

# SYNTHESIS AND X-RAY STUDY OF URANIUM SULPHATE MINERALS<sup>1</sup>

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## ABSTRACT

Attempts have been made to synthesize uranium sulphate minerals. Artificial zippeite having optical properties in agreement with the natural mineral has been prepared. Physical, chemical, optical and x-ray data for zippeite and four other synthetic products are presented.

Artificial zippeite is monoclinic. Space group  $C2/m$ . Unit cell dimensions:  $a=8.81$ ,  $b=14.13$ ,  $c=8.85\text{\AA}$ ,  $\beta=104^{\circ}15'$ . Cell contents:  $2[(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ . Calculated specific gravity 3.68, measured 3.66. Optical properties: biaxial negative;  $nX=1.655$ ,  $nY=1.717$ ,  $nZ=1.765$ ;  $X$ =colorless,  $Y$ =pale yellow,  $Z$ =yellow; orientation,  $X \wedge a=3^{\circ}$ .

The optical properties and x-ray powder pattern of uranopilite from Goldfields, Saskatchewan, are appended.

## INTRODUCTION AND ACKNOWLEDGMENTS

In the summer of 1950, the writer began a research program which had as its objective the synthesis and x-ray study of the uranium sulphate group of minerals. Johannite, medjidite, uraconite, uranochalcite, uranopilite, beta-uranopilite, voglianite, and zippeite are names which occur in mineralogical literature for uranium sulphates. Johannite is well established and the only mineral of this group for which the results of morphological and x-ray studies have been published (Peacock, 1935, and Hurlbut, 1950). The optical properties of uranopilite, recorded by Nováček (1935), have proved to be consistent and have enabled the mineral to be identified in specimens from widespread localities. Chemical analyses by Nováček suggest a composition of  $(\text{UO}_3)_6\text{SO}_3 \cdot 16-17 \text{H}_2\text{O}$  for uranopilite but this composition has not been confirmed. Beta-uranopilite is considered by Nováček to be a dehydration product of uranopilite. Some confusion exists as to the chemical composition and optical properties of zippeite. Nováček (1935) suggested a composition of  $(\text{UO}_3)_2\text{SO}_3 \cdot n\text{H}_2\text{O}$  with  $n$  varying from three to eight. He noted that the refractive indices of zippeite varied over a wide range, and ascribed this variation to the changes in water content. Frondel (1951) suggests that the name zippeite be reserved for a mineral which he has found to give constant optical properties and a distinctive powder diffraction pattern. The descriptions which are recorded for medjidite, uraconite, uranochalcite, and voglianite are so vague that these names have little meaning

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today and cannot be applied to new occurrences of uranium sulphate minerals (Dana, 1951). Crystallographic data on uranopilite and zippeite are lacking, and the optical and chemical properties of these minerals require clarification.

The uranium sulphate minerals occur as clusters of tiny crystals commonly intergrown with other minerals. Museum specimens of these minerals are rare and the labels attached to the specimens are unreliable. Only rarely can material suitable for  $x$ -ray studies be found. The most likely way of establishing the definitive description of such minerals is by the synthesis and  $x$ -ray study of materials having physical, chemical and optical properties similar to those of minerals occurring in nature.

The research program was carried out in the laboratories of the Department of Geological Sciences, Queen's University, Kingston, under the supervision of Dr. L. G. Berry. Uranium oxide compounds were obtained through the courtesy of the Eldorado Mining and Refining Company.  $X$ -ray powder films were kindly loaned for comparison by the U. S. Geological Survey (Trace Elements Laboratory). To the above-mentioned persons and institutions the writer wishes to express his sincere appreciation for assistance rendered.

