PARASCHOEPITE AND EPIIANTHINITE, TWO NEW URANIUM MINERALS FROM SHINKOLOBWE (BELGIAN CONGO)

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Abstract

Paraschoepite, a new mineral with a chemical composition corresponding to the formula $5UO_3 \cdot 9\frac{1}{2}H_2O$ has been found in the uranium mine of Shinkolobwe. Properties: color, yellow; habit, identical with tabular schoepite. X=c, Y=b, Z=a. $\alpha=1.705$, $\beta=1.760$, $\gamma=1.770$. $2V \pm 46^\circ$; r > v. H. = 2-3. G. > 3.3.

Epiianthinite, chemical composition is unknown but probably an uranium hydroxide. Color, yellow. Crystals are prismatic and elongated parallel to b. X=c, Y=b, Z=a. $\alpha=1.70$, $\beta=1.79$, $\gamma=1.793$. 2V very small. Pleochroism, yellow to deep yellow. G.>3.3; H.=2-3.

Paraschoepite and epitanthinite occur in the Shinkolobwe uranium mine (Katanga). They belong to the uranium hydroxide group of minerals whose inter-relationship Charles Palache rightly describes as peculiar. The name paraschoepite appeared to us as very suitable for the first mentioned mineral because it differs very little, both crystallographically and chemically, from schoepite.

In naming the second mineral epiianthinite we specially wished to emphasize the fact that it not only crystallizes on ianthinite, but also that its lattice is in continuity with that of ianthinite; at the same time the name designates its secondary character.

PARASCHOEPITE

Associations and crystallographic properties

Crystals of paraschoepite have been found directly on pitchblende or with secondary uranium minerals. They appear to be very closely associated with becquerelite and are frequently found as deposits on that mineral. The largest crystals observed reach a size of several millimeters. Their habit is tabular and they are orthorhombic in crystallization. Their color is yellow, less greenish than the yellow of schoepite and their transparency is less than that of the latter mineral. The mineral has a very perfect and easy cleavage, making it extremely brittle. The hardness ranges from 2 and 3 and the powder is yellow.

Paraschoepite resembles so closely certain tabular schoepite crystals that it is impossible to distinguish between them without determining their optical properties. Not having available at present any instrument for measuring crystals, we were able however to measure accurately the angles between the edges of crystals placed on the rotating stage of a microscope, and with these data we drew the crystal and showed that the drawings thus obtained (Fig. 1) could be exactly superimposed on drawings of similar schoepite crystals, drawn orthogonally from gnomonic projections. The paraschoepite crystals, which we have examined in this way, lie mostly on face c(001), which is generally better developed than

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the other forms and which is covered with fine striations running parallel to the *b* axis. As shown in Fig. 1, the forms include c(001), b(010), a(100), m(110), n(120), d(011), f(021), x(104) and q(124). This crystal is relatively large; smaller crystals have fewer forms.



FIG. 1. Two views of a crystal of paraschoepite.

Optical properties

Under the microscope crystals of paraschoepite are yellow and translucent; they contain a considerable number of inclusions, apparently of a gaseous nature, which perhaps explains their limited transparency when examined with the naked eye. Zonal growth is nearly always discernible



FIG. 2. Crystal of paraschoepite showing zonal growth. Axial plane is parallel to b(010).

(Fig. 2). Between crossed nicols they react as orthorhombic crystals. The acute bisectrix is perpendicular to c(001); the plane of the optic axes is parallel to b(010); these axes are visible at the edge of the field with a No. 5 Leitz objective (numerical aperture 0.65). If the optic axes are observed on the natural face c(001), it appears as if the axial plane is perpendicular to the striations which cover the face and this is a good characteristic which distinguishes paraschoepite from schoepite.

The indices of refraction as determined by the immersion method are given below.

Pleochroism: Z and Y, yellow; X colorless or nearly so.

Dispersion, r > v.

$\alpha = 1.705$	X = c	$2V \pm 40^{\circ}$
$\beta = 1.760$	Y = b	$B_x(-)$
$\gamma = 1.770$	Z = a	r > v

Chemical properties and composition

Paraschoepite dissolves readily in hydrochloric, nitric and sulfuric acids and gives the uranium reaction; it also contains water but does not give a test for lead.

