Paulscherrerite from the Number 2 Workings, Mount Painter Inlier, Northern Flinders Ranges, South Australia: "Dehydrated schoepite" is a mineral after all

JOËL BRUGGER,^{1,2,*} NICOLAS MEISSER,³ BARBARA ETSCHMANN,¹ STEFAN ANSERMET,³ AND ALLAN PRING²

¹Tectonics, Resources and Exploration (TRaX), School of Earth and Environmental Sciences, University of Adelaide, SA-5005 Adelaide, Australia ²Division of Mineralogy, South Australian Museum, SA-5000 Adelaide, Australia

³Musée Géologique and Laboratoire des Rayons-X, Institut de Minéralogie et de Géochimie, UNIL—Anthropole, CH-1015 Lausanne-Dorigny, Switzerland

ABSTRACT

Paulscherrerite, $UO_2(OH)_2$, occurs as an abundant dehydration product of metaschoepite at the Number 2 Workings at Radium Ridge, Northern Flinders Ranges, South Australia. The mineral name honors the contribution of Swiss physicist Paul Scherrer (1890–1969) to mineralogy and nuclear physics. Individual paulscherrerite crystals are tabular, reaching a maximum of 500 nm in length. Paulscherrerite has a canary yellow color and displays no fluorescence under UV light. Chemically, paulscherrerite is a pure uranyl hydroxide/hydrate, containing only traces of other metals (<1 wt% in total). Bulk (mg) samples always contain admixtures of metaschoepite (purest samples have ~80 wt% paulscherrerite). A thermogravimetric analysis corrected for the presence of metaschoepite contamination leads to the empirical formula $UO_3 \cdot 1.02H_2O$, and the simplified structural formula $UO_2(OH)_2$. Powder diffraction shows that the crystal structure of paulscherrerite is closely related to that of synthetic orthorhombic α -UO₂(OH)₂. However, splitting of some X-ray diffraction lines suggests a monoclinic symmetry for type paulscherrerite, with a = 4.288(2), b = 10.270(6), c = 6.885(5) Å, $\beta = 90.39(4)^\circ$, V = 303.2(2) Å³, Z = 4, and possible space groups P2, $P2_1$, P2/m, or $P2_1/m$.

Paulscherrerite-like material was synthesized using various methods, including heating metaschoepite in water at 150 °C and slow hydration of $UO_3(am)$ in air; material synthesized using hydrothermal techniques displayed peak splitting indicative of monoclinic symmetry. Paulscherrerite has been reported under the name "dehydrated schoepite" as an early weathering product of uraninite/pitchblende in several deposits, such as Shinkolobwe, Zaire; Nopal I deposit, Mexico; and the granitic pegmatites of New Hampshire, U.S.A.

Keywords: Paulscherrerite, new mineral, uranyl hydroxide, "dehydrated schoepite," powder diffraction, Number 2 Workings, Radium Ridge, Northern Flinders Ranges, South Australia

INTRODUCTION

Hydrated uranyl oxy-hydroxides and aims of this paper

More than 170 minerals containing hexavalent uranium (uranyl) are known (Burns 1999), including four closely related uranyl oxide hydrates/hydroxides without interlayer cations that form the schoepite subgroup of the fourmarierite group (Burns 1999): schoepite, metaschoepite, paraschoepite, and "dehydrated schoepite" (Table 1). The empirical chemical formula for these minerals is $UO_3 \cdot xH_2O$ (x = 0.8–2.25), but the nature of the natural uranyl oxide hydrates/hydroxides has been a subject of controversy since the description of schoepite by Walker (1923). Christ and Clark (1960) published the first review providing chemical, single-crystal diffraction and optical data for schoepite, metaschoepite, and paraschoepite from Shinkolobwe, Katanga district, Democratic Republic of Congo. Christ and Clark (1960) also analyzed an orthorhombic "dehydrated schoepite," with the nominal chemical formula UO3·H2O. They demonstrated that this product formed by dehydration of schoepite under mechanical pressure or when schoepite is placed over concentrated H₂SO₄,

0003-004X/11/0203-229\$05.00/DOI: 10.2138/am.2011.3601

but suggested that in nature schoepite dehydrated to metaschoepite (their schoepite II), which appears stable. In the past decade, detailed X-ray powder diffraction (Finch et al. 1997) and singlecrystal studies have provided us with a clearer understanding of the nature of these minerals (Table 1), culminating with refinements of the crystal structures of schoepite and metaschoepite (Finch et al. 1996, 1998; Weller et al. 2000). Schoep and Stradiot (1947) described paraschoepite, $5UO_3 \cdot 9!/2H_2O$, but provided few data. Paraschoepite was reported by Christ and Clark (1960) in a sample mixture consisting of schoepite and "dehydrated schoepite." Finch et al. (1998) failed to identify any paraschoepite in the many samples they examined, and concluded that the sample described by Christ and Clark (1960) as paraschoepite was almost certainly a mixture of metaschoepite, "dehydrated schoepite," and ianthinite.

"Dehydrated schoepite" is the only member of the schoepite subgroup that has not been formally described as a mineral species, despite being a well-established and well-defined phase (e.g., Finch et al. 1998). Here we present a formal description of the mineral paulscherrerite, formerly referred to as "dehydrated schoepite." This description is based on a new occurrence from the Number 2 Workings on Radium Ridge, near Arkaroola,

^{*} E-mail: joel.brugger@adelaide.edu.au

Phase	Schoepite	Metaschoepite	Paulscherrerite	α -UO ₂ (OH) ₂	β -UO ₂ (OH) ₂	γ -UO ₂ (OH) ₂
UO ₃ ·xH ₂ O	x = 2.25	x = 2.00	x = 1.00	x = 1.00	x = 1.00	x = 1.00
Formula	[(UO ₂) ₈ O ₂ (OH) ₁₂]·12H ₂ O	[(UO ₂) ₈ O ₂ (OH) ₁₂]·10H ₂ O	UO ₂ (OH) ₂	UO ₂ (OH) ₂	UO ₂ (OH) ₂	UO ₂ (OH) ₂
Space group	$Pb2_1a$	Pbcn	+	Cmca or C2cb	Pbca	$P2_1/c$
Unit cell						
a (Å)	16.813(5)	16.709(2)	4.288(2)	4.242(1)	5.6438(1)	5.560(3)
b (Å)	14.731(4)	14.7291(2)	10.270(6)	10.302(1)	9.9372(2)	5.522(3)
c (Å)	14.337(3)	14.050(2)	6.885(5)	6.868(1)	6.2867(1)	6.416(3)
β (°)			90.39(4)			112.71(9)
Cell V (Å ³)	3551(2)	3457.8(2)	303.2(2)	300.1(1)	352.6(1)	181.7(5)
Reference	Finch et al. (1996)	Weller et al. (2000)*	This study	Taylor (1971)	Taylor and Hurst (1971)	Siegel et al. (1972)

TABLE 1. Structural and stoichiometric information on some U(VI) oxy-hydroxides, UO₃·xH₂O

Notes: For comparison purposes, the unit cells settings are chosen so that the *b*-axis is perpendicular to the structural sheets, except for γ -UO₂(OH)₂ where the unique axis *b* is parallel to the structural sheets. A bold font emphasizes the axis perpendicular to the structural sheets. * Room-temperature measurement.

+ Probable space groups: P2, $P2_1$, P2/m, or $P2_1/m$.

Northern Flinders Ranges, South Australia. We also provide evidence for a pseudo-orthorhombic (monoclinic) symmetry for natural "dehydrated schoepite," compared with the orthorhombic symmetry reported for the synthetic, stoichiometric α -UO₂(OH)₂ crystals analyzed using single-crystal methods by Taylor (1971) and Taylor and Hurst (1971).

Significance of the "schoepite" subgroup

Schoepite, metaschoepite, and paulscherrerite are important secondary U(VI) phases resulting from the weathering of uranium minerals such as uraninite as well as the corrosion of anthropogenic uranium-bearing solids (Finch and Ewing 1992). Whereas rutherfordine is an important U(VI)-mineral in carbonate-rich groundwater, the oxy-hydroxides of the schoepite subgroup are observed in acidic to near-neutral pH systems (e.g., Brugger et al. 2003b). The latter commonly act as precursors in the formation of more complex and stable assemblages of secondary phases, including metal-uranyl-hydrates such as becquerelite, $Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$, and compregnacite, K₂(UO₂)₆O₄(OH)₆·8H₂O (Sowder et al. 1996; Sandino and Grambow 1994), and uranyl silicates and phosphates (Finch and Ewing 1992). Schoepite and metaschoepite may also form as hydrolysis products of natural uranyl- and alkaline metal sulfates {e.g., natrozippeite or zippeite, (Na,K)₄(UO₂)₆[(OH)₁₀ (SO₄)₃]·4H₂O}, as observed by Ondruš et al. (1997) at Jáchymov (Czech Republic), and at Kletno (Poland) and La Creusaz (Switzerland) by Meisser (2003).