#### SYNTHESIS

*General Considerations.* Uranyl salts are characterized by the bivalent ion  $UO_2$ . Normal uranyl sulphates have a molecular ratio of  $UO_2:SO_4=1:1$ . The suggested compositions of uranopilite and zippeite, respectively, may be written as  $(UO_2)_6SO_4(OH)_{10}\cdot 12H_2O$  and  $(UO_2)_2SO_4(OH)_2\cdot 4H_2O$  showing molecular ratios of  $6UO_2:1SO_4$  and  $2UO_2:1SO_4$ . If the concept of a uranyl radical is retained, these minerals must be regarded as basic uranyl sulphates and their formulas may be rewritten as  $UO_2SO_4\cdot 5UO_2(OH)_2\cdot 12H_2O$  and  $UO_2SO_4\cdot UO_2(OH)_2\cdot 4H_2O$ . The synthesis experiments conducted by the writer were therefore directed towards obtaining basic uranyl sulphates.

The problem of synthesis is complicated by the consideration that the material produced must be suitable for  $x$ -ray studies. To determine the unit cell constants of a compound by means of  $x$ -rays a single crystal of the compound is usually required. For this reason the crystallization of artificial material should take place slowly enough so that single crystals develop instead of clusters of crystal intergrowths. Crystals having dimensions of from 0.1 to 0.5 mm. are most suitable for  $x$ -ray studies.

Three methods of synthesis have been used successfully for the production of artificial minerals. The first method, that of crystallization from a fusion, is not applicable to the problem at hand because of the

hydrous nature of the products sought. The other two methods, which may be included under the term hydrosynthesis, are of practical value in this problem. One method involves crystallization from aqueous solution under elevated conditions of temperature and pressure, and may be termed pressure bomb synthesis. The other type of hydrosynthesis involves crystallization by evaporation or precipitation under conditions of moderate temperature and atmospheric pressure. This method may be termed synthesis at atmospheric pressure.

*Pressure Bomb Synthesis.* The pressure bomb method of synthesis has been used successfully in recent years to produce artificial minerals of many different types. The main disadvantage of using this method is the fact that conditions existing in the pressure bomb do not simulate those which are present during the formation of naturally-occurring uranium sulphate minerals. Many substances, however, have been produced artificially under conditions that are unlikely to exist in nature. Furthermore, the physical-chemical relationships which exist in a bomb of this type are not clearly understood, and the products of chemical reactions under pressure bomb conditions are generally anticipated rather than predicted. The main reason for the increasing popularity of this method of synthesis lies in the nature of the products obtained. It has been found that the products are commonly well crystallized and highly satisfactory for study by *x*-ray methods. If the required products are formed but are not well crystallized, then a simple alteration of the test conditions will generally produce satisfactory material.

A series of pressure bomb experiments were carried out to test the reactions of sulphuric acid solutions of varying strengths on oxides of uranium. Four well-crystallized compounds were produced and studied by optical and *x*-ray methods (Traill, 1951). The four compounds were deep green in color and non-fluorescent, and therefore, probably uranous salts. Compounds of this type are unlikely to occur in nature and thus are of little interest in this investigation.

*Synthesis at Atmospheric Pressure.* Uranium sulphate minerals are formed in nature by the supergene alteration of uraninite. Three processes may be effective in forming the secondary minerals. In the first process, materials contained in circulating solutions react with the uraninite to form secondary minerals by direct alteration. No transportation of uranium is involved in this process. Secondly, the uraninite may be taken into solution by circulating waters and precipitated in the form of secondary minerals by reaction with suitable precipitating agents. The third process involves solution of the uraninite by circulating waters and deposition of secondary minerals as the result of evaporation of the uranium-bearing solutions.

In the first process, a long period of stable conditions and probably some catalytic action would be required to permit the transfer of sulphate ions to take place from the solution to the uraninite. This process is of doubtful value as a method of laboratory synthesis.

Chemical compounds produced by precipitation, as in the second process operative in nature, are generally very fine grained. Material precipitated in the laboratory can sometimes be made more coarsely crystalline by allowing the precipitation to take place slowly at a temperature approaching the boiling point of the solution and by retaining the temperature of the solution near the boiling point for a considerable length of time. Precipitation from solution, as applied to laboratory synthesis is perhaps the most likely way of producing a compound of the required chemical composition. The problem of obtaining the compound in a form suitable for x-ray and optical studies is the main drawback in using this process.