	1.	2.	3.	4.
UO3	89.26	0.312	1	89.31
H_2O	10.73	0.597	1.9	10.69

ANALYSIS OF PARASCHOEPITE

1. Analysis of paraschoepite of Shinkolobwe.

2. Molecular proportions.

3. Molecular ratios on the basis of $UO_3 = 1$.

4. Calculated analysis on the basis of the formula $5UO_3 \cdot 9\frac{1}{2}H_2O$.

Discussion of the formula

The chemical composition of paraschoepite places it in the group of uranium hydroxides, of which the following are already known: becquerelite, schoepite, mineral X (Palache), and fourmarierite. The last named is, it is true, a lead uranate if considered solely from the chemical point of view, but it is equally certain that its crystallographic characteristics place it next to schoepite.

We propose the following formula for paraschoepite: $5UO_3 \cdot 9\frac{1}{2}H_2O$. We should recall here that one of us, after one of the first analyses made of becquerelite and schoepite, gave, in a formula of the $y UO_3 \cdot x H_2O$ type assigned to these minerals, the value $\frac{1}{2}$ for the ratio y:x; the two minerals were at first given the same chemical formula. It must be admitted that these first analyses had been made on samples which could in no wise be claimed to be very pure; lead amongst others was always found to be present, whereas a number of analyses made on isolated and pure crystals of becquerelite and of schoepite had established the fact that these minerals contain no traces of lead.

Later we were able to obtain a sufficient quantity of pure crystals and we have re-analyzed these two minerals. It is in view of the results thus obtained that we realized that it was advisable to give to the coefficients y and x values which differed as little as possible from the molecular ratios found. The chemical composition of the two minerals was thus expressed as follows:

Becquerelite	$4UO_3 \cdot 7H_2O$
Schoepite	$3UO_3 \cdot 7H_2O$

The elementary cells of these minerals as well as of fourmarierite have since then been measured; the following results were obtained:

	Becquerelite	Schoepite	Fourmarierite
a ₀	13.9 Å	14.40Å	14.07Å
b_0	12.55Å	16.89Å	16.72Å
C ₀	14.9 Å	14.75Å	14.40Å

The formula suggested for fourmarierite, $PbO \cdot 4UO_3 \cdot 5H_2O$, corresponds to a molecular weight M, which introduced in the well known formula:

$$n = \frac{V \times d}{M \times 1.65}$$

gives a value for n which is quite acceptable, considering the specific gravity of the mineral. It was not the same for either becquerelite or schoepite; therefore, these minerals were, once more, analyzed and new determinations of specific gravity were made. Finally the following formulae were decided upon:

Becquerelite	$2UO_3 \cdot 3H_2O$
Schoepite	$4UO_3 \cdot 9H_2O$

for which the values of n were considered compatible with both the symmetry and specific gravity.

In the following table the known uranium hydroxides have been placed with some others which are theoretically possible; fourmarierite has been placed at the top of the list because in its formula:

$y \text{ UO}_3 \cdot z \text{ PbO} \cdot x \text{ H}_2\text{O}$ y + z : x = 1

Name Formula $H_2O\%$ x:y UO3% a β r Fourmarierite $4 \text{ UO}_3 \cdot \text{PbO} \cdot 5 \text{ H}_2\text{O}$ 1.00 93.81 6.19 1.920 1.940 $4 \text{ UO}_3 \cdot 5 \text{ H}_2\text{O}$ 1.25 92.70 7.30 -----_ Becquerelite $2 \text{ UO}_3 \cdot 3 \text{ H}_2\text{O}$ 1.50 91.37 8.63 1.725 1.825 1.83 Mineral x $4 \operatorname{UO}_3 \cdot 7 \operatorname{H}_2O$ 1.75 90.08 9.92 1.785 1.81 1.82 5 UO₃ · 9 H₂O 1.80 89.82 10.18 Paraschoepite $5 \text{ UO}_3 \cdot 9\frac{1}{2} \text{ H}_2\text{O}$ 1.90 89.31 10.69 1.705 1.76 1.77 $UO_3 \cdot 2 H_2O$ 2.00 88.81 11.19 Schoepite $4 \text{ UO}_3 \cdot 9 \text{ H}_2\text{O}$ 2.25 87.59 12.41 1.714 1.735 1.69

TABLE OF URANIUM HYDROXIDES

The position we have given to paraschoepite in this series of hydroxides will be noted from the above. It will be interesting to know its crystallographic constants and we hope that they will be published before long.

