CRYSTALLOGRAPHY OF THE URANIUM OXIDES

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The complex suite of oxidation products of uraninite from the Katanga deposits which has been described in recent years, chiefly by Professors Schoep and Buttgenbach, has introduced to mineralogists a great variety of new compounds. The mode of occurrence, however, makes it difficult to isolate these minerals in amounts adequate for satisfactory chemical analysis and, notwithstanding the fairly definite data that exist regarding the crystal form and optical properties of a number of them, the exact chemical nature of several of them is still uncertain. The author has made a small number of crystallographic measurements on minerals of this group which seem, judging by the published descriptions, to be as accurate as those of earlier workers. He has used these measurements in establishing crystal elements which have already been published (9), and it seems proper to place this new data on record. In doing so the results of other studies have been compiled and are here briefly presented.

Schoepite:—Schoepite was first described by Walker (1), who measured and figured a single crystal of prismatic habit. Schoep (2) and (3) also measured crystals and adopted Walker's elements. He notes that the predominant habit, unlike that of Walker's crystal, is tabular parallel to the base. Buttgenbach (4) gave the same forms as Walker but his elements, shown in the table below, differed slightly from those of the earlier writer. Ungemach (5) described several brilliant tabular crystals, one of them very complex with many new forms. In order to simplify the indices of the forms, he suggests doubling the *a* axis of Walker; his elements are in good agreement with those of the latter. Palache measured several crystals, one of them of excellent quality, and calculated axes agreeing closely with those of Walker and Ungemach. In order to determine the question of the proper choice of the unit form, H. Berman of this laboratory measured the dimensions of the unit cell of schoepite by rotation *x*-ray photographs. Because of the high absorption of the mineral, the photographs were not as sharp as was expected, but the result was unambiguous and confirmed the choice of Walker, which is here used.

Becquerelite:—Becquerelite was first described by Schoep and his observations are expanded in his later papers (2) and (3).

TABLE I. AXIAL ELEMENTS OF SCHOEPITE

	a	*c*
Walker (1)	0.426	0.875
Schoep (3)	0.426	0.875
Buttgenbach (4)	0.42757	0.89986
Ungemach (5)	0.4262	0.8744
Palache (unpublished)	0.4253	0.8741
Mean of Walker, Ungemach & Palache	0.4258	0.8745

TABLE II. ANGLES AND FORMS OF SCHOEPITE AND THEIR OBSERVERS

$a=0.4258$ $p_0=2.0538$
$c=0.8745$ $q_0=0.8745$

			ϕ	ρ	Walker	Buttgen-bach	Schoep	Palache	Unge-mach
1	*c*	001	0°00′	0°00′	x	x	x	x	x
2	*b*	010	0°00′	90°00′	x	x	x	x	x
3	*a*	100	90°00′	90°00′	x	x	x	x	x
4	*n*	120	49°35′	90°00′					x
5	*m*	110	66°56′	90°00′	x	x	x	x	x
6	*g*	015	0°00′	9°55′					x
7	*h*	014	0°00′	12°20′					x
8	*i*	027	0°00′	14°01½′					x
9	*k*	012	0°00′	23°37′					x
10	*z*	023	0°00′	30°14½′					x
11	*d*	011	0°00′	41°10′	x	x	x	x	x
12	*f*	021	0°00′	60°14½′	x	x	x	x	x
13	*e*	041	0°00′	74°02½′	x	x			x
14	*x*	104	90°00′	27°10½′	x	x			x
15	*r*	113	66°56′	36°39′					x
16	*s*	112	66°56′	48°08½′				x	x
17	*p*	111	66°56′	65°52′	x	x	x	x	x
18	*q*	124	49°35′	33°59½′	x	x	x	x	x
19	*o*	122	49°35′	53°27′	x	x	x	x	x
20	*u*	144	30°25′	45°24′				x	x
21	*v*	142	30°25′	63°45′					x
22	*t*	121	49°35′	69°39½′					x
23	*w*	342	60°25′	74°14′					x

Buttgenbach (4) gives the same data but adds a number of forms. Ungemach (5) has also measured and figured crystals and added largely to the form series. Tabulated with these results below are the data obtained by Palache on five crystals of good quality.