The third process, that of crystallization from solution by evaporation, is ideally suited for the formation of good crystalline material. A decrease in the rate of evaporation will generally result in an increase in the size of the crystals formed. The main problem involved when this process is used in the laboratory is that of obtaining the particular solution which will yield crystals of the desired compound. A further difficulty arises in the fact that a single solution may yield several different compounds depending on the physical conditions which are operative during crystallization. These problems arise almost invariably in the crystallization of hydrated compounds.

With the above-mentioned thoughts in mind, the writer carried out about 50 synthesis experiments at atmospheric pressure. Space does not permit detailed descriptions of the various combinations of chemicals and procedures which were used. Those experiments which yielded materials of interest are summarized briefly in Table 1, further details are given in the writer's unpublished thesis (Traill, 1951).

*Identification of Products.* The products resulting from each experiment were examined as completely as their nature permitted, within the limitations imposed by the means at the disposal of the writer. In some cases, the information obtained led to positive identification of the compounds, in others it was insufficient and the compounds were not identified. Very little data on uranium sulphates has been published and thus the positive identification of synthetic products by comparison with the published properties of known compounds could not be achieved until exhaustive investigations had been carried out.

The indices of refraction were obtained by immersion in standardized index oils. Specific gravity determinations were made on well-crystal-

TABLE 1. SUMMARY OF SYNTHESSES AT ATMOSPHERIC PRESSURE

Reference Number	Materials Used	Procedure Adopted	Results Obtained
E-1-5	$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ 2 gm. $\text{Na}_2\text{O}_2$ 0.5 gm. $\text{H}_2\text{SO}_4$ (conc) 5 cc. Water 25 cc.	A saturated solution was evaporated slowly at 95° C. in an Erlenmeyer flask closed by a rubber stopper with a capillary opening. (E-1-5 to E-3-4)	Compound W
E-1-6	$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ 2 gm. $\text{CuSO}_4$ 0.8 gm. $\text{Na}_2\text{O}_2$ 0.5 gm. $\text{H}_2\text{SO}_4$ (conc) 5 cc. Water 25 cc.		Copper sulphate and Compound W
E-3-2	Uranyl hydrate $\text{CuSO}_4$ $\text{H}_2\text{SO}_4$ (1:6)		Compound Y
E-3-3	Uranyl hydrate $\text{H}_2\text{SO}_4$ (1:6) $\text{H}_2\text{O}_2$ (30%) 5 cc.		Compound X and Compound Y
E-3-4	Uranyl hydrate $\text{H}_2\text{SO}_4$ (1:6) $\text{CaCO}_3$		Compound Y
E-5-1	Uranyl hydrate 2 gm. $\text{H}_2\text{SO}_4$ (.05 M) 100 cc.	Evaporation in a crystallizing dish at 30° C.	Compound Y
C-1	$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ Water	$\text{NH}_4\text{OH}$ added to give pH 4.5. The ppt. was kept at 95° C. for two weeks.	Fine-grained product gave a powder pattern close to that of zippeite.
C-5	Ur. nitrate 5.02 gm. Cu nitrate 2.41 gm. $\text{K}_2\text{SO}_4$ 3.48 gm. Water 50 cc.	$\text{NH}_4\text{OH}$ added. Evaporation at 25° C. in a crystallizing dish.	Compound Z
C-9	Ur. nitrate 3.58 gm. $\text{K}_2\text{SO}_4$ .62 gm. Water 50 cc.	Evaporation in a crystallizing dish at 30° C.	Compound Y
C-10	$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ Water	$\text{NH}_4\text{OH}$ added to give pH 3.5. Evaporation in a crystallizing dish at 25° C.	Compound V

TABLE 1 (Continued)

