Distinguishing among schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, and related minerals by X-ray powder diffraction

Robert J. Finch[a] and Frank C. Hawthorne
Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada
Mark L. Miller and Rodney C. Ewing
Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131

(Received 22 March 1996; accepted 18 May 1997)

We have calculated X-ray powder-diffraction data for schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, using unit-cell and atomic parameters from the crystal structure ($\boldsymbol{a}$ 14.337, $\boldsymbol{b}$ 16.813, $\boldsymbol{c}$ 14.781, $Z=4$, $D_x=4.87\ \mathrm{g\ cm^{-3}}$). Schoepite crystallizes in space group $P2_1ca$ but is strongly pseudo-centrosymmetric, and observed reflections ($I_{\mathrm{rel}}>0.1\%$) conform to space group $Pbca$. The six strongest reflections for schoepite are [d(Å), hkl (relative intensity)] 7.365, *002* (100), 3.253, *242* (55), 3.626, *240* (36), 3.223, *402* (25), 3.683, *004* (20), 2.584, *244* (18). The calculated intensities of reflections that distinguish space group $Pbca$ from space group $Pbna$ (the space group of metaschoepite), i.e., $h0l$ with h odd and l even, are weak, and may not be evident in experimental powder patterns. The $\boldsymbol{a}$ axis of schoepite (14.34 Å) is significantly longer than that of synthetic metaschoepite (13.98 Å), and the two phases can best be distinguished by their unit-cell parameters. However, potential overlap of the strongest reflections can make identification and unit-cell determination difficult, especially for fine-grained material. Natural samples commonly contain intergrowths of schoepite, metaschoepite, and dehydrated schoepite. The calculated powder pattern for schoepite agrees well with data reported for natural schoepite (PDF 13-241) but shows discrepancies with the data from synthesis products. Data for "synthetic schoepite" indicate that this product was a mixture. Powder data labeled "paraschoepite" in the Powder Diffraction File do not correspond to the mineral of that name. © *1997 International Centre for Diffraction Data.* [S0885-7156(97)00303-5]

Key words: schoepite, metaschoepite, paraschoepite, uranyl oxide hydrate, calculated powder pattern

I. INTRODUCTION

Hydrated uranium(VI) oxy-hydroxides form in oxidizing U-rich meteoric waters and are common weathering products of uraninite, UO_{2+x} (Frondel, 1958; Finch and Ewing, 1992). These minerals occur at many oxidized uranium deposits, where they play an important role in the paragenesis of secondary uranyl minerals that form where uraninite has been exposed to oxidizing meteoric water (Frondel, 1958; Deliens, 1977; Finch and Ewing, 1992; Finch *et al.*, 1992). These and related phases have also been identified as corrosion products of synthetic UO_2 and spent UO_2 nuclear fuel (Finch and Ewing, 1991; Forsyth and Werme, 1992; Wronkiewicz *et al.*, 1992, 1996) and may impact on the long-term corrosion behavior of spent nuclear fuel in a geologic repository.

The crystal structures of the uranium(VI) oxy-hydroxides are based on polyhedral sheets of the form $[(UO_2)_xO_y(OH)_z]^{(2x-2y-z)}$ (Evans, 1963; Miller *et al.*, 1996; Burns *et al.*, 1996). Most contain divalent cations in interlayer sites, but several have electrostatically neutral sheets and contain no interlayer cations. In this latter group, H_2O groups may occupy interlayer sites, bonding adjacent sheets together through H bonds (Finch *et al.*, 1996a). Of the uranium(VI) minerals without interlayer cations, three are chemically and structurally similar: schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, metaschoepite, $UO_3\cdot 2H_2O$ (?), and paraschoepite $UO_3\cdot(2-x)H_2O$ (?) (Christ and Clark, 1960; Christ, 1965; Finch *et al.*, 1996a). Ianthinite, $[(U^{4+})_2(U^{6+}O_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$, and "dehydrated schoepite," $[(UO_2)O_{0.25-x}(OH)_{1.5+2x}]$ $(0\leq x\leq 0.15)$, are also structurally related to the aforementioned minerals and are commonly intergrown with them (Christ and Clark, 1960; Pearcy *et al.*, 1994; Finch *et al.* 1996a, 1996b). Of these five minerals, the crystal structures are known for only two: schoepite (Finch *et al.*, 1996a) and ianthinite (Burns *et al.*, 1997). Two uranyl peroxides are also known: studtite, $UO_4\cdot 4H_2O$ (Walenta, 1974; Čejka *et al.*, 1996), and metastudtite, $UO_4\cdot 2H_2O$ (Deliens and Piret, 1983); however, both peroxides are readily identified by conventional methods and are not discussed here.

The polycrystalline nature of many uranyl compounds makes X-ray powder diffraction the preferred method of phase identification, which is commonly done by matching experimental powder patterns with those reported in the Powder Diffraction File (PDF). Similarities in unit-cell parameters (Table I) and X-ray powder-diffraction patterns among these phases can make correct phase identification difficult. These problems are compounded by disparities among the five patterns for schoepite and related phases reported in the PDF. The aim of this paper is to provide some

---

[a] Present address: Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

0885-7156/97/12(4)/230/9/$6.00

TABLE I. Unit-cell parameters reported for schoepite and related phases (Å).

	Schoepite Ref. 1	Schoepite Ref. 2	Schoepite (syn) Ref. 3	Metaschoepite Ref. 2	Metaschoepite (syn) Ref. 4	Paraschoepite Ref. 2	Ianthinite Ref. 5
a	14.337	14.33	14.36	13.99	13.977	14.12	7.178
b	16.813	16.79	16.66	16.72	16.696	16.83	11.473
c	14.731	14.73	14.74	14.73	14.672	15.22	30.39
	$P2_1ca$	$Pbca$	$Pbca$	$Pbna$	$Pbna$	$Pbca$	$P2_1ca$

References: 1—Finch *et al.* (1996a); 2—Christ and Clark (1960); 3—Peters (1967); 4—Debets and Loopstra (1963); 5—Burns *et al.* (1997).

clarification of the discrepancies among these powder patterns. Toward this end, we calculated the X-ray powder-diffraction pattern for schoepite by using recent structural data (Finch *et al.*, 1996a). The calculated powder pattern is compared to experimental powder patterns reported for schoepite and related phases in the PDF.

