

Studtite, [(UO₂)(O₂)(H₂O)₂](H₂O)₂: The first structure of a peroxide mineral

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ABSTRACT

Studtite, UO₄·4H₂O, and metastudtite, UO₄·2H₂O, are the only minerals thought to contain peroxide. Determination of the structure of studtite has shown it to contain peroxide, with the structural formula [(UO₂)(O₂)(H₂O)₂](H₂O)₂. The structure is monoclinic, space group *C2/c*, *a* = 14.068(6), *b* = 6.721(3), *c* = 8.428(4) Å, β = 123.356(6)°, *V* = 665.6(3) Å³, *Z* = 4. It was refined on the basis of *F*² for 1398 unique reflections collected using MoKα X-radiation and a CCD-based detector to *R*₁ = 3.66%, calculated for the 716 unique observed reflections (*|F_o|* ≥ 4σ_{*F*}). The structure of studtite contains one symmetrically distinct U⁶⁺ cation and four O atoms, two of which occur as H₂O groups. The O-O bond-length in the peroxide group is 1.46(1) Å. The U⁶⁺ cation occurs as part of a linear (UO₂)²⁺ uranyl ion, and each U⁶⁺ cation is bonded to six additional O atoms, two of which are H₂O groups, and four of which are O atoms of peroxide groups. The O-O bonds of two peroxide groups constitute two equatorial edges of each distorted uranyl hexagonal bipyramid. Uranyl polyhedra are polymerized into chains extending along [001] by sharing peroxide groups. Chains are linked by H bonds extending to and from an interstitial H₂O group. It is proposed that studtite forms by incorporating peroxide created by alpha-radiolysis of water, and that radiation is necessary for its formation in nature.

INTRODUCTION

Uranyl minerals display tremendous structural and chemical diversity (Burns 1999). They are important for understanding the genesis of U deposits (Fron del 1958), the mobility of actinides in the vadose zone (Buck et al. 1996; Roh et al. 2000), and alteration of nuclear waste in a geological repository such as Yucca Mountain, Nevada (Wronkiewicz et al. 1996; Finch et al. 1999). Despite their apparent chemical simplicity, the uranyl minerals studtite, UO₄·4H₂O, and metastudtite, UO₄·2H₂O, are fascinating because they are the only reported peroxide minerals. We have determined the crystal structure of studtite using single-crystal X-ray diffractometry and a CCD-based X-ray detector (Burns 1998), and report the details of the only peroxide mineral structure.

Studtite was originally described by Vaes (1947) as a uranyl carbonate from Shinkolobwe, Democratic Republic of Congo, and has since been reported from several localities (Cejka et al. 1996). Using material from Krunkelbach (Meszenschwand, Germany), Walenta (1974) established that studtite is a uranium peroxide hydrate with the formula UO₄·4H₂O. Cejka et al. (1996) provided X-ray powder diffraction data, thermal analysis, and an infrared spectrum for studtite from Krunkelbach.

Studtite and metastudtite may form from alteration of nuclear waste in a geological repository by incorporating peroxide formed by alpha-radiolysis of water (Sattonnay et al. 2001; Amme 2002; McNamara et al. 2002). Most studies of

alteration of UO₂ or commercial spent nuclear fuel under simulated Yucca Mountain conditions have emphasized the importance of uranyl oxide hydrates and uranyl silicates (Wronkiewicz et al. 1996; Finch et al. 1999), and did not note the formation of uranyl peroxides. The design of some of these experiments may have precluded the formation of studtite or metastudtite. Specifically, the experiments of Wronkiewicz et al. (1996) used UO₂ containing depleted U that was not sufficiently radioactive to cause significant formation of H₂O₂ by alpha-radiolysis of water. Recently, McNamara et al. (2002) found extensive formation of studtite on the surface of spent nuclear fuel reacted at 25 °C with de-ionized water for 1.5 years in the atmosphere, and preliminary results indicate that the studtite incorporated significant ²³⁷Np. Sattonnay et al. (2001) observed formation of metastudtite on the surface of UO₂ under irradiation with a ⁴He²⁺ (α-particle) beam, and concluded the peroxide was provided by alpha-radiolysis of water. Burakov et al. (1997) reported that studtite formed on nuclear material (“lava”) following the Chernobyl Nuclear Plant accident. Thus, there is considerable evidence that uranyl peroxides such as studtite and metastudtite will be important alteration phases of nuclear waste, and that these minerals may impact the long-term performance of a geologic repository such as Yucca Mountain.

