

CRYSTAL CHEMICAL STUDIES OF SOME URANYL OXIDE HYDRATES*

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ABSTRACT

Mineralogical and crystal-chemical studies have been made of the closely related uranyl oxide hydrates becquerelite, billietite, fourmarierite, masuyite, schoepite, and vandendriesscheite. An essential feature of the work is the use of *x*-ray precession techniques with carefully selected single crystals to determine accurately the crystallographic constants, the symmetry, and the structural relations of these minerals. Indices of refraction and optical orientation were determined on crystals both identified and oriented by the *x*-ray precession method. Similarly identified crystals were used to obtain the indexed powder pattern data listed. The results obtained on the physical properties, the *x*-ray crystallography, the *x*-ray powder data, and the optical properties are listed and compared with the work of other investigators in the 23 tables of the paper.

Crystals of schoepite and of vandendriesscheite that are apparently single, actually consist of several crystallographically distinct phases in parallel intergrowth. The spontaneous alteration from one phase to another that occurs in these crystals results from loss of water of hydration. All six of the minerals studied yield strikingly similar pseudo-hexagonal diffraction patterns. A reasonable crystal structure based on these patterns consists of $\text{UO}_2(\text{OH})_2$ layers (similar to those proved by Zachariasen to exist in UO_2F_2) parallel to the perfect cleavage (001), with the water of hydration and any cations present in inter-layer positions.

INTRODUCTION

As part of an extensive program of investigation by this laboratory on the mineralogy and geochemistry of the Colorado Plateau, study was initiated of the crystal structures of some uranyl oxide hydrates and related alkaline earth and lead salts. In the following, these minerals will be referred to simply as uranyl oxide hydrates, the term being taken to include any related salts. Prior to structure analysis, accurate determinations were begun of the unit-cell constants and space groups of the following minerals: becquerelite, billietite, fourmarierite, masuyite, schoepite, and vandendriesscheite. As this work progressed it became apparent that the existing literature on these minerals was confused and often contradictory. Therefore our investigation was extended to include redetermination of the indices of refraction and optical orientation for crystals identified from the *x*-ray work. In addition, *x*-ray powder photographs were made from selected crystals of each material. The powder patterns were measured and the lines indexed with the aid of single-crystal *x*-ray precession patterns. All *x*-ray and optical data for each mineral have thus been correlated and have been combined

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with spectrographic analysis whenever enough authentic material was available for such analysis. The results of these studies are presented here. Comparison with earlier findings is given when such comparison appeared warranted, but no exhaustive survey of the literature has been attempted. A comprehensive description of the systematic mineralogy of uranium (including that of the uranyl oxide hydrates) and thorium has recently been published by Frondel (1958).

DESCRIPTION OF MINERAL SPECIMENS

All of the mineral specimens used in this study originated in the Shinkolobwe deposit, Katanga district, Belgian Congo. We are greatly indebted to Professor Clifford Frondel, Harvard University, for making available to us the following specimens, each of which is a type specimen from Dr. J. F. Vaes, Union Minière du Haut Katanga: (1) *billietite*, (HM No. 104455), excellent yellow crystals ranging up to 2 mm. in size, associated with green metatorbernite crystals and powdery pale-yellow rutherfordine; (2) *masuyite*, (HM No. 106524), tiny (<0.1 mm.) reddish-orange to brown-orange crystals, associated with large (to 3 mm. length) pale-yellow lath-like crystals of rutherfordine, yellow crystals of becquerelite, and reddish-orange fourmarierite crystals; (3) *vandriesscheite*, (HM No. 106523), excellent orange crystals (about 0.2 mm. in size), associated with well-developed becquerelite crystals and green metatorbernite crystals, and with powdery pale-yellow rutherfordine.

We are also greatly indebted to Dr. George Switzer, U. S. National Museum, for loaning us the following specimens: (1) *becquerelite* (USNM No. R8387) in fibrous matted crystals; (2) *fourmarierite* (USNM No. R8396), containing orange fourmarierite crystals together with tiny rutherfordine "whiskers" and reddish-brown clumps of goethite crystals; (3) *schoepite* (USNM No. 94712), crystals in various stages of alteration.

DESCRIPTION OF CRYSTALS

Physical properties such as color, habit, and cleavage vary only slightly among the six uranyl oxide hydrates; only billietite and masuyite occur as twins. A summary of these properties for each of the minerals is given in Table 1. It is evident that identification of any one mineral on the basis of these physical properties can be only tentative and x-ray and optical studies are also needed for definitive characterization.

The six minerals can be divided into two color classes: a predominantly yellow group, which includes becquerelite (golden to lemon yellow), billietite (deep golden yellow), and altered schoepite (schoepite II and III, yellow), and a predominantly orange group, which includes

TABLE 1. PHYSICAL PROPERTIES OF URANYL OXIDE HYDRATES

Name	Color	Habit	Twinning	Cleavage
Becquerelite	Golden to lemon yellow, less commonly orange yellow	Usually prismatic, elongated [010]; occasionally tabular on {001}	Not observed	Perfect, (001)
Billietite	Deep golden yellow	Tabular on {001}, pseudo-hexagonal aspect	Usually twins on (110)	Perfect, (001)
Fourmarierite	Reddish orange	Tabular on {001}, elongated [010], pseudo-hexagonal aspect	Not observed	Perfect, (001); secondary, (100)
Masuyite	Reddish to brownish orange	Tabular on {001}, pseudo-hexagonal aspect	Invariably extensively twinned, both on (110) and (130)	Perfect, (001); secondary, (010)
Schoepite I	Amber brown to gold brown	Tabular on {001}, elongated [010], pseudo-hexagonal aspect; (according to Walker (1923) also prismatic elongated [001])	Not observed	Perfect, (001); secondary, (010)
Schoepite II, III	Yellow	As for schoepite I	Not observed	
Vandendriesscheite	Yellowish orange to orange	Prismatic, elongated [100], (010) striated parallel to [100]; also tabular on {001}, elongated [100], pseudo-hexagonal aspect	Not observed	Perfect, (001)

fourmarierite (reddish orange), masuyite (reddish to brownish orange) and vandendriesscheite (yellow orange to orange). Unaltered schoepite (schoepite I) is amber brown to gold brown.

All six minerals are orthorhombic, probably holohedral, and occur in one or both of two common habits: either tabular on {001} with a pseudo-hexagonal outline caused by the presence of forms such as {110}, {111}, {100}, and {010}, or prismatic, elongated along either [100] or [010] and exhibiting a variety of prism forms. Perfect cleavage is always parallel to (001); some secondary cleavages are noted in Table 1. In the present study, billietite, fourmarierite, masuyite, and schoepite were found only as tabular crystals, whereas becquerelite and vandendriesscheite were found both as tabular and as prismatic crystals. Excellent photographs, some in color, of crystals of becquerelite, billietite, fourmarierite, and masuyite-(?) are given by Chervet and Branche (1955). More recently, a remarkably beautiful series of color photographs of a number of uranium minerals, together with brief summaries of the scientific data for these minerals, have been collected in a book by Destas, Vaes, and Guillemin (1958).

Twinning has been reported, and was observed in this study, only for

billietite and for masuyite. Billietite twinning was described by Vaes (1947) and Thoreau (1948); single crystals of billietite are rare although some small ones (about 0.2 mm. cross section) were found on the HM No. 104455 specimen. The common twin we observed has twin and composition plane (110). Masuyite twinning was described by Vaes (1947) and we found it to be exactly as he described it: the twins occurring with (110) and with $(\bar{1}\bar{3}0)$ as twin and composition planes. The twinning is persistent and distinctive, providing the only means we found for differentiating masuyite from fourmarierite under the microscope. The mode of twinning in billietite and masuyite was checked by x -ray precession patterns, as well as by optical study. Fourmarierite was always found as tiny, perfect single crystals, whereas single crystals of masuyite for x -ray study were obtained only by careful cutting of twinned crystals.

No attempt has been made during the present investigation to examine crystal morphology in detail, partly because an extensive literature on this subject already exists. Some of the more comprehensive references are: Schoep (1930) on becquerelite, fourmarierite and schoepite, Thoreau (1948) on billietite and vandendriesscheite, and Vaes (1947) on billietite, masuyite, and vandendriesscheite. Previous studies can be readily correlated with the present x -ray findings provided that the perfect cleavage is always taken as parallel to (001), the elongation direction is identified as noted in Table 1, and the optical orientation is followed as given in Table 16. Because the morphology is so similar for all six minerals, x -ray examination, which provides rapid and accurate differentiation, is preferable to any morphologic study for purposes of identification.

X-RAY CRYSTALLOGRAPHY

Single-crystal x -ray studies were made using quartz-calibrated precession cameras with both Mo/Zr and Cu/Ni radiations (λ MoK α = 0.7107 Å; λ CuK α = 1.5418 Å). Film measurements were corrected for both horizontal and vertical film shrinkage. For all the minerals a characteristic pseudo-hexagonal pattern was obtained for the $hk0$ net, which is the zero level normal to [001] and hence parallel to the cleavage plane (001). A typical pattern is illustrated in Fig. 1. A pseudo-orthohexagonal cell can be defined from these patterns as well as the true orthorhombic cell, and cell constants for each type of cell are given in Table 2. In addition, Table 2 lists the cell volume of the true orthorhombic cell and the possible space groups for each mineral, including alteration forms. Non-centrosymmetric space groups have been included in Table 2 where their possibility exists according to the x -ray data alone. Piezoelectric tests made on an apparatus of the Giebe-Scheibe type gave negative

results, and since the morphology of each of the minerals is clearly holohedral the assignment of centrosymmetric space groups is valid.

Table 2 lists probable chemical formulas and cell contents for all the minerals except masuyite and vandendriesscheite; the corresponding calculated and observed specific gravities are compared in this table. New specific gravity determinations were made of becquerelite (12 mg. sample) and vandendriesscheite (2 mg. sample) with the Berman balance, using toluene as the immersion liquid. Values of the specific gravity for the other minerals are taken from the literature. Discussion of the chemical formulas is included in the section on chemical considerations and crystal structure.

Comparison of the data of the present study with previously reported data is made in Tables 3 through 8, and in the text below. Table 3 deals with becquerelite, Table 4 with billietite, Table 5 with fourmarierite, Table 6 with masuyite, Table 7 with unaltered schoepite (schoepite I), and Table 8 with vandendriesscheite.