II. SCHOEPITE AND RELATED UO_3 HYDRATES

The International Mineralogical Association recognizes three hydrated uranium(VI) oxy-hydroxide minerals with compositions represented by the formula $UO_3\cdot(2\pm x)H_2O$ $(x<1)$ (Nickel and Nichols, 1992). Schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$ (or $4UO_3\cdot 9H_2O$) was originally described by Walker (1923), and the crystal structure was reported by Finch *et al.* (1996a). Schoep and Stradiot (1947) described the related mineral paraschoepite, $5UO_3\cdot 9\ 1/2H_2O$, but provided few data. Christ and Clark (1960) reported paraschoepite in a sample mixture that also contained schoepite and ''dehydrated schoepite.'' Paraschoepite was originally thought to form by partial dehydration of schoepite (Christ and Clark, 1960), but Christ (1965) suggested that schoepite and paraschoepite are polymorphs with different arrangements of O atoms in their structural sheets. Christ and Clark (1960) also described a third related mineral, metaschoepite, formed by the incomplete dehydration of schoepite. Schoepite, metaschoepite, and paraschoepite are structurally and chemically distinct from the four synthetic uranyl hydroxides, α-$UO_2(OH)_2$, β-$UO_2(OH)_2$, γ-$UO_2(OH)_2$, and $U_3O_8(OH)_2$ (Hoekstra and Siegel, 1973), none of which contains structurally bound H_2O groups. As the name implies, ''dehydrated schoepite'' is a naturally occurring dehydration product of schoepite with a structure that can be described as a defect derivative of the synthetic phase α-$UO_2(OH)_2$ (Christ and Clark 1960; Finch *et al.*, 1996b).

There has been debate as to the actual number of structurally unique hydrated uranyl oxy-hydroxide polymorphs (Hoekstra and Siegel, 1973). Most X-ray powder-diffraction studies of synthetic UO_3 hydrates indicate only one phase, equivalent to schoepite (Hoekstra and Siegel, 1973). On the other hand, infrared spectroscopy and thermogravimetric analyses commonly suggest two structurally related phases (Hoekstra and Siegel, 1973). The X-ray powder-diffraction patterns of schoepite and metaschoepite are almost indistinguishable (Hoekstra and Siegel, 1973; Finch *et al.*, 1992), because the U atoms, which contribute most strongly to the diffraction intensities, occupy structurally similar positions in both minerals. Nevertheless, Christ and Clark (1960) were able to identify both minerals and to estimate their unit-cell parameters from precession photographs of single crystals of schoepite with intergrown metaschoepite (Table I). By using their single-crystal data, Christ and Clark (1960) indexed an X-ray powder pattern from a sample mixture of schoepite and metaschoepite (PDF 13-241). Metaschoepite has a smaller unit-cell volume than schoepite, a reflection of the smaller ***a*** cell dimension in metaschoepite (Table I). Schoepite crystallizes in space group $P2_1ca$ but is strongly pseudocentrosymmetric, with apparent space group $Pbca$ (Finch *et al.*, 1996a). The space-group symmetry reported for metaschoepite is $Pbna$ (Christ and Clark, 1960; Debets and Loopstra, 1963).

The synthesis of hydrated uranyl oxy-hydroxides has been reported by numerous authors, and most of these studies used X-ray powder diffraction to identify the run products. Experimental patterns are compared with the five powder patterns reported in the PDF for hydrated uranyl oxy-hydroxides. Because synthesis near room temperature tends to produce a poorly crystalline product (Bruno and Sandino, 1989), most of the reported syntheses have been conducted between approximately 40 and 90 °C. Most of the products synthesized in this temperature range display powder-diffraction patterns that closely resemble the powder pattern of metaschoepite reported by Debets and Loopstra (1963). Above approximately 100 °C, schoepite and metaschoepite dehydrate in water to dehydrated schoepite (Hoekstra and Siegel, 1973), and most syntheses above 100 °C report mixed run products, usually including one or more of the four known uranyl hydroxides in addition to dehydrated schoepite (Hoekstra and Siegel, 1973).

Three of the five powder patterns in the PDF correspond to synthetic preparations, identified as ''schoepite, syn.'' (PDF 29-1376), ''metaschoepite, syn.'' (PDF 43-364), and ''paraschoepite, syn.'' (PDF 23-1461), and we briefly describe the syntheses of these three phases here.

Peters (1967) reported synthesizing schoepite by hydrolyzing an aqueous suspension of UO_3 and heating the product for several hours (temperature unknown). The powder pattern obtained resembles that of the natural sample mixture of schoepite and metaschoepite reported by Christ and Clark (1960). Peters (1967) indexed the powder pattern for the synthetic material as a single phase; however, the unit-cell parameters reported by Peters differ significantly from those of natural schoepite, especially the ***b*** cell dimension (Table I).

Cordfunke (1962) synthesized metaschoepite in aqueous solution at 40 °C, shaking the reaction mixture for 1–4 weeks in order to ''improve crystallinity.'' Debets and Loopstra (1963) indexed the powder pattern obtained from Cordfunke's sample, and the powder-diffraction pattern and unit-cell parameters are closely similar to those reported for metaschoepite by Christ and Clark (1960).