Reference Number	Materials Used	Procedure Adopted	Results Obtained
C-11	Ur. nitrate      5.02 gm. K <sub>2</sub> SO <sub>4</sub> .29 gm. Water             50 cc.	NH <sub>4</sub> OH added to give pH 3.3 Evaporation in a crystallizing dish at 25°C.	Crystals of zippeite formed after several weeks.
C-12	Uranyl hydrate    1 gm. Water               50 cc. H <sub>2</sub> SO <sub>4</sub> (a few drops)	NH <sub>4</sub> OH added to give pH 4.1 Evaporation in a crystallizing dish at 30°C.	Compound V.
C-13	Same as C-12	Same as C-12 but pH 3.6	Compound V.
C-14	Same as C-12	Same as C-12 but pH 2.6	Compound V.
C-17	Uranyl hydrate    1 gm. K <sub>2</sub> SO <sub>4</sub> .5 gm. Water               50 cc. HCl (a few drops)	Same as C-12 but pH 2.6	Compound Z.
C-18	Uranyl hydrate    1 gm. K <sub>2</sub> SO <sub>4</sub> 1 gm. Water               50 cc.	Same as C-12 but pH 3.0	Compound U and Compound Z.
C-19	UO <sub>2</sub> SO <sub>4</sub> · 3H <sub>2</sub> O	Removal of SO <sub>4</sub> <sup>-</sup> by ppt'n as BaSO <sub>4</sub> . Filtrate evaporated at 30°C.	Compound W.
C-20	BaCl <sub>2</sub> sol'n.		
C-21	Water		
C-26	Uranyl sulphate	NH <sub>4</sub> OH added to give pH 4.3 (C-26), 4.1 (C-27)	Fine-grained zippeite formed overnight.
C-27	solution		

lized material by means of the Berman balance. The Weissenberg goniometer and the Buerger precession camera were used for single-crystal *x*-ray studies. Accepted standard procedures of chemical analysis were adopted. Uranium was determined gravimetrically by precipitation with ammonia as the diuranate and ignition to U<sub>3</sub>O<sub>8</sub>. The sulphate content was obtained by precipitation as barium sulphate. Water was determined by the Penfield method for compounds easily deprived of their water, after first mixing the sample with anhydrous sodium tungstate to retain the oxides of sulphur.

#### SYNTHETIC ZIPPEITE

Artificial zippeite was obtained in suitable crystalline form as the product of synthesis experiment C-11. An aqueous solution of uranyl nitrate and potassium sulphate in the molecular ratio of 6:1 was ad-

justed to a pH of 3.3 with ammonium hydroxide and allowed to stand at room temperature for a period of two months. The crystalline product was then examined and found to possess the optical properties of the mineral zippeite. Several  $x$ -ray powder diffraction photographs were taken to ensure the homogeneity of the product. The observed intensities and measured spacings were similar to those obtained from pattern TE 288 of the U. S. Geological Survey Trace Elements Section labelled synthetic zippeite (said to be identical with film TE 251 of natural zippeite). In experiment C-1, a uranyl sulphate solution to which ammonium hydroxide had been added yielded a fine-grained orange precipitate on standing at 95° C. for 12 hours. The precipitate and solution were maintained at that temperature for two weeks. The material gave a powder pattern similar to artificial zippeite but was too fine grained to be identified optically. In experiments C-26 and C-27, fine-grained artificial zippeite crystallized from uranyl sulphate solutions at pH's of 4.3 and 4.1, at 30° C. The material was unsuitable for single-crystal studies.

Clusters of tiny crystals of artificial zippeite are orange yellow in color, but individual crystals have a distinctly greenish tinge. The crystals occur as flat (010) plates with elongate, doubly-terminated, rhombic outlines.

When examined under the polarizing microscope, the crystals are observed to be invariably twinned. Two individuals make up the twin by reflection across the (001) plane. There is no evidence of zoning. A doubly-terminated (010) plate shows a fourling made up of the two individuals when viewed under crossed nicols. The two individuals give acute bisectrix figures indicative of monoclinic symmetry and the optic orientation  $x=b$  and  $Z \wedge a = 3^\circ$ . In the parallel position, the trace of the twin plane disappears giving rise to apparent orthorhombic extinction conditions with  $X=b$ ,  $Y=c$ ,  $Z=a$ . Additional optical properties are listed in Table 2, together with the properties of the natural mineral.