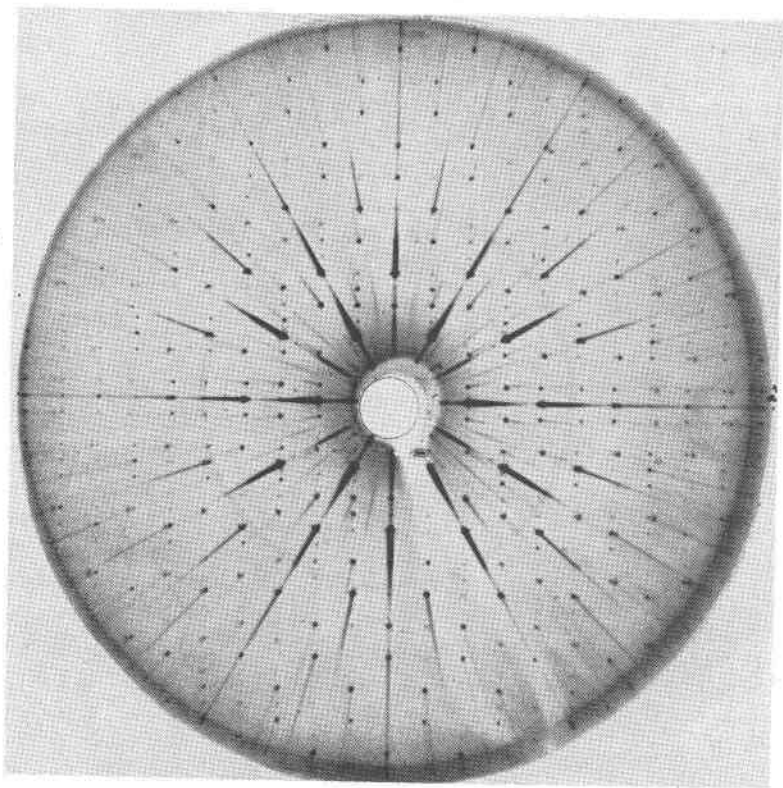


FIG. 1. Characteristic pseudo-hexagonal $hk0$ net, illustrated by schoepite.

TABLE 2. CRYSTAL DATA FOR THE URANYL OXIDE HYDRATES
 (Data of present study unless otherwise noted)

	Becquerelite			Billietite			Fourmarierite			Masuyite			Schoepfite			Vandriesscheite		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	I	II	III	
Cell constants ^a	13.86 Å	7.14 Å	14.00 Å	14.33 Å	13.99 Å	14.12 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å	14.07 Å
<i>a</i>	12.38	12.08	16.47	16.79	16.72	16.83	40.85	40.85	41.31	40.85	41.31	40.85	41.31	40.85	41.31	40.85	41.31	40.85
<i>b</i>	14.96	15.10	14.39	14.73	14.73	15.22	43.33	43.33	43.33	43.33	43.33	43.33	43.33	43.33	43.33	43.33	43.33	43.33
<i>c</i>																		
Pseudo-orthorhombic cell constants																		
<i>a'</i>	<i>a</i> /2 = 6.93	<i>a</i> '/1 = 7.14	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.16	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.06	<i>a</i> /2 = 7.04	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.06	<i>a</i> /2 = 7.04	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.04	<i>a</i> /2 = 7.00	<i>a</i> /2 = 7.04	<i>a</i> /2 = 7.03
<i>b'</i>	<i>b</i> /3 = 4.13	<i>b</i> /3 = 4.03	<i>b</i> /4 = 4.12	<i>b</i> /3 = 4.20	<i>b</i> /4 = 4.04	<i>b</i> /4 = 4.21	<i>b</i> /10 = 4.08	<i>b</i> /4 = 4.18	<i>b</i> /4 = 4.18	<i>b</i> /4 = 4.21	<i>b</i> /4 = 4.21	<i>b</i> /10 = 4.08	<i>b</i> /10 = 4.13	<i>b</i> /4 = 4.18	<i>b</i> /10 = 4.08	<i>b</i> /10 = 4.13	<i>b</i> /10 = 4.08	<i>b</i> /10 = 4.13
<i>c'</i>	<i>c</i> /2 = 7.48	<i>c</i> /2 = 7.55	<i>c</i> /2 = 7.20	<i>c</i> /2 = 7.36	<i>c</i> /6 = 7.10	<i>c</i> /2 = 7.61	<i>c</i> /6 = 7.22	<i>c</i> /2 = 7.36	<i>c</i> /2 = 7.36	<i>c</i> /2 = 7.61	<i>c</i> /2 = 7.61	<i>c</i> /6 = 7.22	<i>c</i> /6 = 7.22	<i>c</i> /2 = 7.36	<i>c</i> /6 = 7.22	<i>c</i> /6 = 7.22	<i>c</i> /6 = 7.22	<i>c</i> /6 = 7.22
Pseudo-hexagonal <i>α'</i>	120.8°	119.4°	120.5°	120.4°	120.0°	120.8°	120.2°	120.4°	120.9°	120.8°	120.8°	120.2°	120.4°	120.9°	120.2°	120.4°	120.2°	120.4°
Volume (true cell) Å ³	2567	1303	3318	3544	43272	3617	24904	3446	3446	3617	24904	25185	24904	3446	24904	25185	24904	25185
Units of UO ₂ (OH) ₂	24	12	32	32	432	32	240	32	32	32	240	240	240	32	240	240	240	240
(true cell)																		
Formula proposed	CaO·6UO ₂ ·11H ₂ O ^b	BaO·6UO ₂ ·11H ₂ O ^b	PbO·4UO ₂ ·4H ₂ O	UO ₂ ·(2+?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O	UO ₂ ·(2-?)H ₂ O
Spec. grav. (calc.)	5.10	5.27	5.76	4.83	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Spec. grav. (obs.)	5.14 ± 0.06	5.28 ± 0.01 ^f	5.74 ± 0.05 ^f	4.8 ^h	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	5.12 ± 0.02 ^d			4.49 ⁱ														
Space Group	<i>Pnma</i> - (No. 62), or <i>Pn2a</i> - (No. 33)	<i>Pnma</i> - (No. 58), or <i>Pn2a</i> - (No. 34)	<i>Bbmm</i> - (No. 63), or <i>Bb2m</i> - (No. 36) or <i>Bbm2</i> - (No. 40)	<i>Pbca</i> - (No. 61)	<i>Pbma</i> - (No. 60)	<i>Pbca</i> - (No. 61)	<i>Pmma</i> - (No. 51), <i>P2ma</i> - (No. 26), or <i>Pm2a</i> - (No. 28)	<i>Pbca</i> - (No. 61)	<i>Pbma</i> - (No. 60)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 60)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)	<i>Pbca</i> - (No. 61)

^a Error ± 0.3%.
^b After Protas (1957).
^c Mineral, Protas (1957).
^d Synthetic, Protas (1937).
^e After Brasseur (1949).
^f Brasseur (1949).
^g Brasseur (1948).
^h Billiet and de Jong (1935).
ⁱ Bignand (1955).

Becquerelite, billietite, and fourmarierite

Cell constants previously reported for becquerelite and billietite are in good agreement with those found during the present study except that a doubled value for a in billietite was given by Frondel and Cuttitta (1953) (Table 4). The doubled value is found if a twin crystal, instead of a single crystal, is examined by [100] rotation x-ray photographs. This result arises from the fact that in billietite, the twinning on (110), following the classical law for pseudo-hexagonal lattices, brings about the almost parallel alignment of the [110] direction of one member of the twin edifice with the [100] direction of its pseudosymmetrically related member. Since, for billietite, $a = 7.14 \text{ \AA}$ and $[110] = 14.03 \text{ \AA}$, i.e. very nearly $2a$, a rotation pattern made around this common direction will have layer-line geometry leading to the doubled value. The smaller value of a originally given by Brasseur (1949) is correct. The calculated

TABLE 3. CRYSTAL DATA FOR BECQUERELITE
Comparison of the results of various investigators

	Present study (Cell constants $\pm 0.3\%$)	Protas (1957)	Frondel and Cuttitta (1953)	Brasseur (1948)	Billiet and de Jong (1935)
a	13.86 \AA	13.86 $\pm 0.03 \text{ \AA}^b$	13.92 $\pm 0.005 \text{ \AA}$	— ^d	13.9 kX
b	12.38	12.42 ± 0.03	12.45 ± 0.005	—	12.55
c	14.96	14.96 ± 0.03	15.09 ± 0.005	—	14.9
$a:b:c$	1.120:1:1.208	(1.116:1:1.205) ^c	(1.118:1:1.212)	—	1.107:1:1.187
Vol. unit cell	2567 \AA^3	(2575 \AA^3)	(2615 \AA^3)	—	2600 kX ³
Formula proposed	CaO·6UO ₃ · 11H ₂ O ^h	CaO·6UO ₃ ·11H ₂ O	7UO ₃ ·11H ₂ O	UO ₃ ·2H ₂ O	2UO ₃ ·3H ₂ O
Z	4	4	4	24	13
Space group	<i>Pnma</i> - (No. 62), prob., or <i>Pn2₁a</i> - (No. 33)	—	<i>Pnma</i>	<i>Pnma</i> ^e	—
Spec. grav. (calc.)	5.10 ± 0.01	(5.08)	5.60	(4.98) ^f	(5.25) ^g
Spec. grav. (obs.)	5.14 ± 0.06	5.12 ± 0.02 mineral 5.10 ± 0.02 synthetic	5.3 (approx.)	5.090 ± 0.035	5.2

^a After Protas (1957).

^b Errors listed are those assigned by original authors.

^c Quantities enclosed in parentheses calculated by present authors from data of original authors, except as indicated in footnotes f and g below.

^d Brasseur states that he found values of a , b , and c in agreement with those of Billiet and de Jong (1935).

^e Brasseur is apparently quoting Wolfe, private communication (1941), in Palache, Berman, and Frondel (1944).

^f Calculated for a , b , c of present study and cell contents 24[UO₃·2H₂O].

^g Calculated for a , b , c of present study and cell contents 13[2UO₃·3H₂O].

TABLE 4. CRYSTAL DATA FOR BILLIETITE
Comparison of the results of various investigators.

	Present Study (Cell constants $\pm 0.3\%$)	Brasseur (1949)	Frondel and Cuttitta (1953)	
<i>a</i>	7.14 ₃ Å	7.10 kX	14.25 Å ^c	13.98 Å ^d
<i>b</i>	12.08	12.06	12.04	12.08
<i>c</i>	15.10	15.06	15.06	15.06
<i>a:b:c</i>	0.591:1:1.250	0.5887:1:1.2486	(1.184:1:1.251)	(1.157:1:1.247)
Vol. unit cell	1303 Å ³	(1290 kX ³) ^b	(2584 Å ³)	(2543 Å ³)
Formula proposed	BaO·6UO ₃ ·11H ₂ O ^a	BaO·6UO ₃ ·11H ₂ O	BaO·6UO ₃ ·11H ₂ O	
Z	2	2	4	
Space group	<i>Pnmm</i> -(No. 58), prob., or <i>Pn2n</i> -(No. 34)	<i>Pnmm</i>	<i>Pmma</i>	
Spec. grav. (calc.)	5.27	(5.27)	5.33	5.40
Spec. grav. (obs.)	—	5.28	5.32	5.36

^a After Brasseur (1949).

^b Quantities in parentheses calculated by present authors from data of original authors.

^c Crystal from HM No. 104456; error in lattice constants listed by authors as ± 0.005 Å.