Synthetic paraschoepite is unknown. The powder pattern, PDF 23-1461, is erroneously labeled "paraschoepite," causing much confusion. These data correspond to a mixed-valence uranium oxide, $UO_{2.86}\cdot 1.5H_2O$, structurally and chemically similar to ianthinite (Cordfunke *et al.*, 1968). The phase $UO_{2.86}\cdot 1.5H_2O$ is not paraschoepite as described either by Schoep and Stradiot (1947) or by Christ and Clark (1960). The powder pattern for $UO_{2.86}\cdot 1.5H_2O$ resembles those of schoepite and metaschoepite (Table III), but this is true of powder patterns for many of the uranyl oxide hydrates, owing to close structural similarities among these phases (Burns *et al.*, 1996).

III. THE CALCULATED POWDER PATTERN FOR SCHOEPITE

A powder-diffraction pattern for schoepite was calculated for Cu $K\alpha$ X-radiation ($\lambda = 1.5418$ Å) with the program POWD (VAX version 12.7; Smith, 1989). Interplanar spacings are reported for 2θ values from 5° to 60° only for reflections with calculated relative intensities 0.5% or greater (Table II).

The calculated relative intensity $I_{hkl}(\text{rel})$ of each reflection is given by

$$I_{hkl}(\text{rel}) = kM_{hkl}LpAT|F_{hkl}|^2.$$

$I_{hkl}(\text{rel})$ is the diffracted intensity on a relative scale, k is a scale factor used to place the data on the relative scale, M_{hkl} is the multiplicity factor, LP is the Lorentz-polarization factor ($\text{LP} = [1 + \cos^2 2\theta]/\sin^2\theta\cos\theta$; where θ is the Bragg angle), A is the absorption factor (see below), T is the Debye–Waller temperature factor [$T = \exp(-B\sin^2\theta/\lambda^2)$; where B is the displacement factor and λ is the X-ray wavelength], and F_{hkl} is the structure factor. Each $I_{hkl}(\text{rel})$ is scaled such that the strongest intensity is equal to 100; for schoepite, this is the 002 interplanar spacing, equivalent to the layer spacing in the schoepite structure.

For a diffractometer, the absorption of X-rays by a flat specimen is independent of scattering angle for a specimen of infinite thickness, and the absorption factor is $A = 1/2\mu$ (Cullity, 1981). A sample can be assumed to be infinitely thick if $\mu t > 2.5$ (μ = effective absorption coefficient; t = sample thickness). The linear absorption coefficient for schoepite is 36.47 mm^{-1} (Finch *et al.*, 1996a), and, assuming a powder with 50% packing efficiency, infinite thickness corresponds to approximately 0.14 mm. To calculate the diffracted intensities for cylindrical Debye–Scherrer samples, the tables of cylindrical absorption factors in terms of μ and r, the sample radius, in the International Tables (1969) are used. When using cylindrical samples of moderate absorbers, absorption causes the front reflection peaks to be relatively weaker then those in the backreflection region, and heavily absorbing samples may split forward reflected beams into two parts. Schoepite may be considered a moderate absorber, and the latter effect has not been reported for schoepite powder patterns.

Schoepite is noncentric, space group $P2_1ca$, and anomalous dispersion is accounted for by generating negative Miller indices, ($-h$-k-l) for each hkl normally generated. The intensity pairs are then averaged and listed under one index. Complex neutral scattering factors are used

TABLE II. Calculated powder pattern for schoepite, $I_{\text{rel}} \geqslant 1\%$ (Cu-$K\alpha$ radiation: $2\theta < 60°$).

hkl	d_{calc}	I (INT)	I (DS)	I (PK)	2θ (PK)
020	8.406	1	0	1	10.52
002	7.365	100	69	100	12.02
021	7.301	1	1		
211	6.019	2	2	2	14.72
221	5.115	1	1	1	17.32
222	4.383	0	1		
123	4.066	0	1		
041	4.042	1	1	1	21.98
213	3.938	1	1	1	22.56
232	3.787	0	1		
004	3.683	20	31	15	24.16
223	3.649	0	1		
240	3.626	36	56	27	24.54
400	3.584	17	27	13	24.82
104	3.567	0	1		
142	3.538	0	1		
410	3.505	1	1		
411	3.410	0	1		
242	3.253	55	100	41	27.40
402	3.223	25	46	19	27.66
043	3.193	0	1		
323	3.172	0	1	1	28.18
412	3.165	1	1		
431	2.958	2	3	1	30.18
511	2.776	0	1		
061	2.753	1	1		
125	2.730	0	1		
144	2.720	0	1		
351	2.703	0	1		
215	2.690	0	1		
441	2.682	0	1		
062	2.619	0	1		
260	2.610	0	1		
244	2.584	18	46	12	34.70
162	2.576	0	1		
433	2.572	1	2	7	34.78
261	2.570	1	2		
404	2.569	9	22	7	34.90
522	2.547	0.5	3		
414	2.539	0	1		
262	2.460	0	1		
006	2.455	5	13	3	36.58
063	2.434	0	1		
106	2.420	0	1		
451	2.419	0	1		
116	2.395	0	1		
443	2.384	0	1		
611	2.336	2	7	2	38.52
126	2.326	0	1		
263	2.305	0	1		
362	2.297	0	1		
621	2.271	0	1		
271	2.251	1	3	1	40.02
064	2.230	0	1		
460	2.208	1	3		
630	2.198	0	1		
453	2.194	0	1		
461	2.183	1	4		
631	2.174	0	1		
363	2.169	0	1		
316	2.166	0	1		
613	2.131	1	4	1	42.38
264	2.129	0	1		
462	2.115	0	1		
435	2.109	0.5	1		
632	2.106	0	1		
080	2.102	5	17	3	43.00
146	2.097	0	1	2	43.12
623	2.082	0	1		
640	2.077	9	33	6	43.54
273	2.066	0	1		
027	2.041	0	1		
515	2.040	0	1		
336	2.035	0	1		
246	2.033	13	47	8	44.54
065	2.030	0	1		

