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Wyartite: Crystallographic evidence for the first pentavalent-uranium mineral

PETER C. BURNS[1] AND ROBERT J. FINCH[2]

[1]Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.
[2]Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.

ABSTRACT

Determination of the structure of wyartite provides the first evidence for a pentavalent-U mineral. The structure of wyartite, $CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$, $Z = 4$, orthorhombic, $a = 11.2706(8)$, $b = 7.1055(5)$, $c = 20.807(1)$ Å, $V = 1666.3(3)$ Å^3, space group $P2_12_12_1$, was solved by direct methods and refined to an agreement index (R) of 4.9% for 2309 unique reflections collected using Mo$K\alpha$ X-radiation and a CCD-based detector. The structure contains three unique U positions; two contain U^{6+} and involve uranyl ions with typical pentagonal-bipyramidal coordination. Seven anions coordinate the other U position, but there is no uranyl ion present. The polyhedral geometry, the bond-valence sum incident at this U site, and electroneutrality requirements, all indicate that this site contains U^{5+}. The $U\phi_7$ (ϕ: O, OH, H_2O) polyhedra share edges and corners to form a unique sheet in which a CO_3 group shares an edge with the $U^{5+}\phi_7$ polyhedron. The structure contains one Ca site coordinated by seven anions. The Ca atom and its associated H_2O groups occupy interlayer sites, along with two H_2O groups that are held in the structure by H bonds only. The $Ca\phi_7$ polyhedron is linked to one adjacent sheet by sharing an edge with the CO_3 group and an O atom with a $U^{6+}\phi_7$ polyhedron. Structural units are linked together through hydrogen bonds only.

INTRODUCTION

Interest in the paragenesis and structures of U minerals arises, in part, because of their role as alteration products of uraninite and other reduced U-ore minerals under oxidizing conditions (Frondel 1958; Finch and Ewing 1992). The U^{6+} phases are also important corrosion products of UO_2 in spent nuclear fuel (Forsyth and Werme 1992; Wronkiewicz et al. 1996), and they may control groundwater concentrations of U in U-contaminated soils (Buck et al. 1996; Morris et al. 1996). A clear understanding of the structural and thermodynamic stabilities of U carbonates is particularly germane to the environmental chemistry of U (Clark et al. 1995; Finch 1997) due to the potentially high mobility of U in carbonate-bearing groundwaters (Langmuir 1978; Grenthe et al. 1994).

Most uranium minerals can be grouped into reduced species in which U occurs primarily as U^{4+}, and oxidized species, in which U is fully oxidized to U^{6+}. To date, no minerals have been described that contain essential U^{5+}. Only two minerals have been described in which U occurs as both U^{4+} and U^{6+}, ianthinite (Burns et al. 1997a) and wyartite (Guillemin and Protas 1959). Guillemin and Protas (1959) first described wyartite, reporting the formula $3CaO·UO_{2.6}UO_{3.2}CO_2·xH_2O$ where x = 12 to 14. In a crystallographic study of type material by X-ray precession photography, Clark (1960) showed that wyartite transforms in air to a phase that she called wyartite II (wyartite, *sensu stricto*, being designated wyartite I). Our interest in the crystal chemistry of U prompted the present structure determination of wyartite, and led to the surprising conclusion that the structure contains essential U^{5+}.

EXPERIMENTAL METHODS

The specimen is from the Shinkolobwe mine, Shaba, Democratic Republic of Congo. We examined the crystal on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector (Burns 1998). Details pertaining to data collection are in Table 1. The unit-cell dimensions (Table 1) were determined and refined by least squares from 3929 reflections, and show that the crystal is wyartite *sensu stricto* ("wyartite I" of Clark 1960).

STRUCTURE SOLUTION AND REFINEMENT

Structure solution and refinement methods are as in Burns (1998). Systematic absences indicate space group $P2_12_12_1$, as noted by Clark (1960) and verified by successful solution and refinement of the structure by direct methods. The final refinement included positional parameters for all atoms, anisotropic-displacement parameters for U and Ca, isotropic-displacement parameters for C and O, and a weighting scheme of structure factors. Details of the structure

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*E-mail: peter.burns.50@nd.edu

