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STRUCTURAL RELATIONS AMONG SCHOEPITE, METASCHOEPITE AND "DEHYDRATED SCHOEPITE"

ROBERT J. FINCH[1] AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

RODNEY C. EWING

Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

ABSTRACT

Schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, transforms slowly in air at ambient temperature to metaschoepite, $UO_3 \bullet nH_2O$ ($n \approxeq 2$), and crystals commonly contain an intergrowth of both minerals. The transformation may be due to the loss of one-sixth of the interlayer H_2O groups in schoepite, and a possible structural formula for metaschoepite is $[(UO_2)_8O_2(OH)_{12}](H_2O)_{10}$. The transformation of schoepite (*a* 14.337, *b* 16.813, *c* 14.731 Å, $P2_1ca$) to metaschoepite (*a* 13.99, *b* 16.72, *c* 14.73 Å, *Pbna*) is characterized by a 2% decrease in the *a* cell dimension, a slight decrease in the *b* dimension, and little or no change in the *c* dimension. Unit-cell changes probably reflect the reorganization of H-bonds. Differences in unit-cell volumes induce strain in crystals in which the transformation to metaschoepite is incomplete, and stored strain energy may be sufficient to rapidly drive the transformation of the remaining schoepite to "dehydrated schoepite" [*a* 6.86, *b* 4.26, *c* 10.20 Å, *Abcm* (?)] when partly altered crystals are exposed to an external stress (*e.g.*, heat, sunlight or mechanical pressure). Metaschoepite is apparently stable in air; canary yellow altered crystals commonly consist of a polycrystalline mixture of "dehydrated schoepite" and metaschoepite. The alteration of schoepite to "dehydrated schoepite" occurs in three steps: (1) loss of all interlayer H_2O from schoepite, causing collapse of the layers, (2) atomic rearrangement within the structural sheets to a configuration that may be similar to that of metaschoepite, and (3) further re-arrangement to a defect α-$UO_2(OH)_2$-type sheet. The complete reaction is $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12} \Rightarrow 8\ [(UO_2)O_{0.25}(OH)_{1.5}] + 12H_2O$. We propose that "dehydrated schoepite" forms an omission solid-solution over the compositional range $UO_3 \bullet 0.75H_2O$ to $UO_3 \bullet H_2O$, represented by the general formula $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ ($0 \leq x \leq 0.25$).

Keywords: schoepite, metaschoepite, uranyl oxide hydrate, uranium minerals, dehydration, phase transformation.

SOMMAIRE

La schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, se transforme lentement en métaschoepite, $UO_3 \bullet nH_2O$ ($n \approxeq 2$), dans l'air à température ambiante; les cristaux contiennent en général un mélange des deux minéraux. La transformation pourrait bien être due à la perte d'un sixième des molécules de H_2O présents dans la schoepite. Il est donc possible que la formule structurale de la métaschoepite soit $[(UO_2)_8O_2(OH)_{12}](H_2O)_{10}$. La transformation de la schoepite (*a* 14.337, *b* 16.813, *c* 14.731 Å, $P2_1ca$) en métaschoepite (*a* 13.99, *b* 16.72, *c* 14.73 Å, *Pbna*) est accompagnée d'une diminution de 2% du paramètre réticulaire *a*, une légère diminution de la dimension *b*, et très peu (ou pas) de changement dans le paramètre *c*. Ces changements témoignent probablement de la réorganisation des liaisons H. Les différences des volumes de la maille qui en résultent mènent à la formation de contraintes dans les cristaux dans lesquels la transformation en métaschoepite est amorcée mais incomplète. L'énergie accumulée pourrait suffire pour causer une transformation rapide de la schoepite résiduelle en "schoepite déshydratée" [*a* 6.86, *b* 4.26, *c* 10.20 Å, *Abcm* (?)] quand les cristaux partiellement altérés reçoivent une contrainte externe, due par exemple à la chaleur, les rayons du soleil, ou bien une pression mécanique. Dans cette situation, la métaschoepite semble stable dans l'air. Les cristaux altérés jaune serin contiennent en général un mélange polycristallin de "schoepite déshydratée" et de métaschoepite. L'altération de la schoepite en "schoepite déshydratée" s'effectuerait donc en trois étapes: (1) perte des molécules de H_2O de la position interfeuillet de la schoepite, causant un affaissement de ces feuillets, (2) une réorganisation des atomes à l'intérieur des feuillets pour atteindre un agencement semblable à celui de la métaschoepite, et (3) réorganisation plus avancée, menant à un feuillet de type α-$UO_2(OH)_2$ avec lacunes. La réaction complète serait donc $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12} \Rightarrow 8\ [(UO_2)O_{0.25}(OH)_{1.5}] + 12H_2O$. Nous considérons la "schoepite déshydratée" exemple de solution solide par omission dans l'intervalle de composition $UO_3 \bullet 0.75H_2O$ à $UO_3 \bullet H_2O$, que représente la formule générale $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ ($0 \leq x \leq 0.25$).

(Traduit par la Rédaction)

Mots-clés: schoepite, métaschoepite, oxyde à uranyle hydraté, minéraux d'uranium, déshydratation, transformation de phases.

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[1] Present address: Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.
E-mail address: finch@cmt.anl.gov

INTRODUCTION

Minerals containing hexavalent uranium play an important part in the transport and fixation of uranium in nature; a knowledge of the phase relations and paragenesis of these minerals is an important part of understanding the geochemistry of uranium (Langmuir 1978, Shock *et al.* 1997, Finch 1997a). The 25 or so uranyl oxide hydrates comprise an important subgroup of the more than 170 known minerals of hexavalent uranium (Finch 1994, Burns *et al.* 1996). The crystal structures of most uranyl oxide hydrates are based on sheets of polyhedra of the form $[(UO_2)_xO_y(OH)_z]^{(2x-2y-z)}$ (Christ & Clark 1960, Evans 1963, Miller *et al.* 1996, Burns *et al.* 1996). Most of these minerals contain divalent cations and H_2O groups in interlayer sites, but several have electrostatically neutral sheets and contain no interlayer cations. In this latter group, adjacent sheets are bonded together through H bonds only (Finch *et al.* 1996a, Finch 1997b). Of the uranyl oxide hydrates without interlayer cations, three are closely related: schoepite, metaschoepite, and paraschoepite. Sometimes called "UO_3 hydrates", these three minerals can be represented by the general formula $UO_3{\bullet}(2 \pm x)H_2O$, where x is less than one (Christ & Clark 1960). The crystal structure is known only for schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$ (Finch *et al.* 1996a), and the structural formula of schoepite corresponds to $x = +0.25$ in the formula of Christ & Clark (1960).

Schoepite occurs at many oxidized uranium deposits, and it may play a key role in the paragenesis of the complex assemblage of uranyl minerals that form where uraninite has been exposed to oxidizing meteoric water (Frondel 1958, Deliens 1977, Finch *et al.* 1992, Finch & Ewing 1992). Schoepite and other uranyl minerals also have been identified as corrosion products of UO_2 and spent nuclear fuel (Wadsen 1977, Wang & Katayama 1982, Forsyth & Werme 1992, Sunder *et al.* 1992, Wronkiewicz *et al.* 1992, 1996, Buck *et al.* 1997, 1998).

During a recent crystal-structure study (Finch *et al.* 1996a), numerous crystals of schoepite were found to alter spontaneously to a mixture of metaschoepite and "dehydrated schoepite," $UO_3{\bullet}0.8H_2O$. Alteration took place over several hours to days following manipulation of single crystals for X-ray examination. The alteration of schoepite was first described by Schoep & Stradiot (1947), and Christ & Clark (1960) proposed dehydration as the mechanism by which schoepite transforms to metaschoepite and paraschoepite (also see Christ 1965). Finch *et al.* (1992) examined schoepite and its dehydration products, but found no evidence for paraschoepite as described by Christ & Clark (1960). Because the structural and paragenetic relationships among schoepite and related uranium minerals are still uncertain, we have examined the alteration of schoepite in more detail.

