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OSWALDPEETERSITE, $(UO_2)_2CO_3(OH)_2•4H_2O$, A NEW BASIC URANYL CARBONATE MINERAL FROM THE JOMAC URANIUM MINE, SAN JUAN COUNTY, UTAH, U.S.A.

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ABSTRACT

Oswaldpeetersite, ideally $(UO_2)_2CO_3(OH)_2•4H_2O$, is a newly discovered hydrated basic uranyl carbonate mineral found in the Jomac uranium mine, Brown's Rim, San Juan County, Utah, U.S.A. It occurs along some bedding planes of a layer of siltstone within the Triassic Shinarump conglomerate. Associated minerals are gypsum, cuprite, antlerite, goethite, lepidocrocite, mbobomkulite, hydrombobomkulite, sklodowskite and two undefined uranium minerals. Oswaldpeetersite occurs as micrometric prismatic crystals (approximately 0.1 × 0.01 × 0.002 mm). These are canary yellow and transparent, with a vitreous luster and pale yellow streak. It does not fluoresce in ultraviolet radiation. The H_{Mohs} is in the range 2–3. $D_{\text{meas}} > 4.10$ g/cm^3, $D_{\text{calc}} = 4.54$ g/cm^3 (empirical formula), 4.50 g/cm^3 (idealized formula). Optically biaxial negative, α 1.583(2), β 1.669(2), γ 1.712(2), and $2V_{\text{calc}} = 67.4(2)°$. Orientation $Z \parallel a$ and elongation positive. The pleochroism is X and Y very pale yellow to colorless, and Z pale yellow. The cleavage and parting are along the elongation. The tenacity is weak, and the fracture, uneven. The habit can be described as acicular. Oswaldpeetersite is monoclinic, $P2_1/c$, with unit-cell parameters refined from powder data: a 4.1425(6), b 14.098(3), c 18.374(5) Å, β 103.62(1)°, V 1042.8(3) Å^3, a:b:c = 0.2938:1:1.3033 and Z = 4. The forms recognized are {100}, {010} and {001}. The strongest eight reflections of the X-ray powder pattern [d(in Å)(I)(hkl)] are: 8.95(65)(002), 7.54(63)(012), 4.55(96)(031), 4.26(60)(014), 3.46(62)(015), 3.32(100)($\bar{1}$14), 3.029(85)(043) and 2.273(62)(062). Electron-microprobe and thermogravimetric analyses gave UO_3 81.47 and H_2O 12.30 wt.%. The CO_2 content was calculated as 6.23 wt.% by difference. The oxide formula is $2.03\,UO_3•1.01\,CO_2•4.88\,H_2O$, and the empirical formula is $(UO_2)_{2.03}(CO_3)_{1.01}(OH)_{2.05}•3.85\,H_2O$. The name honors the Belgian structural crystallographer Maurice Oswald Peeters, University of Leuven, Belgium.

Keywords: oswaldpeetersite, new mineral species, basic uranyl carbonate hydrate, X-ray data, Jomac mine, San Juan County, Utah, U.S.A.

SOMMAIRE

L'oswaldpeetersite, de formule idéale $(UO_2)_2CO_3(OH)_2•4H_2O$, est un carbonate basique hydraté d'uranyle découvert récemment dans la mine d'uranium Jomac, Brown's Rim, comté de San Juan, Utah, aux Etats-Unis. Le minéral se rencontre dans certains plans de stratification d'une couche d'argilite, au sein du conglomérat triassique de Shinarump. L'association minérale est constituée de gypse, cuprite, antlerite, goethite, lepidocrocite, mbobomkulite, hydrombobomkulite, sklodowskite et deux minéraux uranifères indéfinis. Les cristaux prismatiques sont jaune canari et transparents avec un éclat vitreux. La rayure est jaune pâle. Le minéral n'est pas fluorescent aux rayons ultraviolettes. La dureté H_{Mohs} est entre 2 et 3. $D_{\text{mes}} > 4{,}10$ g/cm^3, $D_{\text{calc}} = 4{,}54$ g/cm^3 (formule empirique), 4,50 g/cm^3 (formule idéale). Optiquement biaxe négative, α 1,583(2), β 1,669(2), γ 1,712(2) et $2V_{\text{calc}} = 67{,}4(2)°$, avec orientation optique $Z \parallel a$ et allongement positif. Le pléochroïsme des cristaux est: X et Y jaune très pâle, Z jaune pâle, et le clivage est selon l'allongement. Les cristaux montrent un habitus aciculaire. La tenacité est faible, et la cassure, irrégulière. L'oswaldpeetersite est monoclinique, groupe spatial $P2_1/c$, avec les paramètres de la maille affinés à partir des données sur poudre: a 4,1425(6), b 14,098(3), c 18,374(5) Å, β 103,62(1)°, V 1042,8(3) Å^3, a:b:c = 0.2938:1:1.3033 et Z = 4. Les formes