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TABLE 1. Unit-cell parameters, crystallographic parameters, data statistics, and atom parameters for wyartite

	x	*y*	*z*	‡U_{eq}
U1	0.5595(2)	0.2892(3)	0.23948(6)	113(3)
U2	–0.0593(2)	0.2897(3)	0.23585(5)	109(3)
U3	0.2490(2)	0.2919(1)	0.28343(3)	117(2)
Ca	–0.0734(5)	0.4322(8)	0.0469(3)	232(12)
C	0.241(4)	0.240(3)	0.423(1)	320(64)
O1	0.511(2)	0.310(4)	0.154(1)	197(62)
O2	–0.011(2)	0.314(4)	0.156(1)	206(64)
O3	0.110(1)	0.109(3)	0.2515(9)	62(44)
O4	0.388(2)	0.105(3)	0.267(1)	182(57)
O5	0.610(1)	0.282(3)	0.3205(8)	50(36)
O6	–0.112(2)	0.240(3)	0.316(1)	281(58)
O7	0.100(2)	0.463(3)	0.278(1)	152(55)
O8	0.390(2)	0.474(3)	0.272(1)	158(57)
O9	0.187(2)	0.126(3)	0.380(1)	373(52)
O10	0.224(1)	0.211(3)	0.4817(9)	34(41)
O11	0.286(2)	0.384(3)	0.3966(9)	34(43)
OH12	0.752(3)	0.285(2)	0.1980(6)	156(26)
H_2O13	–0.252(3)	0.235(2)	0.0522(7)	367(40)
H_2O14	0.254(3)	0.363(2)	0.1670(7)	308(36)
H_2O15	0.459(2)	0.028(3)	0.0668(9)	358(51)
H_2O16	0.093(2)	0.629(4)	0.053(1)	161(67)
H_2O17	0.045(2)	0.159(3)	0.016(1)	84(46)
H_2O18	0.209(2)	0.036(3)	0.103(1)	91(48)
H_2O19	–0.079(3)	-0.082(4)	-0.058(2)	254(76)

Data Statistics

a (Å)	11.2706(8)	Crystal size	0.14mm × 0.03mm × 0.01mm
b (Å)	7.1055(5)	Radiation	Mo*K*α
c (Å)	20.807(1)	Data range (2θ)	3-56.7°
V ($Å^3$)	1666.3(3)	Total ref.	10,611
Space group	$P2_12_12_1$	Unique ref.	4006
F(000)	1876	R_{int} (%)	6.9
μ (mm^{-1})	29.5	Unique $\|F_o\| \geq 4\sigma_F$	2309
D_{calc} (g/cm^3)	4.326	Final *R** (%)	4.9
Frame width	0.3° (w)	*S*†	0.98
Frame time	60 s	Abs. Corr.	SADABS

Unit-cell contents: $4\{CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7\}$

* $R = S(|F_o|-|F_c|)/S|F_o|$.
† $S = [Sw(|F_o|-|F_c|)^2/(m-n)]^{–}$, for *m* observations and *n* parameters.
‡ $U_{eq} = U_{eq}$ $Å^2 \times 10^4$.

TABLE 3. Selected interatomic distances (Å) and angles (°) in the structure of wyartite

U1-O5	1.78(2)	U2-O2	1.77(2)
U1-O1	1.87(2)	U2-O6	1.80(2)
U1-O4a	2.32(2)	U2-OH12c	2.26(3)
U1-O8b	2.33(2)	U2-O3	2.32(2)
U1-OH12	2.34(3)	U2-O7	2.35(2)
U1-O4	2.40(2)	U2-O3d	2.36(2)
U1-O8	2.42(2)	U2-O7e	2.39(2)
<U1-O_{Ur}>	1.82	<U2-O_{Ur}>	1.78
<U1-ϕ_{eq}>	2.36	<U2-ϕ_{eq}>	2.34
O5-U1-O1	177(1)	O2-U2-O6	174(1)
U3-O7	2.07(2)	Ca-H_2O16	2.34(3)
U3-O4	2.09(2)	Ca-H_2O15f	2.41(2)
U3-O8	2.06(2)	Ca-O9d	2.41(2)
U3-O3	2.14(2)	Ca-H_2O17	2.44(2)
U3-O9	2.44(2)	Ca-H_2O13	2.45(3)
U3-H_2O14	2.47(1)	Ca-O2	2.51(2)
U3-O11	2.48(2)	Ca-O10d	2.68(2)
<U3-ϕ>	2.25	<Ca-ϕ>	2.46
O7-U3-O4	167.0(9)		
C-O10	1.26(3)	O10-C-O11	128(2)
C-O11	1.26(3)	O10-C-O9	118(3)
C-O9	1.35(3)	O11-C-O9	113(2)
<C-O>	1.29	<O-C-O>	119.7

