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# Metastudtite, $UO_4 \cdot 2H_2O$, a new mineral from Shinkolobwe, Shaba, Zaire

MICHEL DELIENS
*Département de Géologie et de Minéralogie du Musée*
*royal de l'Afrique centrale, B 1980 Tervuren, Belgium*

AND PAUL PIRET
*Laboratoire de Chimie physique et de Cristallographie*
*de l'Université, B 1348 Louvain-la-Neuve, Belgium*

## Abstract

Metastudtite occurs at the Shinkolobwe uranium deposit in Shaba, Zaire. It appears as aggregates of flexible pale yellow fibers. Electron microprobe analysis gave $UO_4$ 88.1%. $H_2O$ by TGA~ 10%. Formula $UO_4 \cdot 2H_2O$. Powder data are similar to those of the synthetic compound and to those of heated studtite ($UO_4 \cdot 4H_2O$). Orthorhombic, probable space group *Immm*, $a = 6.51(1)$, $b = 8.78(2)$, $c = 4.21(1)$Å, Z = 2, d(calc.) = 4.67 mg/cm$^3$. Strongest lines in the X-ray powder pattern are 5.22 (100)(110), 3.54 (80) (101), 4.38 (50)(020) and 3.79 (50)(011). The mineral is optically biaxial positive. $\gamma = 1.760$ (parallel to $c$, fiber axis), $\beta = 1.658$ and $\alpha = 1.640$. Metastudtite is associated with uranophane, kasolite and hydrated uranium-lead oxides. Metastudtite is compared with studtite and lepersonnite.

## Introduction

Two hydrates of uranium peroxide can be synthesized: $UO_4 \cdot 4H_2O$ (below 50°C) and $UO_4 \cdot 2H_2O$ (above 70°C). Both hydrates coexist between 50 and 70°C (Sato, 1961a). A study by thermal decomposition (Sato, 1961b) shows that the formulae adopted above are preferable to $UO_3 \cdot H_2O_2 \cdot 3H_2O$ and $UO_3 \cdot H_2O_2 \cdot H_2O$. X-ray powder patterns of both compounds have been published by Debets (1963).

Vaes (1947) reported the original studtite discovered at Shinkolobwe (Shaba, Zaire) to be a hydrated uranium carbonate as the result of a qualitative chemical analysis. Studying fibers of the same appearance, found at Menzenschwand (Black Forest, Western Germany), Walenta (1974) determined them, by their optical properties and X-ray powder pattern, to be identical to the studtite from Shaba and to the synthetic compound $UO_4 \cdot 4H_2O$. Chemical tests confirmed the composition as that of an oxide (probably a peroxide) and not of a carbonate. Walenta also studied the thermal behavior of studtite. By heating above 60°C, he obtained $UO_4 \cdot 2H_2O$. As the dehydration was irreversible, he suggested the possibility of the natural occurrence of this species.

Since the investigation of Walenta was performed on a sample which was different from the original Shinkolobwe material, we undertook the study of about twenty samples from Shinkolobwe regarded as studtites in several mineralogical collections. Our work indicates the existence of at least 3 different fibrous minerals qualified with the name "studtite" in that deposit:

### *Studtite*

About 12 samples effectively correspond to the original species described by Vaes in 1947. Their properties are identical to those of the Menzenschwand studtite. Their chemical composition corresponds to that given by Walenta (1974): $UO_4 \cdot 4H_2O$. This confirms that Vaes and Walenta worked on fibers of the same nature and that Vaes probably performed his chemical test (release of $CO_2$ by reaction with HCl) either on an impure material or on fibers belonging to another species.

### *Lepersonnite*

Six samples constitute a new mineral species of which the chemical composition and physical properties are distinct from those of studtite. This new mineral is a hydrous uranium, calcium, silicon and rare earth carbonate whose ideal empirical formula is: $CaO \cdot (RE)_2O_3 \cdot 24UO_3 \cdot 8CO_2 \cdot 4SiO_2 \cdot 60H_2O$. It has been described under the name of lepersonnite by Deliens and Piret (1982). Vaes may have performed his test on fibers of this species; leper-

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sonnite and studtite have indeed been found to be closely associated in the samples studied here.

### *Metastudtite*

Finally two samples were identified as being the compound $UO_4 \cdot 2H_2O$ of which this is the first occurrence as a natural phase. A description of this mineral under the name of metastudtite is given below.