The specific gravity was determined by immersion in thallium malonate-thallium formate solutions. The density of the solution in which the material remained suspended was measured on the Berman balance using a cube of galena as a standard. A value of 3.66 was obtained for the specific gravity.

Rotation, zero and first layer Weissenberg films were taken about the axis of elongation ( $a$  axis) of a twinned crystal. Precession photographs were also taken using the  $b$  axis as the precessing axis. The systematic absences of diffraction spots conformed with the criteria of monoclinic space group  $C2/m$ . The unit cell dimensions in Angstrom units are as follows:

$$a = 8.81, \quad b = 14.13, \quad c = 8.85, \quad \beta = 104^\circ 15'.$$

TABLE 2. OPTICAL PROPERTIES OF NATURAL AND ARTIFICIAL ZIPPEITE

		1	2	3	4	5
Indices of Refraction	$nX$	1.64	1.655	1.66	1.66	1.655
	$nY$	1.718	1.72	1.715	1.72	1.717
	$nZ$	1.766	1.77	1.76	1.765	1.765
Optic Sign		(-)	(-)	(-)	(-)	(-)
Pleochroic Formula	$X$	colorless				colorless
	$Y$	pale yellow to yellow				pale yellow
	$Z$	yellow				yellow
Extinction		parallel				parallel or inclined at 3°
Orientation		Z parallel to elongation				$Z/\wedge a = 3^\circ$

1. Anmerk 67071, Frondel (1951).
2. Joachimsthal 69051, Frondel (1951).
3. Joachimsthal 125, Frondel (1951).
4. Joachimsthal 6233, Frondel (1951).
5. Artificial zippeite, Traill (1951).

$\beta$  was obtained by direct measurement on the zero layer precession film.

The chemical analyses of zippeite by Nováček (1935) show the presence of considerable calcium. It seems likely that the material analysed by Nováček contained uranopilite and gypsum in addition to zippeite. The variability of his analyses and optical properties could thus be accounted for. Earlier analyses by Lindacker (1857) are also unreliable. Two chemi-

TABLE 3. ARTIFICIAL ZIPPEITE: CHEMICAL ANALYSIS AND CELL CONTENT

	1	2	3	4	5	6	7	
UO <sub>3</sub>	74.52	75.70	75.11	73.29	72.70	U	6.03	6
SO <sub>3</sub>	13.50	13.25	13.36	13.04	13.56	S	3.83	4
H <sub>2</sub> O	13.81	14.21	14.01	13.67	13.74	O	47.43	48
	101.83	103.16	102.48	100.00	100.00	H	35.70	36

1. Analysis by writer.
2. Analysis by writer.
3. Average of analyses 1 and 2.
4. Average analysis reduced to 100 per cent.
5. Ideal composition for  $2[(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ .
6. Cell content of zippeite,  $M = 2353$ .
7. Ideal cell content for  $2[(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ .



FIG. 1. X-ray powder photograph of artificial zippeite. Cu radiation, Ni filter. Camera radius  $90/\pi$  (1 mm. in film =  $1^\circ$ ).

cal analyses of artificial zippeite were made by the writer (Table 3), and used as a basis for calculation of the unit cell contents.

The unit cell dimensions combined with the measured specific gravity give the molecular weight of the cell contents  $M = 2353$ . In Table 3, this value has been used to determine the atomic content of the unit cell from the average analysis. The computed cell content agrees closely with the ideal figures, clearly indicating a cell content  $2[(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$ . The calculated specific gravity for this cell content is 3.68, in close agreement with the measured value 3.66.

The x-ray powder diffraction pattern of artificial zippeite is shown in Figure 1. Observed intensities and measured spacings, together with the calculated spacings indexed to a minimum  $d = 2.00$ , are listed in Table 4. Close agreement is reached between the measured and calculated spacings.

#### OTHER SYNTHETIC URANIUM SULPHATES

The synthesis experiments at atmospheric pressure (Table 1) yielded crystals of six compounds in addition to zippeite. The six greenish-yellow compounds exhibited brilliant greenish fluorescence when viewed in ultra-violet light. All were soluble in water. None of these compounds are known to occur as minerals.

