# The crystal structure of synthetic autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$

## **ANDREW J. LOCOCK\* AND PETER C. BURNS**

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, Indiana 46556-0767, U.S.A.

## ABSTRACT

Autunite, Ca[(UO<sub>2</sub>)(PO<sub>4</sub>)]<sub>2</sub>(H<sub>2</sub>O)<sub>11</sub>, is amongst the most abundant and widely distributed of the uranyl phosphate minerals, yet because of its pseudo-tetragonal symmetry and rapid dehydration in air, the details of its symmetry, stoichiometry, and structure were previously uncertain. The crystal structure of synthetic autunite was solved by direct methods and refined by full-matrix least-squares techniques to agreement indices  $R_1 = 0.041$ , calculated for the 1497 unique observed reflections ( $|F_o| \ge 4\sigma_F$ ), and  $wR_2 = 0.119$  for all data. Autunite is orthorhombic, space group *Pnma*, Z = 4, a = 14.0135(6), b = 20.7121(8), c = 6.9959(3) Å, V = 2030.55(15) Å<sup>3</sup>. The structure contains the well-known autunite type sheet with composition [(UO<sub>2</sub>)(PO<sub>4</sub>)]<sup>-</sup>, resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra. The calcium atom in the interlayer is coordinated by seven H<sub>2</sub>O groups and two longer distances to uranyl apical O atoms. Two symmetrically independent H<sub>2</sub>O groups are held in the structure only by hydrogen bonding.

## INTRODUCTION

Autunite,  $Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$ , has been recognized for at least 150 years (Brooke and Miller 1852). Owing to its pseudo-tetragonal symmetry and rapid dehydration in air (Sowder et al. 2000), the structure of autunite has never before been determined, and the nature of the interlayer configuration, H<sub>2</sub>O content, and hydrogen bonding were unknown. Autunite is the namesake of the autunite and meta-autunite groups, which consist of ~40 hydrated uranyl phosphate and arsenate minerals (Finch and Murakami 1999). We are interested in the structures, chemistries, and stabilities of autunite-group minerals because of their significance to the environment. They form in abundance and impact the mobility of uranium in phosphate-bearing systems (Sowder et al. 1996), such as the Koongarra uranium deposit in Australia (Murakami et al. 1997). Autunite largely controls the mobility of uranium in soils contaminated by actinides, such as at the Fernald site in Ohio (Buck et al. 1996), and the K1300 locality of the DOE-K 25 site at Oak Ridge, Tennessee (Roh et al. 2000). Autunite-group minerals are bioprecipitated by Citrobacter sp., which is proposed for remediation of groundwater contaminated by heavy metals (Basnakova et al. 1998; Macaskie et al. 2000). They have been found in experiments involving bacteria extracted from the Waste Isolation Pilot Plant repository (Francis et al. 2000). Autunite-group minerals precipitate at reactive barriers that use phosphate to limit the transport of uranium in groundwater (Fuller et al. 2002), and their stabilities under vadose- and saturated-zone conditions may determine the long-term effectiveness of these remediation strategies.

Museum specimens designated as autunite are almost in-

variably meta-autunite; our experiments have shown that autunite is unstable in air, and will dehydrate within minutes, resulting in strained crystals that give very poor quality single-crystal diffraction data. We have developed a technique for the synthesis of superb crystals of autunite, and have collected X-ray diffraction data for a single crystal contained within its mother solution. This has permitted the full determination and refinement of its structure, and elucidation of a probable scheme of hydrogen bonding.

## **PREVIOUS STUDIES**

On the basis of its crystal morphology and biaxial optical character, autunite was thought to have either orthorhombic or monoclinic symmetry by early workers (Goldschmidt 1918; Larsen and Berman 1934; Frondel 1958, and references therein). An X-ray diffraction study conducted by Beintema (1938) indicated that the structure of autunite is tetragonal, space group *I4/mmm*, *a* = 6.989, *c* = 20.63 Å (corrected from kX units to *a* = 7.003, *c* = 20.67 Å in Frondel 1958; see also Bunn 1961), with the measured *a* and *b* dimensions differing by less that 1%. Most modern compilations state autunite is tetragonal (e.g., Strunz and Nickel 2001; Gaines et al. 1997), which implies that its biaxial optical character is anomalous.