EXPERIMENTAL METHODS

We have studied many specimens containing studtite over the past several years; most crystals either diffract very poorly or not at all. The crystal of studtite that provided the structure is from a specimen from Krunkelbach (Meszenschwand, Germany). Crystals were collected from the sample, labeled

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RC4372, during a recent visit to the Belgium Museum of Natural Sciences. Studtite occurs on the specimen as thin acicular crystals that are usually bent. Crystals were selected using a polarizing optical microscope, and showed sharp extinction. Most crystals examined either did not diffract significantly, or gave streaked spots and poor reflection profiles. Superior data was eventually obtained for a crystal with dimensions $200 \times 20 \times 5 \mu\text{m}$ using a Bruker three-circle diffractometer equipped with an APEX CCD detector and MoK α radiation. A sphere of diffraction data to $69^\circ 2\theta$ was collected at room temperature using a crystal-to-detector distance of 4.67 cm, frame widths of 0.3° in ω , and 10 s counting time per frame.

Preliminary analysis of the data resulted in a C-centered unit cell with dimensions $a = 11.82$, $b = 6.75$, $c = 4.24 \text{ \AA}$, $\beta = 93.3^\circ$; this compares well with that given by Cejka et al. (1996) and Walenta (1974). Attempts to solve the structure using this cell failed. Careful re-evaluation of the data revealed several weak reflections requiring the larger C-centered cell given in Table 1, which was refined from 963 reflections using least-squares techniques. Intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical correction for absorption was applied using the program SADABS by modeling the crystal as an ellipsoid. A total of 6416 reflections was collected, of which 1398 were unique, and 716 of the unique reflections were classed as observed ($|F_o| \geq 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms and anomalous-dispersion corrections were taken from International Tables for Crystallography, Vol. IV (Ibers and Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the solution and refinement of the crystal structure in space group $C2/c$. The final refinement included positional parameters of all atoms, anisotropic displacement parameters for non-H atoms, and a weighting scheme of the structure factors. O-H bond-lengths were constrained to be $\sim 0.98 \text{ \AA}$ during refinement. Details of the structure refinement are provided in Table 1. Final atom parameters are given in Table 1, and selected interatomic distances and angles are in Table 2. Calculated and observed structure factors are provided in Table 3¹.

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

a (Å)	14.068(6)	Crystal size (μm)	$200 \times 20 \times 5$			
b (Å)	6.721(3)	Radiation	MoK α			
c (Å)	8.428(4)	Data range (2θ)	$3\text{--}69^\circ$			
β ($^\circ$)	123.356(6)	Total ref.	6416			
V (Å ³)	665.7(3)	Unique ref.	1398			
Space group	$C2/c$	Unique $ F_o \geq 4\sigma_F$	716			
R (000)	656	Final R_i (%)	3.66			
μ (mm ⁻¹)	24.4	Final wR_2 (%)	7.60			
D_{calc} (g/cm ³)	3.73					
Frame width	0.3° (ω)					
Frame time	60 s	Abs. Corr. SADABS				
Unit-cell contents: $4[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$						
	x	y	z	U_{eq}		
U1	0	0	0	0.0193(1)		
O1	0.0073(6)	-0.249(1)	0.074(1)	0.031(2)		
O2	0.0623(6)	0.114(1)	0.3081(9)	0.028(1)		
O3	0.2026(6)	0.038(2)	0.179(1)	0.039(3)		
O4	-0.1565(6)	-0.524(2)	0.061(1)	0.031(2)		
H1	0.255(6)	0.03(2)	0.317(3)	0.03		
H2	0.242(8)	-0.06(1)	0.15(1)	0.03		
H3	-0.102(7)	-0.44(1)	0.06(1)	0.03		
H4	-0.131(9)	-0.662(6)	0.08(1)	0.03		
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	0.0221(2)	0.0241(2)	0.0157(2)	-0.0005(6)	0.0130(1)	-0.0001(7)
O1	0.045(4)	0.027(4)	0.028(3)	-0.002(3)	0.025(3)	0.000(3)
O2	0.032(4)	0.029(4)	0.029(3)	-0.008(3)	0.021(3)	-0.009(3)
O3	0.029(3)	0.061(9)	0.024(3)	-0.006(4)	0.012(3)	0.001(4)
O4	0.030(3)	0.029(6)	0.038(3)	-0.006(4)	0.020(3)	-0.006(4)