^d Crystal from HM No. 104455; error in lattice constants listed by authors as ± 0.005 Å.

angle of obliquity for billietite twinning is $1^{\circ}11'$. Fourmarierite cell constants found in the present study are in reasonable agreement with those reported by Brasseur (1941) (Table 5).

TABLE 5. CRYSTAL DATA FOR FOURMARIERITE
Comparison of the results of various investigators.

	Present study (Cell constants $\pm 0.3\%$)	Brasseur (1941, 1948)
<i>a</i>	14.00 Å	14.07 kX
<i>b</i>	16.47	16.72
<i>c</i>	14.39	14.52 ^b
<i>a:b:c</i>	0.850:1:0.874	(0.842:1:0.868) ^c
Vol. unit cell	3318 Å ³	(3416 kX ³)
Formula proposed	PbO·4UO ₃ ·4H ₂ O ^a	PbO·4UO ₃ ·7H ₂ O
Z	8	8
Space group	<i>Bbmm</i> -(No. 63), prob., <i>Bb2₁m</i> -(No. 36), or <i>Bbm2</i> -(No. 40)	—
Spec. gravity (calc.)	5.76	5.77
Spec. gravity (obs.)	—	5.740 \pm 0.051

^a Best fit to observed specific gravity of Brasseur (1948).

^b The *a*- and *c*-axes of Brasseur (1941) interchanged to conform to convention of present authors.

^c Quantities in parentheses calculated by present authors from data of original author.

Masuyite

The large cell edges given for masuyite in Table 2 and in Table 6 are required by the presence of some faint, diffuse, and relatively sparse spots on the precession patterns. Previous investigators have reported smaller cells: Brasseur (1950) gives $a=14.06$, $b=12.06$, $c=14.25$ kX, and J. W. Frondel in Frondel (1958) gives $a=13.90$, $b=12.31$, $c=14.92$ Å. If the faint spots are neglected, the results obtained in the present study lead to cell edges of $a=13.98$, $b=12.11$, and $c=14.20$ Å, in agreement with Brasseur's values. The value for the length of the c -axis found by J. W. Frondel differs significantly from that found by Brasseur and by us. It does, in fact, agree well with the c for becquerelite, and it is possible that the cell constants given by Frondel (1958) for masuyite are actually those of becquerelite. Brasseur gives the space group *Pcna* for masuyite, in agreement with our findings, the faint spots again being neglected. It was not possible to determine the space group of the large cell. Although great care was exercised in trying to use only single crystals in the x -ray work for masuyite, it is possible that the mineral is twinned on a fine scale, and that this twinning could lead to the large cell edges found. The results of Brasseur and Frondel for masuyite are compared with the results of the present study in Table 6.

Schoepite

Crystals of schoepite that are apparently single yield multiple diffraction patterns. These multiple patterns correspond to the presence of two out of three possible distinct orthorhombic phases in parallel inter-

TABLE 6. CRYSTAL DATA FOR MASUYITE
Comparison of the results of various investigators.

	Present study (Cell constants $\pm 0.3\%$)	Present study— neglecting very weak hkl	Brasseur (1950)	Frondel (1958) ^a
a	41.93 Å	13.98 Å	14.06 kX	13.90 Å
b	24.22	12.11	12.06	12.31
c	42.61	14.20	14.24	14.92
$a:b:c$	1.731:1:1.759	1.154:1:1.172	1.166:1:1.181	1.129:1:1.212
Vol. unit cell	43272 Å ³	2404 Å ³	2415 kX ³	2553 Å ³
Formula proposed	—	—	—	UO ₃ ·2H ₂ O ^b
Space group	—	<i>Pcna</i> -(No. 50)	<i>Pcna</i> -(No. 50)	—

^a Crystallography by J. W. Frondel. The crystal data may be for becquerelite (see Table 3).

^b Chemical analysis by F. Cuttitta. Note, however, that Vaes (1947) described masuyite as a Pb-bearing mineral.

TABLE 7. CRYSTAL DATA FOR SCHOEPITE I (UNALTERED SCHOEPITE)
Comparison of the results of various investigators.

	Present Study (Cell constants $\pm 0.3\%$)	Billiet and de Jong (1935)	Palache (1934); Schoep (1932)
<i>a</i>	14.33 Å	14.40 kX	—
<i>b</i>	16.79	16.89	—
<i>c</i>	14.73	14.75	—
<i>a:b:c</i>	0.854:1:0.877	0.852:1:0.873	0.8516:1:0.8745 ^b
Vol. unit cell	3544 Å ³	3590 kX ³	—
Formula proposed	UO ₃ ·2H ₂ O ^a	4UO ₃ ·9H ₂ O	3UO ₃ ·7H ₂ O ^c
Z	32	8	—
Space group	<i>Pbca</i> -(No. 61)	—	—
Spec. grav. (calc.)	4.83	4.83	—
Spec. grav. (obs.)	—	4.8	4.96 ^c

^a See Frondel (1958) and discussion in text of present paper.

^b Mean of measurements by Walker (1923), Ungemach (1929), and Palache (1934), as reported by Palache (1934).

^c Schoep (1932).

growth in the crystal. The three phases are designated schoepite I, II and III; data are given for these in the appropriate tables of this report.

Examination of the specimen USNM No. 94712 showed that the schoepite crystals are present in various stages of alteration. Commonly, crystals occur that have an amber-brown core completely or partially surrounded by a golden-yellow alteration product. X-ray examination shows that the amber-brown part consists chiefly of schoepite I with small amounts of schoepite II present, and that the yellow alteration product consists either of schoepite II, or of schoepite III, usually with small amounts of schoepite I also present. The fact that schoepite II and schoepite III were not found together in any of the crystals studied does not preclude the possibility that they can occur together, since no exhaustive search was made to test this point. Completely yellow crystals answering the description given for paraschoepite by Schoep and Stradiot (1947) are also present on the specimen. These give the schoepite III pattern. Because of the distinctive x-ray pattern given by the yellow crystals and the excellent agreement of the optical measurements obtained in the present study with those originally given by Schoep and Stradiot in 1947, there can be little doubt as to the validity of paraschoepite. Entirely amber-brown crystals are also present on the specimen. Although these appear to be completely unaltered, they show a weak x-ray pattern corresponding to schoepite II along with the expected strong pattern of schoepite I. The cell constants for schoepite I

agree well with those given by Billiet and de Jong (1935) for "schoepite" (Table 7). Data for schoepite II have not been reported previously. Figure 2 illustrates a portion of an $hk0$ x-ray precession pattern of a schoepite crystal showing the results obtained when two phases are present.

Vandendriesscheite

X-ray patterns of vandendriesscheite are also multiple, corresponding to the presence of two distinct orthorhombic phases present in parallel intergrowth in apparently single crystals. These phases are designated vandendriesscheite I and II and the data for these are given in the appropriate accompanying tables. Crystals of vandendriesscheite occur containing mostly phase I with small amounts of phase II present; crystals with the reverse proportions were also found. Unlike schoepite, the crystals of vandendriesscheite do not change appearance on phase change. However, this phase change does manifest itself in the variability of the β and γ indices of refraction, as well as in the x-ray patterns.

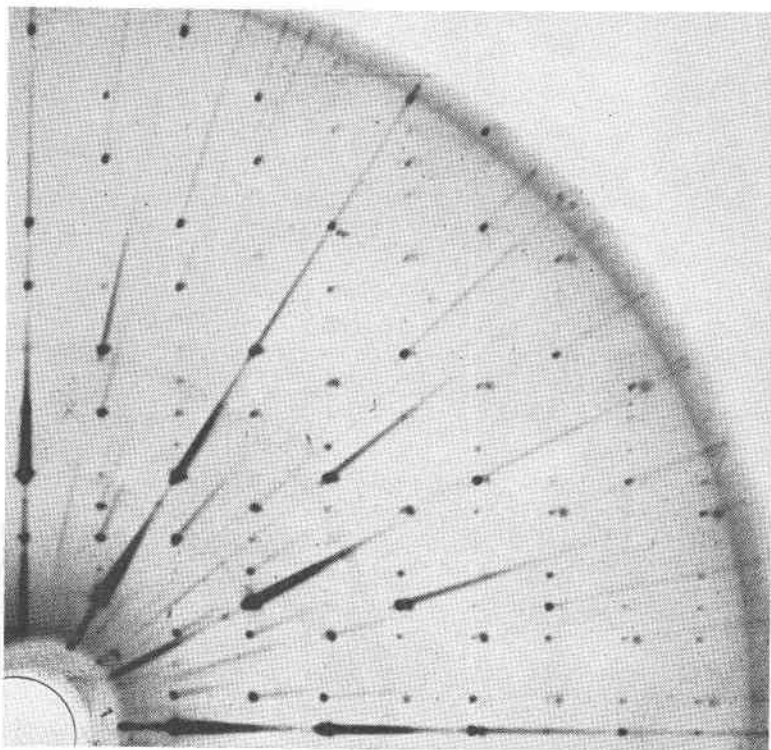


FIG. 2. Enlarged portion of the same pattern shown in Fig. 1 showing the presence of diffraction spots due to two phases in parallel intergrowth.

The weaker reflections leading to the large b -length for both phases of vandendriesscheite (Table 2) are sharp, plentiful, and easily visible on the precession patterns. However, the weaker reflections requiring the large c -axis are, as in masuyite, very faint, diffuse, and relatively sparse. J. W. Frondel in Frondel (1958) has reported values of a , b , and c for four different crystals of vandendriesscheite. The results she obtained are compared with the results of the present study in Table 8. It can be seen from this table that the two sets of results are not in very good agreement. The variability in the cell constants reported in Frondel (1958) was not encountered in the present study, where, however, only crystals from a single specimen were examined. It is stated in Frondel (1958) that a weak set of x -ray reflections was found superimposed on and irrationally related to the main diffraction pattern in Weissenberg photographs of vandendriesscheite. In the present investigation the weak set was found to be unequivocally rational to the main set of reflections. In contrast to masuyite, there was absolutely no indication of any twinning in vandendriesscheite, and consequently no doubt about the validity of the large cell for this reason.

Schoepite and vandendriesscheite appear to alter by spontaneous dehydration at room temperatures. The evidence for this conclusion and a discussion of the complexity of the alteration are given below in the section on chemical considerations and crystal structure. Precession patterns of altered crystals show the usual sharp spots for the parent phase and diffuse spots for the phase resulting from the alteration, due to the fine-grained nature of the alteration product.

X-RAY POWDER DATA

A 114.59 mm. diameter powder camera was used with Cu/Ni and Cr/V radiations (λ CuK α = 1.5418 Å; λ CrK α = 2.2909 Å) to obtain the powder films. Tables 9 through 15 give powder pattern data for the minerals, as follows: becquerelite, Table 9; billietite, Table 10; fourmarierite, Table 11; masuyite, Table 12; schoepite, Table 13; dehydrated schoepite, UO₂(OH)₂, Table 14; vandendriesscheite, Table 15. Measurements from the patterns for becquerelite, fourmarierite, and vandendriesscheite were corrected for film shrinkage; measurements from the other patterns were not, but film shrinkage corrections were negligible for these, as shown by the good agreement between the observed and calculated interplanar spacings. The lower limit measurable for 2θ was about 6°. Calculated interplanar spacings were based on the values of the cell constants as given in Table 2. Indexing of the powder lines was checked by examination of the intensities of the corresponding reflections on the single-crystal precession photographs; estimated in-

TABLE 8. CRYSTAL DATA FOR VANDENDRIESSCHEITE
Comparison of the results of various investigators.