The synthetic products, V, W, Y, and Z, were identified as uranyl sulphate compounds which are listed in Gmelins (1936). A search of chemical literature failed to reveal any comprehensive descriptions of the properties of these compounds. The writer, therefore, has included in this paper a summary of the properties of the four synthetic products (Table 5), and the data obtained from their powder photographs (Table 6). The properties which are recorded in Gmelins agree reasonably well with the corresponding values in Table 5. A discrepancy, however, is found in the specific gravity of compound W (uranyl sulphate trihydrate). The measured and calculated values of 3.84 and 3.88 (Table 5) disagree with the value 3.280 recorded in Gmelins and other handbooks.

Only small amounts of compounds U and X were available for study, and chemical analyses could not be undertaken to establish their identities. The crystallographic, optical, x-ray data, and brief descriptions of

TABLE 4. X-RAY POWDER PATTERN: ARTIFICIAL ZIPPEITE =  $2[(\text{UO}_2)_3(\text{SO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$   
 Monoclinic  $C2/m$ ;  $a=8.81$ ,  $b=14.13$ ,  $c=8.85$  A,  $\beta=104^\circ 15'$

<i>I</i> (Cu)	<i>d</i> (meas)	<i>hkl</i>	<i>d</i> (calc)	<i>I</i> (Cu)	<i>d</i> (meas)	<i>hkl</i>	<i>d</i> (calc)	<i>I</i> (Cu)	<i>d</i> (meas)	<i>hkl</i>	<i>d</i> (calc)
2	8.42	001	8.58			023	2.65			204	2.15
1	7.69	110	7.32	2	2.64	$\bar{3}$ 12	2.65			$\bar{2}$ 43	2.15
10	7.02	020	7.06			$\bar{1}$ 51	2.63			242	2.15
$\frac{1}{2}$	6.24	$\bar{1}$ 11	6.25			113	2.49	2	2.14	203	2.14
2	5.47	021	5.48			151	2.49			004	2.14
		002	4.29			$\bar{1}$ 33	2.49			400	2.13
3	4.27	201	4.27	4	2.48	311	2.48			$\bar{4}$ 02	2.13
		200	4.26			$\bar{2}$ 42	2.48			312	2.11
1	3.87	$\bar{1}$ 31	3.89			$\bar{3}$ 31	2.48			$\bar{4}$ 21	2.10
		022	3.67			241	2.47	1	2.09	$\bar{3}$ 33	2.09
1	3.65	220	3.64			$\bar{1}$ 52	2.36			062	2.07
		$\bar{2}$ 21	3.64	2	2.34	060	2.35			$\bar{2}$ 61	2.07
		202	3.56			$\bar{3}$ 32	2.34			024	2.05
9	3.48	201	3.49			133	2.23			223	2.05
		$\bar{2}$ 22	3.14	$\frac{1}{2}$	2.23	152	2.23			$\bar{2}$ 24	2.05
9	3.13	221	3.12			331	2.22	2	2.04	420	2.04
3	2.85	003	2.86			043	2.22			$\bar{4}$ 22	2.04
		240	2.72	3	2.19	$\bar{4}$ 01	2.20			$\bar{1}$ 53	2.04
		241	2.72			$\bar{1}$ 14	2.19			$\bar{3}$ 51	2.03
$\frac{1}{2}$	2.70	$\bar{2}$ 03	2.71								
		202	2.70								
		150	2.70								

  

<i>I</i>	<i>d</i> (meas)								
6	1.96 A	1	1.53 A	$\frac{1}{2}$	1.30 A	1	1.11 A	$\frac{1}{2}$	0.95 A
1	1.87	1	1.50	2	1.26	1	1.09	$\frac{1}{2}$	0.94
1	1.81	$\frac{1}{2}$	1.46	2	1.24	1	1.07	1	0.93
5	1.75	1	1.42	$\frac{1}{2}$	1.21	1	1.06	$\frac{1}{2}$	0.92
5	1.69	2	1.39	$\frac{1}{2}$	1.20	$\frac{1}{2}$	1.04	$\frac{1}{2}$	0.90
$\frac{1}{2}$	1.63	1	1.37	1	1.18	1	1.01	1	0.89
$\frac{1}{2}$	1.59	$\frac{1}{2}$	1.35	1	1.16	1	0.99		
4	1.56	1	1.31	$\frac{1}{2}$	1.14	1	0.98		

the two compounds are recorded in the writer's unpublished thesis but will not be presented here.