The structures of schoepite (Finch et al. 1996) and metaschoepite (Weller et al. 2000) consist of layers with the stoichiometry $(UO_2)_4O(OH)_6$, formed by edge-sharing UO₇ pentagonal bipyramids (Fig. 1) and interleaved with hydrogen-bonded water molecules. Metaschoepite can form from schoepite via partial dehydration and reorganization of the water molecules within the interleaved sheets so as to form a new hydrogen-bonded array. The topology of the uranyl layers is similar in both minerals, differences being mainly related to the orientations of the UO2 groups with respect to the layers (Weller et al. 2000; Fig. 1). In contrast, the structure of orthorhombic α -UO₂(OH)₂ consists of UO₂(OH)₂ layers formed by edge-sharing UO₈ hexagonal bipyramids (Taylor 1971). As noted by Finch et al. (1998) and illustrated in Figure 1, the uranyl sheets in schoepite/metaschoepite and α -UO₂(OH)₂ are topologically related via the substitution $2(OH) = O^{2-} + vacancy.$

PAULSCHERRERITE, A NEW MINERAL

Occurrence

The type locality for paulscherrerite is the Number 2 Workings, Radium Ridge near Mount Painter, near Arkaroola, Northern Flinders Ranges, South Australia (Australian Grid coordinates: 54J 0339200 m E, 6655430 m N). The occurrence is hosted by the Mesoproterozoic Mount Painter Inlier, which contains large volumes of granites and gneisses highly enriched in U and Th (several tens of parts per million). The radiogenic heat released by these granites was responsible for a longlasting thermal anomaly (Sandiford et al. 1998; Neumann et al. 2000; Elburg et al. 2003). Together with Paleozoic intrusions of granitic and pegmatitic melts, this resulted in long-standing, large-scale hydrothermal activity within and around the Mount Painter area, which continues to this day as evidenced by active hot springs (Brugger et al. 2005). The province contains many small hematite-U ± Cu-Nb-REE deposits, and a large U-rich epithermal system characterized by complex quartz \pm fluorite veins and breccias (Mount Gee-Mount Painter system).

Radium Ridge (including Number 2 Workings) was exploited intermittently for radium between 1906 and 1934 (Coats and Blissett 1971; Brugger et al. 2003a). The Number 2 Workings are centered on a lens of coarse-grained hematite ± quartz, containing locally abundant monazite-(Ce), xenotime-(Y), fluorapatite, and a Ca-Fe-phosphate. Accessory minerals include a metamict, strongly heterogeneous samarskite-group mineral with presentday composition plotting in the ishikawaite [(U,Y,Fe)NbO₄] and Fe-rich samarskite-(Y) [(Y,Fe,U)NbO₄] fields (Hanson et al. 1999), and an unknown primary U-Pb(±Mn)-bearing mineral. This high-temperature Fe-U-Nb-REE mineralization is located at the base of the Mount Gee epithermal system, and is overprinted by the epithermal mineralization. Geochemically, the Number 2 Workings bear some similarities with the 440 My year old diopside-titanite veins deposited at 510 ± 20 °C and located ~3 km South of Number 2 Workings (Bakker and Elburg 2006). At the Number 2 Workings, secondary U minerals occur in the cavities of the epithermal quartz and as replacement of the primary U-bearing mineral, and include metaschoepite, weeksite, beta-uranophane, metatorbernite, soddyite, kasolite, billietite, Ce-rich françoisite (type locality; Meisser et al. 2010), Ba-bearing boltwoodite, spriggite (type locality; Brugger et al. 2004), curite, and barite (Brugger et al. 2003a).



🖲 🌑 Uranium

FIGURE 1. Geometry of the uranyl layers in schoepite, metaschoepite, and α -UO₂(OH)₂. Spheres represent uranium atoms, rods are U-O bonds. The darker spheres represent U1,U2,U5,U6 and U2,U3 in schoepite (Finch et al. 1996) and metaschoepite (Weller et al. 2000), respectively, while the lighter ones represent U3,U4,U7,U8 and U1,U4. The shaded areas are occupied by one oxygen atom in the case of schoepite and metaschoepite, but by two O atoms in α -UO₂(OH)₂, causing the main topological difference between the uranyl sheets and the change in uranyl coordination from a pentagonal bipyramid in schoepite/metaschoepite to an hexagonal bipyramid in α -UO₂(OH)₂.

Together with weeksite, metaschoepite, Fe-Mn-oxy hydroxides, and occasionally spriggite, paulscherrerite is the main mineral replacing the unknown primary U-Pb-(Mn?)-bearing mineral at the Number 2 Workings (Fig. 2a). Paulscherrerite also commonly forms pseudomorphs after platy crystals of metaschoepite in cavities of the late epithermal quartz (Fig. 2b).



FIGURE 2. Paulscherrerite occurrences at Number 2 Workings, Radium Ridge, South Australia. (a) Canary yellow paulscherrerite replacing an unknown primary U-Pb-silicate mineral. Field of view 2 cm. (b) Paulscherrerite replacing elongated platy crystals of metaschoepite associated with β -uranophane in cavities in late, epithermal smoky quartz. Image width: 15 mm. Sample MGL 92689.

Name, type material, and classification

The name honors the contribution of the Swiss physicist Paul Scherrer (1890-1969) to mineralogy and nuclear physics. Scherrer was appointed at the ETH Zürich in 1920 together with Dutch physicist Peter Debye (1936 Nobel Prize in chemistry), and became head of the Physics Institute in 1927. The collaboration between Scherrer and Debye resulted in the development of the powder diffraction theory (e.g., the Scherrer equation), and the design of the Debye-Scherrer X-ray powder diffraction camera, which both had a strong impact on mineralogical sciences. After the initial years of successful research activities in the field of X-ray scattering in crystals, liquids, and gases, Scherrer increasingly turned his attention to nuclear physics. In 1946 he was appointed to the Presidency of the Swiss Study Commission for Atomic Energy, and nuclear and reactor physics developed thanks to his initiative. Scherrer was also instrumental in dissuading the Swiss government from pursuing its own military nuclear program. The name paulscherrerite is chosen in preference

of *scherrerite* because of phonetic confusion with the mineral schairerite, Na₂₁(SO₄)₇ClF₆. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (2008-022). Holotype material (G31382) is deposited in the South Australian Museum, North Terrace, 5000 Adelaide, Australia, and cotype material (MGL 79287) in the Musée Géologique, UNIL-Anthropole, 1015 Lausanne, Switzerland.

In the classification of Strunz and Nickel (2001), paulscherrerite belongs to group 4.GA.20: uranyl hydroxides without additional cation.

Appearance and physical properties

Paulscherrerite occurs most commonly as a microcrystalline powdery product (Fig. 2a) forming part of the mineral assemblage resulting from the weathering of an unknown U-Pb-(Mn?)-bearing mineral. Paulscherrerite commonly replaces metaschoepite, which occurs either in a massive form (Fig. 2b) or as acicular to blocky crystals up to 1 mm in length (Fig. 3a). Paulscherrerite pseudomorphs after metaschoepite crystals display porous surfaces (Fig. 3b) when examined by scanning electron microscopy. The paulscherrerite crystallites reach a maximum length of ~500 nm (Fig. 3c). They are aligned along a crystallographic axis of the replaced metaschoepite. Paulscherrerite crystals show a tabular morphology, with at least one prominent monoclinic prism (Fig. 3c).

Paulscherrerite is canary yellow, with a streak of similar color. It shows no fluorescence under UV-light. The Mohs hardness could not be measured on the powdery material available, and neither cleavage nor fracture was observed. The calculated density is 6.66 g/cm³ for the ideal formula UO₂(OH)₂. Because the mineral occurs in powdery form and is always finely mixed with metaschoepite (10 samples analyzed by XRD), no density measurement using the pycnometer method was undertaken.

No optical properties are reported because the mineral occurs as a powdery replacement product (grain size ≤ 500 nm; Fig. 3c), unsuitable for optical measurements. The average refractive index calculated using the Gladstone-Dale relationship with the constants reported by Mandarino (1981) is *n* (calc.) = 1.874 for the ideal composition UO₂(OH)₂. This value is close to the average value (1.862) measured on synthetic α -UO₂(OH)₂ by Harris and Taylor (1962).

