
O14	0.036(4)	0.099(1)	0.910(2)	0.030(6)						
O15*	0.786(4)	0.607(2)	0.888(2)	0.041(8)						
O16*	1.239(6)	0.493(2)	0.690(2)	0.055(9)						
O17*	1.203(6)	0.571(2)	0.869(3)	0.06(1)						
O18*	0.808(5)	0.498(2)	0.639(2)	0.052(9)						
O19*	0.590(7)	0.476(3)	0.798(3)	0.08(1)						
O20	1.038(4)	0.200(2)	0.670(2)	0.033(6)						

* O atoms of H₂O groups.**TABLE 3.** Bond lengths (Å) and angles (°) for fontanite

U1-O3	1.78(3)	Ca1-O17	2.40(4)
U1-O12	1.82(3)	Ca1-O15	2.44(4)
U1-O7	2.22(3)	Ca1-O3c	2.47(3)
U1-O11	2.22(3)	Ca1-O18	2.48(4)
U1-O10a	2.52(3)	Ca1-O5	2.50(4)
U1-O6b	2.54(3)	Ca1-O4b	2.54(4)
U1-O9	2.56(3)	Ca1-O19	2.55(5)
U1-O13	2.58(3)	Ca1-O16	2.59(4)
O3-U1-O12	177.9(14)	<Ca1-φ>	2.50
<U1-O _{ij} >	1.80		
<U1-O _{eq} >	2.44	C1-O8d	1.25(4)
		C1-O9b	1.27(4)
		C1-O10	1.34(4)
		<C1-O>	1.29
U2-O5	1.75(3)	C2-O13	1.25(4)
U2-O20	1.76(3)	C2-O6b	1.29(4)
U2-O11b	2.19(3)	C2-O2e	1.29(3)
U2-O7	2.22(3)	<C2-O>	1.28
U2-O2	2.37(2)		
U2-O9	2.43(3)		
U2-O10	2.44(3)		
O5-U2-O20	171.8(14)		
<U2-O _{ij} >	1.75		
<U3-O _{eq} >	2.33		
U3-O1	1.71(3)		
U3-O14	1.77(3)		
U3-O7a	2.26(3)		
U3-O11	2.29(3)		
U3-O8	2.41(3)		
U3-O6	2.45(3)		
U3-O13	2.47(2)		
O1-U3-O14	175.8(13)		
<U3-O _{ij} >	1.74		
<U3-O _{eq} >	2.38		

Notes: a: *x* - 1, *y*, *z*; b: *x* + 1, *y*, *z*; c: -*x* + 3/2, *y* + 1/2, -*z* + 3/2; d: *x* + 3/2, -*y* + 1/2, *z* - 1/2; e: *x* - 1/2, -*y* + 1/2, *z* + 1/2

Sheet anion topology

The anion topology of the uranyl carbonate sheet in fontanite, obtained using the procedure of Burns et al. (1996), is shown in Figure 3. This was designated the phosphuranylite anion topology by Burns et al. (1996) and Burns (1999). Fontanite is the only uranyl carbonate that contains a sheet that

TABLE 5. Bond-valence* (v.u.) analysis for the structure of fontanite

	U1	U2	U3	Ca1	C1	C2	Σ
O1			1.93				1.93
O2		0.52				1.31	1.83
O3	1.67			0.26			1.92
O4†				0.21			0.21
O5		1.76		0.24			2.00
O6	0.37		0.45			1.33	2.15
O7	0.70	0.70	0.65				2.06
O8			0.49		1.47		1.96
O9	0.36	0.46			1.40		2.22
O10	0.39	0.45			1.14		1.98
O11	0.70	0.75	0.61				2.06
O12	1.55						1.55
O13	0.35		0.43			1.47	2.24
O14			1.73				1.73
O15†				0.28			0.28
O16†				0.19			0.19
O17†				0.31			0.31
O18†				0.25			0.25
O19†				0.21			0.21
O20		1.75					1.75
Σ	6.09	6.40	6.28	1.94	4.01	4.11	

* Bond valence parameters for uranium from Burns et al. (1997). Calcium and carbon bond-valence parameters are from Brese and O'Keeffe (1991). † O atoms of H₂O groups.

is based upon the phosphuranylite anion topology. It contains pairs of edge-sharing pentagons that share edges with hexagons to form chains that have twice as many pentagons as hexagons, and which have alternating hexagons and pairs of pentagons along the chain length. Adjacent chains of pentagons and hexagons are offset so that hexagons of a given chain are adjacent to pentagons on either side. The chains of pentagons and hexagons are separated by a chain of edge-sharing squares and triangles. The fontanite sheet may be obtained from the anion topology by populating the pentagons and hexagons with uranyl ions, and each triangle with a CO₃ group.

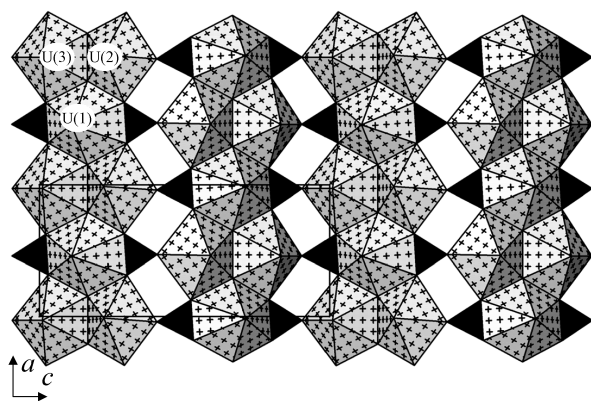


FIGURE 2. Polyhedral representation of the uranyl carbonate sheet in the structure of fontanite projected along [010]. Legend as in Figure 1.