The position in the series which we have given to mineral x is based only on its chemical composition, after deduction of PbO and recalculation to 100%. Furthermore, we repeat that in formulating this table chemical considerations served as a guide.

It may be considered that the formula 5 $UO_3 \cdot 9 H_2O$ might have served equally well to express the chemical composition of paraschoepite, but experience has shown that as far as these uranium hydroxides are concerned it is preferable not to round off the coefficients of either UO_3 or H_2O , given by an analysis of a superior type.

Differences between paraschoepite and schoepite

At first glance the differences between paraschoepite and schoepite are so slight that we take it for granted that one mineral must have been mistaken frequently for the other. Indeed, in so far as we are able to judge without goniometric measurements, the crystals of the two minerals are practically indistinguishable one from the other. An observation of the axial figure and the position of the axial plane is however sufficient; obviously, the determination of the indices of refraction is the infallible way to differentiate between the two minerals.

EPIIANTHINITE

As we mentioned at the beginning of this paper, we assigned the name of epiianthinite to a mineral which occurs as an alteration product of ianthinite. Yet the homogeneity of the alteration product is perfect and its crystalline lattice is in continuity with that of ianthinite.

Herewith is given a brief summary of the history of ianthinite. This mineral is always found implanted directly upon uraninite and fills all its fissures and cavities. The acicular crystals (1-3 mm.) are of prismatic habit; they are black with a brownish violet tinge in reflected but violet in transmitted light. The pleochroism is intense, dark violet to colorless and the appearance of the crystals is shown in Fig. 3. When the orientation suggested by Charles Palache is adopted, the forms are:

 $c(001), g(101), m(103), d(011), f(130) \cdot (3)$



FIG. 3. Crystal of ianthinite.

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For some time one of us had observed that certain ianthinite crystals are edged by a zone that is homogeneous and translucent and yellow in color. It is known that ianthinite is a hydroxide of U^{IV} and that the compounds of U^{IV} oxidize easily to U^{VI} ; at the same time the color changes from green or violet to yellow.

We have now been able to observe all the various stages of the change, passing from pure ianthinite to epiianthinite in which traces of the primary mineral are no longer perceived. Generally the traces of ianthinite inside epiianthinite occur as elongated patches of violet brown (Fig. 4).



FIG. 4. Remnants of unaltered ianthinite in crystal of epiianthinite and optical orientation of epiianthinite.

Optical properties

Epiianthinite crystals, examined under a microscope, are yellow in transmitted light; they have the same perfect cleavage as ianthinite and like the latter are orthorhombic in crystallization. A crystal observed in convergent light on face c(001) exhibits a good interference figure; the acute bisectrix, perpendicular to c(001), is negative; the optic angle is very small and the plane of the optic axes is perpendicular to the elongation, that is to the crystallographic b axis. The pleochroism is marked: X=c pale yellow, Y=b yellow, Z=a deep yellow. The indices of refraction are: $\alpha=1.70$, $\beta=1.79$, $\gamma=1.793$. The traces of ianthinite which one can see in many crystals appear as diffused and elongated shreds parallel to the b axis; they are violet in color and pleochroic; measured in the plane of c(001), their indices of refraction are higher than those of epiianthinite.

Chemical composition

Up to the present we have not been able to determine the chemical composition of the mineral, which has proved practically impossible to purify. It is, of course, a product of the oxidation of ianthinite and its composition can very likely be expressed by $y \text{ UO}_3 \cdot x\text{H}_2\text{O}$. We have, in the past, experimented with the oxidation of ianthinite by immersing the crystals for some minutes in a very dilute solution of hydrogen peroxide at a temperature around 50° C. The experiment was successful but the properties of the yellow crystals thus obtained bore no resemblance to those of epiianthinite; indeed their average index of refraction is only ± 1.60 . Of course, the oxidation took place in water while epiianthinite probably formed under different conditions.

According to L. J. Spencer, ianthinite crystals do not keep their original color when exposed in the cases of the British Museum. He noted that when acquired (1922), the color was purple, but in 1927 it was greenish yellow but crystals that had been mounted in Canada balsam still retained their original color and intense pleochroism. He concluded that the change is evidently due to oxidation in the air of a hydrated uranous oxide to a hydrated uranic oxide (5).

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