X-ray crystallography

In the absence of a suitable crystal, no single-crystal study could be carried out, and the identification of the nature of paulscherrerite relies mainly on its characteristic powder X-ray diffraction pattern (Fig. 4; Table 2; see also Finch et al. 1997). X-ray powder-diffraction data were collected using a Huber Guinier Image Plate G670 camera (South Australian Museum) with CoK α_1 X-radiation (1.78892 Å). NIST SRM 640a silicon power was used as internal standard. Ten samples from different hand specimens were screened using a 100 mm diameter Guinier-Hägg camera (South Australian Museum) under a weak vacuum, with photographic film as a detector and Cr $K\alpha_1$ X-radiation (2.2897 Å). The necessary sample quantity for the latter camera was ~1 mg, while more than 10 mg were necessary to obtain good patterns using the G670 camera. After development, the film was digitized using an optical scanner, the diffractogram was extracted using NIH image (developed at the U.S. National Institute of Health and available at http://rsb.info.nih.gov/nih-image/), and the 2θ scale was calibrated by a linear regression based on the three most intense Si lines.

The measured intensities and peak positions for the holotype are reported in Table 2. Peak positions and intensities were extracted from a full profile fit using the *fityk* software (http://www.unipress.waw.pl/fityk/). The fit included a baseline sub-



FIGURE 3. Scanning electron microscope (SEM) images of metaschoepite crystals from the Number 2 Workings, Radium Ridge, South Australia, replaced by paulscherrerite. (a) Overview of the replaced orthorhombic metaschoepite crystal. (b) Close-up showing the porous nature of the replaced metaschoepite crystal. (c) High-resolution image showing the habit of the paulsherrerite crystals; the largest crystals are ~500 nm in length. Philips XL30 field emission gun SEM at accelerating voltages of 10 to 15 kV (University of Adelaide); images taken in secondary electron mode.



FIGURE 4. X-ray powder pattern of paulscherrerite with the Rietveld fit obtained using a mixture of metaschoepite (Weller et al. 2000) and orthorhombic α -UO₂(OH)₂ (Taylor 1971). The main plot shows the fit and residuals using the Rietveld fit. The inset shows the doubling of some lines, indicative of the reduced symmetry in paulscherrerite relative to the published structure of α -UO₂(OH)₂; both the rietveld (orthorhombic cell) and the LeBail (monoclinic cell) fits are shown in the inset. Miller indices for the most intense lines are shown in the inset (O-orthorhombic cell, M-monoclinic cell).

traction using a spline function, and modeling of peaks using a pseudo-Voigt function.

Rietveld refinement was conducted using the Rietica package (Hunter 1998). The pattern was modeled using a mixture of α -UO₂(OH)₂ (Taylor 1971; Taylor and Hurst 1971; space group *Cmca*) and metaschoepite (Weller et al. 2000). The fit (Fig. 4) shows that paulscherrerite is associated with significant amounts of metaschoepite (~30% metaschoepite, ~70% paulscherrerite); the refined orthorhombic cell for paulscherrerite has a = 4.2876(2) Å, b = 10.2569(3) Å, c = 6.8919(3) Å, V =303.09(2) Å³. The unit cell for the associated metaschoepite is listed in Table 3.

The Rietveld refinement has relatively high residuals (R = 8.5%). Close inspection shows that a few reflections appear to be doublets (inset in Fig. 4), and by excluding the doublets from the Rietveld fit the R value reduced to 4.5%. This relatively high-residual value is mainly related to difficulties in modeling peak shape. The observed peak splitting suggests that the orthorhombic structure reported for synthetic α -UO₂(OH)₂ and that of paulscherrerite differ by a small distortion, which implies monoclinic symmetry for paulscherrerite. We tested this hypothesis by using a Le Bail fit (Le Bail et al. 1988), which showed that when the β angle deviated slightly from 90.0° it was possible to index the experimental pattern with good accuracy (final R = 4.9%; inset in Fig. 4; Table 2).

Hence paulscherrerite is monoclinic (pseudo-orthorhombic), with a = 4.288(2), b = 10.270(6), c = 6.885(5) Å, $\beta = 90.39(4)^{\circ}$, V = 303.2(2) Å³, and Z = 4. The *a*:*b*:*c* ratio calculated from these

unit-cell parameters is 0.4175:1:0.6704. The following space groups explain all 46 reflections listed in Table 2 [tolerance 0.15 °20; program Checkcell (Checkcell: part of the MGP-Suite Suite of programs for the interpretation of X-ray experiments, by Jean Laugier and Bernard Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France. http://www.ingg.fr/LMGP and http://www.ccp14.ac.uk/tutorial/ lmgp/)] P2, P2₁, P2/m, and P2₁/m. P2₁/a also explains all reflections, but is discarded on the ground that the *a* glide is not a subset of the parent structure, orthorhombic α -UO₂(OH)₂. Note that a *C*-centered cell is excluded on the basis of two weak but clearly present reflections: (201), I = 0.5% and (001), I = 0.9%.

Laser Raman spectra were recorded in the range from 4000 to 100 cm⁻¹ with a Renishaw Ramascope 1000 (University of South Australia) using an argon laser (488 nm line) and excitation through a Leica DMLM optical microscope (Si standard, spectral resolution 2 cm⁻¹, unpolarized laser light, random sample orientation). Due to the small excitation volume of Raman (a few cubic micrometers) and the combination with optical microscopy (paulscherrerite and metaschoepite have different yellow tinges), it was possible to record nearly pure spectra for paulscherrerite. The Raman spectra (Fig. 5a) are dominated by a broad band related to v(OH) (~3245–3435 cm⁻¹, with maxima at ~3290 and 3340 cm⁻¹) and an intense band attributed to $v_1(UO_2^{2+})$ centered at 840 cm⁻¹. Weak bands at low wavenumbers (360, 460, 505, and 557 cm⁻¹) are attributed to stretching modes of v(UO) for the planar O atoms (as opposed to axial O atoms in the uranyl group, UO_2^{2+}), based on the interpretation of the IR spectrum

	Measured		Monoclinic cell		Orthorhombic cell					
	20	d _{meas} (Å)	I _{meas} (%)	hkl	d _{calc} (Å)	-	hkl	d _{calc} (Å)	I _{calc} (%)†
MS	13.96	7.359	4.4					200	7.311	100.0
1.	14.83	6.929	0.9		001	6.885				
2.	20.03	5.143	54.8		020	5.135		020	5.128	71.4
MS	28.86	3.589	1.7					024	3.585	30.4
MS	29.50	3.513	0.2					040	3.509	17.1
3.	30.08	3.447	100.0		002	3.442		002	3.446	24.8
4.	30.25	3.428	28.8		111	3.421		111	3.431	100.0
MS	32.26	3.220	4.9					224	3.219	43.1
MS	32.82	3.166	1.9					240	3.164	22.5
5.	36.42	2.862	18.6		022	2.859	2	022	2.860	29.7
*6.	40.14	2.607	0.6		112	2.605	ł	112	2.598	1.9
*7.	40.38	2.592	0.5		112	2.589	J	0.40	2564	0.5
8.	40.84	2.564	6.3		040	2.568		040	2.564	8.5
9.	42.05	2.493	24.4		131	2.490		131	2.492	34.9
10.	43.09	2.404	0.9		140	2.400		041	2.403	0.6
11.	47.77	2.209	0.5		200	2.205		200	2 1 4 4	110
12.	49.50	2.145	6.0		200	2.144		200	2.144	127
13.	52.02	2.030	0.4		201	2.038		042	2.057	12.7
15	53 39	1 991	11.9		113	1 991		113	1 987	27.0
16	53.73	1.979	24.8		113	1.980		220	1.978	11.8
*17.	58.68	1.825	5.8		202	1.825	1	202	1 0 20	0 /
*18.	59.06	1.815	4.9		202	1.814	Ś	202	1.020	0.4
19.	60.11	1.786	10.1		151	1.787		151	1.787	19.1
*20.	61.69	1.745	6.4		133	1.746	l	133	1 742	173
*21.	61.95	1.738	6.2		133	1.738	Ş	155	1.7 42	17.5
22	62 67	1 720	70	{	004	1.721	ļ	004	1,723	2.3
22.	02.07	1.720	7.9	l	222	1.720	Ţ			215
23.	63.08	1.710	8.9		222	1.711	ł	222	1.715	13.6
					.		ι	060	1.709	3.6
24.	65.91	1.644	3.4		240	1.646		240	1.645	4.9
25.	66.46	1.632	5.2		024	1.632		024	1.633	6.2
20. *27	72.07	1.530	2.4		742	1.551	1	062	1.531	5.7
27. *20	73.97	1.407	2.2		242	1,400	}	242	1.484	9.3
20.	76.82	1 440	3.8		153	1 4 3 9	,	153	1 4 4 1	71
30	77.51	1,429	2.3		233	1.439		044	1,430	5.1
*31.	80.22	1.388	2.1		311	1.389	1	211	1 207	7.6
*32.	80.46	1.385	8.7		311	1.385	ſ	311	1.387	7.0
33.	82.39	1.358	3.7		144	1.359	-	171	1.359	9.2
34.	83.24	1.347	0.7		204	1.347		204	1.343	2.4
35.	84.04	1.336	3.1		214	1.335		260	1.337	3.5
36.	86.72	1.303	3.6		224	1.303		115	1.302	5.8
37.	87.23	1.297	6.0		331	1.297		224	1.299	6.5
38.	87.49	1.294	3.5		<u>3</u> 31	1.294		331	1.295	5.5
39.	88.61	1.281	0.4		322	1.281		080	1.282	1.3
40.	91.87	1.245	3.0		262	1.245	•	162	1.246	6.7
*41.	93.69	1.226	1.5		135	1.226	}	235	1.225	7.0
*42.	94.08	1.222	3.9		135	1.222	J	1.00	1 2 1 4	2.0
43.	95.05	1.213	0.5		045	1.213		164	1.214	2.8
44. 45	95.52	1.208	3.6		313 212	1.209		013	1.205	0.5
45. 46	90.52 07 70	1.201	5.5 1.6		313 271	1.201		2/1/	1.202	5.0
	91.20	1.192	1.0		2/1	1.192		544	1.190	0.7