TABLE II. (*Continued.*)

hkl	d_{calc}	I (INT)	I (DS)	I (PK)	2θ (PK)
406	2.026	6	22	5	44.68
127	2.021	0	1		
082	2.021	6	23	6	44.82
463	2.013	1	2	2	44.92
416	2.011	0	1		
165	2.010	0	1		
633	2.006	0	1		
217	2.005	0	1		
445	2.001	0	1		
642	1.9993	12	44	8	45.32
281	1.9981	1	3		
525	1.9961	0	1		
265	1.9536	0	1		
650	1.9478	0	1		
651	1.9310	0	1		
464	1.8935	0.5	2		
634	1.8874	0	1		
455	1.8848	0	1		
652	1.8831	1	2		
327	1.8773	0	1		
283	1.8655	0.5	2		
506	1.8649	0	1		
066	1.8466	0	1		
615	1.8446	1	4		
008	1.8414	3	13	2	49.46
356	1.8315	0	1		
108	1.8264	0	1		
084	1.8253	5	20	3	49.92
118	1.8157	0	1		
480	1.8130	4	17	2	50.28
644	1.8093	8	36	6	50.40
275	1.8018	0	1	2	50.52
800	1.7921	2	8	1	50.92
266	1.7883	0	1		
810	1.7820	0	1		
811	1.7691	0	1		
465	1.7667	0	2		
635	1.7618	0	1		
482	1.7604	7	32	4	51.90
802	1.7413	3	14	2	52.52
138	1.7365	0	1		
812	1.7321	0	1		
437	1.7265	0.5	2		
654	1.7218	0	1		
318	1.7093	0	1		
831	1.6956	2	8		
671	1.6829	1	6		
067	1.6827	0	1		
813	1.6751	0	1		
148	1.6751	0	1		
167	1.6713	0	1		
0101	1.6705	0	1		
285	1.6642	0	1		
527	1.6630	0	1		
565	1.6571	0	1		
672	1.6509	0	1		
744	1.6468	0	1		
338	1.6428	0	1		
248	1.6418	7	36		
466	1.6416	0	1		
0102	1.6391	0	1		
267	1.6382	0	1		
408	1.6379	4	18		
636	1.6376	0	1		
2100	1.6369	0	1		
418	1.6302	0	1		
2101	1.6269	1	4		
484	1.6265	5	25		
833	1.6123	1	5		
804	1.6115	2	8		
673	1.6014	1	4		
2102	1.5972	0	2		
086	1.5966	3	14		
646	1.5858	5	21		
2103	1.5529	1	4		

(Cromer and Mann, 1968) with corrections for anomalous dispersion (Cromer and Liberman, 1970). Anisotropic displacement parameters are used for the U atoms and isotropic displacement parameters are used for the O atoms; these values are tabulated in Finch *et al.* (1996a). Refraction is ignored. Preferred orientation is also ignored, although this may be an important factor in experimental patterns, thereby enhancing 00*l* reflections. The calculated powder pattern is given in Table II.

IV. SCHOEPITE AND THE PDF

Five experimental X-ray powder-diffraction patterns for schoepite and related phases are reported in the PDF: schoepite (natural and synthetic), metaschoepite (synthetic), and paraschoepite (natural and synthetic). The powder patterns for all but synthetic metaschoepite are from film data, and the film data for the minerals were not corrected for film shrinkage (Christ and Clark, 1960). These five powder patterns are compared to the powder pattern calculated for schoepite in Table III.

The *hkl* indexing in Table III is for the calculated schoepite pattern (cf. Table II). Interplanar spacings are listed for calculated relative intensities greater than 0.4%. The most intense reflection for each experimental powder pattern is indicated by a subscript *x*. Additional *hkl* indices reported for synthetic metaschoepite (PDF 43-364) and synthetic schoepite (PDF 29-1376) are also given, and schoepite reflections with *calculated* intensities of 0% are indicated in Table III by an asterisk (*). The indexing for the mixed-phase sample of natural schoepite and metaschoepite is from Christ and Clark (1960) and not from PDF 13-241. The indexing for paraschoepite (labeled *schoepite*, PDF 13-407) also corresponds to that of Christ and Clark (1960) for a (second) mixed-phase sample. The indexing for synthetic schoepite is that given in PDF 29-1376. Interplanar spacings due to impurities of dehydrated schoepite are in parentheses.

A. Natural schoepite (13-241)

This sample contained a mixture of schoepite and metaschoepite (Christ and Clark, 1960). Despite the mixed-phase nature of the sample, the powder pattern is indexed as a single phase in the PDF. The revised indexing does not agree with that proposed by Christ and Clark (1960) and is incorrect, as indicated by the relative intensities of the calculated pattern. On the other hand, the indexing proposed by Christ and Clark (1960) is in excellent agreement with the calculated pattern if the reflections due to metaschoepite are considered (Table III). By using the indexing of Christ and Clark (1960) for each mineral and considering each phase separately, we refined the unit-cell parameters for schoepite ($P2_1ca$): ***a*** 14.30(1), ***b*** 16.77(2), ***c*** 14.659(8) Å; the refined unit-cell parameters for metaschoepite ($Pbna$) are: ***a*** 14.00(1), ***b*** 16.64(3), ***c*** 14.67(1) Å. These values agree well with the reported unit-cell parameters (Table I). Some discrepancy is expected for this film data, because they were obtained from a mixed-phase sample and uncorrected for film shrinkage (Christ and Clark, 1960).

TABLE III. Comparison of X-ray powder-diffraction patterns of schoepite and related phases. (Cu $K\alpha$ radiation: $5<2\theta<60°$).

