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Note

# THERMAL, X-RAY AND INFRARED ABSORPTION SPECTRUM ANALYSES OF A NEW URANYL SULPHATE MINERAL

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The phases of the system $UO_3 \cdot mSO_3 \cdot nH_2O$, which have already been observed, are uranopilite, $6UO_3 \cdot SO_3 \cdot 17H_2O$, and insufficiently described betauranopilite, $6UO_3 \cdot SO_3 \cdot 10H_2O$ [1]. In this paper, a uranyl sulphate mineral was studied, the composition and properties of which differ from uranopilite and betauranopilite indicating that it is probably a new mineral in the system $UO_3$–$SO_3$–$H_2O$. This paper is part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague.

## EXPERIMENTAL

A new mineral phase having the composition $6UO_3 \cdot 0.6SO_3 \cdot 15H_2O$ (M172-NMP inv. No. 68905) and, for comparison, uranopilite specimens (M136B-NMP inv. No. 43866, $6UO_3 \cdot SO_3 \cdot 18H_2O$ and M200, private collection of Z. Mrázek, $6UO_3 \cdot SO_3 \cdot 17H_2O$) were studied. All specimens were found at Jáchymov, Czechoslovakia. Thermal analysis was carried out by use of (a) a Stanton-Redcroft (TG 750) thermobalance (TG): 10°C $min^{-1}$, dynamic air atmosphere, 10 ml $min^{-1}$, (b) a Mettler TA 1 (DTA): 6°C $min^{-1}$, static air atmosphere, reference sample $Al_2O_3$, and (c) micro-DTA by Blažek: 9°C $min^{-1}$, static air atmosphere, reference sample $Al_2O_3$. X-ray diffraction data were obtained using a Rigaku Denki powder diffractometer, with Cu$K\alpha$ radiation and Ni filter, and were indexed using a self-indexing program [2]. Infrared spectra were measured with a Perkin-Elmer spectrophotometer (Model 225: Nujol, KBr micropellets; and Model 325: KBr disks).

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## RESULTS AND DISCUSSION

The symmetry of the uranyl sulphate mineral was calculated to be orthorhombic with lattice parameters $a = 15.065(7)$, $b = 15.704(8)$ and $c = 14.189(8)$ Å, while that of uranopilite was monoclinic with $a = 14.03(3)$, $b = 9.18(1)$, $c = 14.61(2)$ Å, and $\beta = 96.9(2)°$ [3]. The powder diffraction data of the new phase are close to those of minerals from the becquerelite group. The TG curves of the minerals studied are given in Fig. 1, and their DTA curves in Fig. 2. It follows from the TG and DTA curves that all the minerals studied dehydrate in several steps with partial overlapping of dehydroxylation and dehydration (endotherms M172: 140°C and an indication of an endotherm at 200°C; M200: 118, 144, 176°C; M136B: 85, 130, 155°C). Anhydrous phases, all of them X-ray amorphous, are formed in the range 500–600°C. They decompose in the range 600–900°C (endotherms M172: 705°C; M200: 714°C). Crystallization of new phases, $\alpha$-$UO_3$ and $\alpha$-$UO_2SO_4$ was inferred from the exotherms at 623, 653 and 658°C on the DTA curve of M200 [3]. The decomposition of anhydrous M172 runs in one step only ($SO_3$ and $O_2$ loose simultaneously), while a small, essentially separated mass decrease (ca. 0.4 mass%) appears on the TG curves of M200 and M136B in the range 600–660°C, which can be explained as a transformation of $\alpha$-$UO_3$ to $UO_{2.89}$. The remaining oxygen of both samples is released simultaneously with $SO_3$. The thermal decompositions are com-

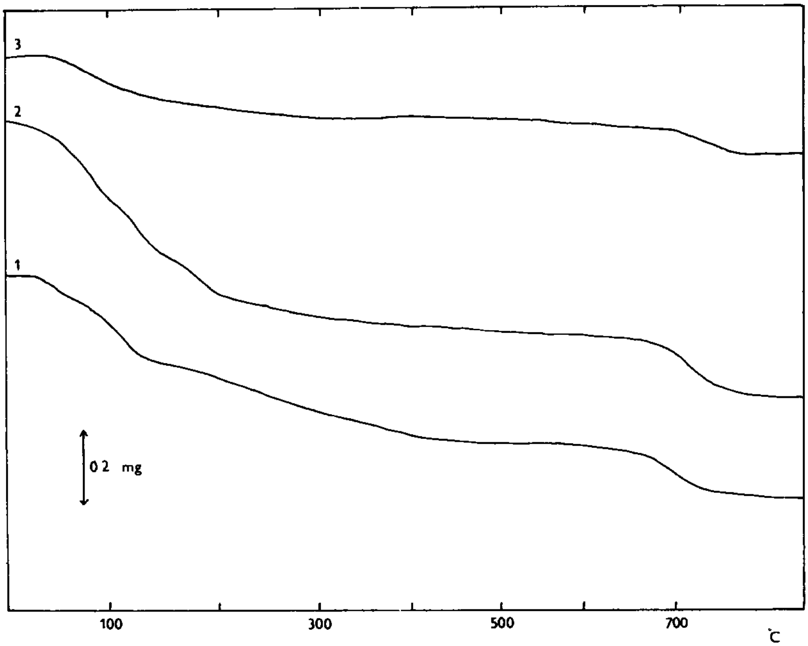

Fig. 1. TG curves of M172 (3.829 mg) (1), M136B (3.796 mg) (2) and M200 (1.351 mg) (3).