 TABLE 2.
 X-ray powder-diffraction data of paulscherrerite (holotype G31382) from Number 2 Workings

Notes: MS = metaschoepite. Starred cells correspond to X-ray diffraction lines that become doublets in the monoclinic cell compared to the orthorhombic cell. Errors on the measured peak positions are ≤ 0.03 °20.

of α -UO₂(OH)₂ by Hoekstra and Siegel (1973). The spectra revealed a splitting of the v₁(UO₂²⁺) mode, with four bands centered at 843, 831, 850, and 864 cm⁻¹ (Fig. 5b), respectively. The v₁(UO₂²⁺) mode is at 848 cm⁻¹ in synthetic α -UO₂(OH)₂ (Bartlett and Cooney 1989). The average U-O distance calculated based on the position of the Raman bands using the empirical relationship of Bartlett and Cooney (1989) is 1.76 Å, similar to the distance retrieved on synthetic, orthorhombic α -UO₂(OH)₂: 1.79(5) Å [from neutron data; Taylor and Hurst (1971)] and 1.71(3) [from X-ray data; Taylor (1971)]. The splitting of the uranyl v₁(UO₂²⁺) Raman band indicates that several different uranyl U-O bond lengths exist in paulscherrerite, in contrast with the structure



FIGURE 5. Raman spectrum of paulscherrerite. (**a**) Full spectral range showing only major bands for uranyl and OH vibrations. (**b**) Detailed view of the $v_1(UO_2^{2*})$, showing splitting of the band. The table shows the position, relative intensity, and width of each band (Gaussian fit), with the corresponding U-O distance calculated using the empirical relationship of Barlett and Cooney (1989).

of orthorhombic α -UO₂(OH)₂, which contains only one such distance (Taylor 1971).

Chemical composition

Chemical analyses were carried out by means of an electron microprobe (Cameca SX50, WDS mode, 20 kV, 20 nA, defocused beam ~5 μ m in diameter; University of Adelaide) on material mounted in epoxy resin and hand-polished using a water-diamond suspension (final polish using 1 μ m diamond). Electron microprobe analyses show that paulscherrerite is an almost pure uranyl oxide-hydroxide/hydrate, with <~1 wt% of minor elements such are rare earth elements, Al, Ba, and Pb (Table 4). The presence of H₂O was confirmed by infrared and Raman spectroscopy, and quantified using thermogravimetric analysis (TGA; Ecole Polytechnique Fédérale, Lausanne).

The empirical formula, using the total water content measured by TGA (see below), based on 1 U atom per formula unit (pfu) and assuming that all U atoms are present as uranyl, is $UO_3 \cdot 1.18H_2O$. Other constituents reported in Table 4 correspond to ≤ 0.001 atoms pfu each. The empirical formula corrected for contamination by metaschoepite is $UO_3 \cdot 1.02H_2O$, within error of the simplified structural formula $UO_2(OH)_2$. The latter formula requires: $UO_3 \cdot 9.96$, $H_2O \cdot 6.04$, Total 100.00 wt%.

As the available paulscherrerite always exists in powder form and is intimately admixed with significant amounts of metaschoepite, TGA was the preferred method of water measurement, as this method can distinguish between crystal water

TABLE 3. Comparison of unit cells and chemical formulas for minerals and synthetic phases related to schoepite and paulscherrerite

Mineral	Formula and notes	a (Å)	b (Å)	<i>c</i> (Å)	β(°)	V (ų)	Space group	
Schoepite and metaschoepite								
Schoepite, Finch et al. (1996)	[(UO ₂) ₈ O ₂ (OH) ₁₂](H ₂ O) ₁₂	16.813(5)	14.731(4)	14.227(3)	3550.9(4)	Pb2₁a		
Metaschoepite (synth) @ 150 K, Weller et al. (2000)	[(UO ₂) ₈ O ₂ (OH) ₁₂]·10H ₂ O	16.7063(5)	14.6861(4)	13.9799(3)	3430.0(1)	Pbcn		
Metaschoepite (synth) @ room T, Weller et al. (2000)	[(UO) ₈ O ₂ (OH) ₁₂]·10H ₂ O	16.709(2)	14.7291(2)	14.050(2)	33457.8(2)	Pbcn		
Metaschoepite synthesis (US3) ^{††}	[(UO ₂) ₈ O ₂ (OH) ₁₂]·10H ₂ O*	16.6958(6)	14.6741(7)	13.9713(5)	3422.9(2)	Pbcn		
Metaschoepite mixed with paulscherrerite in G31382 ⁺⁺	[(UO ₂) ₈ O ₂ (OH) ₁₂]·10H ₂ O	16.678(3)	14.622(3)	14.037(3)	3423(1)	Pbcn		
Paulscherrerite, "dehydrated schoepite" (DS) and α-UO ₂ (OH),								
α-UO ₂ (OH) ₂ , Taylor (1971)	UO ₂ (OH) ₂ †	4.2888	10.2524	6.8919	orth.	303.04	Стса	
DS slow hydration of UO₃(am)††	$UO_2(OH)_2$	4.2807(1)	10.2239(3)	6.8984(2)	orth.	301.91(2)) Cmca	
DS G46, 150 °C‡‡	UO ₂ (OH) ₂ §	4.2883(2)	10.1862(7)	6.9067(3)	90.507(3)	301.69(3)) –	
DS COGEMA††	$UO_2(OH)_2$	4.2826(2)	10.2356(3)	6.8821(3)	90.22(1)	301.68(2)) –	
Paulscherrerite G31382, this study‡‡	UO ₂ (OH) ₂ **	4.288(2)	10.270(6)	6.885(5)	90.39(4)	303.2(2)	-	

* Metaschoepite US3 was synthesized by placing UO₃(am) in water at room temperature. After aging in solution for 12 months at room temperature, the load consisted of fine-grained metaschoepite. Two X-ray diffraction peaks at 3.226(2) and 3.593(2) Å cannot be explained by the crystal structure of Weller et al. (2000). + The α -UO₂(OH)₂ crystal measured by Taylor (1971) was probably synthesized via cooling of β -UO₂(OH)₂ (Hoekstra and Siegel 1973).

 \pm Prepared by standing UO₃(am) in air for 24 months. After 8 months poorly crystalline α-UO₂(OH)₂ was obtained. The unit cell reported here is for material after 24 months, which had sharp diffraction peaks and consisted of 18.0(7) mol% metaschoepite and 82.0(7) mol% α-UO₂(OH)₂ (from Rietveld analysis).

§ Synthesized by placing synthetic metaschoepite (see US3) at 150 °C in water for 11 days.

|| Commercial yellow UO₃(am) manufactured by COGEMA and purchased from LOBOSI PROLABO, Paris, France, in 1981. It now consists of 56.4(5) mol% metaschoepite and 43.6(7) mol% α -UO₂(OH)₂ (from Rietveld analysis). The mixture also contains an unknown additional phase with an X-ray powder diffraction peak at 3.216(1) Å. ** G31382 is the paulscherrerite holotype, and consists of a fine-grained mixture of paulscherrerite with ~30 wt% metaschoepite. Rietveld refinement using the orthorhombic cell for α -UO₂(OH)₂ (Taylor 1971) gave a = 4.2876(2) Å, b = 10.2569(3) Å, c = 6.8919(3) Å, V = 303.09(2) Å³.

 \uparrow Unit cell from Rietveld refinement.

‡‡ Unit cell from Le Bail fit.

groups and hydroxyl anions. Protas (1959) and Čejka (1999; p. 583) provide TGA data for metaschoepite. Upon heating, metaschoepite {[(UO₂)₈O₂(OH)₁₂]·10H₂O} loses 10 H₂O between 60 and 125 °C (molecular water), and 6 H₂O corresponding to 12 hydroxyl groups between 135 and 450 °C. The TGA curves of metaschoepite are similar to those of synthetic UO₃·2H₂O, and show endotherms at 130 and 300 °C (dehydration and dehydroxylation), at 630 and 700 °C (transition of α -UO₃ to U₃O₈), and an exotherm at 480 °C corresponding to α -UO₃ crystallization from amorphous UO₃.