PREVIOUS WORK

The International Mineralogical Association recognizes three structurally related hydrated oxyhydroxide minerals of of hexavalent uranium, with compositions that can be represented by the general formula $UO_3{\bullet}(2 \pm x)H_2O$ ($x < 1$) (Nickel & Nichols 1991). Schoepite was originally described by Walker (1923), and the crystal structure was reported by Finch *et al.* (1996a). Schoep & Stradiot (1947) described paraschoepite, $5UO_3{\bullet}9\frac{1}{2}H_2O$, but provided few data. Christ & Clark (1960) reported the presence of paraschoepite from a sample mixture that also contained schoepite and "dehydrated schoepite". Paraschoepite is considered to form by partial dehydration of schoepite (Schoep & Stradiot 1947, Christ & Clark 1960), although Christ (1965) suggested that schoepite and paraschoepite are polymorphs. Christ & Clark (1960) described a third related mineral, metaschoepite, $UO_3{\bullet}2H_2O$, also formed by partial dehydration of schoepite. Metaschoepite was identified from precession photographs of apparently single crystals of schoepite, in which additional diffraction spots indicated that the two minerals are in parallel growth.

Owing to difficulties in obtaining suitable single-phase mineral samples, much of what is known about schoepite is based on studies of synthetic analogues (Hoekstra & Siegel 1973, Smith *et al.* 1982). Schoepite and metaschoepite are difficult to distinguish on the basis of X-ray powder-diffraction data alone, and the name "schoepite" is commonly applied to any mineral or synthetic preparation with a formula close to $UO_3{\bullet}2H_2O$. Synthetic $UO_3{\bullet}2H_2O$ is most commonly prepared by heating run products in water above approximately 50°C. When prepared this way, unit-cell parameters commonly correspond most closely to those of metaschoepite (Christ & Clark 1960, Debets & Loopstra 1963, Finch *et al.* 1997), although mixtures of synthetic schoepite and metaschoepite also are common (Peters 1967, Finch *et al.* 1997). Paraschoepite has not been synthesized and remains the least well defined of the three related minerals described by Christ & Clark (1960).

Schoepite, metaschoepite and paraschoepite are structurally and chemically distinct from the four uranyl hydroxides, α-$UO_2(OH)_2$, β-$UO_2(OH)_2$, γ-$UO_2(OH)_2$, and $U_3O_8(OH)_2$ (Hoekstra & Siegel 1973, Smith *et al.* 1982), none of which contains structurally bound H_2O groups. When natural schoepite, metaschoepite, or synthetic $UO_3{\bullet}2H_2O$ dehydrate in air at ambient temperatures, or in water near 100°C, the phase that results is approximately isostructural with α-$UO_2(OH)_2$ (Taylor & Hurst 1971), but with a composition between $UO_3{\bullet}0.72H_2O$ (Peters 1967) and $UO_3{\bullet}0.9H_2O$ (O'Hare *et al.* 1988); the most commonly reported composition is $UO_3{\bullet}0.8H_2O$ (Dawson *et al.* 1956, Hoekstra & Siegel 1973). Christ & Clark (1960) obtained $UO_3{\bullet}0.8H_2O$ by dehydrating natural schoepite over H_2SO_4, calling the product "dehydrated

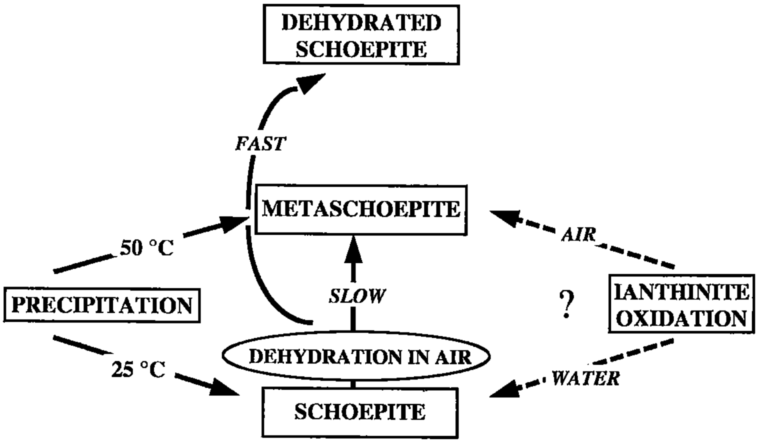

FIG. 1. Representation of the natural phase relationships among schoepite, metaschoepite and dehydrated schoepite, as inferred from natural occurrences and experimental studies (see text).

schoepite." "Dehydrated schoepite" also occurs naturally, but it has not achieved official mineral status. It is readily identified from powder-diffraction patterns, partly because of an intense peak corresponding to ~5.1 Å, the 002 diffraction maximum (Finch *et al.* 1992). Figure 1 illustrates the paragenetic relationships among schoepite, metaschoepite and "dehydrated schoepite", as inferred from natural occurrences and experimental studies (Christ & Clark 1960, Smith *et al.* 1982, Finch *et al.* 1992, 1996c).

The dehydration of schoepite to $UO_3{\bullet}0.8H_2O$ is irreversible, with "dehydrated schoepite" remaining unchanged, even in humid air, for long periods (Dawson *et al.* 1956, Christ & Clark 1960). $UO_3{\bullet}0.8H_2O$ does not react in water at near-ambient temperatures (Dawson *et al.* 1956), and reaction in hot water (≥ 100°C) yields a range of compositions, from approximately $UO_3{\bullet}0.9H_2O$ near 100°C, to stoichiometric $UO_3{\bullet}H_2O$ above ~290°C (Hoekstra & Siegel 1973, O'Hare *et al.* 1988). The ranges of thermal stability for the $UO_2(OH)_2$ polymorphs, as well as for schoepite and metaschoepite, are indicated in Figure 2. Phases with compositions from $UO_3{\bullet}0.8H_2O$ to $UO_3{\bullet}H_2O$ are isostructural with α-$UO_2(OH)_2$, and "dehydrated schoepite" is the name commonly applied to any α-$UO_2(OH)_2$-type phase within this compositional range. To explain the irreversible dehydration of schoepite, Sobry (1973) proposed that schoepite might contain hydronium ions (H_3O^+); however, Finch *et al.* (1996a) demonstrated that only neutral H_2O groups occur in schoepite, leaving unanswered the question of why the transformation of schoepite to $UO_3{\bullet}0.8H_2O$ is irreversible.

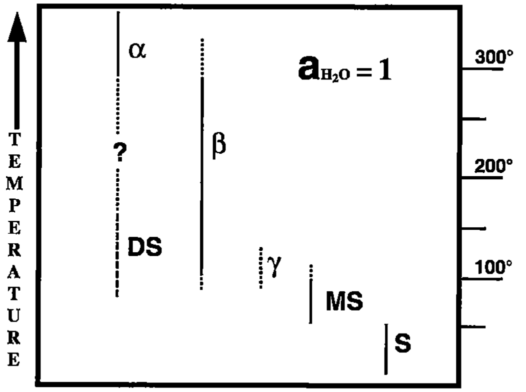

FIG. 2. Thermal stability of schoepite (S), metaschoepite (MS), dehydrated schoepite (DS) and the $UO_2(OH)_2$ polymorphs (α, ß, γ) in water. Lines are solid where the stability field for each phase is established with a high degree of certainty, and dashed where less certain or metastable. The question mark along the tie line between α-$UO_2(OH)_2$ and DS indicates the uncertain nature of this solid solution. The stability fields were deduced from experimental studies and natural occurrences (Christ & Clark 1960, Smith *et al.* 1982), as well as data reported here.