#### **EXPERIMENTAL METHODS**

Single crystals of autunite were grown over the course of four months by slow diffusion of 0.1 M H<sub>3</sub>PO<sub>4(aq)</sub> and 0.1 MUO<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>6(aq)</sub> into a Ca-bearing silica gel formed by the hydrolysis of a mixture (1:10) of (CH<sub>3</sub>O)<sub>4</sub>Si<sub>(liq)</sub> and 0.1 MCa(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4(aq)</sub>. The crystals are biaxial negative; 2V is ~30°. A suitable crystal was sealed in a glass capillary (0.5 mm external diameter) with a volume of its diluted growth solution, and mounted on a Bruker PLATFORM three-circle X-ray

<sup>\*</sup> E-mail: alocock@nd.edu

	X	У	Ζ	$U_{ m eq}$	Occupancy%	Wyckoff Position		
U1	1250(1)	5412(1)	7498(1)	12(1)	100	8 <i>d</i>		
P1	1245(2)	5003(1)	2478(2)	13(1)	100	8 <i>d</i>		
Ca1	1251(2)	7500	4501(4)	29(1)	86.0(7)	4 <i>c</i>		
01	1235(5)	4551(2)	7482(5)	26(1)	100	8 <i>d</i>		
02	1250(4)	6278(2)	7472(5)	21(1)	100	8 <i>d</i>		
O3	1252(4)	5440(2)	733(7)	29(1)	100	8 <i>d</i>		
O4	373(4)	4560(4)	2451(5)	28(2)	100	8 <i>d</i>		
O5	2118(4)	4557(3)	2553(5)	32(2)	100	8 <i>d</i>		
O6	1206(4)	5452(2)	4226(7)	23(1)	100	8 <i>d</i>		
07	7591(7)	2500	2851(13)	41(3)	100	4 <i>c</i>		
08	2368(5)	6647(4)	3510(11)	72(2)	100	8 <i>d</i>		
O9	126(4)	6645(3)	3438(11)	63(2)	100	8 <i>d</i>		
O10	10002(9)	2500	2833(13)	55(3)	100	4 <i>c</i>		
011	1263(6)	7500	757(11)	39(2)	100	4 <i>c</i>		
012	3257(5)	6614(4)	-255(10)	62(2)	100	8 <i>d</i>		
O13	759(5)	3379(3)	243(10)	57(2)	100	8 <i>d</i>		
H1	7260(40)	2830(20)	2220(90)	50	100	8 <i>d</i>		
H2	1970(40)	6330(30)	4120(90)	50	100	8 <i>d</i>		
H3	2210(60)	6540(50)	2150(40)	50	100	8 <i>d</i>		
H4	330(50)	6191(14)	3350(100)	50	100	8 <i>d</i>		
H5	80(60)	6650(40)	2010(30)	50	100	8 <i>d</i>		
H6	10370(40)	2851(18)	2330(90)	50	100	8 <i>d</i>		
H7	1300(50)	7056(12)	440(100)	50	100	8 <i>d</i>		
H8	2720(40)	6740(40)	580(90)	50	100	8 <i>d</i>		
H9	3972(16)	6550(50)	-270(140)	50	100	8 <i>d</i>		
H10	680(50)	3819(16)	750(90)	50	100	8 <i>d</i>		
H11	1483(14)	3360(50)	220(130)	50	100	8 <i>d</i>		
			Data Stat	istics				
a (Å)		14.0135(6)	Crystal size		0.46 mm >	imes 0.46 mm $ imes$ 0.06 mm		
b (Å)		20.7121(8)	R <sub>int</sub>		0.098			
<i>c</i> (Å)		6.9959(3)	Unique reflection	ons	4318			
V (ų)		2030.55(15)	Unique   <i>F</i> <sub>o</sub>   > 4	σ <sub>F</sub>	1497			
Space gro	oup	Pnma	Refinement me	ethod	Full-matrix	x least-squares on <i>F</i> <sup>2</sup>		
F(000)*		1760	Parameters va	ried	168			
μ (mm <sup>-1</sup> )*		16.443	$R_1$ † for $ F_0  > 4$	$\sigma_F$	0.041			
$D_{calc} (g/cm^3)^*$ 3.167(1)		3.167(1)	$R_1$ † all data		0.086			
Radiation Mo <i>K</i> a		Μο <i>Κ</i> α	wR <sub>2</sub> ‡ all data		0.119			
Total reflections 29,471		29,471	Goodness of fit	t all data	0.944			
Data range ( $\theta$ ) 2.9		2.91 to 34.50°	Max. min. peak	⟨s ( <i>e</i> /ų)	3.66, -6.5	51		
Unit-cell c	contents	4{Ca[(UO <sub>2</sub> )(PO <sub>4</sub> )] <sub>2</sub> (H <sub>2</sub> O)	1}					
Notes 11	is defined as an	a third of the trees of the	wthe genelized 11 tensor					

**TABLE 1.** Atomic positions (×10<sup>4</sup>), displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>), unit-cell parameters, crystallographic parameters, and data statistics for synthetic autunite

Note: U<sub>eq</sub> is defined as one third of the trace of the orthogonalized U<sub>ii</sub> tensor.