To assess the reliability of our TGA, we measured a synthetic metaschoepite (US3; see Fig. 6; unit-cell constants in Table 3). US3 looses 7.01 wt% H₂O over the range 40 to 150 °C, corresponding to 10.04 H₂O pfu. A further 4.45% weight loss occurs between 150–450 °C, corresponding to 6.38 H₂O molecules pfu. This is ~5% higher than the stoichiometric hydroxyl contents of 12 OH⁻ pfu, a value that may be explained by the presence of small amounts of carbonates in the product, as revealed by the infrared spectrum (Fig. 7). The TGA spectrum of US3 also shows a small loss of ~0.4 wt% between 515 and 560 °C, and a further weight loss of ~1.1% between 610 and 675 °C, the latter corresponding to the transition of α -UO₃ to UO_{2.67} according to Čejka (1999). The total weight loss between 500 and 700 °C is 1.61 wt%, which we interpret as a loss of 0.33 O per U atom, in accordance with the expected stoichiometry of the final product, UO_{2.66}.

The paulscherrerite cotype shows a loss of $1.14 \text{ wt}\% \text{ H}_2\text{O}$ up to 150 °C (Fig. 6), which we attribute to the loss of molecular water in the associated metaschoepite. There is a further loss of 5.78 wt% between 150 and 465 °C, which corresponds to $0.99 \text{ H}_2\text{O}$ molecule pfu on the basis of one U pfu. Assuming that the water loss to 150 °C corresponds to the loss of hydration water contained in metaschoepite mixed with paulscherrerite (Table 3), we can calculate that the investigated sample contains about 16 wt% metaschoepite. This number is lower than the value of 30 wt% found by Rietveld refinement for an aliquot of the sample used in the TGA. The resulting composition of the paulscherrerite is UO₃·1.02H₂O, in excellent agreement with the stoichiometry of synthetic α -UO₂(OH)₂.

TABLE 4. Chemical composition of type specimen for paulscherrerite

		<i>, , , , , , , , , ,</i>		
Constituent	wt%	Range	Stand. dev.	Probe standard
UO₃	92.91	91.69–93.66	0.57	UO ₂ (synthetic)
Al ₂ O ₃	0.07	<0.05-0.24	0.08	Albite
BaO	0.02	<0.05-0.13	0.04	Barite
La ₂ O ₃	0.05	<0.04-0.14	0.06	Glass
CeO ₂	0.02	<0.04-0.12	0.04	Glass
Nd ₂ O ₃	0.06	<0.04-0.52	0.16	Glass
PbO	0.09	<0.05-0.33	0.10	Crocoite
Subtotal	93.22	92.12-94.49	0.58	
H ₂ O _{tot} (TGA, <i>T</i> < 465 °C)*	6.92			
Total	100.14			

Note: Water analyzed using TGA, other elements via electron microprobe (average of 20 point analyses).

* H_2O loss at T < 150 °C: 1.14 wt%, attributed to molecular water in admixtures of metaschoepite. Other analyzed minor constituents: <0.05 wt% Na₂O; <0.07 wt% P₂O₅; <0.05 wt% CaO; <0.05 wt% MnO; <0.05 wt% FeO; <0.10 wt% Y₂O₃; <0.09 wt% Pr₂O₃; <0.06 wt% Sm₂O₃.

SYNTHESIS OF PAULSCHERRERITE-LIKE MATERIAL: "Dehydrated schoepite"

The empirical phase relationships among schoepite, metaschoepite, and "dehydrated schoepite" were summarized by Finch et al. (1998), and an updated representation of their conclusions is shown in Figure 8. As pointed out by Hoekstra and Siegel (1973), stoichiometric α -UO₂(OH)₂ so far has only been synthesized via cooling of β -UO₂(OH)₂, and the only single-crystal data available are for this material. Unfortunately the details of the synthesis of the crystal used by Taylor (1971) are not reported, but were part of a 1958 patent application (Harris and Taylor 1962). The products synthesized via other routes appear to be waterdeficient, with water contents corresponding to UO₃·0.8-0.9H₂O (Table 5). This non-stoichiometry is probably related to the substitution $2(OH)^- = O^{2-} + vacancy$ (Fig. 1; Finch et al. 1998), leading to the structural formula $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ (x = 0 to 0.25) for "dehydrated schoepite" (paulscherrerite from the type locality has x ~ 0.25). All published reports about "dehydrated schoepite" assume an orthorhombic symmetry for the phase, based on the similarity of the powder diffraction pattern with that calculated for the structure of α -UO₂(OH)₂ provided by



FIGURE 6. Thermogravimetric analysis of paulscherrerite and related phases. Heating rate of 10 °C/min, under N_2 -flux.

FIGURE 7. Infrared spectra of paulscherrerite and related phases. *Notes.* The absorbance peak at 1384 cm⁻¹ in synthetic metaschoepite was not reported by Urbanec and Čejka (1979), and may correspond to contamination by an unknown carbonate. KBr pressed disk; paulscherrerite 1.5 mg; $UO_2(OH)_2$ COGEMA 1.7 mg; $UO_2(OH)_2$ [$UO_3(am)$ after 24 months] 1.7 mg; synthetic metaschoepite 1.5 mg.

Taylor (1971). In the following we use " α -UO₂(OH)₂" to refer to a stoichiometric compound with the crystal structure given by Taylor (1971), and "dehydrated schoepite" as a general term to designate compounds with stoichiometry UO₃·0.75–1.00H₂O and a unit cell closely related to that of α -UO₂(OH)₂; this usage includes paulscherrerite.

"Dehydrated schoepite" has been synthesized using several routes (Table 5; Fig. 8). Vochten and Blaton (1999) synthesized $UO_3 \cdot 0.8H_2O$ by heating synthetic rutherfordine, (UO)₂CO₃, in water at 100 °C for 30 days. Their TGA curve shows dehydration between 200 and 450 °C with a total loss of water (5.04 wt%) corresponding to 0.8 mole of water per U atom. Vochten and Blaton (1999) reported a powder pattern that shows clear evidence for monoclinic symmetry in their compound (doublet lines at 1.743/1.725 and 1.343/1.334 Å), as well as IR data similar to those obtained for paulscherrerite.

Unit cells refined on the basis of X-ray powder diffraction data for paulscherrerite, α -UO₂(OH)₂, and "dehydrated schoepite" synthesized using various different methods are summarized in Table 3. We succeeded in forming a mixture of metaschoepite

and "dehydrated schoepite" simply by leaving amorphous UO₃ $[UO_3(am)]$ in air for two years. $UO_3(am)$ was synthesized following the method of O'Hare et al. (1988) by roasting uranyl peroxide (made from uranyl nitrate) at 500 °C for 8 h. After 8 months, the orange product had turned yellow, and displayed broad diffraction lines characteristic of α -UO₂(OH)₂ (Fig. 9). After 24 months, the product was well crystallized, containing about 80% of paulscherrerite and 20% metaschoepite (Fig. 9; Table 3). Interestingly, this α -UO₂(OH)₂ does not display any evidence of monoclinic distortion, while the α -UO₂(OH)₂ prepared via hydrothermal method (G46) and a sample obtained from COGEMA showed evidence for such a distortion (Fig. 9; Table 3). While TGA curves of paulscherrerite and the COGEMA material are very similar-with all significant features appearing at similar temperatures-the material obtained by slow hydration of UO₃(am) in air has a more complex evolution. In particular, there is near-continuous water loss up to 235 °C in the latter material, while water (from metaschoepite admixtures) is lost by 150 °C in paulscherrerite and 195 °C in the COGEMA sample (Fig. 6). Correcting for the metaschoepite admixtures based upon water loss to 195 and 235



FIGURE 8. Reactions among schoepite, metaschoepite, "dehydrated schoepite" (including paulscherrerite), and α -UO₂(OH)₂ based on natural occurrences and experimental studies (see text). Modified from Finch et al. (1998). Paulscherrerite at the type locality (Radium Ridge) forms via dehydration of metaschoepite (bold arrow) at *T* <100 °C.