DISTINGUISHING SCHOEPITE AND METASCHOEPITE

Where X-ray powder diffraction is the only analytical method available, schoepite and metaschoepite can be distinguished only by precise determination of unit-cell parameters (Finch *et al.* 1997) (Tables 1, 2). In addition, both natural and synthetic samples may contain a mixture of schoepite and metaschoepite, in which case the two are best identified by using full-pattern-fitting methods such as Rietveld refinement (Finch *et al.* 1992, 1995, 1997). A *C*-centered subcell can be described for both schoepite and metaschoepite, with approximate dimensions, *a'* = 7.15, *b'* = 4.2, *c'* = 7.35 Å (Christ & Clark

TABLE 1. UNIT-CELL PARAMETERS REPORTED FOR SCHOEPITE AND SYNTHETIC $UO_3{\cdot}2H_2O$ (Å)

MINERALS					
mineral	*a*	*b*	*c*	method used	ref.
schoepite	*14.40	*16.89	*14.75	rotation photos	[1]
schoepite	14.23	16.72	14.62	Debye-Scherrer camera	[2]
schoepite	14.33	16.79	14.73	precession	[3]
metaschoepite	13.99	16.72	14.73	precession	[3]
paraschoepite	14.13	16.83	15.22	precession	[3]
schoepite	14.34	16.81	14.73	single-crystal diffractometer	[4]
SYNTHETIC $UO_3{\cdot}2H_2O$					
synth. temp.	*a*	*b*	*c*	method used	
40°C	13.977	16.696	14.672	diffractometer	[5]
"heated several hrs."	14.36	16.66	14.74	Debye-Scherrer camera	[6]
	†14.35	†16.71	†14.74	†recalculated	[6,7]
	†14.08	†16.71	†14.74	†recalculated	[6,7]
60°C	13.984	16.701	14.673	Debye-Scherrer camera	[8]

References: [1] Billiet & de Jong (1935); [2] Protas (1959); [3] Christ & Clark (1960); [4]; Finch *et al.* (1996a); [5] Debets & Loopstra (1963); [6] Peters (1967); [7] Finch *et al.* (1997); [8] Sobry (1973).

Notes: * units are in kX. † Data of Peters (1967) but unit-cell parameters are recalculated by Finch *et al.* (1997) for two phases.

TABLE 2. AXIAL RATIOS REPORTED FOR NATURAL SCHOEPITE AND RELATED MINERALS

	a/b	*c/b*	method used	ref.
schoepite	0.852†	0.875	optical goniometer	[1]
schoepite	0.852†	0.875	optical goniometer	[2]
*schoepite (?)	0.855†	0.900	optical goniometer	[3]
schoepite	0.852	0.874	optical goniometer	[4]
schoepite	0.851†	0.874	optical goniometer	[5]
schoepite	0.852	0.873	XRD (rotation & powder)	[6]
schoepite	0.851	0.874	XRD (powder)	[7]
schoepite	0.853	0.877	XRD (precession)	[8]
metaschoepite	0.837	0.881	XRD (precession)	[8]
paraschoepite	0.839	0.904	XRD (precession)	[8]
schoepite	0.853	0.876	XRD (4-circle diffractometer)	[9]
synthetic	0.837	0.879	XRD (powder)	[10]
synthetic	0.862	0.885	XRD (powder)	[11]
	0.843	0.882	recalculated	[11,12]
	0.859	0.882	recalculated	[11,12]
synthetic	0.837	0.879	XRD (powder)	[13]

References: [1] Walker (1923); [2] Schoep (1924); [3] Buttgenbach (1924); [4]; Ungemach (1929); [5] Palache (1934); [6] Billiet & de Jong (1935); [7] Protas (1959); [8] Christ & Clark (1960); [9] Finch *et al.*(1996a); [10] Debets & Loopstra (1963); [11] Peters (1967); [12] Finch *et al.* (1997); [13] Sobry (1973).

Notes: * Buttgenbach (1924) reported the optic axis parallel to (001), not (010) (Walker 1923; Christ & Clark 1960). † *a/b* values are twice those reported by Walker (1923), Schoep (1924), Buttgenbach (1924) and Palache (1934).

1960, Finch 1994). This subcell corresponds to the approximate positions of U atoms at (0,0,0) and (0,0,½), and the strongest diffraction-maxima for both minerals are those corresponding to this subcell. These strong diffraction-maxima give rise to a pseudohexagonal net in *hk*0 precession photographs, a characteristic of most uranyl oxide hydrates (Christ & Clark 1960, Finch 1994). The subcell in schoepite has nearly the same dimensions in the plane of the sheets (a'–b' plane) as does α-$UO_2(OH)_2$ and, by analogy, "dehydrated schoepite" (Taylor & Hurst 1971, Smith *et al.* 1982).

Although their X-ray powder patterns are closely similar, schoepite and metaschoepite are readily distinguished by single-crystal diffraction techniques (Christ & Clark 1960). Systematic absences are diagnostic because schoepite displays diffraction aspect *Pbca*, whereas metaschoepite displays diffraction aspect *Pbna*. The two minerals are therefore readily distinguished in *h*0*l* precession photographs, in which $h = 2n$ for schoepite and $h + l = 2n$ for metaschoepite. In addition, *hk*0 precession photographs of schoepite and metaschoepite are distinctly different. Both minerals are characterized by the same apparent systematic absences in *hk*0 photographs, and both display the same strong subcell reflections: those for which $h = 2n$ and $k = 4n$. The next most intense group of diffraction spots in *hk*0 photographs of both schoepite and metaschoepite are those for which $h = 2n$ and $k = 4n \pm 1$. In schoepite,

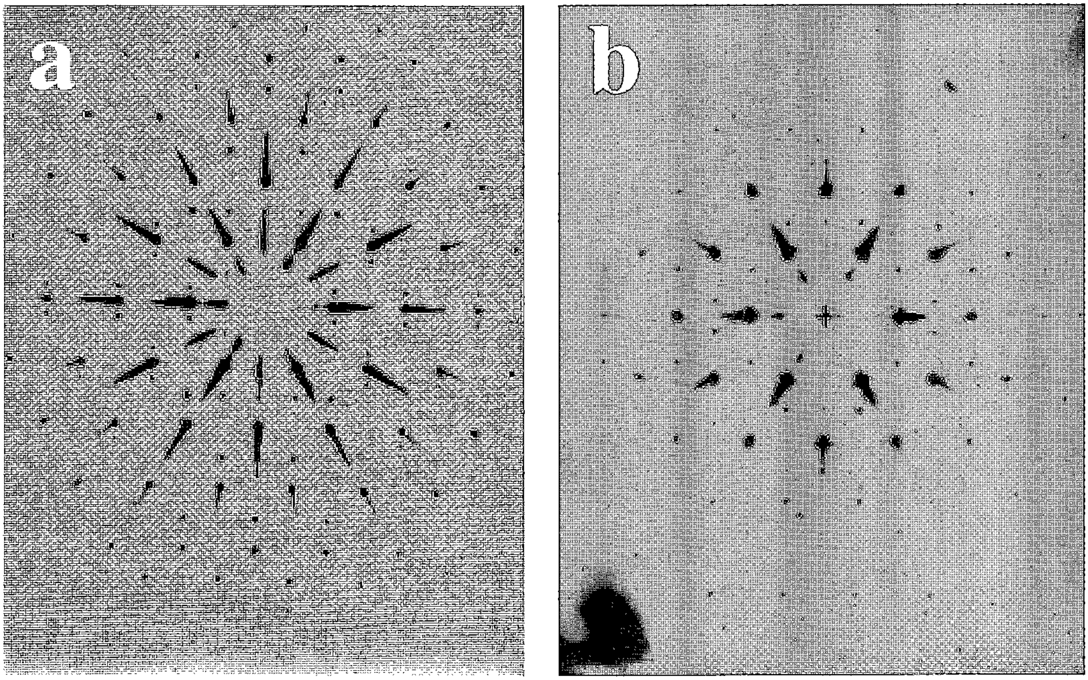

FIG. 3. Comparison of *hk0* precession photographs of (a) schoepite and (b) metaschoepite.

these appear as satellites beside the strong subcell reflections in *hk*0 photographs (Fig. 3a), whereas they do not appear as satellites, but between the subcell reflections along *a** in photographs of metaschoepite (Fig. 3b). When mounting crystals of good optical quality for precession photography, crystallographic orientations are readily determined optically because the optic planes of both schoepite and metaschoepite are parallel to (010) (Walker 1923, Christ & Clark 1960). Mounting crystals for precession analysis with the rotation axis perpendicular to the plane of the optic axis (parallel to *a*) allows one to obtain both *hk*0 and *h*0*l* photographs and thus to unambiguously distinguish schoepite and metaschoepite or to identify a composite pattern (*cf.* Fig. 1 of Christ & Clark 1960).