\* Calculated with full occupancy of all atomic positions.

 $\dagger R_1 = [\Sigma ||F_0| - |F_c|]/\Sigma |F_0|.$ 

 $\ddagger wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}, w = 1/(\sigma^2(F_0^2) + (a \cdot P)^2, P = 1/3 \max(0, F_0^2) + 2/3F_c^2, a = 0.0537.$ 

diffractometer operated at 50 keV and 40 mA and equipped with a 4K APEX CCD detector with a crystal to detector distance of 4.7 cm. A sphere of three-dimensional data was collected using graphite-monochromatized MoKa X-radiation and frame widths of  $0.3^{\circ}$  in $\omega$ , with count-times per frame of 5 seconds. Data were collected over the range  $6^{\circ} \le 2\theta \le 70^{\circ}$  in 4.5 hours; comparison of the intensities of equivalent reflections measured at different times during data collection showed no significant decay. Determination of the unit cell (Table 1) was based upon the location of centered diffraction maxima from several hundred frames of data, and the final cell was refined using 6903 reflections and least-squares techniques. The a unitcell dimension reported here is double that of earlier work; this larger dimension was confirmed by 683 observed ( $I > 3\sigma$ ) reflections in the sphere of data. The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption correction was applied by modeling the crystal as a plate and rejecting data within 3 degrees of the primary X-ray beam. This procedure lowered  $R_{int}$  for 5750 intense reflections from 0.381 to 0.089.

Systematic absences of reflections were consistent with space group Pnma. 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 Version 5 series of programs was used for the solution and refinement of the crystal structure. The structure was solved in space group Pnma using direct methods and was refined based on  $F^2$  for all unique data. A structure model including anisotropic displacement parameters for all non-hydrogen atoms converged, and gave an agreement index  $(R_1)$  of 0.041, calculated for the 1497 observed unique reflections ( $|F_0| \ge 4\sigma_F$ ). The final value of  $wR_2$  was 0.119 for all data using the structure-factor weights assigned during least squares refinement. An empirical correction factor for extinction refined to 0.0019(1). The atomic positional parameters and displacement parameters are given in Table 1, and selected interatomic distances and angles are in Table 2. Anisotropic dis-

U1-O1 U1-O2 U1-O3* U1-O4† U1-O5‡ U1-O6 <u1-0></u1-0>		1.784( 1.794( 2.264( 2.276( 2.289( 2.291( 2.12	5) 5) 5) 6) 6) 5)	01-U1-02 01-U1-03 01-U1-04 01-U1-05 01-U1-06	* † ‡	178.9(i 91.79 90.8(i 92.3(i 91.70	2) )(15) 3) 3) )(15)	
P1-O3 P1-O4 P1-O5 P1-O6 <p1-o></p1-o>		1.519( 1.529( 1.534( 1.537( 1.53	5) 6) 6) 5)	03-P1-04 03-P1-05 04-P1-05 03-P1-06 04-P1-06 05-P1-06		110.7(3 112.4(3 106.0(3 106.3(3 110.1(3 111.4(3	3) 3) 3) 3) 3) 3) 3)	
Ca1-O8§ Ca1-O8 Ca1-O(7) Ca1-O(9) Ca1-O(9) Ca1-O(10 Ca1-O(11 Ca1-O(2) Ca1-O(2) <ca1-o></ca1-o>	 § ))   )	2.461( 2.463( 2.485( 2.485( 2.562( 2.619( 3.275( 2.68	7) 7) 9) 7) 7) 12) 9) 5) 5)	O8§-Ca1- O8§-Ca1- O8§-Ca1- O8§-Ca1- O8§-Ca1- O8§-Ca1- O8§-Ca1- O8§-Ca1-	08 07   09 09§ 010   011 02 02§	91.8(; 78.0(; 146.2(; 78.9(; 129.9(; 73.4(; 137.2(; 67.9(;	3) 3) 3) 2) 2) 2) 3) 2)	
07-H1 08-H2 08-H3 09-H5 010-H6 011-H7 012-H9 013-H10 013-H11	0.94(2 0.96(2 1.00(2 0.99(2 1.00(2 0.95(2 0.95(2 0.95(2 0.98(2 1.01(2 0.98(2 1.02(2	2) 2) 2) 2) 2) 2) 2) 2) 2) 2) 2) 2) 2)	H1012 H206 H3012 H406 H5013 H6013 H702 H8011 H8011 H809 H1004 H1108	1.93(2) 2.11(2) 2.24(2) 2.05(2) 1.97(2) 1.91(2) 2.63(2) 2.57(2) 2.12(2) 2.07(2) 1.99(2) 2.00(2)	07-H1 08-H2 09-H4 09-H5 010-H6 011-H7 012-H8 012-H8 012-H9 013-H11 013-H1	012 06 012 06 013 02 013 02 011 08 09 004 108	162 154 124 150 147 151 141 143 136 139 163 144	
<i>Note:</i> Symmetry transformations used to generate equivalent atoms: * $x + z + 1$								