TABLE III. AXIAL ELEMENTS OF BECQUERELITE

	a	*c*
Schoep (2)	0.5722	0.6173
Schoep (3)	0.5537	0.5938
Schoep (6)	0.5537	0.5938
Buttgenbach (4)	0.5537	0.5938
Ungemach (5)	0.5591	0.6056
Palache (unpub.)	0.55905	0.6044
Mean of last two	0.5591	0.6050

In order to bring about closer similarity to the elements of schoepite the *c* axis is doubled and the elements of becquerelite adopted in this paper are therefore:—

$$a=0.5591 \quad p_0=2.1642$$
$$c=1.2100 \quad q_0=1.2100$$

The five crystals measured by the author were tabular parallel to the base and elongated parallel to *b*. The data on which are based the forms observed by him and not by others are as follows:—

		ϕ	ρ	
a	100	90°00′	90°00′	2 faces, good quality
n	130	30°50′	90°00′	2 faces, fair quality
h	051	0°00′	80°13′	1 face, poor quality
j	308	90°00′	38°55′	1 face, poor quality
		89°34′	38°22′	1 face, poor quality
r	332	60°39′	74°28′	1 face, good quality
s	221	60°52′	78°23′	line face, fair quality
		60°24′	78°55′	line face, fair quality
y	124	41°40′	39°45′	1 face, poor quality

"Mineral X":—A mineral occurring at Great Bear Lake, Canada, with other oxidation products of pitchblende and probably a lead-free oxide of uranium, was described by Palache and Berman (10). The elements of this mineral are intermediate between those of schoepite and becquerelite. Like them it is platy parallel to a direction of perfect cleavage which is taken as basal. The analysis, made on very little material which was impure, was unsatisfactory

TABLE IV. ANGLES AND FORMS OF BECQUERELITE AND THEIR OBSERVERS

$a=0.5591$ $p_0=2.1642$
$c=1.2100$ $q_0=1.2100$

			ϕ	ρ	Schoep	Buttgen-bach	Unge-mach	Palache
1	*c*	001	0°00′	0°00′	x	x	x	x
2	*b*	010	0°00′	90°00′	x	x	x	x
3	*a*	100	90°00′	90°00′			x	x
4	*n*	130	30°48′	90°00′			x	x
5	*m*	110	60°47½′	90°00′	x	x	x	x
6	*e*	011	0°00′	50°25½′	x	x	x	x
7	*g*	031	0°00′	74°36′		x		
8	*z*	041	0°00′	78°19½′			x	
9	*h*	051	0°00′	80°37′			x	x
10	*i*	106	90°00′	19°50′		x		x
11	*f*	104	90°00′	28°25′	x	x	x	x
12	*k*	3.0.10	90°00′	33°00′	x	x		
13	*A*	103	90°00′	35°48½′		x	x	
14	*j*	308	90°00′	39°03½′			x	x
15	*l*	7.0.18	90°00′	40°05′			x	
16	*q*	205	90°00′	40°53′			x	
17	*t*	5.0.12	90°00′	42°02½′			x	
18	*u*	7.0.16	90°00′	43°26′			x	
19	*d*	102	90°00′	47°15½′	x	x	x	x
20	*v*	508	90°00′	53°31½′			x	
21	*o*	112	60°47½′	51°06′½			x	
22	*p*	111	60°47½′	68°02′		x	x	
23	*r*	332	60°47½′	74°57′				x
24	*s*	221	60°47½′	78°36′				x
25	*y*	124	41°48½′	39°04′				x
26	*x*	122	41°48½′	58°22′			x	x
27	*w*	322	69°33½′	73°54′		x	x	x

but seems to indicate the composition $UO_3 \cdot 2H_2O$. The elements, forms and angles are as follows:

	$a=0.490$	$p_0=2.12$	
	$c=1.04$	$q_0=1.04$	
		ϕ	ρ
n	120	45°35′	90°00′
d	011	0°00′	46°11′
f	021	0°00′	64°22′
p	111	63°54′	67°07′

Fourmarierite:—Fourmarierite was first described by Buttgenbach (8) and nothing has been added to his description of the crystal form. As originally oriented the cleavage was made macropinacoidal. By interchanging *a* and *c*, making the cleavage basal, a closer relation to schoepite appears, and for this paper this change has been made. The elements of Buttgenbach, recalculated to this position are:—

$a=0.4056$ $p_0=2.1775$
$c=0.8832$ $q_0=0.8832$

The forms become:—

Buttgenbach		New Position		ϕ	ρ
h′	100	*c*	001	0°00′	0°00′
$m_{\frac{1}{2}}$	110	*d*	011	0°00′	41°27′
b	111	*s*	122	50°57′	54°30′

Ianthinite:—Ianthinite was first described by Schoep (6) and his data for the crystal form remain the sole source of information. The cleavage is taken as the macropinacoid and the habit is tabular parallel to this form. Schoep's elements, given below, were calculated from the angle ρ of (011) and the angle ϕ of (130). However, by changing the position so that *a* (Schoep) becomes *c*, and *b* (Schoep) becomes *a*, both cleavage and optical orientation fall into parallelism with those of preceding minerals. This new orientation is adopted here and the result is shown in the table.