TABLE 5.	Summary of results of previous studies of "dehydrated schoepite": This table attempts to present an exhaustive view of the mentions
	of "dehydrated schoepite" in nature, as well as a selection of critical studies conducted on synthetic material

Reference	X-ray powder diffraction results	Water determination	Type of material investigated
Dawson (1956)	Guinier camera, but none	UO₃·0.85H₂O based on weight	Synthesized by (1) hydration of "UO ₃ "
	of the monoclinic peak	loss to 700 °C (to U₃O ₈).	in steam at 120 °C, (2) reaction of "UO ₃ "
	splitting reported.		in water at 180 °C.
Christ and Clark (1960)	Doublet at 1.826/1.807 Å can be	Assume UO ₂ (OH) ₂ based on loss of 5.4%	Natural from the Shinkolobwe
	indexed in monoclinic setting,	water upon heating of synthetic	deposit, Katanga district,
	but not in orthorhombic setting.	schoepite UO ₃ ·2H ₂ O between 60 and 180 °	C Democratic Republic of Congo.
		(Bignand 1955). 5.4 wt% water correspond	ds
		to UO ₃ ·0.91H ₂ O.	
Hoekstra and Siegel (1972)	Raw data not reported.	TGA analyses on three synthetic	Synthesized via three different
		compounds are reported, but the	methods: (1) heating γ -UO ₃ in water
		wt% H_2O are not given, and the	at 100 °C for several days;
		plotted spectra do not display	(2) heating amorphous UO ₃
		a y-scale. Given stoicniometries:	In water at 100°C for several days;
		(1) UO₃•0.8H₂O; (2) UO₃•0.8H O;	(3) cooling of γ -UU ₂ (OH) ₂ .
		(2) UO ₃ ·0.8H₂O; (2) UO (OH)	
O'Hare et al. (1988)	Raw data not reported	$(3) 00_2(01)_2$.	Synthesized by reacting LIO (am)
0 Hale et al. (1900)	Naw data not reported.	loss to 800 °C (to 11.0.)	in water 45–50 °C for 5 days
Vochten and Blaton (1999)	Clear evidence for monoclinic symmetry	TGA. 5.04 wt% weight loss between	Synthesized by heating synthetic
	in their compound: doublets	25 and 450 °C, resulting in formula	rutherfordine $(UO)_2O_2$ in water at
	at 1.743/1.725 and 1.343/1.334 Å.	UO ₃ ·0.8H ₃ O.	100 °C for 30 days.
Pearcy et al. (1994)	Raw data not reported.	n/a	Natural from the Nopal I deposit,
	•		Chihuahua, Mexico.
Korzeb et al. (1997)	Mixture dominated by metaschoepite;	TGA; mixture dominated by	Natural from the Palermo No. I and
	no evidence for monoclinic distortion.	metaschoepite.	Ruggles granitic pegmatites,
			Grafton County, New Hampshire, U.S.A

°C, respectively, the empirical formula for "dehydrated schoepite" in the COGEMA sample is $UO_3 \cdot 0.9H_2O$, and that from the sample left out for 24 months is $UO_3 \cdot 0.8H_2O$.

Dawson et al. (1956) reported that $UO_3(am)$ in contact with water at about 180 °C yields orthorhombic α -UO₂(OH)₂; and based on TGA results, they reported that the product was nonstoichiometric, with composition UO₃·0.8H₂O (Table 5). O'Hare et al. (1988) synthesized "dehydrated schoepite" using the same method, but at a lower temperature of 45–50 °C (5 days reaction time), and obtained the composition $UO_3 \cdot 0.9H_2O$. Hoekstra and Siegel (1973) provide the best systematic characterization of "dehydrated schoepite" to date; they note that the unit cell, IR spectra, and TGA data for this phase vary slightly depending on the method of synthesis. Only material obtained via cooling of



FIGURE 9. XRD patterns for UO₃(am) after 8 and 24 months in air, showing increase in crystallinity of the formed α -UO₂(OH)₂. The inset compares different synthetic α -UO₂(OH)₂ to paulscherrerite. See Table 4 for details about samples.

the β -UO₂(OH)₂ phase was stoichiometric [i.e., α -UO₂(OH)₂], while material prepared from UO₃(am) or γ -UO₂(OH)₂ contained less than one water pfu (UO₃·0.8H₂O) even when synthesized at 300 °C and 2 kbar.

All the above studies agree that the formation of "dehydrated schoepite" is an irreversible process. In contrast, Sowder et al. (1999) obtained a compound with nominal composition $UO_3 \cdot 0.9H_2O$ (from TGA) by drying synthetic metaschoepite at 105–150 °C. This product quickly rehydrated to form poorly crystalline metaschoepite in water at room temperature. Unfortunately, the product is poorly characterized. The identity of their dehydration product with "dehydrated schoepite" is based on a major X-ray diffraction line at 5.9 Å [compared to ~5.1 Å in α -UO₂(OH)₂]. The major line at ~3.44 Å is replaced by several lines in their diffractogram (XRD patterns shown only to d = 2.98 Å). Hence, this unknown phase is not shown in Figure 8.

DISCUSSION

A note on nomenclature: "Dehydrated schoepite" vs. paulscherrerite

A consensus has emerged in the mineralogical literature that "dehydrated schoepite" is isostructural with α -UO₂(OH)₂ (Taylor 1971) but is water-deficient, with the formula commonly given as UO₃·0.8H₂O (range 0.8 to 0.9 H₂O; Table 5). A review of the literature (Table 5) reveals that before the present study there was no determination of water in natural "dehydrated schoepite," a reflection of the fact that the mineral so far has been found only in powdery form (crystallites <1 μ m in size) and in fine intergrowths with other uranyl minerals.

The reported occurrences of "dehydrated schoepite" were all identified on the basis of X-ray powder diffraction data (Table 5); however, only Christ and Clark (1960) reported good quality powder XRD data, and their table of diffraction lines includes a doublet at 1.826/1.807 Å, one of the strongest split peaks (Table 2) in paulscherrerite. It is worth noting that discerning such a small monoclinic distortion with the use of powder diffraction will be exacerbated by the very small crystallites (less than a few tens of nanometers), as this results in considerable diffraction peak broadening. Also, in the absence of space group determination based on a single-crystal study, it is usually not possible to distinguish between an orthorhombic cell and a monoclinic cell with β close to 90° (e.g., Bevan et al. 2002). The only available single-crystal data for "dehydrated schoepite" are for a stoichiometric α -UO₂(OH)₂, probably synthesized via cooling of γ -UO₂(OH)₂ (Taylor 1971; Hoekstra and Siegel 1973).

Hence, there is currently no hard evidence that paulscherrerite from the Number 2 Workings is structurally different from the reported occurrences of "dehydrated schoepite" in nature. The confusion on the nature of "dehydrated schoepite" appears to have evolved from comparison between partial data sets obtained on material synthesized via different routes (e.g., Berlepsch et al. 2003 for a similar example). Further work is required to confirm and investigate the origin of the monoclinic distortion of paulscherrerite vs. α -UO₂(OH)₂, and about the variability in water content and stoichiometry of paulscherrerite, and its possible correlation with unit cell and symmetry. Polytypism is the most likely explanation for the slight structural variations affecting "dehydrated schoepite"; these do not warrant new mineral names, and are dealt with using suffixes (e.g., Guinier et al. 1984). In this context, the paulscherrerite type material provides a solid reference point on which to build our understanding of the nature of "dehydrated schoepite" in natural and engineered environments.

Occurrences of paulscherrerite

Recent assessment of the thermodynamics of metaschoepite and β -UO₂(OH)₂ by Kubatko et al. (2006) concluded that metaschoepite (and probably schoepite) may be metastable under all conditions. At 298.15 K, the Gibbs free energy for the reaction

 $UO_3 \cdot 2H_2O$ (metaschoepite) = β - $UO_2(OH)_2 + H_2O(l)$ is

 $\Delta_r G_1 = \Delta G_f^0 [UO_2(OH)_2] + \Delta G_f^0 (H_2O) - \Delta G_f^0 (metaschoepite)$ $= -1398.7 \pm 1.8 - 237.4 + 1632.0 \pm 4.0 = -4.1 \pm 4.4 \text{ kj/mol.}$

The enthalpy of formation of "dehydrated schoepite" with $UO_2 \cdot 0.9H_2O$ stoichiometry was measured using solution calorimetry by O'Hare et al. (1988) on material synthesized via hydration of $UO_3(am)$ at 90 °C. For the reaction

 $UO_3 \cdot 2H_2O$ (metaschoepite) = $UO_2 \cdot 0.9H_2O + 1.1H_2O(1)$

the Gibbs free energy of reaction at standard conditions is

 $\Delta_r G_2 = \Delta G_{f}^{0}(\text{UO}_3 \cdot 0.9\text{H}_2\text{O}) + 1.1\Delta G_{f}^{0}(\text{H}_2\text{O}) - \Delta G_{f}^{0}(\text{metaschoepite}) = -1374.4 \pm 2.6 - 1.1 \times 237.4 + 1632.0 \pm 4.0 = -3.5 \pm 4.8 \text{ kj/mol.}$

The Gibbs free energy for the transformation of β -UO₂(OH)₂ to UO₃·0.9H₂O at 25 °C is

 β -UO₂(OH)₂ = UO₃·0.9H₂O + 0.1H₂O(l)

 $\Delta_r G_3 = \Delta G_1^{0}(UO_3 \cdot 0.9H_2O) + 1.1 \Delta G_1^{0}(H_2O) - \Delta G_1^{0}[\beta - UO_2(OH)_2] = -1374.4 \pm 2.6 - 0.1 \times 237.4 + 1398.7 \pm 1.8 = 0.6 \pm 3.2 \text{ kJ/mol}.$

Overall, these calculations based on calorimetric results give little energy difference between metaschoepite, "dehydrated schoepite," and β -UO₂(OH)₂, which suggests that kinetic effects probably play a major role in controlling the paths by which "dehydrated schoepite" forms (Fig. 8).