TABLE 2. Selected interatomic distances (Å) and angles (°) for autunite. Ca[(UO<sub>2</sub>)(PO<sub>4</sub>)]<sub>2</sub>(H<sub>2</sub>O)<sub>11</sub>

-x. -v + 1. -z + 1.

-x + 1/2, -y + 1, z + 1/2

-x + 1, -y + 1, -z + 1.

|| x - v + 3/2. z.

O-H…O angles were obtained from SHELXL and rounded to the nearest degree.

placement parameters and structure factors are given in Tables 3 and 4 respectively.<sup>1</sup>

Possible hydrogen atom positions were located in difference-Fourier maps calculated following refinement of the model. As is typical for uranium minerals, it was very difficult to locate the hydrogen atoms on the basis of the X-ray data alone. Hydrogen atoms were inserted into the model at positions consistent with weak peaks in the difference-Fourier maps, as well as expected hydrogen atom positions derived from crystal-chemical arguments. Their positions were refined using the constraint that O-H bond-lengths be ~0.96 Å and have fixed isotropic displacement parameters. It was necessary to constrain the separations of the H4-H5, H3-H8, H6-H6, and H1-H1 atom pairs to reasonable values (~1.5 Å). The refinement provided a crystal-chemically reasonable hydrogen bonding network.

<sup>1</sup>For a copy of Tables 3 and 4, Document item AM-03-021, 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.

#### STRUCTURE DESCRIPTION

Autunite contains the well-known autunite-type sheet formed by the sharing of vertices between uranyl square bipyramids and phosphate tetrahedra, with composition  $[(UO_2)(PO_4)]^-$  (Fig. 1). The interlayer contains Ca atoms coordinated by seven H<sub>2</sub>O groups with bond-lengths in the range 2.461 to 2.619 Å (Table 2). The Ca site is also located 3.275 Å from uranyl ion O atoms of the sheets on either side; if these correspond to weak bonds they serve to link the sheets directly through the Ca atom. The Ca position refined to 86% occupancy; charge balance is interpreted to be maintained by oxonium, in analogy with chernikovite (Atencio 1988; Morosin 1978). There are two additional H<sub>2</sub>O groups that are located in the interlayer where they are held in position only by hydrogen bonding.

Bond valence analysis was performed using the parameters of Burns et al. (1997) for <sup>[6]</sup>U<sup>6+</sup>, Brown and Altermatt (1985) for P and Ca, and Ferraris and Ivaldi (1988) for hydrogen. The bond valence sums at the U, P, and Ca sites are 6.11, 5.06 and 1.71 valence units, respectively. These results are consistent with formal valences of U<sup>6+</sup>, P<sup>5+</sup>, and Ca<sup>2+</sup>. Proposed hydrogen bonds for autunite are provided in Table 2, and their contributions to the bond-valence sums of the anions (calculated from the donor to acceptor distances) are shown in Table 5. In most cases the acceptor anion for each hydrogen bond is unambiguous, and the hydrogen bond distances range from 1.91 to 2.24 Å for nine of the hydrogen bonds. The bond associated with H7 may be accepted by O2, but the long H-acceptor distance of 2.63 Å indicates that this interaction is very weak. There are two possible acceptor anions for the bond associated with H8, O8 at 2.12 Å and O11 at 2.57 Å. Both belong to H<sub>2</sub>O groups that are bonded to Ca; their bond-valence requirements are met



FIGURE 1. Polyhedral representation of the structure of autunite Ca[(UO<sub>2</sub>)(PO<sub>4</sub>)]<sub>2</sub>(H<sub>2</sub>O)<sub>11</sub>, projected along [001]. The uranyl polyhedra are shown in gray and the phosphate tetrahedra are stippled. The Ca atoms are shown as large spheres, and the H<sub>2</sub>O groups (with O atoms labeled) are shown as small spheres. The long interatomic distances from Ca to  $O_{Ur}$  (3.275 Å) are shown as dashed lines.