Christ & Clark (1960) stated that they obtained precession photographs of paraschoepite that were distinctive; however, they did not reproduce a photograph, reporting only an X-ray powder pattern for paraschoepite with admixed "dehydrated schoepite". We were unable to obtain any precession photographs that could be attributed to paraschoepite. Some crystals of schoepite with dark inclusions commonly produced precession photographs indicating inclusions in parallel growth with schoepite (or nearly so). The most common inclusions we found are becquerelite, fourmarierite, vandendriesscheite, and ianthinite. Ianthinite, $[U^{4+}_2(U^{6+}O_2)_4O_6(OH)_4](H_2O)_9$, is known to oxidize to schoepite or metaschoepite (Schoep & Stradiot 1947, Guillemin & Protas 1959, Burns *et al.* 1997) (Fig. 2), and the X-ray powder pattern for paraschoepite reported by Christ & Clark (1960) can be interpreted as a composite pattern of metaschoepite, "dehydrated schoepite", and ianthinite (Finch *et al.* 1997). Whatever the true nature of paraschoepite, we were unable to identify it in any samples that we studied.

EXPERIMENTAL

Single crystals of schoepite were removed from two museum samples (91.62 and B3616) originally from the Shinkolobwe mine, Shaba, southern Congo. Both samples contain uraninite, uranyl carbonates, uranyl oxide hydrates and uranyl silicates. Schoepite crystals were taken directly from the surface of sample B3616, whereas crystals were extracted from the interior of sample 91.62 by breaking it open. Unit-cell parameters of single crystals were measured either on a four-circle diffractometer or by precession photography (Table 3). Precession photographs were taken for two of three principal orientations (*hk*0 photographs and either 0*kl* or *h*0*l* photographs).

During a structural study of schoepite (Finch *et al.* 1996a), cleavage fragments from several crystals of

TABLE 3. MEASURED UNIT-CELL PARAMETERS (Å) FOR SCHOEPITE AND METASCHOEPITE CRYSTALS (THIS STUDY)

	a[†]	*b*[†]	*c*[†]	comments
B3616				
[‡] sc-c(2)	14.0	16.72	14.7	metaschoepite, broad maxima
sc-f	14.074(7)	16.717(7)	14.70(1)	metaschoepite, stable (coated)
sc-e	14.17(1)	16.74(1)	14.68(2)	stable (coated)
[‡] sc-c(1)	14.26	16.72	14.69	before alteration to metaschoepite: *sc-c*(2)
[*] sc-d(2)	14.296(3)	16.775(4)	14.713(4)	stable (coated)
sc-a	14.301(3)	16.788(4)	14.712(4)	altered to DS and MS
[*] sc-d(1)	14.308(3)	16.793(2)	14.706(3)	stable (coated)
sc-b	14.31	16.76	14.71	altered to DS and MS
91.62				
schod	14.06	16.74	14.58	crystal heated in water: 65(±8)°C for 19 d.
schoc	14.30	16.74	14.72	subsequently heated in air at 120°C for 1 hr.
schoa	14.308(2)	16.808(3)	14.705(4)	stable (not coated)
schob	14.337(3)	16.813(5)	14.731(4)	stable (not coated)

[†] Standard deviations are ±1σ in the last decimal place; standard deviations for precession data are not reported.
[‡] *sc-c(1)* and *sc-c(2)* are the same sample. Unit-cell parameters of *sc-c(2)* were not determined as precisely as for *sc-c(1)* due to the poor qualityof precession photographs after transformation to metaschoepite.
[*] *sc-d(1)* and *sc-d(2)* are the same crystal, but data was recollected on *sc-d(2)* after six months.

schoepite had been extracted from sample B3616. Several months later, many of the schoepite crystals that remained in the sample had altered. The cores of most altered crystals were composed of a fine-grained yellow powder, whereas crystal rims remained more or less translucent yellow. These altered crystals were removed from sample B3616, and X-ray powder diffraction data were collected on the powdered material from the cores of the altered schoepite crystals. To avoid possible further reaction, the altered material was not ground. Unit-cell parameters of the phases comprising the altered material were determined by Rietveld refinement (Finch *et al.* 1995) using known structures as starting models (Taylor & Hurst 1971, Finch *et al.* 1996a), and uranium positions only for metaschoepite (Table 4); atomic parameters were not refined.

In order to examine the stability and possible transformation of schoepite in water at elevated temperature, several single crystals of schoepite from sample 91.62 were heated at 65 ± 8°C in deionized water for seven to nineteen days. Precession photographs of these crystals were taken after heating. In addition, a single crystal (*schoc*, dimensions: 0.20 × 0.30 × 0.05 mm) of inclusion-free fresh schoepite from sample 91.62 was mounted on a glass fiber and heated in air for one hour at 120°C. Precession photographs were taken of this sample before and after heating.

TABLE 4. ATOMIC PARAMETERS USED IN RIETVELD-REFINEMENT MODEL FOR METASCHOEPITE[*]

Pbna	*a* 14.074(3)	*b* 16.717(3)	*c* 14.697(13)
Site	*x*	*y*	*z*
U(1)	-0.0196 (5)	-0.1450 (7)	0.2471 (7)
U(2)	0.0059 (5)	-0.3749 (7)	0.2457 (7)
U(3)	0.2680 (5)	-0.2403 (7)	0.2231 (7)
U(4)	0.2670 (5)	-0.0091 (7)	0.2651 (7)

[*] Crystal *sc-f* (sample B3616); atomic positions determined by direct methods. Final R index of 19.5%; isotropic displacement parameters only. $Z = 8$.

X-ray intensity data from one crystal of metaschoepite that clearly displayed diffraction aspect *Pbna* (*sc–f*, sample B3616) were collected on a single-crystal diffractometer (Table 3). We attempted to determine the structure; however, the quality of the data was too poor to allow a reasonable solution of the structure. Only the U positions could be determined (Table 4), and these were used in our structural model of metaschoepite for Rietveld refinement of unit-cell parameters from powdered samples containing metaschoepite.

RESULTS

Spontaneous alteration of schoepite in air (25°C)

We found that the relative stabilities of schoepite from the two samples (91.62 and B3616) were different. Nearly all crystals of schoepite from the surface of sample B3616 altered following manipulation and removal of cleavage fragments. Altered crystals became clouded or opaque, including crystals extracted for X-ray analysis and many crystals remaining on the sample. Alteration was inhibited in some crystals extracted from B3616 by coating them with hair spray, and these did not alter further for more than two years (Table 3). In contrast, schoepite crystals from sample 91.62 were not coated, and these did not alter during this study (after more than two years of storage in air; all crystals from sample 91.62, however, have now altered). Unit-cell parameters and axial ratios of schoepite crystals from sample 91.62 are consistent with those reported for schoepite (Tables 1, 2), whereas unit-cell parameters of schoepite from sample B3616 are more variable, with values ranging from those of schoepite to those characteristic of metaschoepite (Table 1, Fig. 4). As noted above, crystals from sample B3616 were obtained from the surface of the sample, whereas crystals from sample 91.62 were extracted from its interior.

Although *measured* unit-cell parameters vary continuously between those of schoepite and metaschoepite

(Table 3), many of these are average values of cell parameters for the two minerals intergrown in one crystal. Individual diffraction-maxima for intergrown schoepite and metaschoepite are not readily resolvable with film data or a four-circle diffractometer. However, our diffractometer data indicate asymmetrical peaks owing to the presence of two phases in several crystals. Crystals consisting of both minerals are usually optically homogeneous and cannot be identified by optical examination; if a sufficient component of each mineral is present in a crystal, however, precession photographs may display a distinctive composite pattern (Christ & Clark 1960).

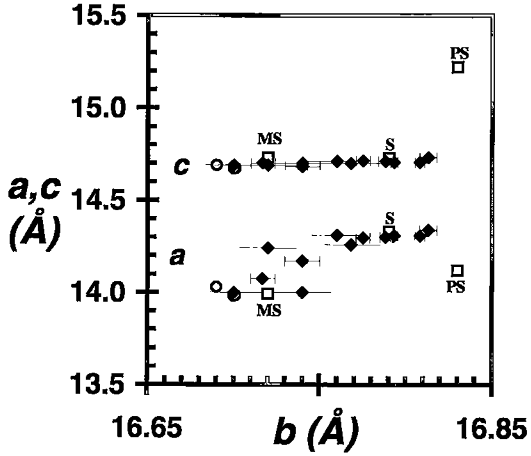

FIG. 4. Unit-cell parameters of schoepite and metaschoepite from Table 3 (filled symbols) and values reported elsewhere (hollow symbols; Table 1). Diamonds and squares represent minerals; open squares are for natural schoepite (S), metaschoepite (MS) and paraschoepite (PS) (Christ & Clark 1960) (Table 1). Circles represent synthesis products (Debets & Loopstra 1963, Peters 1967, Sobry 1973). Estimated uncertainties for diffractometer data indicate ±1σ (closed-end error bars) (Table 3); uncertainties for precession data are estimated: ±0.15% of the measured unit-cell parameters (open-ended error bars). Estimated uncertainties for the *a* and *c* cell edges are less than the extent of the data points at the scale shown. Uncertainties for data from other studies are not indicated. Values for paraschoepite (PS) are shown for completeness; however, the status of paraschoepite is uncertain. (*Note*: Horizontal axis is greatly expanded compared to the vertical axis.)