S_S Ref. 2	‡S_N Ref. 1	Schoepite		MS_S Ref. 3	‡MS_N Ref. 1	PS_N Ref. 1	IAN_N Ref. 4	PS_S Ref. 5
d_{obs}	d_{obs}	d_{calc}	hkl	d_{obs}	d_{obs}	d_{obs}	d_{obs}	d_{obs}
		8.7669	111	8.64				
		8.4065	020	8.33				
						7.59	7.63_x	7.53_x
7.37_x	7.35_x	7.3655_x	002	7.33_x	7.35_x	7.28_x		
		7.3013	021					
		6.5062	121	6.439				
6.65†		6.5941	210					
		6.1044	112	6.055			5.90	5.92
		6.0186	211					
		5.5399	022	5.510				
		5.4546	220	5.364			5.35	5.32
		5.1152	221	5.035				
						(5.08)		5.07
		4.9200	131	4.871				
	4.46	4.4777	113	4.452	4.46	4.43		
		4.3835	222	4.326				
		4.3882	311	4.291				4.26
		4.2033	040	4.174				
		4.0419	041	4.013				4.02
		3.9384	213					
		2.8997	312	3.829				
						3.78	3.81	3.76
3.69	3.66	3.6828	004	3.667	3.66	3.66		
	3.62	3.6259	240	3.583	3.58	3.59		
		*3.6186	322	3.559			3.59	3.56
3.59	3.58	3.5843	400	3.493	3.49	3.51		
3.52		3.5304	331					
		*3.5208	241	3.482				
		3.5055	410					
						(3.44)		
		3.4102	411	3.330		(3.39)	3.35	3.32
		*3.3558	313	3.307				
3.235	3.24	3.2531	242	3.220	3.21	3.22	3.24	3.22
		3.2229	402	3.156	3.162	3.162		3.17
3.170		3.1958	151					
		3.1653	412					
		*3.0195	430	2.959			2.95	2.961
2.985		2.9916	152					
		2.9580	431					
		2.9169	243	2.889				2.920
						(2.885)		
		2.8443	115	2.832				2.839
		2.8281	234	2.804				
	2.810	2.8135	252					
2.780		2.7759	511					
		2.7528	061	2.734				
		2.7034	351	2.668			2.69	2.665
		2.6817	441	2.634				2.645
		2.6099	260	2.585			2.61	2.587
2.580		2.5838	244	2.563				
		2.5721	433					
	2.571	2.5686	404	2.529	2.530			
2.550		2.5698	261					
		2.5465	522					
		2.5391	414			(2.539)		
		2.5152	531	2.462			2.53	2.513
						(2.481)		2.490
		2.4565	424	2.420				
2.455	2.446	2.4552	006	2.445	2.446	2.450		
		2.3953	116	2.383			2.39	2.384
		2.3657	610	2.3068	2.31			2.363
	2.31	2.3358	611					
2.285		2.2967	362					
		2.2892	335	2.2674				
2.260		2.2774	270					
		2.2710	621				2.30	2.273

TABLE III. (*Continued.*)

S_S Ref. 2 d_{obs}	‡S_N Ref. 1 d_{obs}	Schoepite d_{calc}	Schoepite hkl	MS_S Ref. 3 d_{obs}	‡MS_N Ref. 1 d_{obs}	PS_N Ref. 1 d_{obs}	IAN_N Ref. 4 d_{obs}	PS_S Ref. 5 d_{obs}
		2.2554	415	2.2259			2.24	2.259
		*2.2524	612	2.2010				
		2.2507	271					2.219
		2.1900	155	2.1771				
		2.1832	461	2.1528				2.169
		2.1335	173	2.1184			2.15	2.158
		2.1313	613					2.129
						(2.110)		
	2.090	2.1016	080	2.0863	2.090			
2.090		2.0972	146					
2.060		2.0806	081	2.0661				
		2.0773	640	2.0342				
2.040		2.0590	181			(2.053)	2.07	2.053
		2.0330	246	2.0195			2.03	2.040
		2.0255	406	2.0038				
		2.0210	082	2.0072				
2.000		2.0167	280			(2.018)		
		2.0110	463	1.9888			1.992	2.005
		1.9993	642	1.9599				1.972
1.980		1.9923	174				1.956	
		1.9321	083	1.9194			1.929	1.935
		1.9259	472	1.9030			1.899	
		1.9310	651	1.8951				
		*1.9131	643	1.8775				
		1.8771	554	1.8496				
1.849		1.8555	563					
		1.8414	008	1.8348				
		1.8253	084	1.8140			1.842	1.822
1.823		1.8247	446					
		*1.8201	247	1.8089				
1.8024		1.8130	480	1.7925				
		1.8093	644	1.7789			1.794	1.779
		1.7921	800	1.7474				
		1.7739	427	1.7566				1.770
		1.7691	811	1.7263				
		1.7604	482	1.7412			1.746	1.723
		1.7413	802	1.6998				
		*1.7332	193	1.7208				
		*1.7007	483	1.6819				
		1.6956	831					
		1.6880	517	1.6681				
		1.6829	671	1.6559			1.681	1.687
		1.6418	248	1.6326				1.661
		1.6379	408	1.6250				
		1.6269	2101	1.6137				
		1.6265	484	1.6098				1.622
		1.6123	833					
		1.6115	804	1.5774				
		1.6014	673					1.609
		1.5966	086	1.5869				
		1.5858	646	1.5644			1.582	1.585
								1.580
		1.5529	2103	1.5414				

References: 1—Christ and Clark (1960); 2—Peters (1967); 3—Debets and Loopstra (1963); 4—Guillemin and Protas (1959); 5—Cordfunke *et al.* (1968).
Notes: S_N = natural schoepite, S_S = synthetic schoepite, MS_N = natural metaschoepite, MS_S = synthetic metaschoepite, PS_N = natural paraschoepite, IAN_N = natural ianthinite; PS_S = synthetic "paraschoepite" ($UO_{2.86} \cdot 1.5H_2O$). Indexing is for the calculated schoepite pattern (Table II); *d* spacings indicated for all $I_{calc} > 0.4\%$ plus additional diffraction maxima for synthetic metaschoepite (PDF 43-364) and synthetic schoepite (PDF 29-1376). Indexing for (natural) schoepite, metaschoepite, and paraschoepite are from (Christ and Clark, 1960); indexing for synthetic schoepite is from the PDF 29-1376. The most intense reflection for each pattern is indicated by a subscript *x*; *d* spacings for "dehydrated schoepite" ($UO_3 \cdot 0.75H_2O$) are in parentheses.