	Present study (Cell constants $\pm 0.3\%$)		Present study—neglecting very weak <i>hkl</i>		Frondel (1958) ^a			
	I	II	I	II	Crystal 1	Crystal 2	Crystal 3	Crystal 4
<i>a</i>	14.07 Å	14.07 Å	14.07 Å	14.07 Å	13.96 Å	14.12 Å	14.01 Å	13.99 Å
<i>b</i>	40.85	41.31	13.62	13.77	14.36	16.75	16.80	16.44
<i>c</i>	43.33	43.33	14.44	14.44	14.41	14.72	14.68	14.30
<i>a:b:c</i>	0.344:1:1.061	0.341:1:1.049	1.033:1:1.061	1.022:1:1.049	0.972:1:1.003	0.843:1:0.879	0.834:1:0.874	0.851:1:0.870
Vol. unit cell	24904 Å ³	25185 Å ³	2767 Å ³	2798 Å ³	(2889 Å ³) ^b	(3481 Å ³)	(3455 Å ³)	(3289 Å ³)
Formula proposed	—	—	—	—	PbO·7UO ₃ ·12H ₂ O ^c	PbO·7UO ₃ ·12H ₂ O ^d	PbO·7UO ₃ ·12H ₂ O ^e	—
Z	—	—	—	—	(4)	(4)	(4)	(4)
Spec. grav. (calc.)	—	—	—	—	5.61	4.66	4.69	—
Spec. grav. (obs.)	5.45	—	—	—	5.46	—	4.72	—

^a Crystallography by J. W. Frondel.

^b Quantities in parentheses calculated by present authors from data of original authors.

^c Chemical analysis by F. Cutilita.

^d Chemical analysis by F. A. Gonyer.

tensities for the single-crystal reflections are included in the tables, where feasible. All calculated interplanar spacings are given for $d \geq 2.5$ Å except in Table 15 for vandendriesscheite, where, because of the large cell, the listing is for $d \geq 3.0$ Å. However, all observed spacings smaller in value than these could be satisfactorily accounted for. Tables 9 through 15 also give observed powder data found by other investigators and believed by us to be reliable.

Each of these six uranyl oxide hydrates can be identified from its powder pattern provided certain precautions are observed. Material chosen for the powder spindle should, of course, be carefully selected for homogeneity. A sharp clear pattern with maximum line resolution is required. With the commonly used 114.59 mm. diameter camera, a small diameter (*ca.* 0.2 mm.) powder spindle is desirable, and line-focus, rather than spot-focus, radiation is recommended. With good patterns, becquerelite, billietite, and schoepite can be promptly identified. Powder patterns of schoepite always show lines corresponding to each of the two or three possible phases, but their presence does not prevent correct overall identification of the material as schoepite. Fourmarierite, masuyite, and vandendriesscheite can easily be distinguished as a group from the other three minerals, but identification of any one of the three is more difficult. Comparison of the powder data given in Tables 11, 12, and 15 shows that fourmarierite, masuyite and vandendriesscheite can be differentiated if the powder patterns are good. However, single-crystal x -ray studies, preferably by precession methods, provide the best and certainly the most rapid and convenient means of unambiguously distinguishing among these various uranyl oxide hydrates and their alteration products.

OPTICAL DATA

Indices of refraction were measured with Na light ($\lambda = 589 \text{ m}\mu$). Cargille's High Series liquids were used and the indices of the liquids were checked on a Leitz-Jelley refractometer. No special effort was made to keep the temperature constant; room temperatures were $25^\circ \pm 5^\circ$ C. Optical orientation was in each case checked on crystals for which crystallographic directions had been identified by precession x -ray work.

Values found in the present study for the indices of refraction and observed V_α , as well as data on pleochroism and optical orientation, are summarized in Table 16. Comparison between data of the present study and data reported by other investigators is made in Tables 17 through 23. Table 17 is for becquerelite, Table 18 for billietite, Table 19 for fourmarierite, Table 20 for masuyite, Table 21 for schoepite I, Table 22 for schoepite III, and Table 23 for vandendriesscheite.

All the uranyl oxide hydrates are biaxial negative with $X=c$ in each

TABLE 9. X-RAY POWDER DATA: BECQUERELITE

Calculated		Present Study			Frondel and Cuttitta (1953) ¹		Protas (1957)			
		Measured			Measured		Measured $d(\text{\AA})$			
		Single Crystal	$d(\text{\AA})$	Powder Cu/Ni $\lambda = 1.5418 \text{\AA}$	$d(\text{\AA})$	Cu/Ni	Natural Mineral	Synthetic Mineral		
hkl	d_{hkl}	I	I	d_{hkl}	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
101	10.17	*								
011	9.54	*			(8.51) ²	1				
111	7.86	*								
002	7.48	VS	100	$7.44 \pm .05$	7.50	10	7.54	FF	7.48	FF
200	6.93	a								
102	6.58	S	3	$6.56 \pm .04$	6.63	2	6.59	mf	6.59	mf
201	6.29	a								
020	6.20	*	1	$6.21 \pm .04$	6.24	1	6.22	mf	6.22	mf
210	6.05	w					6.05	mf	6.05	mf
112	5.81	a					5.81 ³	mf	5.81 ³	mf
211	5.61	m	1	$5.59 \pm .03$	5.63	1				
121	5.29	*								
202	5.08	a							4.78	ff
022	4.77	w								
212	4.70	w								
103	4.69	m	6	$4.68 \pm .02$	4.71	6	4.71	mf	4.71	mf
013	4.63	a								
220	4.62	w								
122	4.51	*								
301	4.41	w			4.31	1			4.40	f
221	4.41	a								
113	4.39	a								
311	4.16	a								
203	4.05	w							4.05	f
031	3.981	a								
302	3.931	w-							3.92	f
222	3.930	*								
213	3.848	a							3.84	f
131	3.826	a								
312	3.747	a								
123	3.740	a								
004	3.740	VS	30	$3.73 \pm .015$	3.75	8	3.74	m	3.73	m
104	3.611	m	3	$3.61 \pm .02$					3.61	f
321	3.595	a								
230	3.548	VS	21	$3.54 \pm .015$	3.56	8	3.55	F,FF	3.55	F,FF
132	3.498	w-								
114	3.467	w-								
400	3.465	VS	4	$3.45 \pm .015$	3.48	2	3.47	m	3.46	m
231	3.452	S								
303	3.389	m								
223	3.388	a	4	$3.37 \pm .015$	3.39	2	3.40	m	3.39	m
401	3.376	VS								
410	3.337	w-								
322	3.319	a								
204	3.291	a								
313	3.269	*								
411	3.257	a								
232	3.206	VS	35	$3.20 \pm .01$	3.22	9	3.21	F,FF	3.20	F,FF
024	3.202	w-								
214	3.181	w								
033	3.181	w								
402	3.144	VS	4	$3.14 \pm .01$	3.13	1	3.15	mF	3.14	mF
124	3.120	w								
133	3.100	w							3.10	f
040	3.098	w								
412	3.048	a								
420	3.024	a								
331	3.016	a								
323	2.973	*								
421	2.964	m	3	$2.959 \pm .007$	2.97	2	2.97	mf	2.97	mf
141	2.963	a								
105	2.925	w								
015	2.908	w								
304	2.907	w								
224	2.907	a								
233	2.891	m	3	$2.894 \pm .006$	2.88	3				
042	2.862	w								

¹ See also Frondel, Riska, and Frondel (1956).² Must be β reflection for 002.³ Possibly a typographical error and should be 5.61.

TABLE 9 (continued)

Calculated		Present Study		Frondel and Cuttitta (1953) ¹		Protas (1957)				
		Measured		Measured		Measured $d(\text{\AA})$				
		Single Crystal	$d(\text{\AA})$	Powder Cu/Ni $\lambda = 1.5418 \text{\AA}$	$d(\text{\AA})$	Cu/Ni	Natural Mineral		Synthetic Mineral	
332	2.847	a								
115	2.846	a								
403	2.846	m	3	2.848 ± .006			2.86	mf	2.85	mf
314	2.830	*								
240	2.828	a								
422	2.804	a								
142	2.803	a								
241	2.779	a								
413	2.773	*								
205	2.747	w	3	b { 2.74 to 2.71	2.73	1				
501	2.726	a								
134	2.718	w								
215	2.682	a								
511	2.662	w-							2.67	f
430	2.654	a								
242	2.645	a								
125	2.645	a								
324	2.632	*								
333	2.620	*								
431	2.614	a								
502	2.599	a								
423	2.586	*								
143	2.585	a								
234	2.574	m	9	2.566 ± .006	2.58	7	2.58	m	2.58	m
512	2.544	w-								
404	2.542	m	1	2.53 ± .01			2.55	mf	2.54	mf
341	2.536	a								
305	2.511	w								
225	2.511	a								
432	2.502	a								
			2	2.483	2.47	2			2.49	ff
			4	2.441	2.44	2			2.45	f
			3	2.378	2.38	2	2.40	mf	2.38	mf
			3	2.305	2.31	3	2.31	m	2.31	m
			2	2.197	2.21	1	2.22	f	2.25	f
			4	2.102	2.11	2			2.21	f
			3	2.065	2.07	3	2.07	mf	2.12	f
			6	2.036	2.04	4	2.04	mf	2.07	mf
							2.04	mf	2.04	mf
							2.02	f	2.02	f
			4	1.989	1.994	4	2.00	m	2.00	m
			6	1.935	1.943	5				
			2	1.891	1.893	2				
			3	1.869	1.875	2				
			3	1.846	1.848	2				
			1	1.826						
			2	1.807	1.814	1				
			4	1.771	1.773	3				
			4	1.721	1.725	3				
			2	1.686	1.681	2				
			3	1.670						
			3	1.615	1.614	2				
			3	1.597	1.600	2				
			3	1.560	1.564	2				
			2	1.541	1.541	1				

Plus many additional weak lines.
 a = observed to be absent.
 b = broad.
 * = not measured.
 Film No. 7861, corrected for shrinkage.

Plus many additional weak lines.