CRYSTAL STRUCTURE OF STUDTITE

The structure determination definitively establishes that studtite is a peroxide mineral. The structure contains U^{6+} , O^{2-} , H_2O , and the $(\text{O}_2)^{2-}$ peroxide group. The structural formula is $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$, with the constituents of the structural unit contained within square brackets. Note that this formula is chemically identical to $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, the previously accepted formula for studtite.

The structure of studtite contains one symmetrically unique U^{6+} cation and four O atoms, two of which (O3 and O4) correspond to H_2O groups. A pair of symmetrically equivalent O2 atoms are bonded to form a peroxide group, with an O2-O2 separation of $1.46(1) \text{ \AA}$. The U^{6+} cation is strongly bonded to two O1 atoms, resulting in a linear $(\text{UO}_2)^{2+}$ uranyl ion (designated U_r). The U^{6+} cation is also bonded to six O atoms arranged at the equatorial vertices of a distorted hexagonal bipyramid that is capped by the O_{U_r} atoms. Four of the equatorial vertices are O2 atoms, which correspond to two peroxide groups, and the other two are H_2O (O3) groups. The bond within the peroxide group is parallel to the equatorial plane of the hexagonal bipyramid, and defines an equatorial edge of the polyhedron (Fig. 1a).

Polymerization of the uranyl polyhedra occurs by sharing of peroxide O-O equatorial edges, resulting in chains that are parallel to $[001]$ (Fig. 1a). Adjacent chains are linked only by hydrogen bonds that extend to and from the O4 position located between the chains (Fig. 2). Hydrogen bonds donated by the O3 atoms, which are located at the equatorial position of the uranyl polyhedra, are accepted by two symmetrically distinct O4 atoms. The O4 atom donates two H bonds that are accepted by an O_{U_r} atom of an adjacent chain (O1), and by O2 of the peroxide group.

The only other structure of an inorganic uranyl peroxide compound was reported for synthetic $\text{Na}_4(\text{UO}_2(\text{O}_2)_3)(\text{H}_2\text{O})_9$ by Alcock (1968). In this structure, uranyl hexagonal bipyramids contain three peroxide groups arranged at the equatorial edges of the polyhedra. Uranyl polyhedra are linked only through bonds to low-valence cations.

¹For a copy of Table 3, Document AM-03-036 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.

TABLE 2. Selected interatomic distances (Å) and angles ($^\circ$) in the structure of studtite

U1-O1	$1.768(7) \times 2$	O2-O2	$1.46(1)$
U1-O2	$2.351(6) \times 2$		
U1-O2	$2.364(6) \times 2$		
U1-O3	$2.396(7) \times 2$		
O1-U1-O1	180		
O3-H1	0.98	H1...O4	1.72
O3-H2	0.97	H2...O4	1.99
H1-O3-H2	94	O3-H1...O4	177
		O3-H1...O4	128
O4-H3	0.97	H3...O1	1.94
O4-H4	0.97	H4...O2	1.76
H3-O4-H4	110	O4-H3...O1	173
		O4-H4...O2	161