#### APPENDIX: URANOPILITE FROM GOLDFIELDS, SASKATCHEWAN

Through the generosity of Dr. S. C. Robinson of the Geological Survey of Canada, the writer obtained a specimen of pitchblende richly encrusted with a bright yellow mineral. The yellow mineral was studied optically, and a powder pattern was obtained. Both the optical proper-

TABLE 5. SUMMARY OF URANIUM SULPHATE SYNTHETIC PRODUCTS

Compound	V	W	Y	Z
Cell contents	4[UO <sub>2</sub> SO <sub>4</sub> · (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> · 2H <sub>2</sub> O]	8[UO <sub>2</sub> SO <sub>4</sub> · 3H <sub>2</sub> O]	4[2UO <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> SO <sub>4</sub> · 5H <sub>2</sub> O]	4[UO <sub>2</sub> SO <sub>4</sub> · K <sub>2</sub> SO <sub>4</sub> · 2H <sub>2</sub> O]
Space group	<i>P2<sub>1</sub>/n</i>	<i>Pbnm</i>	<i>Pmnn</i>	<i>Pmnb</i>
Unit cell dimensions	<i>a</i> 20.53 Å <i>b</i> 7.30 <i>c</i> 7.74 <i>β</i> 99°25'	12.58 Å 17.00 6.73	12.86 Å 12.99 11.57	11.55 Å 13.78 7.28
Specific gravity (measured)	3.07	3.84		3.33
Specific gravity (calculated)	3.10	3.88	3.16	3.31
Chemical analysis	UO <sub>3</sub> 52.90 SO <sub>3</sub> 30.13 NH <sub>3</sub> } 17.90 H <sub>2</sub> O } 100.93	UO <sub>3</sub> 69.13 SO <sub>3</sub> 19.01 H <sub>2</sub> O 13.78 101.92	UO <sub>3</sub> 57.46 SO <sub>3</sub> 26.54 H <sub>2</sub> O n.d.	UO <sub>3</sub> 48.74 SO <sub>3</sub> 27.31 K <sub>2</sub> O qual. H <sub>2</sub> O 6.98
Indices of refraction	<i>n<sub>X</sub></i> n.d. <i>n<sub>Y</sub></i> 1.555 <i>n<sub>Z</sub></i> 1.600	1.574 1.589 1.593	1.555 1.586 1.586	n.d. 1.529 1.575
Pleochroic formula	<i>X</i> colorless <i>Y</i> colorless <i>Z</i> pale green	colorless pale green greyish green	colorless pale yellow pale yellow	not pleochroic
Orientation		<i>Z=c</i>	<i>Z=c</i>	

ties and the powder diffraction data are in agreement with those of the mineral uranopilite.

The mineral has a silky lustre which gives the crust a velvety appearance. It emits a bright greenish fluorescence when viewed in ultra-violet light. The crust is made up of bundles of tiny fibres grouped together in the form of rosettes and also intergrown in a completely random manner. Because of the fibrous habit, the writer was unable to select a single crystal for study by single-crystal *x*-ray methods.

Several powder diffraction photographs were taken using Cu radiation, and the material was found to give a distinctive pattern (Table 7).