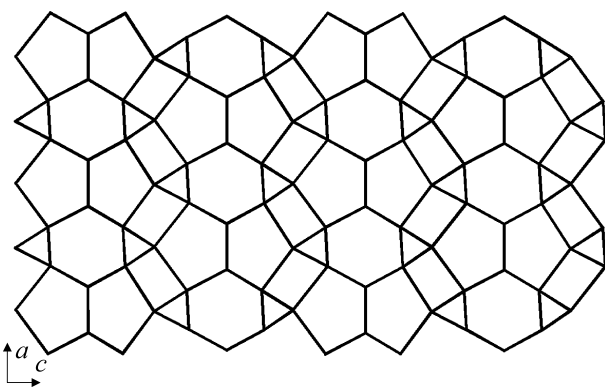


FIGURE 3. The sheet anion topology corresponding to the fontanite sheet, derived using the method of Burns et al. (1996). This anion topology is designated the phosphuranylite anion topology.

DISCUSSION

Mineral structures based upon the phosphuranylite anion topology

In addition to the uranyl carbonate sheet in fontanite, there are several other populations of the phosphuranylite anion topology that occur in the structures of uranyl phosphates, uranyl selenites, and uranyl sulfates. In uranyl phosphates, each pentagon and hexagon is populated by a uranyl ion, and phosphate tetrahedra populate the triangles of the sheet, such that the faces of the tetrahedra match the triangles of the anion topology. Several topologically distinct uranyl phosphate sheets result from differing orientations of the phosphate tetrahedra, and are the basis of several uranyl phosphate minerals (listed in Burns 1999).

Guilleminite (Cooper and Hawthorne 1995), $\text{Ba}[(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2](\text{H}_2\text{O})_3$, and marthozite (Cooper and Hawthorne 2001), $\text{Cu}[(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2](\text{H}_2\text{O})_8$, contain uranyl selenite sheets that are based upon the phosphuranylite anion topology. The pentagons and hexagons of the anion topology are populated by uranyl ions, and the triangles correspond to Se^{4+}O_3

pyramids that are distorted owing to the presence of a lone pair of electrons on the Se^{4+} cation.

The structure of johannite (Mereiter 1982), $\text{Cu}[(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2](\text{H}_2\text{O})_8$, contains uranyl sulfate sheets based upon the phosphuranylite anion topology. Pentagons of the anion topology are populated by uranyl ions, the faces of sulfate tetrahedra correspond to the triangles of the topology, and the hexagons are vacant.

Relationship to structures of uranyl carbonates

Twenty-six uranyl carbonate minerals have been described (Mandarino 1999), although the structures have been reported for only eleven. In general, uranyl carbonates that crystallize under alkaline conditions involve the uranyl tricarbonate cluster of composition $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$. These clusters are typically linked by bonds to low-valence cations and by H bonds, thus Burns et al. (1996) and Burns (1999) grouped them with structures based upon finite clusters of polyhedra of higher bond valence. Under more acidic conditions, uranyl carbonates containing sheets are dominant. The structure of rutherfordine, $[(\text{UO}_2)(\text{CO}_3)_3]$, contains sheets of uranyl hexagonal bipyramids and carbonate triangles (Finch et al. 1999), and the corresponding sheet anion topology involves only hexagons and triangles (Burns 1999). The structure of wyartite, $\text{Ca}[\text{U}^{5+}(\text{UO}_2)_2(\text{CO}_3)_4(\text{OH})](\text{H}_2\text{O})_7$, contains sheets of uranyl pentagonal bipyramids and carbonate triangles that is based on the $\beta\text{-U}_3\text{O}_8$ anion topology with triangles, squares, and pentagons (Burns and Finch 1999). Bijvoetite, $[(\text{Y,REE})^{3+}(\text{H}_2\text{O})_{25}(\text{UO}_2)_{16}\text{O}_8(\text{OH})_8(\text{CO}_3)_{16}](\text{H}_2\text{O})_{14}$, contains complex sheets of uranyl pentagonal and hexagonal bipyramids, carbonate triangles, and (Y,REE) polyhedra, and has a novel sheet anion topology containing pentagons, hexagons, squares, and trapezoids (Li and Burns 2001b). The structure of roubaulite, $[\text{Cu}_2(\text{UO}_2)_5(\text{CO}_3)_2\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_4$, contains sheets of uranyl pentagonal and hexagonal bipyramids, carbonate triangles, and $\text{Cu}^{2+}\phi_6$ octahedra (Ginderow and Cesbron 1985), which are based upon an anion topology with triangles, squares, pentagons, and hexagons. The roubaulite sheet is most closely related to that of fontanite; they contain identical chains of edge-sharing uranyl pentagonal and hexagonal bipyramids and carbonate triangles. In the fontanite sheet, these chains are directly linked, whereas in the rutherfordine sheet, they are linked through $\text{Cu}^{2+}\phi_6$ octahedra.

ACKNOWLEDGMENTS

This research was supported by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy, grant DE-FG07-97ER14820. We are grateful to M. Deliens, l'Institut Royal des Sciences Naturelles de Belgique in Brussels, for providing the specimens used in this study. K.A. Hughes was supported by a GAANN Fellowship.

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MANUSCRIPT RECEIVED JULY 29, 2002

MANUSCRIPT ACCEPTED NOVEMBER 22, 2002

MANUSCRIPT HANDLED BY MARIA BRIGATTI