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des cristaux sont {100}, {010} et {001}. Les huit raies les plus intenses du spectre de diffraction X [*d*(en Å)(*I*)(*hkl*)] sont: 8,95(65)(002), 7,54(63)(012), 4,55(96)(031), 4,26(60)(014), 3,46(62)(015), 3,32(100)($\bar{1}$14), 3,029(85)(043) et 2,273(62)(062). L'analyse chimique à la microsonde électronique et par thermogravimétrie a donné: UO_3 81,47 et H_2O 12,30%. La quantité de CO_2, obtenue par différence, est 6,23%. La formule en termes d'oxydes correspond à 2,03 UO_3•1,01 CO_2•4,88 H_2O, et la formule empirique est $(UO_2)_{2,03}(CO_3)_{1,01}(OH)_{2,05}$•3,85$H_2O$. Le nom du minéral souligne les contributions du cristallographe structural Maurice Oswald Peeters de l'Université de Leuven, Belgique.

Mots-clés: oswaldpeetersite, nouvelle espèce minérale, carbonate basique hydraté d'uranyle, données de diffraction X, mine Jomac, comté de San Juan, Utah, Etats-Unis.

INTRODUCTION

Up to now, only three uranyl carbonates without additional cations have been described as minerals: rutherfordine, UO_2CO_3 (Marckwald 1906), joliotite, UO_2CO_3•$2H_2O$ (Walenta 1976) and blatonite, UO_2CO_3•H_2O (Vochten & Deliens 1998).

Oswaldpeetersite, ideally $(UO_2)_2CO_3(OH)_2$•$4H_2O$, is the first known *basic* uranyl carbonate mineral devoid of other cations in its structure. This mineral was discovered at the Jomac uranium mine, Brown's Rim, San Juan County, Utah, U.S.A., by Patrick Haynes, of Cortez, Colorado, geologist and mineral collector. After haynesite, $(UO_2)_3(SeO_3)_2(OH)_2$•$5H_2O$ (Deliens & Piret 1991), and blatonite, UO_2CO_3•H_2O (Vochten & Deliens 1998), oswaldpeetersite is the third new uranium-bearing mineral species originating from the Jomac uranium mine. The Jomac mine was initially (1950–1979) owned by Alliance Nuclear Inc. of Spokane, Washington, and then (1983–1985) by Birco Development of Moab, Utah. The mines of the district, including the Jomac mine, are now closed and are part of the Glen Canyon National Recreation Area.

The Commission on New Minerals and Mineral Names, IMA, approved *oswaldpeetersite* in October 2000 (IMA 2000–34). Type material is deposited in the mineralogical collection of the Royal Belgian Institute of Natural History, Brussels, Belgium, under catalogue number R.C. 5166. The mineral name honors Maurice Oswald Peeters (b. 1945), structural crystallographer at the University of Leuven, Belgium, and researcher in the field of uranium mineralogy.

OCCURRENCE

The rock in which oswaldpeetersite occurs belongs to the Triassic Shinarump conglomerate, which is rich in organic material such as black coal-bearing smears and logs of partially petrified wood. Coconinoite is the most common U^{6+}-bearing mineral at the Jomac mine and is found scattered throughout the conglomerate, locally replacing organic debris. Oswaldpeetersite occurs, associated with gypsum, along bedding planes of a layer of siltstones within the conglomerate. Additional associated minerals are cuprite, antlerite, goethite, lepidocrocite, mbobomkulite, hydrombobomkulite, sklodowskite and two undefined uranium minerals.

MORPHOLOGY AND PHYSICAL PROPERTIES

Oswaldpeetersite most commonly occurs as micrometric prismatic crystals arranged in radiating groups, rarely distributed on layers of gypsum. The dimensions of the crystals are approximately $0.1 \times 0.01 \times 0.002$ mm. SEM photomicrographs (Figs. 1A, B), taken at two different magnifications, show typical arrangements of the crystals, which are heavily striated lengthwise. The forms recognized are {100}, {010} and {001}. The habit can be described as acicular. The mineral is canary yellow, transparent with a vitreous luster and a pale yellow streak. The Mohs hardness is estimated to be between 2 and 3, the cleavage and the parting are along the elongation, the tenacity is weak, and the fracture is uneven. A density greater than 4.10 g/cm^3 was found using the flotation method at 25°C in Clerici solution. The calculated density, based on the empirical formula, is 4.54 g/cm^3, and that based on the idealized formula is 4.50 g/cm^3. Oswaldpeetersite is soluble with effervescence in dilute HCl.