Notes: a = 1-*x*, y+½, ½-*z*; b = 1-*x*, *y*-½, ½-*z*; c = *x*-1, *y*, *z*; d = -*x*, *y*+½, ½-*z*; e = -*x*, *y*-½, ½-*z*; f = *x*-½, ½-*y*, *z.*

refinement are provided in Table 1. Final atom parameters are given in Tables 1 and 2,[1] and selected interatomic distances and angles are given in Table 3. Calculated and observed structure factors are provided in Table 4.[1]

RESULTS

U coordination

The structure of wyartite contains three symmetrically distinct U positions. The U1 and U2 cations are each strongly bonded to two O atoms with U-O bond-lengths of ~1.8 Å, forming nearly linear $(UO_2)^{2+}$ uranyl ions (Ur) (Table 3). Each of these two U atoms is further coordinated by four O atoms and an $(OH)^–$ group forming pentagonal bipyramids capped by O_{Ur} atoms. Bond-valence sums at the U1 and U2 sites, calculated with the coordination-specific parameters of Burns et al. (1997b), are 5.78 and 6.18 v.u., respectively, consistent with U^{6+} ions.

The U3 site is not associated with a uranyl ion. Although U3 has seven anions at the corners of a pentagonal bipyramid (Fig. 1, Table 3), the apical ligands are O7 and O4, with U-O bond-lengths of 2.07(2) and 2.09(2) Å, respectively, and the O7-U3-O4 bond-angle is 167.0(9)º. Thus the shortest U-O bonds of the U3ϕ_7 polyhedron are ~0.3 Å longer than the average U-O_{Ur} bond of 1.79(3) Å for $U^{6+}\phi_7$ pentagonal bipyramids in well-refined structures (Burns et al. 1997b). The U3ϕ_7 polyhedron contains four short (~2.1 Å) and three long (~2.4 Å) bonds, with a mean bond-length of 2.25 Å. A bond-valence analysis shows that U3 is coordinated by six O atoms and one H_2O group. Two of the O atoms of the bipyramid are shared with a CO_3 group (Fig. 1). The sum of bond-valences incident at the U3 site, calculated by using general bond-valence parameters for U from Burns et al. (1997b), is 5.07 v.u., in accord with the occurrence of U^{5+} in this site.

Ca and C coordination

The unique Ca site in the structure is coordinated by three O atoms and four H_2O groups, with an average Ca-ϕ bond-length of 2.46 Å. The C site is coordinated by three O atoms in a distorted triangular arrangement, with an average C-O bond-length of 1.29 Å and an average O-C-O bond-angle of 119.7º. Bond-valence sums incident at the Ca and C sites, calculated by using bond-valence parameters from Brese and O'Keeffe (1991), are 1.89 and 3.96 v.u., respectively.

Structural sheets of uranyl polyhedra

The structural sheet in wyartite is topologically unique. The U1ϕ_7 and U2ϕ_7 pentagonal bipyramids share equatorial edges to form chains parallel to the *b* axis. These chains are cross-linked by sharing edges with the U3ϕ_7 pentagonal bipyramids, forming a complex heteropolyhedral sheet parallel to (001) (Fig. 2a). The U3ϕ_7 pentagonal bipyramid also shares an equatorial

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[1] For a copy of Tables 2 and 4, Document AM-99-022 contact the Business Office of the Mineralogical Society of America. Deposit items may also be available on the American Mineralogist web site (see inside back cover of a current issue for a web address).

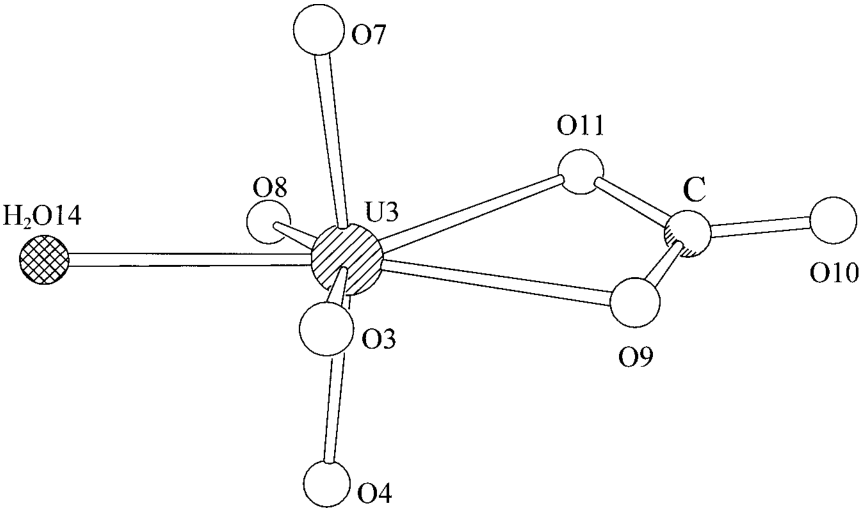

FIGURE 1. Coordination environment about the U3 site in the structure of wyartite.

edge with the CO_3 group, which lies approximately perpendicular to the plane of the structural sheet (Fig. 2).