*Schoepite reflections with *calculated* intensities less than 0.01%.

‡Data for natural schoepite (S_N) and metaschoepite (MS_N) are from the same sample (Christ and Clark, 1960).

†This *d* spacing does not agree well with the reported unit-cell parameters of schoepite or metaschoepite (Table I).

B. Synthetic schoepite (29-1376)

This sample is reported to be a single phase (Peters, 1967), and the powder pattern resembles that of the natural sample of mixed schoepite and metaschoepite described above (Christ and Clark, 1960). However, the reported unit-cell parameters differ significantly from those of schoepite; the ***b*** cell dimension is particularly short (Table I). Several *d* spacings and their relative intensities are also at variance with schoepite powder patterns reported elsewhere (Table III). The indexing reported in PDF 29-1376 is not that proposed by Peters (1967) and has been revised from his original indexing.

This powder pattern can be reindexed as a mixture of schoepite and metaschoepite. Seven diffraction maxima can be indexed on the schoepite unit cell, giving refined cell parameters ***a*** 14.35(3), ***b*** 16.71(2), ***c*** 14.74(1) Å ($P2_1ca$), and eight diffraction maxima can be indexed on the metaschoepite unit cell, giving refined cell parameters: ***a*** 14.08(1), ***b*** 16.71(1), ***c*** 14.74(1) Å ($Pbna$) (note that some diffraction maxima can be indexed on both unit cells). Eleven diffraction maxima cannot be attributed uniquely to either phase: 6.65, 2.985, 2.285, 2.260, 2.060, 2.040, 2.000, 1.980, 1.849, 1.823, and 1.8024 Å. Given the extensive overlap of schoepite and metaschoepite reflections, the poor fit for those diffraction maxima with values less than ~2 Å is probably a result of overlapping peaks from both phases. The two low-intensity diffraction maxima, 2.985 and 2.285 Å, may correspond to overlapped metaschoepite diffraction peaks (Table III). The 6.65 Å *d* spacing (20% relative intensity) is most problematic, as no diffraction maxima are reported (or calculated) with this *d* spacing for schoepite or metaschoepite (Tables II and III). Furthermore, a *d* spacing of 6.65 Å for the 210 reflection does not even agree with the unit-cell parameters reported by Peters (1967). We conclude that the 6.65 Å *d* spacing is spurious and not representative of either schoepite or metaschoepite.

C. Synthetic metaschoepite (43-364)

This powder pattern and reported unit-cell parameters are closely similar to those of natural metaschoepite (Christ and Clark, 1960) (Table I). Although the powder pattern of synthetic metaschoepite also closely resembles that of schoepite (Table III), there are important differences that can be used to distinguish between metaschoepite and schoepite with powder-diffraction data. Nine diffraction maxima in the powder pattern of synthetic metaschoepite correspond to interplanar spacings with zero intensity in the calculated pattern for schoepite (Table III): 322, 241, 313, 430, 612, 643, 247, 193, and 483; and each is marked with an asterisk in Table III. The 241 reflection of metaschoepite (10% relative intensity) is the strongest of these nine reflections; the relative intensities of the other eight reflections are at or below 5%. X-ray powder-diffraction data obtained from samples that contain metaschoepite may display these diffraction maxima, although the 241 reflection may be the only one observed in most experimental patterns.

D. Natural paraschoepite (13-407)

This powder pattern was obtained from a mixture of paraschoepite, schoepite, and dehydrated schoepite (Christ and Clark, 1960). Nonetheless, the powder pattern is labeled *schoepite* and is indexed as a single phase in the PDF (Table III). Reindexing only those diffraction maxima that can be unambiguously assigned to either schoepite or metaschoepite [d(Å), hkl:7.28, 002; 4.43, 113; 3.66, 004; 3.162, 402; 2.450, 006] allows us to refine the unit-cell parameters, giving ***a*** 14.03(3), ***b*** 16.70(5), ***c*** 14.67(2) Å ($Pbna$). These are in good agreement with the unit-cell parameters of metaschoepite (Table I). Of the 11 remaining diffraction maxima, nine can be assigned to dehydrated schoepite (shown in parentheses in Table III and noted in PDF 13-407), and two can be assigned to ianthinite (several ianthinite diffraction maxima also overlap with diffraction maxima for dehydrated schoepite and metaschoepite). Ianthinite is a common precursor of schoepite (Schoep and Stradiot, 1947; Finch and Ewing, 1992; Pearcy *et al.*, 1994; Burns *et al.*, 1997), and oriented inclusions of ianthinite within crystals of schoepite are common (Schoep and Stradiot, 1947). Although Christ and Clark (1960) identified paraschoepite from single-crystal precession photographs, we have obtained precession photographs of metaschoepite with oriented intergrowths of ianthinite or becquerelite that closely mimic the data reported for paraschoepite (our unpublished results). We conclude, therefore, that the sample described by Christ and Clark (1960) as paraschoepite was a mixture of metaschoepite, dehydrated schoepite, and ianthinite, as proposed by Finch *et al.* (1992).

E. "Synthetic paraschoepite" (23-1461)

Synthetic paraschoepite is unknown, and the mislabeling of this powder pattern has caused confusion. These data were obtained from a mixed-valence uranium oxide, $UO_{2.86}\cdot 1.5H_2O$, similar to ianthinite (Cordfunke *et al.*, 1968). The phase $UO_{2.86}\cdot 1.5H_2O$ is not paraschoepite as described by either Schoep and Stradiot (1947) or Christ and Clark (1960). The powder pattern for $UO_{2.86}\cdot 1.5H_2O$ resembles those of schoepite and metaschoepite (Table III), but the X-ray powder patterns of many uranyl oxide hydrates are similar because of their close structural similarities. As noted above, the apparent match with paraschoepite is possible only if diffraction maxima in the paraschoepite powder pattern that correspond to dehydrated schoepite are also included (Table III). Although Cordfunke *et al.* (1968) did not index this powder pattern or report unit-cell parameters, the PDF data are indexed and unit-cell parameters are reported there. The unit-cell parameters are different from those of known uranyl oxide hydrates, and this indexing is probably in error; the unit-cell parameters of $UO_{2.86}\cdot 1.5H_2O$ are probably similar to those of ianthinite (Guillemin and Protas, 1959) (Table III).