X-ray powder-diffraction data from powdered material obtained from crystals in sample B3616 that had altered in the laboratory indicate that the resulting material is a mixture of metaschoepite and "dehydrated schoepite", in some cases with minor schoepite. Crystals from sample B3616 did not decompose homogeneously. Instead, small regions that had decomposed to polycrystalline material were surrounded by a deep yellow clouded rim. These rims had developed cleavage fractures parallel to (010) (Fig. 5). Precession photographs of the rims of altered crystals demonstrate that they commonly contain intergrown schoepite and metaschoepite, and that their unit-cell parameters are closest to those of metaschoepite. In a previous study, schoepite crystals from sample 91.62 that had been ground and left in a sealed glass vial for three months also decomposed to a mixture of metaschoepite, "dehydrated schoepite" and minor schoepite (Finch *et al.* 1992). The spontaneous alteration of powdered schoepite from sample 91.62 at room temperature contrasts with the relative stability of single crystals from the same sample, a difference probably caused by grinding. Nevertheless, alteration of schoepite crystals from sample B3616 yielded the same products as the alteration of powdered schoepite from sample 91.62 (Finch *et al.* 1992). There has been no further visible change in sample B3616 after more than two years. "Dehydrated schoepite" does not replace the remaining metaschoepite. This observation is consistent with previous findings that metaschoepite and dehydrated schoepite are stable with respect to further change (Christ & Clark 1960, Finch *et al.* 1992).

One crystal of schoepite from sample B3616 [crystal *sc–c*(1), Table 3] altered spontaneously overnight at 20°C to metaschoepite [*sc–c*(2)] during a ten-hour X-ray exposure. As a result of the transformation, the crystal changed from translucent sulfur yellow to deep golden yellow with numerous inclusions. We propose that before the transformation, this crystal contained minor metaschoepite. Though additional spots attributable to metaschoepite are not evident in the *hk*0 precession photograph taken of this crystal before the transformation, the existence of metaschoepite is indicated by the shortened *a* cell dimension before the transformation (Table 3). The transformation of this crystal was characterized by a 2% decrease in the *a* cell dimension, from 14.26 Å to 14.0 Å; there is no measurable change in the *b* or *c* cell dimensions (Table 3). The appearance of weak diffraction-spots in the *h*0*l* photograph with *h* and *l* both odd indicate a space-group change from $P2_1ca$ (pseudo-*Pbca*) for schoepite to *Pbna* for metaschoepite. The strongest diffracted intensities in *hk*0 photographs of both schoepite and metaschoepite are for $h = 2n$ and $k = 4n$. The next most intense diffraction-spots in the *hk*0 photograph of schoepite differ from those in the *hk*0 photograph of metaschoepite. Although there is no change in systematic absences, the *hk*0 photographs of schoepite and metaschoepite are distinctive (Fig. 3). Our results indicate that most (if not all) crystals from the surface of sample B3616 that had altered spontaneously in the laboratory consist of intergrown schoepite and metaschoepite, whereas crystals taken from the interior of sample 91.62 contained little or no metaschoepite (Table 3).

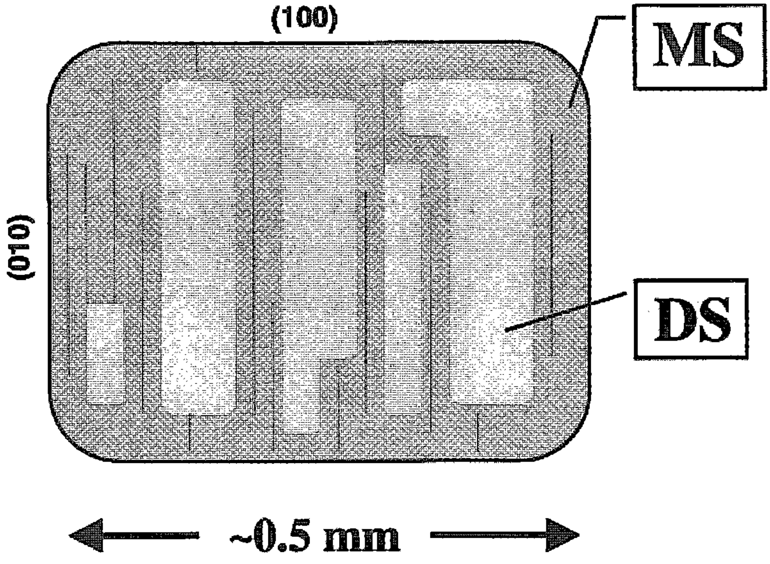

FIG. 5. Schematic representation of an altered crystal of metaschoepite plus "dehydrated schoepite". Light regions represent "dehydrated schoepite" (DS), and dark regions are metaschoepite (MS). Dashed lines indicate the (010) cleavage developed in metaschoepite following transformation from schoepite. The size is indicated for a typical altered crystal from sample B3616.

Schoepite alteration in water (~65°C)

Schoepite crystals heated in deionized water became brittle and developed abundant inclusions. Most of the crystals altered in this way have opaque cores, although their rims remain translucent and optically continuous. Optical examinations indicate that many inclusions are fluid, but fine-grained opaque inclusions were observed in several samples (comprising less than ~5 vol.%). The optic axial angles ($2V_\alpha$) of altered crystals range between 65° and 80° (estimates within approximately ± 5°), consistent with the optical properties reported for schoepite (Christ & Clark 1960).

Precession photographs of crystals heated in water closely resemble the composite pattern in precession photograph reported by Christ & Clark (1960) and photographs obtained from the rims of altered crystals on sample B3616. Photographs taken with the X-ray beam parallel to the structural sheets (*h*0*l* or 0*kl* photographs) display streaking parallel to c^*, suggesting disorder. Minor streaking perpendicular to c^* also is evident, but streaking in *hk*0 photographs is relatively minor. Precession photographs exhibit more fogging than photographs of unaltered crystals. Diffraction spots are broad compared to those of unaltered crystals, but are similar to those in precession photographs of metaschoepite crystal *sc–c*(2) (Fig. 3b) and remnant metaschoepite from the rims of altered crystals from sample B3616. Spot broadening, streaking and film fogging prevented us from determining unit-cell dimensions of schoepite and metaschoepite separately, where both are present, such that we report average values only.

The average *a* cell dimension of crystals heated in water is 14.0 Å, and none was found with *a* greater than 14.1 Å. The average *b* cell dimension is 16.7 Å, regardless of duration of heating. The *c* cell dimension was difficult to measure precisely, owing to streaking, but values range from 14.6 Å to 14.8 Å. Evidence for the ~10.2 Å *c* cell dimension characteristic of "dehydrated schoepite" is not apparent (Christ & Clark 1960, Finch *et al.* 1992). However, if present, inclusions of "dehydrated schoepite" would not be apparent in precession photographs if not crystallographically oriented with metaschoepite. The poor quality of most *h*0*l* photographs made systematic absences difficult to determine. Diffraction spots corresponding to subcell reflections in *hk*0 photographs ($h = 2n$ and $k = 4n$) and *h*0*l* photographs ($h = 4n$ and $l = 2n$) remain the most intense, as for unaltered schoepite (and metaschoepite). One crystal, after being heated for nineteen days, had a very short *c* dimension (14.6 Å) and an intermediate *a* dimension (14.06 Å). The *hk*0 photograph of this crystal indicates that *h* is always even and that there is no restriction on *k* (*k* is even for observed 0*k*0 spots). The *h*0*l* photograph of this crystal unambiguously displayed diffraction spots for which the sum (*h* + *l*) is always even, consistent with an *n*-glide parallel to (010); however, diffraction spots for which both *h* and *l* are odd are extremely weak. No 0*kl*-oriented photograph was obtained for this crystal. X-ray intensity data from this crystal were collected on a single-crystal diffractometer, from which we attempted to determine the structure; however, the quality of the data was too poor to allow a reasonable solution of the structure or stable refinement.