TABLE 10. X-RAY POWDER DATA: BILLIETITE

Calculated		Present Study			Frondel and Cuttitta (1953) ¹		Protas (1956)						
<i>hkl</i>	<i>d_{hkl}</i>	Measured			Measured		Measured <i>d</i> (Å)						
		Single Crystal	<i>d</i> (Å)	Powder Cu/Ni $\lambda = 1.5418 \text{ \AA}$	<i>d</i> (Å)	Cu/Ni	Natural Mineral		Synthetic Mineral				
		I	I	<i>d_{hkl}</i>	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I			
011	9.43	a											
002	7.55	VS	100	7.56 ± .05		7.53	10	(7.74) ²	m-F	(7.69) ²	mF		
101	6.46	*	2	6.51 ± .04				7.40	FF	7.40	FF		
110	6.15	w	2	6.13 ± .03									
020	6.04	w											
111	5.69	*	2	5.73 ± .03									
102	5.19	*											
112	4.77	a											
022	4.72	m	6	4.70 to		4.59	2	4.68	f	4.61	f		
013	4.65	m		4.62									
121	4.41	w											
103	4.12	a											
122	3.936	a											
113	3.895	a											
031	3.890	a											
004	3.775	VS	25	3.78 ± .015		3.77	9	3.74	F,FF	3.74	F,FF		
200	3.571	S	9	3.58 ± .015									
130	3.507	VS	18	3.51 ± .01		b3.54	5	3.51	mF	3.47	mF		
201	3.476	w											
131	3.416	w	1	3.42 ± .01									
123	3.400	w											
211	3.340	*											
104	3.338	a											
202	3.228	S	18	3.23 ± .01									
114	3.217	w-											
024	3.201	w											
132	3.181	VS	35	3.183 ± .008		3.17	8	3.19	F,FF	3.16	F,FF		
033	3.144	a											
212	3.119	a											
220	3.074	w											
040	3.020	m	2	3.030 ± .008		3.02	1	3.01	ff	3.01	ff		
221	3.012	*											
015	2.930	w	2	2.928 ± .007		2.89	1	2.91	ff				
124	2.921	a											
203	2.913	a											
133	2.878	a											
222	2.847	*	1	2.85 ± .01						2.85	ff		
213	2.832	a											
042	2.804	S	3	2.798 ± .007		2.79	2	2.79	ff	2.78	ff		
105	2.782	a											
141	2.735	w											
115	2.711	w-											
231	2.631	*											
223	2.624	*											
142	2.610	w											
204	2.594	m	6	2.60 to		2.56	3	2.57	mf	2.55	mf		
134	2.570	S		2.56									
214	2.537	a											

¹ See also Frondel, Riska, and Frondel (1956).² Possibly β reflection for 002, otherwise not indexable.

TABLE 10 (continued)

Calculated		Present Study			Fron del and Cuttitta (1933) ¹		Protas (1956)			
<i>hkl</i>	<i>d_{hkl}</i>	Measured			Measured		Measured <i>d</i> (Å)			
		Single Crystal	Powder Cu/Ni $\lambda = 1.5418 \text{ \AA}$		<i>d</i> (Å)	Cu/Ni	Natural Mineral		Synthetic Mineral	
		I	I	<i>d_{hkl}</i>	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I
125	2.527	w								
*	2.519									
006	2.517	S	4	2,520 ± .006	2.49	4	2.50	mf	2.50	mf
			3	2.313	2.30	2	2.31	mf	2.29	mf
			2	2.271						
			1	b { 2.21 to 2.19	d 2.19	1	2.20	f	2.19	f
			4	2.124	2.10	3	2.12	f	2.11	f
			9	2.053	2.03	6	2.05	m	2.03	m
			2	2.015						
			4	1.983	1.970	4				
			6	1.950	1.940	2				
					1.898	1				
			4	1.888	1.872	3				
					1.812	1				
			3	1.803	1.790	2				
			2	1.705	1.676	3				
			2	1.664	1.654	4				
		Plus many additional weak to moderate lines.			Plus many additional weak to moderate lines.					
		Film No. 7829, not corrected for shrinkage.								
		b = broad								
		d = diffuse								
		a = observed to be absent								
		* = not measured								

case. Since the cleavage and tabular habit favor appearance of {001}, β and γ indices are readily determined. The birefringence, $\gamma - \beta$, is usually small, the largest difference being 0.02. Accurate measurement of the α index is more difficult, and for the poor quality, thin crystals of masuyite this difficulty was not overcome. For billietite, fourmarierite, and unaltered schoepite (schoepite I), the optic angle $2V_\alpha$ was measured by universal-stage methods on crystals having the tabular habit, and the corresponding α index calculated from the standard equation:

$$\alpha = (\gamma\beta \sin V_\alpha)(\gamma^2 - \beta^2 \sin^2 V_\alpha)^{-1/2}$$

No calculated V_α angles are listed because examination of the equations given by Mertie (1942) shows that for large indices of refraction, a large error (10 to 15°) is associated with a calculated V_α . The indices of refrac-

TABLE 11. X-RAY POWDER DATA: FOURMARIERITE

Calculated		Present Study			Bignand (1955)	
		Measured			Measured	
		Single Crystal	$d(\text{\AA})$	Powder Cu/Ni $\lambda = 1.5418 \text{\AA}$	$d(\text{\AA})$	Cu/Ni
<i>hkl</i>	d_{hkl}	I	I	d_{hkl}	d_{hkl}	I
101	10.04	*				
111	8.57	*	1	8.55 ± .06		
020	8.23	w				
002	7.20	VS	100	7.20 ± .04	7.12	FF
200	7.00	m				
210	6.44	m	3	6.42 ± .03	6.36	f
121	6.37	*				
022	5.42	a				
220	5.33	w				
202	5.02	m	1	5.04 ± .02		
131	4.82	m	3	4.82 ± .02		
212	4.80	w				
103	4.54	w				
301	4.44	w				
113	4.38	S	9	4.36 ± .02	4.31	f
230	4.32	m				
311	4.29	a				
222	4.29	*				
040	4.12	m	2	4.13 ± .015		
123	3.975	*				
321	3.908	S	3	b) 4.00 to 3.90		
141	3.809	a				
232	3.704	m				
004	3.599	VS	50	3.58 ± .015	} 3.53	FF
042	3.574	w				
240	3.549	VS	18	3.55 ± .015		
400	3.500	VS	6	3.50 ± .01		
133	3.499	*				
331	3.451	w				
410	3.424	m				
303	3.345	w				
024	3.297	w				
313	3.279	w	1	3.28 ± .01		
420	3.221	a				
204	3.200	a				
242	3.183	VS	50	3.178 ± .008	} 3.16	FF
402	3.147	VS	12	3.143 ± .007		
214	3.142	a				
151	3.129	S				
323	3.099	*				
412	3.091	S	2	3.095 ± .007		
143	3.050	*		3.046 ± .007		
341	3.018	w				
224	2.983	*				
250	2.980	m	<1	2.97 ± .01		
430	2.952	w				
422	2.940	w-				
333	2.857	*				
105	2.820	a				
115	2.779	w-				
234	2.765	*				

TABLE 11 (continued)

Calculated		Present Study			Bignand (1955)	
		Measured			Measured	
		Single Crystal	$d(\text{Å})$	Powder Cu/Ni $\lambda=1.5418 \text{ Å}$	$d(\text{Å})$	Cu/Ni
hkl	d_{hkl}	I	I	d_{hkl}	d_{hkl}	I
252	2.753	a				
501	2.749	a				
060	2.744	m				
432	2.730	S	4	$2.724 \pm .006$	2.71	m
511	2.711	w				
044	2.709	w	<1	$2.70 \pm .01$		
125	2.667	*				
153	2.666	*	1	$2.65 \pm .01$		
440	2.666	w				
161	2.648	w				
351	2.645	a				
521	2.607	w				
343	2.596	*				
062	2.564	w				
260	2.555	w				
244	2.527	*	9	$2.520 \pm .006$	} 2.51	m
404	2.509	S	4	$2.503 \pm .006$		
135	2.508	*				
442	2.500	m				
			4	2.389		
			<1	2.340		
			<1	2.311		
			2	2.229		
			2	2.181		
			2	2.136		
			3	2.056		
			4	2.030	} 2.02	mf
			4	2.010		
			12	b { 1.987 to	} 1.96	F
				1.972		
			4	1.951	1.93	f
			3	1.900	1.88	f
			4	1.793	1.83	f
			4	1.767	1.75	mf
			4	1.719	} 1.70	f
			2	1.698		
			4	1.600	1.58	mf

a = observed to be absent
b = broad
* = not measured

There are additional weak lines with $I \geq 2$ for $d_{hkl} < 1.97 \text{ Å}$; these are not listed.

Film No. 11911, corrected for shrinkage.

Plus 3 additional weak lines.

Original data of Bignand (1955) given in kX units.

TABLE 12. X-RAY POWDER DATA: MASUYITE

Calculated		Measured	
hkl	d_{hkl}	$d(\text{\AA})$ Cu/Ni	
		I	d_{hkl}
006	7.10	100	7.08 ± .05
		6	4.36 ± .02
		6	4.30 ± .02
0.0.12	3.551	35	3.56 ± .01
660	3.496	70	3.52 ± .01
12.0.0	3.494	21	3.48 ± .01
666	3.137	12	3.16 ± .01
12.0.6	3.135	50	3.12 ± .01
12.0.12	2.491	6	2.51 ± .01
6.6.12	2.491	12	2.484 ± .007
		4	2.38 ± .01
0.0.18	2.367	9	2.36 ± .01
		4	2.27 ± .01
		4	2.12 ± .01
0.12.0	2.019	} 18	2.008 ± .004
18.6.0	2.017		
		9	1.973 ± .008
		b 17	1.95 ± .01
		4	1.79 ± .01
		12	1.766 ± .004
		9	1.745 ± .006
		4	1.72 ± .006
		9	1.690 ± .004
		4	1.613 ± .006
		4	1.598 ± .006
		6	1.578 ± .006
		4	1.559 ± .006

Plus additional weak lines.
 Film No. 11912, not corrected for shrinkage.
 b=broad

tion measured in the present study are considered good to ± 0.005 unless otherwise noted, and an estimated error has been assigned to the calculated α values from study of the limits of error attached to the associated observed data.