OPTICAL CHARACTERISTICS

Oswaldpeetersite is biaxial negative. The indices of refraction, measured at 589–599 nm, are α 1.583(2), β 1.669(2) and γ 1.712(2). The calculated $2V$ value is 67.4(2)°. The optical orientation is $Z \parallel a$, and the elongation is positive. Dispersion was not observed. The pleochroism is X and Y very pale yellow to colorless, and Z pale yellow. Oswaldpeetersite, like rutherfordine, does not fluoresce under 360 nm light; this contrasts with joliotite, which strongly fluoresces, and with blatonite, which strongly fluoresces greenish yellow in ultraviolet radiation.

X-RAY CRYSTALLOGRAPHY

Because of the small dimensions of the crystals, we were unable to determine the crystal structure, the unit cell and space group by single-crystal X-ray diffraction. X-ray powder-diffraction data were recorded with a Guinier–Hägg camera using monochromatic Cu$K\alpha_1$ radiation (λ 1.5406 Å). Silicon powder (SRM–640) was used as an appropriate internal standard. Relative intensities of the diffraction lines were measured with an LS–20 line scanner (Key Instruments, Täby, Sweden). The peak positions were determined by using the computer

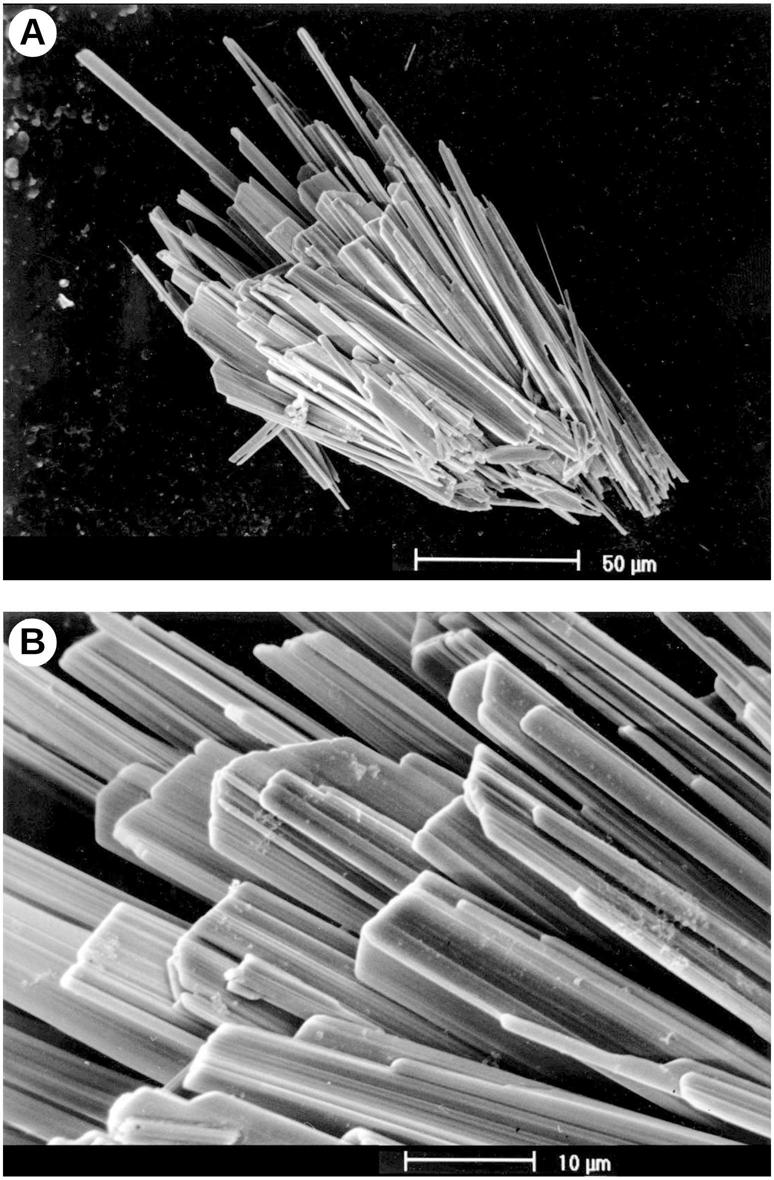

FIG. 1. A. SEM photomicrograph of a radiating group of oswaldpeetersite crystals. Scale bar: 50 µm. B. Closeup of A showing striations and morphology. Scale bar: 10 µm.