Dehydration of schoepite in air (120°C)

In order to examine short-term structural changes that occur as schoepite dehydrates, we heated a thin (~0.02 mm) crystal of schoepite from sample 91.62 (*schoc*) in air for one hour. Before heating, the crystal was translucent yellow with no indication of metaschoepite (Table 3). After one hour at 120°C, the crystal was a deep golden yellow and contained abundant inclusions, visually similar to crystal *sc–c*(2) after it had transformed to metaschoepite. Detailed optical examination of the mounted crystal was not possible, and the crystal disaggregated when we attempted to remove it from the glass rod after examination by precession.

Precession photographs of crystal *schoc* after heating display broad diffraction spots, and most show concentric streaking, spanning arcs of a few degrees (Fig. 6). The only diffraction spots apparent in *h*0*l* photographs are those for which $h = 4n$ and $l = 2n$ (indexing refers to the original schoepite); in *hk*0 photographs, the strongest diffraction spots are those for which $h = 2n$ and $k = 4n$. These strong reflections correspond to the *C*-centered subcell described above, but with a *c* dimension of ~10.2 Å. As noted, these are the approximate cell dimensions of $UO_3{\bullet}0.8H_2O$ or "dehydrated schoepite" (Dawson *et al.* 1956). Many of the most intense subcell reflections in the *hk*0 photograph are split (Fig. 6a). In one quadrant, the split reflections are 480, 640, 800, 880, and 10,4,0 (plus symmetrically related spots in the remaining quadrants); no split spots are apparent in *h*0*l* photographs (Fig. 6b), and there is no evidence for the ~7.35 or 14.7 Å repeat along the *c* axis, as is characteristic for metaschoepite. In addition to the strong subcell reflections, several low-intensity spots are evident in *hk*0 photographs (visible on a light table only and not apparent in Fig. 6a; they are indicated in Fig. 6c). These low-intensity spots define a pattern resembling that of metaschoepite ($h = 2n$ and $k = 4n \pm 1$) and are not split (Fig. 6c). The pattern of these lower-intensity spots resembles that observed in precession photographs of metaschoepite (Fig. 3b).

Two crystallographically related phases are clearly evident from the *hk*0 photograph of crystal *schoc* after heating (Fig. 6c). One phase (phase 1) displays relatively strong spots only, whereas the other (phase 2) displays both strong spots as well as the low-intensity spots. We can describe cell dimensions for two phases (*a* and *b* axes parallel to the *a* and *b* axes of the original schoepite): for phase 1, $a = 6.96$ Å, and $b = 4.18$ Å; for phase 2, $a = 7.1$ Å and $b \cong 16.2$ Å; (note that the *a* dimension of phase 2 may be 14.2 Å, as no upper level photographs were obtained; however, no evidence for the longer *a*-cell dimension is evident in *h*0*l* photographs either). Both phases display the same repeat-distance along *c*: 10.2 Å. Of course, phase 1 is approximately equivalent to "dehydrated schoepite". It has a shorter *a* and a longer *b* than reported for $UO_3{\bullet}0.8H_2O$, for which $a = 6.86$, $b = 4.26$, $c = 10.20$ Å (Dawson *et al.* 1956) (Note: cell dimensions of Dawson *et al.* are transposed *cab* compared to α-$UO_2(OH)_2$: Taylor 1971). The unit-cell volumes of phase 1 and $UO_3{\bullet}0.8H_2O$ are approximately equivalent: $V_{\text{phase 1}} = 296.7$ Å^3, $V_{DS} = 298.1$ Å^3. The combination of the *hk*0 diffraction character and unit-cell dimensions of phase 2 suggests that it possesses a structural sheet similar to that of metaschoepite.

DISCUSSION

The transformation of schoepite to metaschoepite

Our data are consistent with the observations of Christ & Clark (1960) that natural crystals of schoepite commonly consist of intergrown schoepite and metaschoepite (Table 3). The transformation from schoepite to metaschoepite at ambient temperatures is slow; however, the rate varies widely among samples, and crystals may last for geologically long periods (Finch *et al.* 1996b). The transformation of crystals from the surface of sample B3616 seems to have progressed further than for crystals obtained from within sample 91.62 (Table 3). We attribute this to the relative isolation from the atmosphere of crystals within sample 91.62. We did not determine whether the transformation of schoepite to metaschoepite is reversible; however, the structural role of interlayer H_2O groups in most uranyl minerals suggests that H_2O cannot be removed from interlayer sites without structural modification (Finch *et al.* 1996c, Finch 1997b). The H_2O groups in schoepite occupy well-defined positions and constitute part of a complex H-bond network in which all H_2O groups link *via* H-bonds across adjacent structural units (Finch *et al.* 1996a). There are no occluded H_2O groups in schoepite, such that their removal would leave the structural sheets unaffected (Hawthorne 1992, Finch 1997b).

Two of the twelve interlayer H_2O groups in schoepite are more weakly bonded than the remaining ten (Finch *et al.* 1996a); the transformation of schoepite to metaschoepite may be related to the loss of these two H_2O groups. The other ten H_2O groups evidently remain within the interlayer of metaschoepite, because the structural sheets do not collapse as a result of the transformation (Table 3). Removing only the two most weakly bonded H_2O groups should induce relatively minor changes to H-bonding. Differences in the diffracted intensities in *hk*0 precession photographs fol-