Whenever the presence of two or more phases was indicated by x-ray study, as in the cases of schoepite and vandendriesscheite, the indices of refraction were found variable within a given range, the variability affecting chiefly the β and γ indices. Schoepite I was identified as original, unaltered schoepite, not only by comparison of its cell constants with

TABLE 13. X-RAY POWDER DATA: SCHOEPITE

Calculated			Schoepite				Dehydrated Schoepite		
Phase	hkl	d _{hkl}	Measured—Sample 1			Measured—Sample 2		Measured	
			d(Å) I	Cu/Ni d _{hkl}	d(Å) Cr/V d _{hkl}	d(Å) I	Cu/Ni d _{hkl}	d(Å) I	Cu/Ni d _{hkl}
III	002	7.61	6	7.59 ± .05	7.56 ± .05				
I, II	002	7.37	100	7.28 ± .05	7.35 ± .05	100	7.35 ± .05		
			70	5.08 ± .02	5.07 ± .02			100	5.09 ± .02
			1	4.43 ± .03		1	4.46 ± .03		
III	004	3.805	3	3.78 ± .015	3.79 ± .01				
I, II	004	3.682	15	3.66 ± .015	3.69 ± .01	50	3.66 ± .01		
I	240	3.622				1	3.62 ± .02		
III	240	3.614							
II	240	3.588	}	6	3.59 ± .015	3.585 ± .007	1	3.58 ± .02	
I	400	3.582							
III	400	3.530							
II	400	3.498	12	3.51 ± .01	3.495 ± .007	2	3.49 ± .01		
			25	3.44 ± .01	3.430 ± .006			25	3.45 ± .01
			9	3.39 ± .01	3.380 ± .006			17	3.39 ± .01
III	242	3.265							
I	242	3.250				9	3.24 ± .01		
II	242	3.227	}	12	3.22 ± .01		3	3.21 ± .01	
I	402	3.222							
III	402	3.202							
II	402	3.159	6	3.162 ± .008	3.165 ± .006	3	3.162 ± .008		
			12	2.885 ± .007	2.872 ± .005			7	2.890 ± .007
						1	2.81 ± .01		
III	404	2.588							
I	404	2.568				4	2.571 ± .006		
III	006	2.537	12	2.539 ± .006	2.539 ± .003	1	2.53 ± .01	6	2.542 ± .003
II	404	2.536	9	2.481 ± .006	2.480 ± .003			b	7 2.48 ± .01
I, II	6	2.455	1	2.45 ± .01		9	2.446 ± .006		
			1	2.11 ± .01	Film No. 12262, corrected for shrinkage.	<1	2.31 ± .01	4	2.117
			4	2.053 ± .002		<1	2.09 ± .01	4	2.060 ± .002
			9	2.018 ± .002				5	2.023 ± .002
			Plus many additional weak lines.			Plus many additional weak lines.		Plus many additional weak lines.	
			Film No. 12119, not corrected for shrinkage.			Film No. 11904, not corrected for shrinkage.		Film No. 12293, not corrected for shrinkage.	
								b=broad	

those reported by Billiet and de Jong (1935) but also by the close agreement of its indices of refraction with those originally given by Walker (1923), as shown in Table 21. Schoepite III has indices of refraction in accord with those reported by Schoep and Stradiot (1947) for paraschoepite (Table 22). One reason that schoepite II has been considered an intermediate product is that crystals identified by x-ray study as prin-

cipally schoepite II invariably gave values of β and γ indices of refraction ranging somewhere between the values given by schoepite I and those given by schoepite III. Vandendriesscheite crystals also undergo an alteration process similar to the one that occurs in schoepite, and have more

TABLE 14. X-RAY POWDER DATA: DEHYDRATED SCHOEPITE

Present Study		Bignand (1955)		Zachariasen (1944)	
Measured		Measured		Calculated ²	
$d(\text{\AA})$	Cu/Ni	$d(\text{kX})$	Cu/Ni		
I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
100	5.09	F	5.05	5.10	002
		f	(3.76) ¹		
25	3.45	FF	3.44	3.43	200
17	3.39			3.41	111
		f	3.16		
7	2.890	m	2.85	2.85	202
		f	2.72		
6	2.542	m	2.53	2.55	004
b 7	2.48	m	2.45	2.48	113
4	2.117	f	2.12	2.13	020
4	2.060	f	2.05	2.05	204
5	2.023				
4	1.993	mF	1.97	1.98	311
4	1.954			1.97	022
4	1.826				
<4	1.80			1.81	220
6	1.774	mF	1.77	1.78	115
<4	1.72			1.733	313
				1.725	400
4	1.698	m	1.69	{ 1.708	222
				{ 1.698	006
<4	1.67				
<4	1.63	m	1.63	1.636	024
				1.626	402
<4	1.541	m	1.52	1.52	206
<4	1.484	m	1.48		
<4	1.444	m	1.43		
<4	1.350	mf	1.35		

Film No. 12293, not corrected for shrinkage.
b=broad

¹ Possibly β reflection for $d=3.44$.

² Calculations based on face-centered orthorhombic cell with $a=6.86 \pm .03$, $b=4.27 \pm .03$, $c=10.19 \pm .06 \text{\AA}$.

TABLE 15. X-RAY POWDER DATA: VANDENDRIESSCHEITE

Calculated		Measured				
Phase I		Single Crystal	Powder			
<i>hkl</i>	d_{hkl}		$d(\text{\AA})$ Cu/Ni		$d(\text{\AA})$ Cr/V	
		I	I	d_{hkl}	I	d_{hkl}
006	7.22	VS	100	7.25 ± .05	S	7.23 ± .05
210	6.93	m	2	6.94 ± .04		
060	6.81	m	2	6.81 ± .04		
230	6.25	w	3	6.33 ± .04		
240	5.79	m	2	5.77 ± .04		
236	4.72	(w) ¹	2	4.71 ± .04		
119	4.53	w-	10	4.53 ± .03	w-	4.55 ± .03
246	4.52	(m)				
270	4.49	w	10	4.45 ± .02	w-	4.45 ± .03
129	4.45	m				
0.0.12	3.611	VS	100	3.61 ± .015	S	3.62 ± .007
0.10.6	3.566	m	b 25	3.53 ± .03	w-	3.56 ± .01
0.2.12	3.556	m				
2.10.0	3.532	VS	b 25	3.53 ± .03	w	3.53 ± .01
400	3.517	VS				
410	3.504	m	b 75	3.17 ± .03	w-	3.49 ± .01
2.1.12	3.203	(w)				
0.6.12	3.190	w	b 75	3.17 ± .03	b m	3.18 ± .03
349	3.190	(w-)				
2.2.12	3.173	(w-)	b 75	3.17 ± .03		
2.10.6	3.173	(VS)				
406	3.162	VS				
416	3.153	(m)				
2.4.12	3.064	(m)	2	3.06 ± .01		
470	3.013	m	2	3.01 ± .01		
			2	2.94		
			b 8	2.80		
			5	2.722		
			2	2.66		
			25	2.522	b w	2.531
			10	2.401	w	2.418
			b 3	2.29		
			b 3	2.18		
			5	2.058		
			15	2.034		
			40	1.985		
			3	1.961		
			2	1.914		
			2	1.877		
			2	1.861		
			10	1.800		
			3	1.791		
			8	1.773		
			2	1.726		
			2	1.716		

Plus additional weak lines.

Film No. 12337 corrected for shrinkage.

b = broad

Plus additional lines with I ≤ 10.

Film No. 11903, not corrected for shrinkage.

b = broad

¹ Parentheses used for intensities extrapolated from lower-level patterns.

TABLE 16. OPTICAL DATA FOR URANYL OXIDE HYDRATES^a

(Data of present study unless otherwise noted)

	Bequerelite	Billietite	Fourmarierite	Masyite	Schoepite I (unaltered)	Schoepite III (paraschoepite)	Vandendries- scheite
α	1.730	1.730 ^e	1.85 ± 0.01 ^d	1.785 ^e	1.690 ± 0.003 ^f	1.700	1.780
β	1.825	1.800	1.885 ± 0.01	1.895 ± 0.01	1.714 ± 0.003 ^f	1.750	1.850 ± 0.01
γ	1.830	1.805	1.890 ± 0.01	1.915 ± 0.01	1.735 ± 0.003 ^f	1.770	1.860 ± 0.01
2V _{α} (obs.)	32° ± 3 ^b	37° ± 2 ^c	50° ± 2 ^c	~50 ^g	75° ± 2 ^c	40° ± ϵ	60° ± 2 ^c
X	<i>c</i> , pale yellow	<i>c</i> , pale greenish yellow	<i>c</i> , colorless ^d	<i>c</i> , pale yellow ^e	<i>c</i> , pale yellow	<i>c</i> , pale yellow	<i>c</i> , colorless
Y	<i>a</i> , deep yellow	<i>a</i> , greenish yellow	<i>a</i> , pale amber yellow	<i>b</i> , amber yellow	<i>b</i> , golden yellow	<i>b</i> , golden yellow	<i>b</i> , golden yellow
Z	<i>b</i> , deep yellow	<i>b</i> , deep yellow	<i>b</i> , amber yellow	<i>a</i> , amber yellow	<i>a</i> , golden yellow	<i>a</i> , golden yellow	<i>a</i> , golden yellow

^a Dispersion, $r > v$ for all. Values for α , β , γ are ± 0.005 unless otherwise indicated.^b Protas (1957).^c Brasseur (1949).^d Larsen and Berman (1934). Error in α estimated by present authors.^e Frondel (1958).^f Walker (1923).^g Schoep and Stradiot (1947).

TABLE 17. OPTICAL DATA FOR BECQUERELITE

	Present Study	Protas (1957)	Frondel and Cuttitta (1953)	Brasseur (1948)	Schoep and Stradiot (1948)	Palache and Berman (1933)
				($\lambda = 578 \text{ m}\mu$)		
α	1.730 ± 0.005	1.725	1.730		1.725	1.735
β	1.825 ± 0.005	1.815	1.805	1.798 ± 0.007	1.825	1.820
γ	1.830 ± 0.005	1.825	1.720	$1.822 \pm .006$	1.83	1.830
$2V_\alpha$ (obs.)		$32^\circ \pm 3^\circ$	$\sim 30^\circ$		$30^\circ \pm$	30°
X	<i>c</i> , pale yellow	colorless	<i>c</i> , pale yellow		<i>c</i> , colorless	<i>c</i> , colorless
Y	<i>a</i> , deep yellow	yellow	<i>a</i> , deep golden yellow		<i>a</i> , yellow	<i>b</i> , yellow
Z	<i>b</i> , deep yellow	yellow	<i>b</i> , deep golden yellow		<i>b</i> , yellow	<i>a</i> , yellow

TABLE 18. OPTICAL DATA FOR BILLIETITE

	Present Study	Frondel and Cuttitta (1953)		Brasseur (1949) ($\lambda = 578 \text{ m}\mu$)	Schoep and Stradiot (1948)	Vaes (1947)
		H.U.M. No. 104456	H.U.M. No. 104455			
α	$1.76 \pm 0.05^*$	1.730	1.725	1.730	1.73	
β	1.800 ± 0.005	1.810	1.780	1.822	1.82	
γ	1.805 ± 0.005	1.815	1.790	1.8285	1.83	
$2V_\alpha$ (obs.)	$37^\circ \pm 2^\circ$	$\sim 35^\circ$	$\sim 35^\circ$	47°	$36^\circ \pm$	36°
X	<i>c</i> , pale greenish yellow	<i>c</i> , pale yellow		<i>c</i> Dichroism	<i>c</i> , colorless	<i>b</i> , colorless
Y	<i>a</i> , greenish yellow	<i>a</i> , deep golden yellow		<i>a</i> , of Vaes (1947)	<i>a</i> , yellow	<i>c</i> , greenish yellow
Z	<i>b</i> , deep yellow	<i>b</i> , deep golden yellow		<i>b</i> , confirmed	<i>b</i> , deep yellow	<i>a</i> , amber

* Value for α calculated from observed values of β , γ and V_α .