TABLE 6. X-RAY POWDER PATTERNS (Cu radiation, Ni filter)

Compound V		Compound W		Compound Y		Compound Z	
<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)
10	6.71 A	6	6.76 A	1	8.34 A	2	7.38 A
4	5.91	1	5.72	2	7.02	10	6.81
7	5.28	1	5.51	10	6.32	2	6.07
7	4.98	10	5.01	4	5.61	10	5.54
6	4.48	4	4.37	2	5.15	1	5.22
3	3.93	1	4.10	$\frac{1}{2}$	4.44	5	4.58
3	3.77	9	3.99	4	4.27	5	4.44
2	3.59	3	3.49	3	4.00	6	3.65
9	3.38	3	3.41	$\frac{1}{2}$	3.71	3	3.51
3	3.21	3	3.34	$\frac{1}{2}$	3.48	3	3.43
7	3.06	1	3.22	1	3.40	4	3.30
7	2.87	2	3.05	6	3.19	5	3.08
$\frac{1}{2}$	2.73	2	2.95	1	3.08	5	3.00
$\frac{1}{2}$	2.64	6	2.79	$\frac{1}{2}$	3.02	1	2.88
4	2.56	1	2.71	1	2.87	2	2.73
$\frac{1}{2}$	2.45	1	2.58	5	2.76	1	2.65
1	2.38	8	2.50	1	2.70	2	2.51
5	2.33	$\frac{1}{2}$	2.44	3	2.61	2	2.37
4	2.25	$\frac{1}{2}$	2.37	$\frac{1}{2}$	2.49	2	2.30
3	2.17	5	2.32	$\frac{1}{2}$	2.39	4	2.23
1	2.10	1	2.24	1	2.34	1	2.19
5	2.06	1	2.21	2	2.22	1	2.13
2	1.99	2	2.14	4	2.13	1	2.09
1	1.93	2	2.07	2	2.04	2	2.04
1	1.89	1	1.99	1	1.98	3	1.96
$\frac{1}{2}$	1.85	1	1.96	1	1.92	2	1.87
$\frac{1}{2}$	1.82	2	1.90	1	1.88	2	1.80
3	1.77	2	1.85	2	1.84	2	1.76
2	1.73	7	1.79	1	1.80	2	1.72
1	1.70	2	1.74	1	1.75	2	1.69
1	1.69	1	1.68	3	1.70	4	1.65
2	1.65	1	1.63	$\frac{1}{2}$	1.66	1	1.62
2	1.62	1	1.59	$\frac{1}{2}$	1.59	1	1.59
2	1.59	3	1.56	2	1.55	2	1.52
$\frac{1}{2}$	1.56			1	1.51	2	1.48
$\frac{1}{2}$	1.54			1	1.47	1	1.41
$\frac{1}{2}$	1.50			3	1.43	1	1.40
1	1.44			3	1.40	1	1.37

TABLE 7. URANOPILITE: X-RAY POWDER PATTERN (Cu radiation, Ni filter)

<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)
3	8.76 Å	$\frac{1}{2}$	3.95 Å	6	2.88 Å	2	2.14
3	7.97	$\frac{1}{2}$	3.82	2	2.72	1	2.11
10	6.97	3	3.60	4	2.66	4	2.00
5	5.87	1	3.47	$\frac{1}{2}$	2.56	2	1.95
6	5.44	1	3.34	$\frac{1}{2}$	2.49	$\frac{1}{2}$	1.89
1	5.07	1	3.24	$\frac{1}{2}$	2.40	3	1.81
2	4.60	1	3.03	$\frac{1}{2}$	2.33		
9	4.21	1	2.95	$\frac{1}{2}$	2.24		

A powder pattern of uranopilite (TE 604) was borrowed from the Trace Elements Section of the U. S. Geological Survey for comparison with that of the mineral from Goldfields. The measurements obtained from the two patterns showed good agreement.

Rotation films were taken about the axis of elongation of several tiny bundles of fibres. The films yielded a value of 8.91 Å for the lattice period along the axis of elongation.

For the mineral from Goldfields, the writer determined the following optical properties: indices of refraction,  $nX=1.620$ ,  $nY=1.624$ ,  $nZ=1.630$ ; strong dispersion; not pleochroic; inclined extinction,  $Y \wedge$  elongation =  $16^\circ-17^\circ$ . These properties are in close agreement with the properties of uranopilite recorded by several investigators and summarized by George (1949).

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