Interlayer connectivity

The wyartite structure is shown projected along [010] in Figure 2b. The interlayer contains the $Ca\phi_7$ polyhedron as well as two H_2O groups that are connected to the structure only by hydrogen bonds. The CO_3 group projects into the interlayer and shares an edge with the $Ca\phi_7$ polyhedron. Thus, the $Ca\phi_7$ polyhedron is connected to one structural sheet by sharing an edge with the CO_3 group, as well as an O_{Ur} atom of the $U2O_2$ uranyl ion. All three $Ca\phi_7$ polyhedral elements are shared with a single structural sheet. The remaining $Ca\phi_7$ polyhedral elements are four interlayer H_2O groups, so that structural sheets are connected to each other through a network of hydrogen bonds only. This explains the perfect and easy (001) cleavage in wyartite (Guillemin and Protas 1959).

EVIDENCE FOR PENTAVALENT U IN WYARTITE

Evidence for U^{5+} in wyartite is provided by (1) the geometry of the $U3\phi_7$ polyhedron, (2) the sum of bond-valence incident at the U3 site, and (3) the electroneutrality principle. We first consider the coordination environment about the U3 site. Whereas all known U^{6+} cations in well-refined mineral structures include a uranyl ion (Burns et al. 1997b), the distorted pentagonal-bipyramidal $U3\phi_7$ polyhedron in wyartite has no uranyl ion, which is not consistent with U^{6+} at this site. U^{4+} occurs in pentagonal bipyramidal coordination in UNb_2O_7 (Busch and Gruehn 1994) and $U(UO_2)(PO_4)_2$ (Bénard et al. 1994); however, mean bond-lengths in those compounds are 2.30 and 2.32 Å, respectively, and the shortest U-O bond-length in either structure is 2.17 Å. The $U3\phi_7$ polyhedral geometry is quite similar to $U^{5+}\phi_7$ pentagonal bipyramids in the four compounds of Table 5.

The bond-valence parameters for U (Burns et al. 1997b) can discriminate between U valence states, giving bond-valence

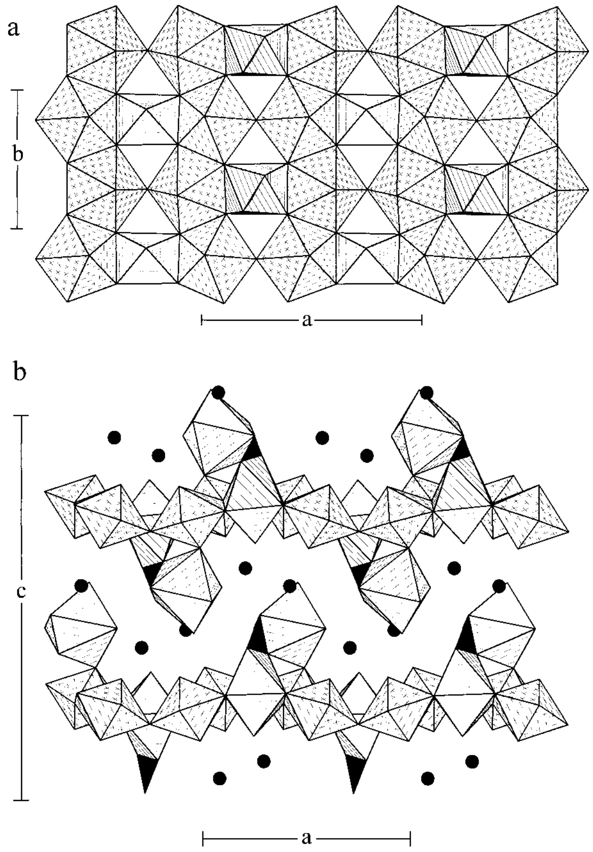

FIGURE 2. Polyhedral representations of the structure of wyartite. (**a**) Sheets of polyhedra projected along [001]. (**b**) Structure projected along [010]. The $U1\phi_7$ and $U2\phi_7$ polyhedra are shown shaded with crosses; $U3\phi_7$ polyhedra are shown shaded with parallel lines, and CO_3 groups are shown as black triangles. The $Ca\phi_7$ polyhedra are shown shaded with broken parallel lines and H_2O groups that are held in the structure by hydrogen bonds only are shown as black circles.