TABLE 19. OPTICAL DATA FOR FOURMARIERITE

	Present Study	Frondel (1958)	Larsen and Berman (1934)
α	$1.863 \pm .025^*$	1.865	1.85
β	1.885 ± 0.01	1.900	1.92
γ	1.890 ± 0.01	1.904	1.94
$2V_\alpha$ (obs.)	$50^\circ \pm 2^\circ$	55°	large
X	<i>c</i>	<i>c</i> , colorless	<i>a</i> , colorless
Y	<i>a</i> , pale amber yellow	<i>b</i> , pale yellow	<i>c</i> , pale yellow
Z	<i>b</i> , amber yellow	<i>a</i> , yellow	<i>b</i> , deeper yellow

* Value for α calculated from observed values for β , γ and V_α .

TABLE 20. OPTICAL DATA FOR MASUYITE

	Present Study	Frondel (1958)	Vaes (1947)
α		1.785	
β	1.895 ± 0.01	1.906	between 2.11 and 2.15
γ	1.915 ± 0.01	1.917	
$2V_\alpha$ (obs.)		$\sim 50^\circ$	large
X	<i>c</i>	<i>c</i> , pale yellow	<i>b</i>
Y	<i>b</i> , amber golden yellow	<i>b</i> , deep golden	<i>a</i> †, orange yellow
Z	<i>a</i> , amber golden yellow	<i>a</i> , deep golden	<i>c</i> , orange yellow

† Vaes (1947) gives $n_m = a$ but states that the P.O.A. is perpendicular to *c*.

TABLE 21. OPTICAL DATA FOR SCHOEPITE I

	Present Study	Larsen and Berman (1934)	Walker (1923)
α	$1.70 \pm 0.01^*$	1.690	1.690 ± 0.003
β	1.720 ± 0.005	1.714	1.714 ± 0.003
γ	1.735 ± 0.005	1.735	1.735 ± 0.003
$2V_\alpha$ (obs.)	$75^\circ \pm 2^\circ$	large	
X	<i>c</i> , pale yellow	<i>c</i> , colorless	<i>c</i> , colorless
Y	<i>b</i> , golden yellow	lemon yellow	lemon yellow
Z	<i>a</i> , golden yellow	lemon yellow	lemon yellow

* Value for α calculated from observed β , γ and V_α .

TABLE 22. OPTICAL DATA FOR SCHOEPITE III

	Present Study	Schoep and Stradiot (1947), for paraschoepite
α	1.700 ± 0.005	1.705
β	1.750 ± 0.005	1.760
γ	1.770 ± 0.005	1.770
$2V_\alpha$ (obs.)		$40^\circ \pm$
X	<i>c</i> , pale yellow	<i>c</i> , colorless
Y	<i>b</i> , golden yellow	<i>b</i> , yellow
Z	<i>a</i> , golden yellow	<i>a</i> , yellow

TABLE 23. OPTICAL DATA FOR VANDENDRIESSCHEITE

	Present Study	Frondel (1958)*				Vaes (1947)
		(1)	(2)	(3)	(4)	
α	1.780±0.005	1.790	1.785	1.760	—	—
β	1.850±0.01	1.840	1.810	1.824	1.882	>1.884
γ	1.860±0.01	1.845	1.820	1.828	1.890	>1.884
$2V_{\alpha}$ (obs.)	60°±2°	medium	medium	50°	medium	large
X	<i>c</i> , colorless		<i>c</i> , nearly colorless			<i>b</i> , nearly colorless
Y	<i>b</i> , golden yellow		<i>b</i> , golden yellow			<i>a</i> , orange yellow
Z	<i>a</i> , golden yellow		<i>a</i> , golden yellow			<i>c</i> , orange yellow

* Values in each column are for crystals with unit cell reported under the corresponding column number in Table 8. Material of (2) from Great Bear Lake; measurements by Palache and Berman (1933). Others from Katanga; measurements by J. W. Frondel.

than normal variation in the values of the β and γ indices of refraction for different crystals. In general, indices of refraction for these minerals must be considered in connection with *x*-ray evidence for purposes of identification.

CHEMICAL CONSIDERATIONS AND CRYSTAL STRUCTURE

Semiquantitative spectrographic analysis for Pb, Ca, Ba, and Sr was carried out on 2 mg samples of crystals of each mineral except masuyite; schoepite was examined only as schoepite I. So few crystals of masuyite were available that neither spectrographic analysis nor specific gravity determination were feasible. The following results were obtained from the spectrographic analysis:

Sample	Pb	Ca	Ba	Sr
Becquerelite from HM No. 106523	.0X	X.	.00X	.0X
Becquerelite from HM No. 106524	.0X	X.	.00X	.0X
Becquerelite from USNM No. R8387	.0X	.X	.00X	.0X
Billietite from HM No. 104445	.0X	.0X	X.	.0X
Schoepite from USNM No. 94712	.0X	.X	.0X	.0X
Fourmarierite from USNM No. R8396	X.	.0X	.00X	.0X
Vandendriesscheite from HM No. 106523	X.	.0X	.00X	.0X

(X is in weight percentage.)

H. J. Rose, Jr., analyst.

These chemical results are best explained in terms of the crystal structure concepts discussed below.

All of these uranyl oxide hydrates yield *x*-ray patterns on which the strong reflections are distributed according to the demands of a primitive

pseudo-hexagonal cell (Figure 1), with cell edges for the several minerals varying from $a' = 4.0 \text{ \AA}$ to $a' = 4.2 \text{ \AA}$, and $c' = 7.1 \text{ \AA}$ to $c' = 7.6 \text{ \AA}$. The intensities of the strong reflections follow an essentially normal form-factor decline with increasing $(\sin \theta)/\lambda$. These minerals all have perfect (001) cleavage. With these experimental results and a knowledge of the structures of similar compounds, it is immediately possible to derive many of the essential features of the structures of the uranyl oxide hydrates.

A number of compounds containing hexavalent uranium have been studied, including anhydrous uranyl fluoride, UO_2F_2 , (Zachariasen, 1948a), calcium uranate, $\text{Ca}(\text{UO}_2)\text{O}_2$, (Zachariasen 1948b), and rutherfordine, UO_2CO_3 , (Christ *et al.*, 1955). The structures of these three compounds are alike in that they consist of stacked infinite layers of fluoride, oxygen, or carbonate ions, respectively, with uranyl, $(\text{O-U-O})^{++}$, ions normal to the layers, the uranium of the uranyl ion being contained in the layer. A drawing of the structure of the UO_2F_2 layer of uranyl fluoride, taken from Zachariasen (1948a), is shown in Figure 3. Calcium uranate contains similar $[\text{UO}_2\text{O}_2]_n^{-2n}$ layers, with Ca^{++} ions, in eightfold coordination, located half-way between successive layers. In the uranyl oxide hydrates there are undoubtedly infinite $\text{UO}_2(\text{OH})_2$ layers quite similar to those found in UO_2F_2 and CaUO_2O_2 , and with dimensions close to those of

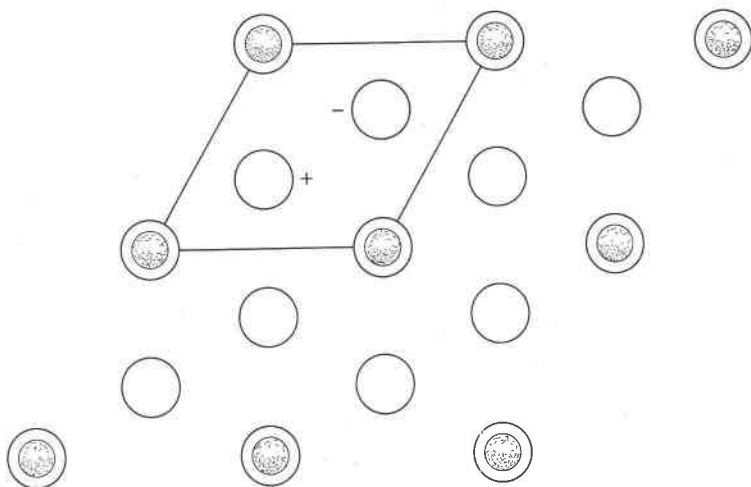


FIG. 3. A drawing of the structure of the UO_2F_2 layer of uranyl fluoride (after Zachariasen, 1948a). Circles with stippled centers represent uranyl groups lying normal to the plane of the drawing with oxygen atoms 1.91 \AA above and below the plane, and with the uranium in the plane. The large open circles indicate fluorine atoms at distances of 0.61 \AA above, (+), and below, (-), the plane. The $\text{UO}_2(\text{OH})_2$ layers in the uranyl oxide hydrates are similar to the UO_2F_2 layer shown here.

UO_2F_2 . In crystals of CaUO_2O_2 and UO_2F_2 the successive hexagonal layers are displaced, in accordance with the rhombohedral symmetry of the crystals, in order to allow room for the packing of the oxygens of the uranyl groups. The distance between consecutive layers in UO_2F_2 is 5.22 Å, and in CaUO_2O_2 is 5.84 Å. The similar hexagonal $\text{UO}_2(\text{OH})_2$ layers in the uranyl oxide hydrates are stacked directly over one another with the distance between consecutive layers varying from 7.1 to 7.6 Å. This larger separation presumably serves to provide space to accommodate the water molecules and the cations, such as Pb^{++} , Ba^{++} , and Ca^{++} , contained in the uranyl oxide hydrates.

Although the structure and composition of the layers of the uranyl oxide hydrates seem entirely clear, the structure and even the exact composition of the interlayer content is considerably less apparent, and the clarification of these properties for each of the minerals must await a complete crystal structure analysis. Some preliminary studies with Patterson and electron density maps have been carried out on billietite during the present investigation and the results obtained are in agreement with the conclusions given above. The structure work is continuing and will be reported upon at a later date.

From these crystal structure considerations and the probable chemical content of the minerals, as listed in Table 2, the oxide formulas can be rewritten as follows: schoepite I, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$; becquerelite, $\text{Ca}(\text{OH})_2 \cdot 6\text{UO}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, billietite, $\text{Ba}(\text{OH})_2 \cdot 6\text{UO}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, and fourmarierite, $\text{Pb}(\text{OH})_2 \cdot 4\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The general formula for these compounds, $x\text{MeO} \cdot y\text{UO}_3 \cdot z\text{H}_2\text{O}$, can be written as $x\text{Me}(\text{OH})_2 \cdot y\text{UO}_2(\text{OH})_2 \cdot (z-x-y)\text{H}_2\text{O}$ (Christ and Clark, 1955). An alternative general structural formulation of the oxide formula, $x\text{MeO} \cdot y\text{UO}_3 \cdot z\text{H}_2\text{O}$, is $\text{Me}_x [(\text{UO}_2)_y \text{O}_{2x} (\text{OH})_{2(y-x)}] \cdot (z-y+x)\text{H}_2\text{O}$, where the brackets enclose the layer composition. Under this formulation billietite, e.g., would be written $\text{Ba}[(\text{UO}_2)_6 \text{O}_2 (\text{OH})_{10}] \cdot 6\text{H}_2\text{O}$.