V. DISCUSSION

Between 5° and 80° 2θ, there are 1119 allowed reflections in the calculated X-ray powder-diffraction pattern of schoepite. Most of these reflections (~95%) have calculated intensities below 1%, and will be difficult to observe above background, unless enhanced by preferred orientation. Also, in this range, all reflections that are not in accord with the extinction conditions of the b glide in space group $Pbca$

$(0kl,\ k=2n)$ have calculated relative intensities below 0.1%. Additional hkl reflections, which would be systematically absent in $Pbna$ but allowed in $Pbca$ ($h0l$, with h odd and l even) have calculated intensities below 1% (Table II). Schoepite powder data are approximately consistent with $Pbna$ symmetry, and it is only with difficulty that X-ray powder diffraction for schoepite and metaschoepite can be used to distinguish between space groups $Pbca$, $Pbna$, and $P2_1na$. In the absence of single-crystal methods, the most reliable way to distinguish schoepite and metaschoepite from their X-ray powder-diffraction data is to compare their unit-cell parameters (Table I).

An additional difficulty in distinguishing between data for schoepite and metaschoepite is that several of the most diagnostic reflections overlap. Of the most intense reflections, five occur between 24° and 28° 2θ; 004, 240, and 400 are within 1.4° 2θ of each other, and 242 and 402 are within 1.0° 2θ (Table II). Overlap of diffraction peaks will be most severe for fine-grained or poorly crystalline samples due to peak broadening, a problem that is common among synthesis products and uranium minerals. Profile-fitting programs may be used to decompose overlapping peaks and are especially useful for examining samples that may be mixtures (Finch *et al.*, 1992).

The temperature of synthesis can be another important consideration in distinguishing between synthetic schoepite and synthetic metaschoepite. Schoepite is stable in water below approximately 40 °C, whereas metaschoepite is stable between approximately 40 and 90 °C (Cordfunke, 1962; Finch *et al.*, 1996b). Natural schoepite crystals alter spontaneously in air to metaschoepite by losing some molecular H_2O (Christ and Clark, 1960), and many natural samples are mixtures of schoepite and metaschoepite (Christ and Clark, 1960; Finch *et al.*, 1996b). Schoepite may also decompose directly to dehydrated schoepite:

$$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}\Rightarrow 8[(UO_2)O_{0.25}(OH)_{1.5}]+12H_2O,$$

and the three-phase mixture, schoepite + metaschoepite + dehydrated schoepite, is common in natural samples (Finch *et al.*, 1996b). Other minerals that occur intergrown with schoepite or metaschoepite include ianthinite, becquerelite, fourmarierite, and vandendriesscheite. Inclusions of these minerals and dehydrated schoepite with schoepite and/or metaschoepite can give rise to X-ray powder patterns similar to that attributed to paraschoepite (PDF 13-407; Christ and Clark, 1960).

VI. CONCLUSIONS

(1) The X-ray powder-diffraction pattern of schoepite is consistent with $Pbca$ symmetry and differs little from that of metaschoepite with $Pbna$ symmetry. Thus powder-diffraction patterns of schoepite are difficult to distinguish from those of metaschoepite, based on peak positions and intensities alone.

(2) The calculated powder pattern for schoepite shows good agreement with the experimental powder pattern of natural schoepite in the PDF (13-241), provided that additional diffraction maxima due to metaschoepite are considered. Intensity variations in experimental powder patterns of schoepite are common due to preferred (001) orientation.

(3) The powder pattern for natural "paraschoepite" (PDF 13-407) is a composite pattern from a three-phase mixture of metaschoepite + dehydrated schoepite + ianthinite.

(4) The powder pattern for "synthetic schoepite" (PDF 29-1376) is a composite pattern from a two-phase mixture of schoepite and metaschoepite. Furthermore, the 6.65 Å 210 d spacing (20% relative intensity) is spurious and not characteristic of either schoepite or metaschoepite.

(5) The powder pattern for "synthetic paraschoepite" (PDF 23-1461) is mislabeled, and these data are from a mixed-valence uranium oxide, $UO_{2.86}\cdot 1.5H_2O$, related to ianthinite.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through Major Equipment, Operating and Infrastructure grants to F.C.H. R.J.F. gratefully acknowledges an NSERC International Fellowship. Financial support for R.C.E. was provided by DOE-BES (Grant No. DE-FG03-95ER14540). Helpful comments by two anonymous reviewers improved the manuscript.

Burns, P. C., Finch, R. J., Hawthorne, F. C., Miller, M. L., and Ewing, R. C. (**1997**). "The crystal structure of ianthinite, $[U^{4+}{}_2(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$, a possible phase for Pu^{4+} incorporation during oxidation of spent nuclear fuel," J. Nucl. Mater. (in press).

Burns, P. C., Miller, M. L., and Ewing, R. C. (**1996**). "U^{6+} minerals and inorganic phases: A comparison and hierarchy of crystal structures," Can. Mineral. **34**, 845–880.

Bruno, J., and Sandino, A. (**1989**). "The solubility of amorphous and crystalline schoepite in neutral to alkaline aqueous solutions," in *Scientific Basis for Nuclear Waste Management XII*, edited by W. Lutze and R. C. Ewing [Mater. Res. Soc. Symp. Proc. **127**, 871–878].