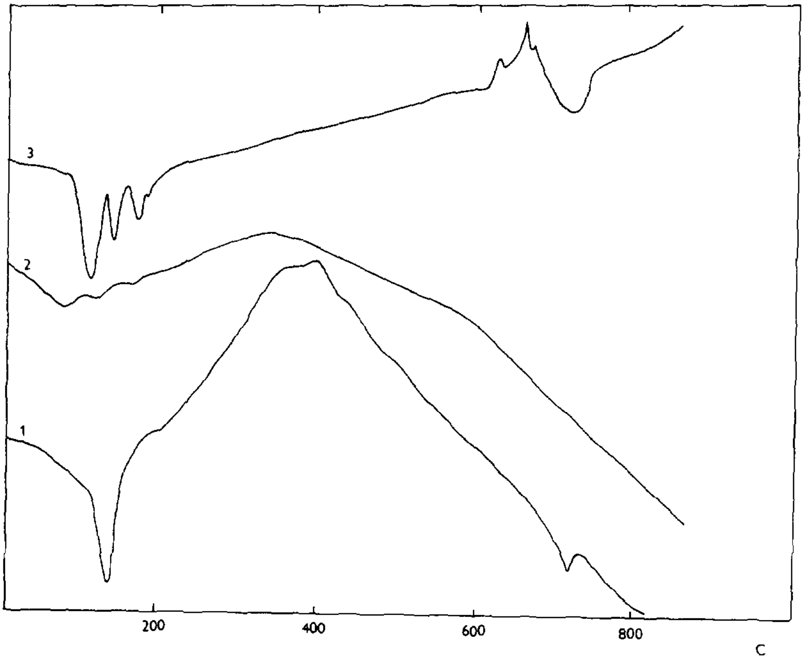

Fig. 2. DTA curves of M172 (7.06 mg) (1), M136B (3.86 mg) (2) and M200 (20 mg) (3).

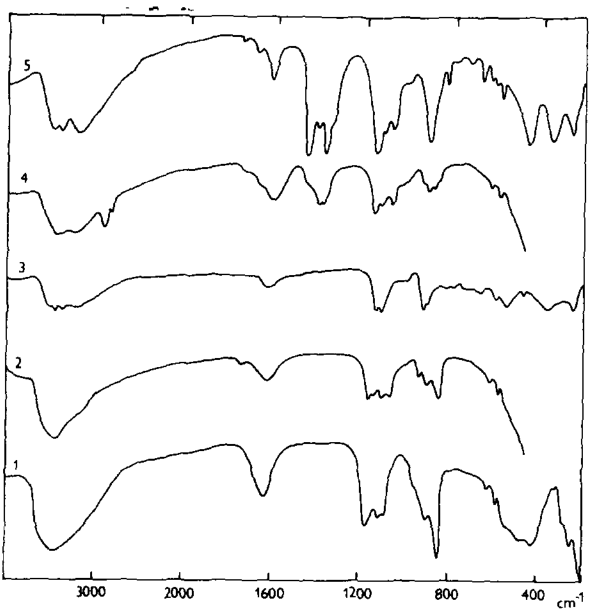

Fig. 3. IR spectra of M172 ((1) Nujol, (2) KBr), M136B ((3) Nujol, (4) KBr) and M200 ((5) KBr).

pleted at 884 (M172 and M136B) and 858°C (M200) with the formation of $U_3O_8$.

KBr micropellet preparation (pressure, temperature) influenced the character of the IR spectrum of M172, as was observed in the case of other natural uranyl sulphates. The IR spectra of the specimens studied are given in Fig. 3. In the IR spectra of M172 in Nujol, sharp absorption bands at 668 and 853 $cm^{-1}$ entirely disappear with KBr micropellets, an absorption band $\delta H_2O$ 1619 $cm^{-1}$ splits, simultaneously, an absorption band at about 1590 $cm^{-1}$ appears, and a shoulder on the absorption band $\nu_3 UO_2^{2+}$ at about 935 $cm^{-1}$ can be observed. The arrangement of OH absorption bands is also changed. It can be inferred from the comparison of the IR spectra of M172 and of M200 and M136B that the character of $SO_4^{2-}$ absorption bands of M172 is different, and is rather similar to the IR spectra of some zippeites in these ranges. The frequency of the $\nu_3 UO_2^{2+}$ band in the Nujol spectrum is lower, and the most intense absorption band of uranopilite at 935–945 $cm^{-1}$ does not appear with micropellets. The $\nu_3$ and $\nu_4 SO_4^{2-}$ splittings are nearly the same, while they change substantially in uranopilite on passing from Nujol to micropellets, the $\nu_3 SO_4^{2-}$ splitting increases and $\nu_4 SO_4^{2-}$ frequencies are higher. The IR spectra of all three phases in micropellets are very similar in this range. M172 possesses an additional weak, but sharp absorption band at 1681 $cm^{-1}$ in the range of $\delta H_2O$.

The uranyl sulphate mineral studied has a composition and properties different from uranopilite and betauranopilite. It is characterized by a layer structure close to the crystal structure of becquerelite-type minerals. The $SO_4^{2-}$ groups are present in uranyl layers together with $OH^-$ which may also join the layers. Water molecules in the interlayer space contribute to the linking of layers by the formation of hydrogen bonds. It is probable that the composition of this mineral phase may vary in a greater range and can be generally expressed as: $(UO_2)_6 \cdot (SO_4)_{1-x} \cdot (OH)_{10+2x} \cdot (10-x)H_2O$.

## REFERENCES

1 C. Frondel, U.S. Geol. Surv. Bull., 1064 (1958) 400 pp.

2 B Hájek and J. Ondráček, Silikaty, 27 (1983) 115.

3 J. Čejka, Z. Mrázek and Z. Urbanec, in L. Káčer (Ed.), 9th Czechoslovak Conference on Thermal Analysis, Bratislava, 1982, Slovak Chemical Society, pp. 87–88.