"Dehydrated schoepite" has been reported from several environments, as well as in many experimental studies dedicated to environmental uranium mineralogy or to using uraninite as analog for the UO₂ found in some high-level radioactive waste. Paulscherrerite is a relatively common early alteration product of uraninite. Christ and Clarke (1960) analyzed "dehydrated schoepite" in schoepite crystals from Shinkolobwe (Katanga district, Democratic Republic of Congo), but showed that at least some of it may have formed from schoepite in the laboratory. Finch et al. (1992) and Finch and Ewing (1992) also observed abundant "dehydrated schoepite" together with schoepite or metaschoepite as a weathering product of uraninite from the Shinkolobwe mine. They attributed the formation of the mineral to weathering under oxidizing near-surface conditions, in a monsoonal environment characterized by extremes of wet and dry conditions. Finch et al. (1992) showed that dehydration also occured during museum storage of the specimen, and could be distinguished easily from environmental dehydration by the lack of overprinting by subsequent groundwater interaction. Pearcy et al. (1994) described a similar occurrence at the Nopal I deposit, Chihuahua, Mexico. Korzeb et al. (1997) identified "dehydrated schoepite" as an early product of uraninite weathering in the Ruggles and Palermo granitic pegmatites, New Hampshire, U.S.A.; they (erroneously) suggested a hydrothermal origin of the weathering (>100 °C) based on the lack of molecular water in paulscherrerite. Finally, Lind et al. (2009) identified "dehydrated schoepite" in soils contaminated during a fire at a depleted uranium (DU) ammunition storage facility in Kuwait in 1992, but not on DU impact residues in Kuwait or Kosovo.

Under oxidizing conditions, the solubility of uranium in solutions containing uraninite and other U⁴⁺-bearing materials can be limited by the growth onto the leached surface of secondary phases such as uranyl hydrates and carbonates: effectively the aqueous U-concentration becomes controlled by the newly formed uranyl minerals, and the solution remains heavily undersaturated with respect to uraninite (e.g., Trocellier et al. 1998). Several experimental studies regarding the rate of dissolution of uranium have observed the formation of "dehydrated schoepite." "Dehydrated schoepite" appeared within a few days on aluminum-based nuclear fuels exposed to a basic (pH ~8.4) groundwater from Yucca Mountain at 90 °C (Kaminski and Goldberg 2002). Trocellier et al. (1998) leached $UO_{2,1}$ using synthetic water with a composition similar to a thermal, granitehosted groundwater, and observed "dehydrated schoepite" in at least one experiment (162 days at pH 8.0, 96 °C). They observed that UO₂(OH)₂ appeared to limit U solubility under oxidizing conditions (Eh = 145-242 mV).

Secondary uranyl minerals can also form as uranyl-bearing solutions interact with the surface of minerals in rocks and soils. Schindler et al. (2004) conducted free-drift experiments in which the (104) surface of calcite was exposed to uranyl-bearing solutions of variable pH. In their acidic runs (initial pH 2.5, final 4.5) at 25 °C they observed the growth of schoepite, becquerelite, and wyarthite-(II). The same experiment at 100 °C showed the initial presence of "dehydrated schoepite" that was replaced by becquerelite after 2 to 3 days of contact time. Altogether, these experimental studies emphasize the importance of paulscherrerite as a transient product during weathering of uraninite/ pitchblende and interaction between uranyl-rich groundwater and minerals.

Summer air temperatures at the Number 2 Workings commonly exceed 40 °C (Australian Bureau of Meteorology, Arkaroola station), and the surface rock temperature in the black massive hematite ore forming the gangue of paulscherrerite can exceed 70 °C. Transformation of metaschoepite to "dehydrated schoepite" has been observed in our study in water at 150 °C, and transformation of rutherfordine to "dehydrated schoepite" was observed at 100 °C by Vochten and Blaton (1999). The 70 °C temperature is also close to the conditions of the studies of Schindler et al. (2004), Kaminski and Goldberg (2002), and Trocellier et al. (1998) (90–100 °C), in which "dehydrated schoepite" was produced via interaction of water with U-rich material.

In summary, paulscherrerite appears to be a relatively common secondary mineral forming from the oxidation of uraninite and pitchblende. Although we applied state-of-the-art techniques to characterize paulscherrerite, we still do not have an adequate explanation why it is monoclinic and its close analog, synthetic α -UO₂(OH)₂, is not. The significance of the variable UO₃/H₂O reported in other studies of "dehydrated schoepite" (Table 5) also needs to be further investigated. In the absence of better single crystals of natural paulscherrerite, systematic studies using modern methods of "UO₂(OH)₂" synthesized under a range of conditions and methods may help to understand the relationships between paulscherrerite and orthorhombic α -UO₂(OH)₂ and the significance and extent of non-stoichiometry in these phases.

ACKNOWLEDGMENTS

Thanks to Daniel Baumann (Swiss Federal Institute of Technology, Lausanne) for performing the thermogravimetric and IR analyses and to Judge Bevan for discussions about crystallography. The manuscript benefitted from insightful comments by R. Finch, M. Cuney, R.L. Frost, J. Grice, R. Peterson, and E. Grew.

REFERENCES CITED

- Bakker, R.J. and Elburg, M.A. (2006) A magmatic-hydrothermal transition in Arkaroola (northern Flinders Ranges, South Australia): From diopside-titanite pegmatites to hematite-quartz growth. Contributions to Mineralogy and Petrology, 152, 541–569.
- Bartlett, J.R. and Cooney, R.P. (1989) On the determination of uranium-oxygen bond lengths in dioxouranium(VI) compounds by Raman spectroscopy. Journal of Molecular Structure, 193, 295–300.
- Berlepsch, P., Armbruster, T., Brugger, J., Criddle, A.J., and Graeser, S. (2003) Tripuhyite, FeSbO₄, revisited. Mineralogical Magazine, 67, 31–46.
- Bevan, D.J.M., Rossmaith, E., Mylrea, D.K., Ness, S.E., Taylor, R.M., and Cuff, C. (2002) On the structure of aragonite—Lawrence Bragg revisited. Acta Crystallographica, B58, 448–456.
- Bignand, C. (1955) Sur les propriétés et les synthèses de quelques minéraux uranifères. Bulletin de la Société Française de Minéralogie et Cristallographie, 78, 1–26.
- Brugger, J., Ansermet, S., and Pring, A. (2003a) Uranium minerals from Mt Painter, Northern Flinders Ranges, South Australia. Australian Journal of Mineralogy, 9, 15–31.
- Brugger, J., Burns, P., and Meisser, N. (2003b) Contribution to the mineralogy of acid drainage of Uranium minerals: Marécottite and the zippeite group. American Mineralogist, 88, 676–685.
- Brugger, J., Krivovichev, S.V., Berlepsch, P., Meisser, N., Ansermet, S., and

Armbruster, T. (2004) Spriggite, $Pb_3(UO_2)_6O_8(OH)_2(H_2O)_3$, a new mineral with β -U₃O₈-type sheets: Description and crystal structure. American Mineralogist, 89, 339–347.