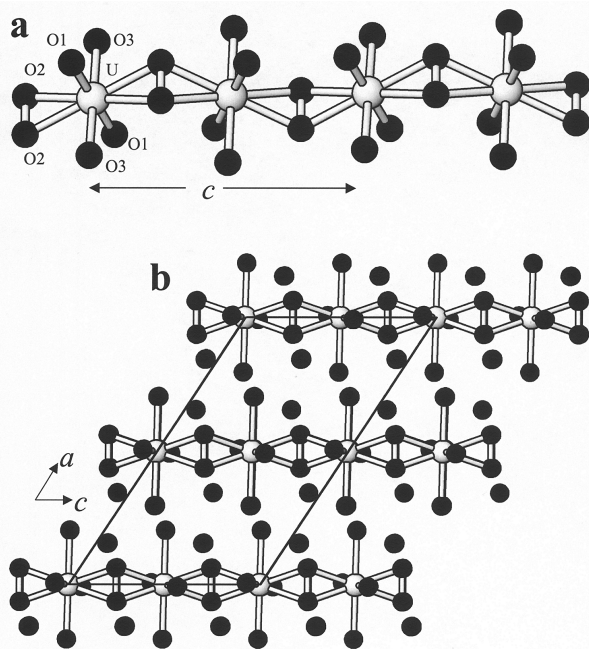


FIGURE 1. The structure of studdite. (a) The chain of uranyl polyhedra extending along [001], projected approximately along [010]. (b) The structure projected along [010].

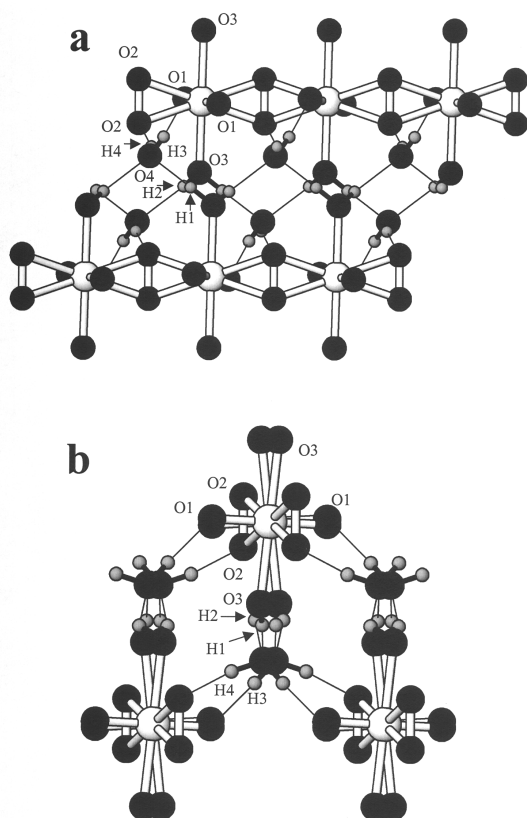


FIGURE 2. Hydrogen bonding in the structure of studdite projected along [010] (a) and [001] (b).

Metastuddite, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, probably contains the same chains of uranyl polyhedra as studdite, but it involves only H_2O that is bonded to U. Metastuddite is probably orthorhombic, and Deliens and Piret (1983) reported the unit cell as $a = 6.50$, $b = 8.78$, $c = 4.21$ Å. In light of the structure determination for studdite, it is likely that the correct unit cell of metastuddite is larger than previously thought, as the repeat length of the chain of uranyl polyhedra in studdite is 8.4 Å, and is not compatible with the 4.2 Å cell dimension.

DISCUSSION

Structures of uranyl oxide hydrate minerals are almost invariably based upon sheets of uranyl polyhedra, with low-valence cations and H_2O groups located between the sheets (Burns 1999). Studdite presents a major departure from this theme; polymerization of uranyl polyhedra occurs in only one dimension. The presence of peroxide at the equatorial positions of the uranyl polyhedra results in hexagonal bipyramids that are significantly distorted, with the peroxide O-O edge lengths of 1.46 Å. The typical O-O edge-length in a uranyl hexagonal bipyramid is ~ 2.4 Å (Burns et al. 1997). The distortion of the polyhedra imposed by incorporation of peroxide may preclude two-dimensional polymerization into a stable structure.

Studdite and metastuddite are the only known peroxide minerals. Studdite is readily synthesized by adding peroxide to a U-bearing solution (Debets 1963). The existence of peroxide in a natural system may be indicative of exceptionally oxidizing conditions. However, it is possible that studdite grows by incorporating peroxide created by alpha-radiolysis of water. Studdite has only been observed in nature in close association with other uranium minerals (usually uraninite), thus radiation may be important for its formation. Accumulation of peroxide created by radiolysis in pore fluids, or by evaporative concentration, may lead to sufficient concentrations for incorporation into growing crystals of studdite or metastuddite.

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