Elements of Ianthinite

Schoep		Palache (new position)	
$a=0.8646$	$p_0=0.7713$	$a=0.4998$	$p_0=2.5938$
$c=0.6669$	$q_0=0.6669$	$c=1.2964$	$q_0=1.2964$

Forms and Angles of Ianthinite

Schoep (observed)				Palache		(Observed angles transformed to new position)		Calculated	
		ϕ	ρ			ϕ	ρ	ϕ	ρ
a	(100)	90°00′	90°00′	*c*	001	—	—	—	—
**g*	(130)	21°05′	90°00′	*g*	101	90°00′	68°55′	90°00′	68°55′
m	(110)	49°09′	90°00′	*m*	103	90°00′	40°48½′	90°00′	40°51′
**f*	(011)	0°00′	33°42′	*f*	130	33°42′	90°00′	33°42′	90°00′
d	(101)	90°00′	37°41′	*d*	011	0°00′	52°19′	0°00′	52°21′

Curite:—Curite was first described by Schoep (6) and little has since been added to our knowledge of its crystal form. The simple crystals are minute and rather poor, and there is a cleavage, determined by Berman to be parallel to the direction taken as the macropinacoid. Two crystals were measured in this laboratory and their angles were averaged with those of Schoep for determination of elements.

	ϕ	ρ
Schoep, five crystals average for (111)	46°18½′	43°25′
Palache and Berman, two crystals average for (111)	45°52′	43°07′
Weighted mean for (111)	46°11′	43°20′

The elements are:—

$a=0.9595 \qquad p_0=0.6808$

$c=0.6532 \qquad q_0=0.6532$

Attempts to so transform the position of curite that its elements more nearly resembled those of other members of this series were unsuccessful.

General Relations:—The peculiar relations of these six minerals are unclear and must remain so until more is known of their chemical nature. All are orthorhombic and a general similarity exists in their cleavage and their crystallographic elements. To bring this out more clearly they are tabulated below. The column showing optical orientation has been prepared by Mr. Berman after the study of measured crystals.

TABLE V. SOME PROPERTIES OF THE URANIUM OXIDES

	Formula	Optical Orientation	Cleavage	a	$c=q_0$	p_0
Schoepite	$3UO_3 \cdot 7H_2O$	$X=c$ $Y=b$	001	0.4258	0.8745	2.0538
"Mineral X"	$UO_3 \cdot 2H_2O$ (?)	$X=c$ $Y=b$	001	0.490	1.04	2.12
Becquerelite	$4UO_3 \cdot 7H_2O$	$X=c$ $Y=b$	001	0.5591	1.2100	2.1642
Ianthinite	$2UO_2 \cdot 7H_2O$	$X=c$ $Y=b$	001	0.4998	1.2964	2.5938
Fourmarierite	$PbO \cdot 4UO_3 \cdot 5H_2O$	$X=c$ $Y=a$	001	0.4056	0.8832	2.1775
Curite	$2PbO \cdot 5UO_3 \cdot 4H_2O$	$Z=c$ $Y=a$	100	0.9595	0.6532	0.6808

The formulae assigned to schoepite and becquerelite are those of Schoep's latest paper (7). They are based on water determinations alone, made on microchemical samples, and are certainly open to question. The mean values of all the water determinations published on both minerals certainly indicate their probable identity of composition with the formula $UO_3 \cdot 2H_2O$.

It will be seen that there is a close similarity in the elements of five of these six minerals, curite alone being widely different. This similarity is closest between schoepite and fourmarierite, amounting almost to identity of form, but their optical orientation and chemical composition are different. If the values of $p_0(=c/a)$ of the first four are compared, it will be seen that they increase more or less regularly from schoepite onward. When structural studies have been made, some explanation of this peculiar set of relations may be discovered, but at present they simply have to be termed anomalous.

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