TABLE 5. Comparison of the U3ϕ_7 polyhedral geometry in wyartite with $U^{5+}\phi_7$ polyhedra in synthetic compounds

				U-ϕ (Å)				O-U-O (°)	Valence sum (v.u.)	Ref.
Wyartite U3	2.07	2.09	2.06	2.14	2.44	2.47	2.48	167.0	5.07	
U_2MoO_8	2.06	2.06	2.11	2.18	2.36	2.46	2.73	178.1	4.92	1
	2.08	2.08	2.13	2.15	2.32	2.35	2.58	164.1	5.12	
$USbO_3$	1.93	2.02	2.13	2.30	2.35	2.43	2.50	173.0	5.23	2
UVO_5	2.05	2.07	2.21	2.21	2.30	2.30	2.32	179.9	5.26	3
$U_5O_{12}Cl$	2.06	2.06	2.25	2.25	2.30	2.30	2.54	178.9	4.95	4

Notes: 1 = Serezhkin et al. (1973); 2 = Dickens and Stuttard (1992); 3 = Dickens et al. (1992); 4 = Cordfunke et al. (1985).

sums ~5 v.u. for structural sites that contain U^{5+}. The bond-valence sum at the U3 site in wyartite is 5.07 v.u. Bond-valence parameters for U^{4+} (Brese and O'Keeffe 1991) give 5.05 v.u. for the U3 site, also indicating U^{5+}.

All atoms in the wyartite structure occur at general positions in space group $P2_12_12_1$ (Table 2). The valence of the U1 and U2 cations (6+) is not in question, and the structure contains one Ca^{2+} and one C^{4+}. Bond-valence sums incident at the anion sites (neglecting contributions from H), calculated using the parameters of Brese and O'Keeffe (1991) for Ca-O and C-O bonds, and Burns et al. (1997b) for U-O bonds, indicate there are 11 O^{2-} ions (bond-valence sums ~2 v.u.), one $(OH)^-$ group (bond-valence sum 1.2 v.u.), and seven H_2O groups (bond-valence sums <0.4 v.u.). The sum of cation charges (ignoring U3 and H) is +18; the sum of anion charges is –23 (accounting for OH^- and H_2O groups). In order to maintain charge neutrality, the valence of the U3 cation must be 5+. The structural formula of the studied wyartite crystal is therefore $CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$.

DISCUSSION

The two mixed-valence U minerals, ianthinite and wyartite, are alteration products of uraninite and always occur in close proximity to dissolving uraninite (Frondel 1958; Guillemin and Protas 1959). The conditions of formation of these minerals are poorly understood. Synthesis requires partial reduction of uranium in solution (Bignand 1955). In nature, biologic respiration and organic decomposition, along with uraninite oxidation, may decrease groundwater pO_2 and increase pCO_2, resulting in anoxic or moderately reducing conditions conducive to the precipitation of mixed-valence U minerals.

Until now a valence state of 5+ has not been shown for U in a mineral structure (see Burns et al. 1997b for a summary of synthetic compounds that contain U^{5+}). Dissolution of a U^{5+}-bearing phase in acid solution leads to disproportionation of U^{5+} into U^{4+} and U^{6+}, which explains the empirical formula determined for wyartite with U^{4+} and U^{6+} (Bignand 1955).

The formation of wyartite has implications for U geochemistry. The U^{5+} valence state is considered unstable in most natural waters; however, Langmuir (1978) reports that UO_2^+ is the predominant dissolved U species in groundwaters with pH between 1 and 6 and Eh between –0.1 and +0.2 V. Langmuir's calculations are based on 0.273 V for the redox half reaction $U^{4+} + 2H_2O = UO_2^{2+} + 4H^+ + 2e^-$. The CRC Handbook reports a value of 0.327 V for the same reaction (Vanysek 1998), although Grenthe et al. (1994) accept the lower value.

The reduction of dissolved UO_2^{2+} to U^{4+} may be kinetically inhibited, as this requires exchange of two electrons and a change in coordination. Reduction of UO_2^{2+} to UO_2^+ may be more favorable, and the persistence of UO_2^+ may promote precipitation of a U^{5+}-bearing mineral such as wyartite. The solution complex $UO_2^+.UO_2^{2+}$ disproportionates at a much slower rate than UO_2^+ alone, and UO_2^+ in solution is stabilized in the presence of UO_2^{2+} due to the formation of the $UO_2^+:UO_2^{2+}$ complex (Arland 1986). Wyartite is not common: that it oxidizes in air to schoepite or dehydrated schoepite (Gauthier et al. 1981) may contribute to its rarity.

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