## Occurrence and associations

Metastudtite has been found in two samples from Shinkolobwe (Shaba, Zaire) preserved in the mineralogical collection of the Musée royal de l'Afrique centrale. The first sample is a grey dolomitic rock, brecciated and deeply altered. The surface is almost completely covered with yellow and orange coatings in which the following minerals have been identified: grey fibers of rutherfordine; prismatic tablets of amber yellow becquerelite; red pseudohexagonal crystals of masuyite; red-orange short crystals of kasolite and red microcrystals of wölsendorfite. The latter crystals serve as support for two small radiated nodules of metastudtite. These nodules are pale yellow and have a diameter of about 1.2 mm. The second sample is a massive block of purple black uraninite. One face is covered with a thick yellow coating. It is mainly composed of needles of uranophane, which form rounded structures, and short crystals of soddyite. A few aggregates of flexible and silky fibers of metastudtite are mixed with uranophane (Fig. 1). The fibers are pale yellow and up to 3 mm in length. A few orange nodules of kasolite and powdered yellow uranopilite complete the association.

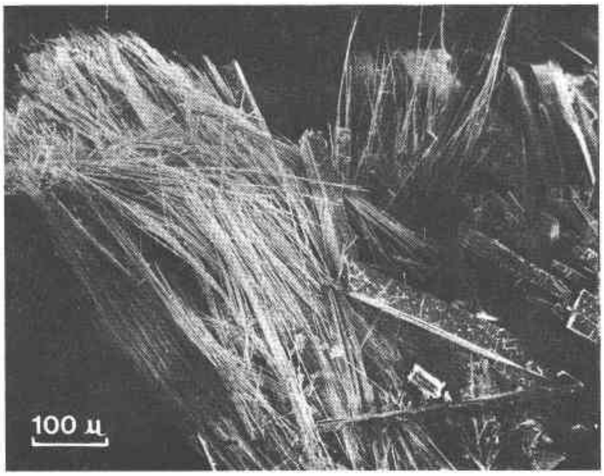

Fig. 1. Scanning electron photomicrograph of fibrous metastudtite (*left*) and tabular uranophane (*right*).

## Physical and optical properties

The small amount of metastudtite available and the minute diameter of individual fibers (~0.001 mm) do not permit the determination of some physical properties such as cleavage, hardness and density. The streak is yellowish and the luster silky.

Under the microscope, metastudtite appears as pale yellow fibers or elongated tablets. No pleochroism was observed. The mineral is biaxial positive with refractive indices $\gamma = 1.760 \pm 0.002$, $\beta = 1.658 \pm 0.002$ and $\alpha = 1.640 \pm 0.002$ ($2V$ calculated 47.7°). $Z = c$ (direction of elongation). According to Walenta (1974) the dihydrate has higher indices of refraction than studtite ($\gamma = 1.680$ and $\alpha = 1.537$). He provides only $\alpha = 1.758$ for metastudtite. This agrees closely with the value for $\gamma$ determined in this study. The mineral does not fluoresce under short or long wave ultraviolet light.

## Chemical composition

An electron microprobe analysis was performed in the Centre d'Analyse par Microsonde des Sciences de la Terre (CAMST) (Laboratory of Petrography of the University of Louvain, Belgium, analyst: J. Wautier). Low potential was used in order to avoid the destruction of the needles. Usual corrections were applied by the mean of a ZAF program. Using metallic uranium as the standard, the mean of 3 analyses gave $UO_3$ 83.4% or $UO_4$ 88.1%. TGA analysis on a 0.5 mg sample gave ~10% water. This value is regarded as approximate because of the small sample size. The ideal formula $UO_4 \cdot 2H_2O$ requires $UO_4$ 89.3% and $H_2O$ 10.7%.

Metastudtite is soluble without effervescence in hot HCl.

## X-ray data

The X-ray powder data (Table 1) show the identity between metastudtite and the synthetic compound $UO_4 \cdot 2H_2O$ (Debets, 1963 and Walenta, 1974). Two additional lines at 7.25 and 3.18Å correspond to the strongest lines of hydrated uranium–lead oxides such as fourmarierite. This latter compound occupies the fiber core of some fibers of metastudtite where it appears as a reddish thread.