The probable chemical formulas listed in Table 2 are those which give the best agreement with all the data available at the present time. The x-ray findings afford two checks on these formulas: densities can be calculated, and a count of the total number of $\text{UO}_2(\text{OH})_2$ units per cell can be made. It can be seen from Table 2 that the agreement between calculated and observed specific gravities is excellent. The total number of $\text{UO}_2(\text{OH})_2$ units per cell must be an integral multiple of the number of uranium atoms given in a chemical formula, in order for that formula to be acceptable. This rule is obeyed for the chemical formulas listed in Table 2.

The chemical composition of becquerelite has been considered as uncertain (Fron del, 1958); however, the recent work of Protas (1957) clearly

establishes becquerelite as a calcium uranyl oxide hydrate, in agreement with the results of the spectrographic analysis of the present study. Protas (1957) gives the formula of becquerelite as $\text{CaO} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$. The observed specific gravity obtained in the present study, and those found by Protas (1957) for both synthetic and natural becquerelites, are in excellent agreement with the specific gravity calculated on the basis of this chemical formula, as shown in Table 2. In the present study, one becquerelite sample (USNM No. R8387) showed a lower calcium content than the other two examined. Because of the small samples used in the spectrographic analysis, this result may not be real. On the other hand, it may indicate a variable calcium content. It has been suggested that becquerelite may be formulated as a compound in which some of the uranium may be substituted by barium or lead (Fron del and Cuttitta, 1953). This kind of substitution would lead to decreasing density with increasing barium or lead. It is observed, in fact, that the opposite is true, as would be predicted on the basis of the interlayer positioning of cations described above. Because the uranium is undoubtedly present in these compounds in uranyl groups any substitution of the uranyl by spherical cations seems extremely unlikely.

Billietite is the barium analog of becquerelite, and the formula $\text{BaO} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$, assigned by Brasseur (1949), is in excellent agreement with the x -ray and spectrographic results of the present study and with the results of various chemical analyses (Fron del, 1958), including that for the synthetic billietite prepared and analyzed by Protas (1956).

The formula $\text{PbO} \cdot 4\text{UO}_3 \cdot 7\text{H}_2\text{O}$, proposed by Brasseur (1941, 1946) for fourmarierite is consistent with the x -ray results of the present study except for the water content. The cell constants found by us are probably more accurate than those of Brasseur, and when combined with his specific gravity value of 5.74 lead to the formula $\text{PbO} \cdot 4\text{UO}_3 \cdot 4\text{H}_2\text{O}$. However, because the contribution of the water to the specific gravity of any of these minerals is small, it is difficult to determine precise water values for them in this way.

No new results on the chemistry of masuyite were obtained in this study.

Fron del (1958) gives the formula of vandendriesscheite as near $\text{PbO} \cdot 7\text{UO}_3 \cdot 12\text{H}_2\text{O}$. It will be noted from Table 2 that consideration of the number of pseudo-orthohexagonal cells contained in the large true cell leads to a true cell content of 240 units of $\text{UO}_2(\text{OH})_2$. This result would require slight modification of the formula above, since 240 is not an integral multiple of 7. Our observed specific gravity for vandendriesscheite is 5.45, in excellent agreement with the value of 5.46 given for crystal 1 in Fron del (1958), as shown in Table 8. The cell constants of the present

study, when combined with the formula $\text{PbO} \cdot 7\text{UO}_3 \cdot 12\text{H}_2\text{O}$, yield a calculated specific gravity of 5.86. This disagreement between calculated and observed specific gravities is a second indication that the formula requires modification, and may be variable as stated in Frondel (1958).

DEHYDRATION PHENOMENA IN SCHOEPITE AND VANDENDRIESSCHEITE

As mentioned above, crystals of schoepite commonly occur with an amber-brown core completely or partially surrounded by a derivative golden-yellow rim which retains the morphology of the original crystal, and which itself yields single-crystal patterns. The brown part consists chiefly of schoepite I, and the yellow part mostly of schoepite II or schoepite III. Examination under the binocular microscope reveals that the rim is usually threaded by numerous small tubes, lying approximately parallel to (001), radiating from the brown core to the external surface of the crystal. These tubes are considered to be tunnels that have developed to permit the escape of water from schoepite I, with the resulting formation of schoepite II or schoepite III. X-ray study shows that crystals in all stages of alteration occur on the specimen USNM No. 94712. A number of these crystals have been examined from time to time over a period of months, and it has been found that the crystals continually alter, with the alteration process always proceeding with the formation of schoepite II or III and with concomitant decrease in the relative amount of schoepite I. The rate at which the crystals alter varies considerably. Experiments with large x -ray dosages have shown that the alteration is independent of the x -ray diffraction experiment, and is truly spontaneous. The brown crystals will continue to alter toward the yellow ones, as evidenced by x -ray studies, even if the crystals are kept in an atmosphere saturated with water vapor at room temperature; completely yellow crystals (schoepite III) will not alter toward the brown when kept in such an environment. When completely brown crystals are put over concentrated H_2SO_4 in a closed vessel a yellow powder forms in a matter of hours; completely yellow crystals so treated do not alter. The yellow powder yields an x -ray pattern designated as that of "dehydrated schoepite" in Tables 13 and 14. Bignand (1955) found that synthetic schoepite heated between 60° and 180° C. lost 5.4% water, and that the remaining product gave an x -ray powder pattern different from that of the original schoepite. The pattern obtained by Bignand is in excellent agreement with that obtained by us for dehydrated schoepite, as shown in Table 14. If it is considered that natural schoepite has the formula $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, and therefore contains 11.2% water, the loss of 5.4% water observed by Bignand would lead to the approximate formula $\text{UO}_3 \cdot \text{H}_2\text{O}$, or $\text{UO}_2(\text{OH})_2$, for dehydrated schoepite. It has been reported (Katz and

Rabinowitch, 1951, p. 285) that there are four polymorphic crystalline modifications of $\text{UO}_3 \cdot \text{H}_2\text{O}$, all stable at room temperature. For one of these modifications, Zachariassen (1944) gives the following data: orthorhombic, $a=6.86$, $b=4.27$, $c=10.19$ Å, uranium atoms in face-centered array. This form of $\text{UO}_3 \cdot \text{H}_2\text{O}$ will account for nearly all the lines found for dehydrated schoepite (Table 14). Dawson *et al.* (1956) report that UO_3 in contact with water at about 180° C. yields orthorhombic $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$. The cell dimensions listed by these authors for $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ are in excellent agreement with those of Zachariassen for $\text{UO}_3 \cdot \text{H}_2\text{O}$, as given above.

We have also observed that when an amber-brown crystal of schoepite is teased with a dissecting needle the crystal disintegrates into a yellow powder around the point of contact of the needle. X-ray examination shows that this yellow powder is mostly dehydrated schoepite. It is believed that the pressure of the needle results in cleavage on a very fine scale, parallel to (001), thus permitting the rapid escape of water. When an amber-brown crystal with a golden-yellow rim is used in this experiment, or is dehydrated over concentrated H_2SO_4 , the rim retains its original form, and remains otherwise unchanged. These experiments are interpreted to have the following significance. When allowed to alter naturally, the amber-brown crystals will slowly form golden-yellow crystals which are apparently stable toward further change. Schoepite I, corresponding to the amber-brown crystals, and schoepite II or III, corresponding to the golden-yellow crystals, all have slightly different cell constants and x-ray intensity distributions. It seems likely that these differences result from a loss of a small part of the interlayer water (the water in excess of that needed to form $\text{UO}_2(\text{OH})_2$ layers) from schoepite I, with consequent slight rearrangement of the atomic structure. The $\text{UO}_2(\text{OH})_2$ layers are parallel to (001), and if the interlayer water contributes to the binding together of these layers, then loss of some of the water would result in an increase in c . This increase does occur in going from schoepite I to schoepite III. All of these results indicate that under room conditions, schoepite I is thermodynamically unstable with respect to schoepite II, which in turn is unstable toward schoepite III. Although schoepite I alters to dehydrated schoepite under mechanical pressure, crystals of schoepite II or III do not appear to do so. We have no explanation for this observation. Natural schoepite (schoepite I) (Fron del, 1958), and the corresponding synthetic compound (Hüttig and Schroeder, 1922), (Bignand, 1955) appear to contain slightly more than two moles of H_2O per mole of UO_3 . Accordingly, in Table 2 the formula for schoepite I is given as $\text{UO}_3 \cdot (2+?)\text{H}_2\text{O}$. Since schoepite II and III are considered to result from spontaneous loss of water from schoepite I, these are given the formula $\text{UO}_3 \cdot (2-?)\text{H}_2\text{O}$.

That variations in x -ray powder patterns of "schoepite" are found is readily understood in view of the foregoing analysis. The patterns will vary both with the way in which material is selected from a given specimen, and with the method of preparation of the powder sample. The results from the powder patterns measured in the present study are given in Table 13. Sample 1 (Table 13) consisted of a mixture of yellow powder and yellow crystal fragments from the specimen USNM No. 94712. It can be seen from Table 13 that this sample contained schoepite II and schoepite III, with a large proportion of $\text{UO}_2(\text{OH})_2$ also present. Sample 2 was made up of crystals from the same specimen, selected without regard to their stage of alteration. From Table 13 it can be seen that this sample consisted of a mixture of schoepite I and schoepite II. Apparently, no detectable amount of $\text{UO}_2(\text{OH})_2$ was produced in the preparation of this sample.

Vandendriesscheite crystals with varying proportions of phase I and phase II (Table 2) occur on the specimen HM No. 106523. No study was made to determine which of the two phases persisted with time. However, it was found that when a clear orange crystal of vandendriesscheite, consisting principally of phase I, was put in a container over concentrated H_2SO_4 , the crystal became cloudy, tiny tubes appeared as with schoepite, and the x -ray precession pattern of the altered crystal showed that phase II was now the dominant phase. The x -ray powder pattern data, given in Table 15, are indexed on the basis of phase I. It would be difficult to differentiate the two phases with powder pattern data only.

NOMENCLATURE

Throughout this paper, the designations schoepite I, II, and III, and vandendriesscheite I and II have been used for the several phases encountered. These designations are simple and convenient, and are precisely defined in terms of the lattice constants of the phases. In order to relate these terms to the more customary mineralogical nomenclature it is proposed that the name "schoepite" be retained for schoepite I, and that schoepite II be called "metaschoepite." Schoepite III is clearly paraschoepite. Similarly, it seems desirable to use the name "vandendriesscheite" for vandendriesscheite I, and to call vandendriesscheite II, "metavandendriesscheite." These relationships are summarized as follows:

Schoepite I = schoepite
 Schoepite II = metaschoepite
 Schoepite III = paraschoepite
 Vandendriesscheite I = vandendriesscheite
 Vandendriesscheite II = metavandendriesscheite

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