Čejka, J., Sejoora, J., and Deliens, M. (**1996**). "New data on studtite, $UO_4\cdot 4H_2O$, from Shinkolobwe, Shaba, Zaire," Neues Jahrb. Mineral. Mh. **H3**, 125–134.

Christ, C. L., and Clark, J. R. (**1960**). "Crystal chemical studies of some uranyl oxide hydrates," Am. Mineral. **45**, 1026–1061.

Christ, C. L. (**1965**). "Phase transformations and crystal chemistry of schoepite," Am. Mineral. **50**, 235–239.

Cordfunke, E. H. P., Prins, G., and Van Vlaanderen, P. (**1968**). "Preparation and properties of the violet 'U_3O_8 hydrate,' " J. Inorg. Nucl. Chem. **30,** 1745–1750.

Cordfunke, E. H. P. (1962). "On the uranates of ammonium-I. The ternary system NH_3–UO_3–H_2O," J. Inorg. Nucl. Chem. **24,** 303–307.

Cromer, D. T., and Liberman, D. (**1970**). "Relativistic calculations of anomalous scattering factors," J. Chem. Phys. **53,** 1891–1898.

Cromer, D. T., and Mann, J. B. (**1968**). "X-ray scattering factors computed from numerical Hartree–Fock wave functions," Acta Crystallogr. **A24,** 321–324.

Cullity, B. D. (**1981**). *Elements of X-ray Diffraction* (Addison-Wesley, Reading, Mass.), p. 555.

Debets, P. C., and Loopstra, B. O. (1963). "On the uranates of ammonium-II. X-ray investigations in the system NH_3–UO_3–H_2O," J. Inorg. Nucl. Chem. **25,** 945–953.

Deliens, M. (**1977**). Associations de minéraux secondaires d'uranium à Shinkolobwe (région du Shaba, Zaïre)," Bull. Soc. Fr. Minéral. Cristallogr. **100**, 32–38.

Deliens, M., and Piret, P. (**1983**). "Metastudtite, $UO_4\cdot H_2O$ a new mineral from Shinkolobwe, Shaba, Zaire," Am. Mineral. **68,** 456–458.

Evans, H. T. (**1963**). "Uranyl ion coordination," Science **141**, 154–158.

Finch, R. J., Cooper, M. A., Hawthorne, F. C., and Ewing, R. C. (**1996a**). "The crystal structure of schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$," Can. Mineral. **34**, 1071–1088.

Finch, R. J., Hawthorne, F. C., and Ewing, R. C. (**1996b**). "Schoepite and dehydrated schoepite," in *Scientific Basis for Nuclear Waste Management XIX*, Murphy, W. M., and Knecht, D. A., eds. [Mater. Res. Soc. Symp. Proc. **412,** 361–368].

Finch, R. J., and Ewing, R. C. (**1992**). "The corrosion of uraninite under oxidizing conditions," J. Nucl. Mater. **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," Radiochim. Acta **58/59,** 433–443.

Finch, R. J., and Ewing, R. C. (**1991**). "Uraninite alteration in an oxidizing environment and its relevance to the disposal of spent nuclear fuel," SKB Technical Report No. **91–15** (Swedish Nuclear Fuel and Waste Management Co., Stockholm), p. 114.

Forsyth, R., and Werme, L. O. (**1992**). "Spent fuel corrosion and dissolution," J. Nucl. Mater. **190,** 3–19.

Frondel, C. (**1958**). Systematic Mineralogy of Uranium and Thorium. U. S. Geol. Surv. Bulletin No. **1064,** 400.

Guillemin, C., and Protas, J. (1959). "Ianthinite et wyartite," Bull. Soc. Fr. Minéral. Cristallogr. **82,** 80–86.

Hoekstra, H. R., and Siegel, S. (**1973**). "The uranium trioxide–water system," J. Inorg. Nucl. Chem. **35,** 761–779.

International Tables for X-ray Crystallography (**1969**). (Kynoch, Birmingham, England, p. 558).

Miller, M. L., Finch, R. J., Burns, P. C., and Ewing, R. C. (**1996**). "Description and classification of uranium oxide hydrate sheet anion topologies," J. Mater. Res. **11,** 3048–3056.

Nickel, E. H., and Nichols, M. C. (**1992**). *Mineral Reference Manual* (Van Norstrand Reinhold, New York, p. 250).

Pearcy, E. C., Prikryl, J. D., Murphy, W. M., and Leslie, B. W. (**1994**). "Alteration of uraninite from the Nopal I deposit, Peña 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," Appl. Geochem. **9**, 713–732.

Peters, J.-M. (**1967**). "Synthesis et étude radiocristallographique d'uranates synthétiques du type oxyde double d'uranyle," Mem. Soc. R. Sci. Liège, ser. 5, vol. 14, fasc. 3, 6–59.

Schoep, A., and Stradiot, S. (**1947**). "Paraschoepite and epiianthinite, two new uranium minerals from Shinkolobwe (Belgian Congo),"Am. Mineral. **32,** 344–350.

Smith, D. K. (**1989**). POWD, a computer program for calculating X-ray powder diffraction patterns. VAX version 12.7—5 June, 1989. Department of Geosciences, The Pennsylvania State University.

Walker, T. L. (**1923**). "Schoepite, a new uranium mineral from Kasolo, Belgian Congo," Am. Mineral **8**, 67–69.

Walenta, K. (**1974**). "On studtite and its composition,"Am. Mineral. **59,** 166–171.

Wronkiewicz, D. J., Bates, J. K., Wolf, S. F., and Buck, E. C. (**1996**). "Ten-year results from unsaturated drip tests with UO_2 at 90 °C: Implications for the corrosion of spent nuclear fuel," J. Nucl. Mater. **238,** 78–95.

Wronkiewicz, D. J., Bates, J. K., Gerding, T. J., Veleckis, E., and Tani, B. S. (**1992**). "Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90 °C," J. Nucl. Mater. **190,** 107–127.