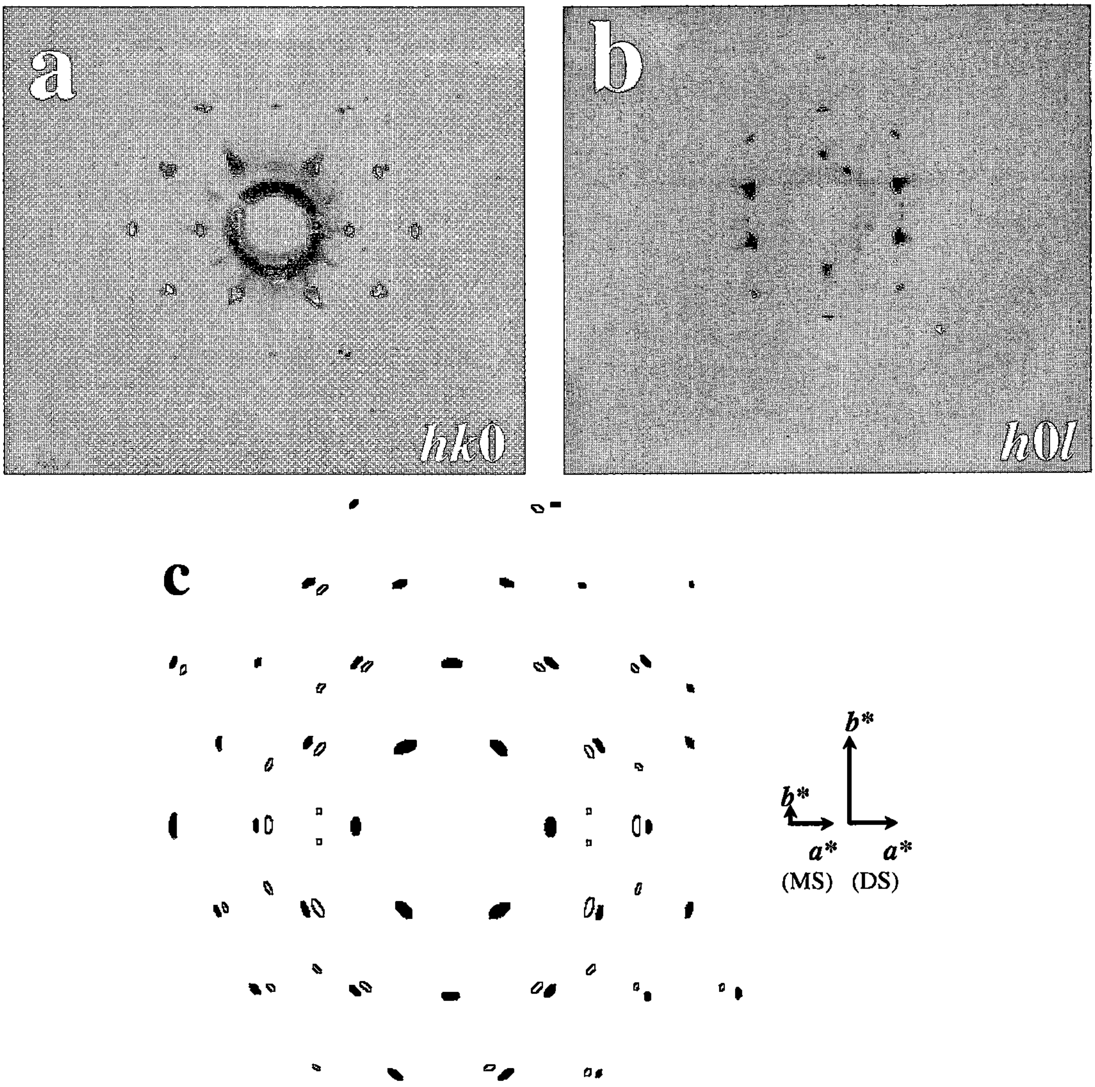

FIG. 6. Precession photographs of crystal *schoc* after heating in air at 120°C for one hour (a) *hk*0 photograph; (b) *h*0*l* photograph; (c) Representation of the *hk*0 precession photograph in (3a) with weak diffraction spots enhanced. The pattern indicates the intergrowth of two phases, one with an α-$UO_2(OH)_2$-type sheet: "dehydrated schoepite" (phase 1, filled spots), and one with a structural sheet that may resemble that of metaschoepite (phase 2, hollow spots). Reciprocal axes are indicated at right and labeled "DS" for phase 1 and "MS" for phase 2.

lowing the transformation of schoepite to metaschoepite clearly reflect structural rearrangement parallel to the sheets (Fig. 3), probably the result of modified H-bond arrangements. If the transformation to metaschoepite is due to the loss of one-sixth of the interlayer H_2O groups from schoepite, then a possible structural formula for metaschoepite is $[(UO_2)_8O_2(OH)_{12}](H_2O)_{10}$, equivalent to $UO_3{\bullet}2H_2O$.

Figure 7 shows the structural environment of the two weakly bonded H_2O groups in schoepite, *W*(5) and *W*(11). Every H_2O group in schoepite is H-bonded to an OH group within the structural sheet. *W*(5) and *W*(11) act as H-bond acceptors for *OH*(5) and *OH*(11), respectively; they also act as donors to two (or three) uranyl O atoms in the adjacent sheet, each at a distance

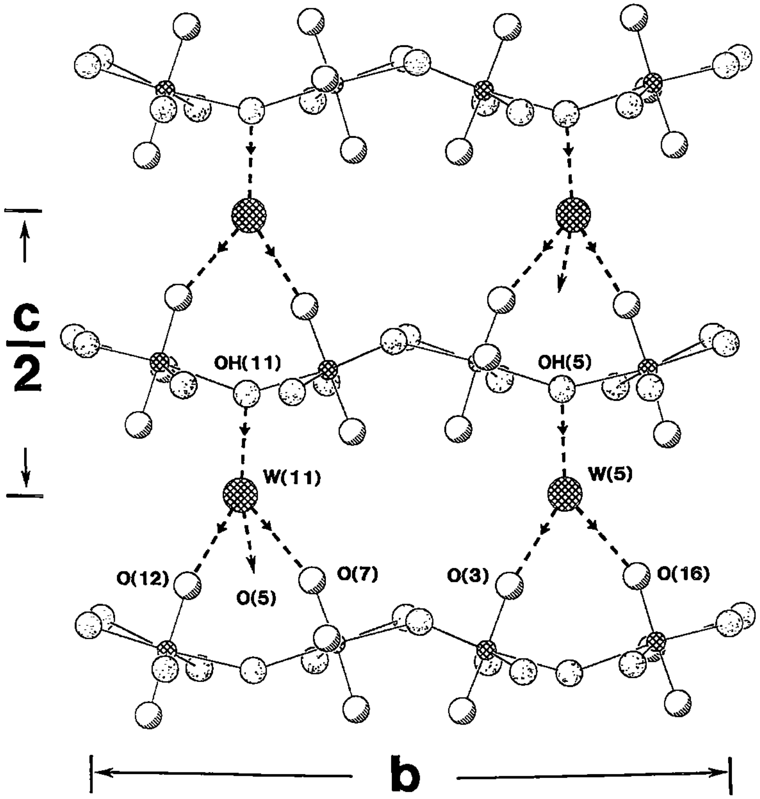

FIG. 7. Atomic arrangement and H-bond interactions between the structural sheet in schoepite and the two H_2O groups not members of the pentagonal H_2O rings, *W*(5) and *W*(11). View along [100], $x \approx 0.25$. O(5) is behind the plane of the illustration.

of ~2.9 Å (Fig. 7). Removal of *W*(5) and *W*(11) therefore leaves the corresponding OH groups (and uranyl O atoms) underbonded. If the bond-valence contribution of *OH*(5) and *OH*(11) to their respective H atoms remains approximately 0.8 valence units (*vu*) each, the removal of *W*(5) and *W*(11) leaves those H atoms underbonded by ~0.2 *vu*. Expected O–O distances for H-bond interactions are less than 3.1 Å (Baur 1972). H-bonds associated with O–O distances of 3.1 to 2.95 Å and O–H–O angles in the range 110 – 135° correspond to an H–O bond strength of 0.05 to 0.07 *vu* (Brown 1976a, b). If the H atoms from *OH*(5) and *OH*(11) each form a trifurcated H-bond of ~0.07 *vu* to the three uranyl O atoms in the adjacent sheet, their bond-valence requirements can be satisfied.

The nearest O atoms that may act as H-bond acceptors for *OH*(5) and *OH*(11) are uranyl O atoms to which *W*(5) and *W*(11) are H-bond donors in schoepite. Each of two groups of three uranyl O atoms, *O*(5), *O*(7), *O*(12), and *O*(3) *O*(14), *O*(16), define a plane that is approximately 5.0 Å from *OH*(11) and *OH*(5), respectively. Each group of three uranyl O atoms forms a nearly equilateral triangle, with each uranyl O atom approximately equidistant from the OH groups in the adjacent sheet. In order to establish H-bonds from *OH*(11) and *OH*(5) to uranyl O atoms in the adjacent sheet, the sheets must pucker by ~2.4 Å, or approximately 1.2 Å cooperative puckering of both sheets. Accompanied by slight shifting along [100], this puckering will leave a distance of ~3.0 Å between *OH*(11) and *OH*(5) and the three uranyl O atoms in the adjacent sheet, and O–H–O angles of approximately 135°. Such a configuration is consistent with bond-valence contributions of 0.05 to 0.07 *vu* from the uranyl O atoms to the H atoms and is comparable to multiple H-bonds in other phases (Brown 1976b).

The remaining ten H_2O groups originally in schoepite remain within the interlayer after the transformation to metaschoepite. There is a complex network of H-bonding among these ten interlayer H_2O groups, as well as between them and the structural sheets (Finch *et al.* 1996a). The loss of one or more of these interlayer H_2O groups will profoundly disrupt H-bonding interactions (Finch 1997b), and spontaneous dehydration of metaschoepite is not expected at ambient temperatures. This explains the apparent stability of metaschoepite in air (Christ & Clark 1960, Finch *et al.* 1992, 1996b, c) and also explains why there is little or no change in (002) layer spacing when *W*(5) and *W*(11) are lost from schoepite (Table 3, Fig. 4). The unit-cell volume of metaschoepite is smaller than that of schoepite, owing to an approximately 0.3 Å decrease in the *a* cell dimension. The shorter *a* dimension in metaschoepite may reflect shifting and puckering of the layers as well as changes to the configuration of interlayer H_2O groups. Only slight distortions of the pentagonal H_2O rings and small shifts in the positions of uranyl O atoms are required to make the schoepite structure conform with the *Pbna* symmetry of metaschoepite.