program SCANPI (Johansson *et al.* 1980). The X-ray-diffraction spectrum shows 56 diffraction peaks, which were indexed by the program TREOR (Werner *et al.* 1985). Indexing converged to monoclinic symmetry and the unique space-group $P2_1/c$. The unit-cell parameters, refined by the least-squares program PIRUM (Werner 1969), are: *a* 4.1425(6), *b* 14.098(3), *c* 18.374(5) Å, β 103.62(1)°, *a*:*b*:*c* = 0.2938:1:1.3033, *V* = 1042.8(3) Å^3, *Z* = 4. The figure of merit values are M(20) = 10, F(20) = 17(0.018752,65). A fully indexed powder-diffraction pattern is given in Table 1.

CHEMICAL COMPOSITION

Crystals of oswaldpeetersite were chemically analyzed with a Cameca SX–50 electron microprobe. An energy-dispersion scan indicated no elements with Z greater than 8, other than uranium. Quantitative analyses were performed at 10 points using a beam size of 2 μm, an operating voltage of 15 kV, and a beam current of 20 nA. Synthetic UO_2 was used as the standard. The mean content of UO_3 is 81.47 wt.% (range 76.72 – 84.21%). The H_2O content was determined with a thermogravimetric analyzer (TGA 2950, TA Instruments). The heating rate was 5°/min, with a constant flow of N_2 at 50 mL/min. The combined loss of H_2O and OH is complete at 170°C and corresponds to a H_2O content of 12.30 wt.%. The content of CO_2, calculated by difference, is 6.23 wt.%. The oxide formula, calculated on the basis of 13 atoms of oxygen, is $2.03\ UO_3{\bullet}1.01\ CO_2{\bullet}4.88\ H_2O$. The empirical formula, taking into account electroneutrality, is $(UO_2)_{2.03}(CO_3)_{1.01}(OH)_{2.05}{\bullet}3.85\ H_2O$. The ideal formula is $(UO_2)_2CO_3(OH)_2{\bullet}4H_2O$. Calculations of the Gladstone–Dale relationship, made using the constants of Mandarino (1981), yielded a compatibility index of 0.0470 for the empirical formula and 0.0428 for the ideal formula, indicative of good agreement between the physical and chemical data.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR OSWALDPEETERSITE

hkl	d_{obs}	d_{calc}	*I*	*hkl*	d_{obs}	d_{calc}	*I*
002	8.95	8.928	65	230	1.850	1.850	17
012	7.54	7.543	63	0010	1.786	1.786	36
021	6.55	6.557	35	081	1.753	1.754	9
013	5.49	5.484	7	049	1.729	1.729	36
031	4.55	4.544	96	147	1.710	1.711	6
004	4.46	4.464	38	$\bar{1}67$	1.688	1.689	19
014	4.26	4.256	60	$\bar{2}28$	1.660	1.660	16
$\bar{1}12$	3.88	3.888	26	$\bar{2}47$	1.603	1.603	10
033	3.68	3.688	43	$\bar{2}56$	1.568	1.568	10
111	3.62	3.617	18	$\bar{2}48$	1.536	1.537	12
$\bar{1}22$	3.51	3.508	27	244	1.525	1.525	10
015	3.46	3.462	62	$\bar{1}.5.10$	1.515	1.515	12
$\bar{1}14$	3.32	3.321	100	$\bar{1}78$	1.479	1.480	12
034	3.23	3.237	44	$\bar{2}71$	1.439	1.438	13
130	3.060	3.057	41	$\bar{1}.10.1$	1.335	1.335	17
043	3.029	3.033	85	$\bar{2}84$	1.329	1.328	43
035	2.842	2.844	47	$\bar{1}.10.3$	1.321	1.321	20
051	2.787	2.785	31	$\bar{3}27$	1.300	1.300	20
$\bar{1}41$	2.682	2.684	10	0.10.7	1.234	1.234	14
141	2.567	2.566	36	267	1.218	1.219	10
036	2.516	2.514	10	$\bar{3}39$	1.215	1.215	8
$\bar{1}27$	2.297	2.296	18	2.0.10	1.203	1.203	9
062	2.273	2.272	62	198	1.177	1.177	14
152	2.168	2.166	20	$\bar{2}.10.4$	1.156	1.156	19
$\bar{2}02$	2.071	2.071	34	$\bar{2}.8.10$	1.154	1.154	21
$\bar{2}12$	2.049	2.049	28	353	1.141	1.141	14
$\bar{2}11$	2.034	2.033	25	$\bar{3}72$	1.136	1.136	16
$\bar{2}33$	1.886	1.886	33	335	1.134	1.134	16

Guinier–Hägg camera, diameter 100 mm, Cu$K\alpha_1$ radiation, exposure time 45 min., intensities measured using LS–20 line scanner (Key Instruments, Sweden).