A similar association has been observed in some studtites. Yellow studtite fibers with reddish fiber core have been heated to 100°C for 2 hours. The X-ray powder pattern of heated material shows the

Table 1. X-ray powder patterns for natural metastudtite, synthetic $UO_4 \cdot 2H_2O$ and heated studtite

| | | Metastudtite Shinkolobwe | | Synthetic $UO_4 \cdot 2H_2O$ | | Heated natural studtite | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Present study | | Debets,1963 | | Walenta,1974 | | Present study | |
| hkl | $d_c$ | $d_o$ | I/Io | $d_o$ | I/Io | $d_o$ | I/Io | $d_o$ | I/Io |
| | | 7.25† | 50b | | | | | 6.27†† | 30 |
| 110 | 5.23 | 5.22 | 100 | 5.23 | 100 | 5.24 | 10 | 5.23 | 100 |
| 020 | 4.39 | 4.38 | 50 | 4.39 | 33 | 4.41 | 7 | 4.394 | 50 |
| | | | | | | | | 3.985†† | 20 |
| 011 | 3.796 | 3.79 | 50 | 3.80 | 33 | 3.80 | 7 | 3.798 | 40 |
| 101 | 3.535 | 3.538 | 80 | 3.53 | 34 | 3.54 | 8 | 3.534 | 70 |
| | | | | | | | | 3.378†† | 20 |
| 200 | 3.255 | 3.214<br>3.180† | 50b | 3.25 | 15 | 3.26 | 6 | 3.253 | 20 |
| | | | | | | | | 3.152††<br>3.075†† | 30<br>20 |
| 121 | 2.753 | 2.756 | 30 | 2.75 | 21 | 2.75 | 5 | 2.753 | 30 |
| 130 | 2.669 | 2.669 | 20 | 2.667 | 21 | 2.67 | 5 | 2.667 | 30 |
| 220 | 2.615 | | | 2.611 | 9 | 2.61 | 3 | 2.616 | 5 |
| | | | | | | | | 2.572††<br>2.536†† | 5<br>5 |
| 211 | 2.471 | 2.467 | 20 | 2.469 | 19 | 2.47 | 5 | 2.468 | 25 |
| 031 | 2.403 | 2.398 | 20 | 2.402 | 15 | 2.40 | 4 | 2.406 | 20 |
| 040 | 2.195 | 2.191 | 5 | 2.193 | 5 | 2.19 | 2 | 2.199 | 5 |
| 310<br>002 | 2.107<br>2.105 | 2.103 | 15 | 2.105 | 12 | 2.10 | 5 | 2.102 | 20 |
| 112 | 1.953 | 1.950 | 15 | 1.953 | 13 | 1.955 | 4 | 1.954 | 20 |
| 231 | 1.933 | 1.928 | 15 | 1.932 | 13 | 1.927 | 5 | 1.931 | 20 |
| 301 | 1.929 | | | 1.926 | 8 | | | | |
| 022 | 1.898 | | | 1.898 | 5 | | | | |
| 141 | 1.865 | 1.859 | 10 | 1.863 | 13 | 1.862 | 3 | 1.860 | 5b |
| 240 | 1.820 | 1.815 | 3 | 1.818 | 4 | 1.819 | 1 | 1.807 | 3 |
| 202 | 1.768 | 1.767 | 10 | 1.767 | 6 | 1.768 | 4 | 1.771 | 15 |
| | | | | + 24 lines | | + 24 lines | | + 6 lines | |

*Pattern obtained in 114.6 mm diameter camera using Cu Kα nickel-filtered X-radiation. Intensities estimated visually (Present study)*
*b = broad line*
*† = line of hydrated U-Pb oxide such as fourmarierite*
*†† = line of curite.*

association of the major metastudtite with curite, a hydrated uranium-lead oxide (lines at 6.27, 3.985, 3.378, 3.152 and 3.075Å particularly).

The refinement of the cell constants using our powder data does not differ significantly from the values given by Walenta (1974). Therefore these latter values have been adopted here: $a$ = 6.51(1), $b$ = 8.78(2), $c$ = 4.21(1)Å, Z = 2, calculated density = 4.67 mg/cm$^3$ Orthorhombic, probable space group *Immm* (Debets, 1963). Single crystal studies gave only the values of the $c$ axis: 4.2±0.1Å.

## Nomenclature and conservation

The name metastudtite was chosen for the new mineral because it is a dehydration product of studtite. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA.

The type specimen of metastudtite is preserved in the mineralogical collection of the Musée royal de l'Afrique centrale (Tervuren, Belgium) under the number RGM 13748. There exists a cotype RGM 13755 in the same collection.

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