Differences in the unit-cell volumes of schoepite and metaschoepite must induce strain in crystals that contain both phases. This strain may promote further transformation of crystals that have partly converted to metaschoepite when manipulated or otherwise stressed (*e.g.*, by exposure to heat or sunlight), which would explain why some schoepite crystals spontaneously decompose to "dehydrated schoepite" at room temperature when manipulated in the laboratory (Christ & Clark 1960, Finch *et al.* 1996a). Domains already transformed to metaschoepite do not decompose in this way, hence the incomplete conversion of crystals to "dehydrated schoepite" when they alter spontaneously (Fig. 5).

Another effect of the transformation of schoepite to metaschoepite is embrittlement of crystals and the appearance of a (010) cleavage. This secondary cleavage is manifested as subparallel fractures in metaschoepite (Fig. 5), which may explain striations parallel to *a* observed on the (001) face of paraschoepite crystals (Schoep & Stradiot 1947). The (010) cleavage may help reduce strain by acting as shear planes along which adjacent domains within a crystal may contract differentially along [100]. Cleavage planes are also potential pathways for H_2O released from schoepite. As only H-bonds link structural sheets and H_2O groups in schoepite and metaschoepite, embrittlement may also be a manifestation of changes in H-bonding and the establishment of sheet-to-sheet H-bonds in metaschoepite, as observed in curite (Mereiter 1979).

Transformation of schoepite to "dehydrated schoepite"

The short *c* dimension of crystal *schoc* after one hour at 120°C indicates that heating in air caused complete collapse of layers in schoepite. This structural collapse must reflect the loss of all interlayer H_2O groups from schoepite, for which $\frac{1}{2}c \cong 7.36$ Å, and recrystallization of an α-$UO_2(OH)_2$-type layer structure, with $\frac{1}{2}c \cong 5.1$ Å. The collapse of layers in schoepite occurs rapidly and completely as all interlayer H_2O is lost. Domains within the structural sheets apparently undergo rearrangement from the schoepite configuration before alteration to a sheet structure that may be similar to that of metaschoepite, as indicated by weak diffraction-spots that resemble the diffraction pattern in precession photographs of metaschoepite (Fig. 6c). The "metaschoepite-like" domains (phase 2) are laterally continuous with the α-$UO_2(OH)_2$-type sheets of "dehydrated schoepite" (phase 1). The structural relationship between the sheets in schoepite and those in α-$UO_2(OH)_2$ is shown schematically in Figure 8. The structural sheet of schoepite is essentially an ordered α-$UO_2(OH)_2$ defect-structure with 1/8 of the anion positions in α-$UO_2(OH)_2$ vacant and 1/8 of the anions shifted toward the vacancies; differences in the U positions between the two sheet types are minor (Fig. 8).

Our results indicate that the complete structural rearrangement required to convert schoepite into the α-$UO_2(OH)_2$-type structure of "dehydrated schoepite" proceeds in three steps. The first two steps are rapid: (1) loss of all interlayer H_2O; (2) concomitant rearrangement of the structural sheet to a metastable intermediate structure with a metaschoepite-like sheet (phase 2). The first two steps are represented by a single reaction:

$$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12} \Rightarrow [(UO_2)_8O_2(OH)_{12}] + 12H_2O \quad (1)$$

The third step requires relaxation of the structural sheets from the configuration of the metastable intermediate to the configuration of the sheet in "dehydrated schoepite" (phase 1):

$$[(UO_2)_8O_2(OH)_{12}] \Rightarrow 8\,[(UO_2)O_{0.25}(OH)_{1.5}]. \quad (2)$$

The right-hand side of reaction (2) represents a structure-derivative of α-$UO_2(OH)_2$ in which anion vacancies are disordered. The composition of "dehydrated schoepite" on the right is $UO_3{\bullet}0.75H_2O$, close to that first reported by Dawson *et al.* (1956), $UO_3{\bullet}0.8H_2O$, and essentially the same as reported by Peters (1967) for a phase produced by thermal decomposition of synthetic $UO_3{\bullet}2H_2O$ between 250° and 400°C: $UO_3{\bullet}0.72H_2O$.

The replacement of some OH groups by O atoms, combined with vacancies in the structural sheets, requires that hydrogen-bonding in "dehydrated schoepite" is substantially reduced compared to that in stoichiometric α-$UO_2(OH)_2$. The proportion of anion vacancies in "dehydrated schoepite" is 1:8, *i.e.*, one anion vacancy per unit cell in "dehydrated schoepite". When placed in contact with water, some of these vacancies may be filled by OH groups, as $UO_3{\bullet}0.9H_2O$ is the composition attained in water below 150°C (Protas 1959, Peters 1967, O'Hare *et al.* 1988); the corresponding structural formula is $[(UO_2)O_{0.1}(OH)_{1.8}]$. The proportion of anion vacancies is reduced from 1:8 in $UO_3{\bullet}0.75H_2O$ to 1:20 in $UO_3{\bullet}0.9H_2O$. The reduction in vacancies enhances H-bonding between adjacent sheets and explains why "dehydrated schoepite" reacts in water to give stoichiometric α-$UO_2(OH)_2$ at higher temperatures (Dawson *et al.* 1956, Smith *et al.* 1982), but does not hydrate at any temperature (Hoekstra & Siegel 1973). The observed compositional series between "dehydrated schoepite" and α-$UO_2(OH)_2$ can be explained by an omission solid-solution with the general formula $[(UO_2)O_{0.25-x}(OH)_{1.5+2x}]$, with x varying from zero in "dehydrated schoepite" to 0.25 in α-$UO_2(OH)_2$.

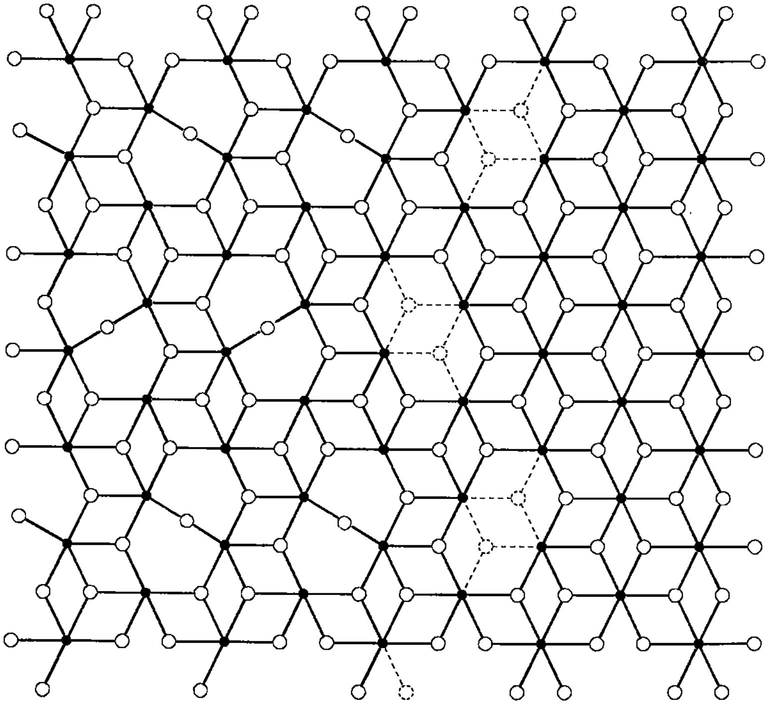

FIG. 8. Schematic representation of the structural sheet in schoepite (Finch *et al.* 1996a) illustrating its relationship to the structural sheet in stoichiometric α-$UO_2(OH)_2$ (Taylor & Hurst 1971) (right). Filled circles are uranyl ions (uranyl O atoms not shown); open circles are O atoms of the sheets (O^{2-} and OH^-): solid circles represent occupied positions, dotted circles are vacancies in α-$UO_2(OH)_2$ that are replaced by a single O atom in the schoepite-type sheet. The structural sheet in "dehydrated schoepite" has the same composition as the schoepite sheet ($UO_3{\bullet}0.75H_2O$), and therefore must consist predominantly of five-coordinated uranyl ions; however, the high degree of order that gives rise to the larger unit-cell in schoepite and metaschoepite is absent in "dehydrated schoepite", in which anion vacancies are disordered, giving rise to the α-$UO_2(OH)_2$-type unit cell.

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