TABLE 2. INFRARED-ABSORPTION BANDS IN OSWALDPEETERSITE

Wavenumber, (cm^{-1})	Vibrational mode	Ref.
3437 (bs)	ν (OH) stretching	(1)
1636(m)	δ (H–O–H) bending	(3)
1520 (m), 1374 (m)	ν_3 (CO_3^{2-}) antisymmetric stretching	(2)
1114 (vw)	ν_1 (CO_3^{2-}) symmetric stretching	(2)
915 (w)	ν_3 (O–U–O) antisymmetric stretching	(1)
804(vw)	ν_2 (CO_3^{2-}) out-of-plane bending	(4)
724 (vw)	ν_4 (CO_3^{2-}) in-plane bending	(4)
670 (w)	OH libration (?)	(4)
537(vw), 419(w)	Not assigned	

Band intensities: m: medium, w: weak, vw: very weak, bs: band shape. References: (1) Cejka *et al.* (1996), (2) Botto *et al.* (1989), (3) Farmer (1974), (4) Nakamoto (1963).

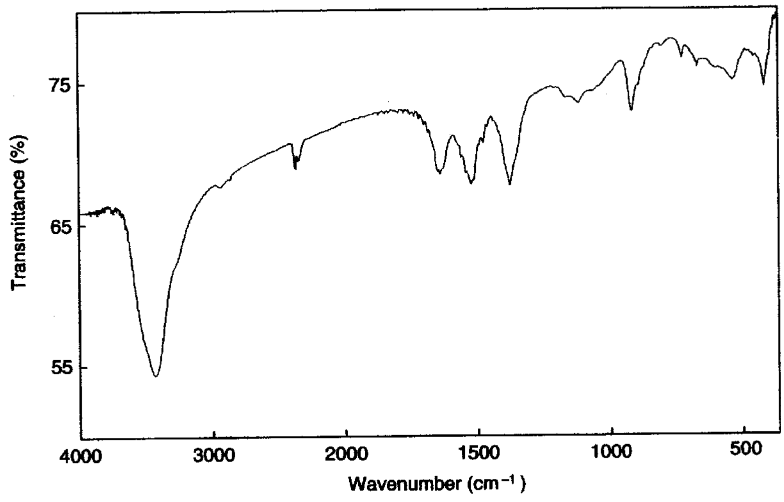

FIG. 2. Fourier-transform infrared spectrum of oswaldpeetersite.

INFRARED SPECTROSCOPY

The infrared spectrum was recorded by using the KBr dispersion technique (1 mg sample in 300 mg KBr) with a Bruker Vector 22 Fourier-transform infrared spectrometer over the range 400–4000 cm^{-1}. The infrared-absorption spectrum is shown in Figure 2. The assignments of absorption bands are summarized in Table 2.

FORMATION AND STABILITY

Cjeka & Urbanec (1988) stated that in synthesis experiments in the system UO_3–CO_2–H_2O, the phases $UO_2CO_3 \bullet nH_2O$ and $UO_2(CO_3)_{1-x}(OH)_{2x} \bullet nH_2O$ ($n \geq 0$) were characterized. In aqueous solutions, below a pH of 5, the dominant species is UO_2^{2+} in the presence of minor quantities of $(UO_2)_2(OH)_2^{2+}$, UO_2OH^+ and fractions of $(UO_2)_3(OH)_5^+$ and $(UO_2)_4(OH)_7^+$. At higher values of pH, the uranyl ion hydrolyzes and forms a number of polymeric hydroxide complexes according the reaction

$$x\,UO_2^{2+} + y\,H_2O \longrightarrow (UO_2)_x(OH)_y^{(2x-y)} + y\,H^+.$$

At a pH between 4.8 and 6.4, $(UO_2)_2(OH)_5^+$ is the dominant cationic species. In the presence of CO_2, anionic uranyl hydroxyl carbonate and uranyl carbonate species will be formed. At a pH between 6.5 and 8, the anionic complex $(UO)_2CO_3(OH)_3^-$ is dominant (Burns & Finch 1999). As a consequence, the following reaction can be considered at a pH between 6 and 7:

$$(UO_2)_2CO_3(OH)_3^- + (UO_2)_3(OH)_5^+ \longrightarrow$$
$$(UO_2)_2CO_3(OH)_2 + 3\,UO_2(OH)_2.$$

After hydration, the solid phase oswaldpeetersite can be expected to form.

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