	01	02	O3	O4	O5	O6	07	08	O9	O10	011	012	O13	Total
U1	1.69	1.66	0.71	0.69	0.68	0.68								6.11
P1			1.30	1.27	1.25	1.24								5.06
Ca1		0.03 <sup>x2→</sup>					0.26	0.26 <sup>x2→</sup>	0.25 <sup>x2→</sup>	0.20	0.17			1.71
H1							0.83 ×2↓					0.17		1.0
H2						0.13		0.87						1.0
H3								0.85				0.15		1.0
H4						0.14			0.86					1.0
H5									0.84				0.16	1.0
H6										0.81 <sup>x2↓</sup>			0.19	1.0
H7		0.08									0.92 ×2↓			1.0
H8								0.15			0.08 <sup>x2↓</sup>	0.69		1.0
H9									0.15			0.85		1.0
H10				0.14									0.86	1.0
H11								0.15					0.85	1.0
Total	1.69	1.77	2.01	2.10	1.93	2.19	1.92	2.28	2.10	1.82	2.17	1.86	2.06	

FABLE 5. Bond val	lence analysis t	for synthetic au	utunite (v.u.)
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essentially without the bond from H8. It is possible that the H8 bond is three-centered (bifurcated), with both the O8 and O11 atoms accepting the bond locally. Both O8 and O11 lie essentially in the same plane as O12 and H8; the sum of the O-H angles around H8 is 359°, consistent with a three-centered hydrogen bond arrangement (Jeffrey 1997).

The hydrogen bond network in autunite is illustrated in Figure 2. Hydrogen bonds extend from the  $H_2O$  groups to acceptors within the sheets, as well as to other  $H_2O$  groups located in the interlayer. The O2 uranyl ion O atom accepts the very weak H7 hydrogen bond. Three stronger hydrogen bonds extend from the  $H_2O$  groups to anions (O4 and O6) that are at the equatorial vertices of the uranyl square bipyramids, and that are also shared with the phosphate tetrahedra. Site O9 corresponds to a  $H_2O$  group bonded to a Ca atom, and accepts a single hydrogen bond. Sites O8 and O11 participate in a three-centered hydrogen bond from H8, and O8 accepts an additional hydrogen bonds and accept two hydrogen bonds, resulting in approximately tetrahedral coordination environments.

### DISCUSSION

Autunite dehydrates to meta-autunite rapidly in air (except at high relative humidity) (Sowder et al. 2000; Takano 1961). Loss of O12 and O13 from autunite results in the formula  $Ca[(UO_2)(PO_4)]_2(H_2O)_7$ . Details of the structure of meta-autunite are unclear, and there may be several different hydration states in nature. Collapse of the interlayer spacing is presumably associated with removal of H2O groups from the interlayer, and strengthening of the interactions between the Ca cation and the uranyl ion O atoms within the sheets on either side. Our structure determination indicates that the Ca position in the interlayer is significantly underbonded, with only 1.71 valence units incident upon it, including the possible weak bonds to the uranyl ion O atoms. If these interactions are ignored, the bond-valence sum to Ca is only 1.65 valence units. We suggest that rapid dehydration of autunite in air is associated with the underbonding at the Ca site; removal of the O12 and O13 H<sub>2</sub>O groups, coupled with collapse of the structure, will significantly increase the bond valence incident upon the Ca site because the interactions with the uranyl phosphate sheets should be enhanced.



**FIGURE 2.** Projection of the structure of autunite  $Ca[(UO_2) (PO_4)]_2(H_2O)_{11}$  along [001] showing the proposed hydrogen bonding network. The hydrogen atoms are shown as small pale gray spheres, the O atoms as large dark gray spheres, and the H…O bonds as thin rods; both possible H…O bonds for H8 are illustrated. The Ca-O<sub>Ur</sub> interactions have been omitted for clarity. Only those O atoms participating in the hydrogen bonding network have been labeled. Note that a mirror plane parallel to the uranyl phosphate sheets passes through the plane of the Ca atoms.

#### **ACKNOWLEDGMENTS**

This research was supported by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy, grant DE-FGO7-97ER14820. We thank S. Krivovichev, R. Finch, and an anonymous reviewer for their comments on the manuscript.

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MANUSCRIPT RECEIVED MARCH 10, 2002 MANUSCRIPT ACCEPTED OCTOBER 9, 2002

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