- Brugger, J., Long, N., McPhail, D.C., and Plimer, I. (2005) An active amagmatic hydrothermal system: The Paralana hot springs, Northern Flinders Ranges, South Australia. Chemical Geology, 222, 35–64.
- Burns, P.C. (1999) The crystal chemistry of uranium. In P.C. Burns and R. Finch. Eds., Uranium: Mineralogy, geochemistry and the environment, vol. 38, p. 23–90. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Čejka, J. (1999) Infrared spectroscopy and thermal analysis of uranyl minerals. In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, geochemistry and the environment, vol. 38, p. 521–622. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Christ, C.L. and Clark, J.R. (1960) Crystal chemical studies of some uranyl oxide hydrates. American Mineralogist, 45, 1026–1061.
- Coats, R.P. and Blissett, A.H. (1971) Regional and economic geology of the Mount Painter province. Department of Mines, Geological Survey of South Australia, Bulletin, 43, 426 pp.
- Dawson, J.K., Wait, E., Alcock, K., and Chilton, D.R. (1956) Some aspects of the system uranium trioxide-water. Journal of the Chemical Society, 3531–3540.
- Elburg, M., Bons, P., Foden, J., and Brugger, J. (2003) A newly defined Late Ordovician magmatic-thermal event in the Mt Painter Province, northern Flinders Ranges, South Australia. Australian Journal of Earth Sciences, 50, 611–631.
- Finch, R.J. and Ewing, R.C. (1992) The corrosion of uraninite under oxidizing conditions. Journal of Nuclear Materials, 190, 133–156.
- Finch, R.J., Miller, M.L., and Ewing, R.C. (1992) Weathering of natural uranyl oxide hydrates: schoepite polytypes and dehydration effects. Radiochimica Acta, 58, 433–443.
- Finch, R.J., Cooper, M.A., and Hawthorne, F.C. (1996) The crystal structure of schoepite, [(UO₂₎₈O₂(OH)₁₂](H₂O)₁₂. Canadian Mineralogist, 34, 1071–1088.
- Finch, R.J., Hawthorne, F.C., Miller, M.L., and Ewing, R.C. (1997) Distinguishing among schoepite, (UO₂)₈O₂(OH)₁₂·12H₂O, and related minerals by X-ray powder diffraction. Powder Diffraction, 12, 230–238.
- Finch, R.J., Hawthorne, F.C., and Ewing, R.C. (1998) Structural relations among schoepite, metaschoepite and "dehydrated schoepite." The Canadian Mineralogist, 36, 831–845.
- Guinier, A., Bokij, G.B., Boll-Dornberger, K., Cowley, J.M., Ďurovič, S., Jagodzinski, H., Krishna, P., de Wolff, P.M., Zvyagin, B.B., Cox, D.E., and others (1984) Nomenclature of polytype structures. Acta Crystallographica A, 40, 399–404.
- Hanson, S.L., Simmons, W.B., Falster, A.U., Foord, E.E., and Lichte, F.E. (1999) Proposed nomenclature for samarskite-group minerals: new data on ishikawaite and calciosamarskite. Mineralogical Magazine, 63, 27–36.
- Harris, L.A. and Taylor, A.J. (1962) A pressure-induced phase transformation in a UO₃ monohydrate. Journal of the American Ceramic Society, 45, 25–28.
- Hoekstra, H.R. and Siegel, S. (1973) The uranium trioxide-water system. Journal of Inorganic and Nuclear Chemistry, 35, 761–779.
- Hunter, B.A. (1998) Rietica—A visual Rietveld program. Commission for Powder Diffraction Newsletter, 20, 21.
- Kaminski, M.D. and Goldberg, M.M. (2002) Aqueous corrosion of aluminum-based nuclear fuel. Journal of Nuclear Materials, 304, 182–188.
- Korzeb, S.L., Foord, E.E., and Lichte, F.E. (1997) The chemical evolution and paragenesis of uranium minerals from the Ruggles and Palermo granitic pegmatites, New Hampshire. Canadian Mineralogist, 35, 135–144.
- Kubatko, K.A., Helean, K., Navrotsky, A., and Burns, P.C. (2006) Thermodynamics of uranyl minerals: enthalpies of formation of uranyl oxide hydrates. American Mineralogist, 91, 658–666.
- Le Bail, A., Duroy, H., and Fourquet, J.L. (1988) Ab-initio structure determination of LiSbWO₆ by X-ray powder diffraction. Materials Research Bulletin, 23, 447–452.
- Lind, O.C., Salbu, B., Skipperud, L., Janssens, K., Jaroszewicz, J., and Nolf, W.D. (2009) Solid state speciation and potential bioavailability of depleted uranium particles from Kosovo and Kuwait. Journal of Environmental Radioactivity, 100, 301–307.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. Part IV: The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.
- Meisser, N. (2003) La minéralogie de l'uranium dans le massif des Aiguilles Rouges (Alpes occidentales). Ph.D. thesis, Université de Lausanne, Switzerland, 255

p. (www.unil.ch/gse/page14040_en.html)

- Meisser, N., Brugger, J., Ansermet, S., Thélin, P. and Bussy, F. (2010) Françoisite-(Cc), a new mineral species from La Creusaz uranium deposit (Valais, Switzerland) and from Radium Ridge (Flinders Ranges, South Australia): Description and genesis. American Mineralogist, 95, 1527–1532.
- Neumann, N., Sandiford, M., and Foden, J. (2000) Regional geochemistry and continental heat flow: Implications for the origin of the South Australian heat flow anomaly. Earth and Planetary Science Letters, 183, 107–120.
- O'Hare, P.A.G., Lewis, B.M., and Nguyen, S.N. (1988) Thermochemistry of uranium compounds. XVII. Standard molar enthalpy of formation at 298.15 K of dehydrated schoepite (UO₃·0.9H₂O). Thermodynamics of (schoepite+dehydrated schoepite+water). Journal of Chemical Thermodynamics, 20, 1287–1296.
- Ondruš, P., Veselovský, F., Hlousek, J., Skála, R., Vavrín, I., Fryda, J., Čejka, J., and Gabasová, A. (1997) Minerals of the Jáchymov (Joachimsthal) ore district. Journal of the Czech Geological Society, 42, 3–76.
- Pearcy, E.C., Prikryl, J.D., Murphy, W.M., and Leslie, B.W. (1994) Alteration of uraninite from Nopal I Deposit, Pena Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. Applied Geochemistry, 9, 713–732.
- Protas, J. (1959) Contribution à l'étude des oxydes d'uranium hydratés. Bulletin de la Société française de Minéralogie et Cristallographie, 82, 239–272.
- Sandiford, M., Hand, M., and McLaren, S. (1998) High geothermal gradient metamorphism during thermal subsidence. Earth and Planetary Science Letters, 163, 149–165.
- Sandino, M.C.A. and Grambow, B. (1994) Solubility equilibria in the U(VI)-Ca-K-CI-H₂O system; transformation of schoepite into becquerelite and compreignacite. Radiochimica Acta, 66/67, 37–43.
- Schindler, M., Hawthorne, F.C., Putnis, C., and Putnis, A. (2004) Growth of uranylhydroxy-hydrate and uranyl-carbonate minerals on the (104) surface of calcite. Canadian Mineralogist, 42, 1683–1697.
- Schoep, A. and Stradiot, S. (1947) Paraschoepite and epiianthinite, two new minerals from Shinkolobwe (Belgian Congo). American Mineralogist, 32, 344–350.
- Siegel, S., Hoekstra, H.R., and Gebert, E. (1972) The structure of γ-uranyl dihydroxide, UO₂(OH)₂. I. The structure of γ-uranyl dihydroxide, UO₂(OH)₂. Acta Crystallographica, B28, 3469–3473.
- Sowder, A.G., Clark, S.B., and Field, R.A. (1996) The effect of silica and phosphate on the transformation of schoepite to becquerelite and other uranyl phases. Radiochimica Acta. 74, 45–49.
- (1999) The transformation of uranyl oxide hydrates: the effect of dehydration on synthetic metaschoepite and its alteration to becquerelite. Environmental Science and Technology, 33, 3552–3557.
- Strunz, H. and Nickel, E.H. (2001) Strunz Mineralogical Tables, 9th Edition, 870 pp. E. Schweizerbart'sche Verlagsbuchhandlung, Berlin and Stuttgart.
- Taylor, J.C. (1971) The structure of α form of uranyl hydroxide. Acta Crystallographica, B27, 1088–1091.
- Taylor, J.C. and Hurst, H.J. (1971) The hydrogen atom locations in the α and β forms of uranyl hydroxide. Acta Crystallographica, B27, 2018–2022.
- Trocellier, P., Cachoir, C., and Guilber, S. (1998) A simple thermodynamic model to describe the control of the dissolution of uranium dioxide in granitic groundwater by secondary phase formation. Journal of Nuclear Materials, 256, 197–206.
- Urbanec, Z. and Čejka, J. (1979) Infrared spectra of rutherfordine and sharpite. Collection of Czechoslovak Chemical Communications, 44, 1–9.
- Vochten, R. and Blaton, N. (1999) Synthesis of rutherfordine and its stability in water and alkaline solutions. Neues Jahrbuch f
 ür Mineralogie-Monatshefte, 1999, 372–384.
- Walker, T.L. (1923) Schoepite, a new uranium mineral from Kasolo, Belgian Congo. American Mineralogist, 8, 67–69.
- Weller, M.T., Light, M.E., and Gelbrich, T. (2000) Structure of uranium(VI) oxidedihydrate, UO₃·2H₂O; synthetic meta-schoepite (UO₂)₄O(OH)₆·5H₂O. Acta Crystallographica, B56, 577–583.

MANUSCRIPT RECEIVED MAY 11, 2010 MANUSCRIPT ACCEPTED SEPTEMBER 1, 2010

MANUSCRIPT HANDLED BY EDWARD GREW