An XRD, SEM and TG study of a uranopilite from Australia

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ABSTRACT

A uranopilite from The South Alligator River, Northern Territory, Australia, has been studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) with EDAX attachment, and thermogravimetry in conjunction with evolved gas mass spectrometry. The XRD shows that the mineral is a pure uranopilite with few if any impurities. The SEM images show that the uranopilite consists of elongated crystals, up to 50 μm long and 5 μm wide. Thermogravimetry combined with mass spectrometry shows that dehydration occurs at ~31ºC resulting in the formation of metauranopilite. The first dehydration step over $20-71$ºC corresponds to a decrease of 5.4 wt.%, equivalent to 6.076 H_2O. The second dehydration step, over the temperature range $71-162.4$ºC corresponds to a decrease of 4.7 wt.%, equivalent to 5.288 H_2O, making a total of 11.364 moles of H_2O, close to 12 H_2O for uranopilite.

Dehydroxylation takes place over the temperature range $80-160$ºC. The loss of sulphate occurs at higher temperatures in two steps at 622 and 636ºC. A mass loss also occurs at 755ºC, accounted for by evolved oxygen.

Introduction

WITH the potential increased use of uranium as an energy source comes a host of environmental problems among which are the handling of waste products of the uranium mining industry, including many secondary minerals. What is not clearly understood is that many of these minerals are soluble to a significant extent and therefore may be transported in groundwaters. Among these secondary minerals of environmental importance are the sulphates including uranopilite.

Uranyl sulphate minerals are largely alteration, i.e. hydration-oxidation, products of uraninite. They are important where sulphides are being oxidized providing dissolved sulphate to groundwater that can complex with UO_2^{2+} ions to form relatively stable uranyl sulphate complexes in solution. Evaporation is necessary for precipita-tion of uranyl sulphates (Finch and Murakami, 1999). These hydration processes are strongly pH dependent and are therefore caused by hydrolysis. This leads to the formation of uranyl sulphates of the uranopilite-type minerals, when sufficient concentrations only of UO_2^{2+} and SO_4^{2-} are present. Alternatively, zippeite-type minerals can be formed in the systems, where low valence cations M^+ and/or M^{2+} are in sufficient concentra-tions. Uranyl sulphate minerals may therefore be classified as intermediates formed in regions rich in uraninite and sulphides (pyrite), the alteration of which leads to the origin of acid solutions containing sulphate anions (Meisser, 2003). Paragenetic sequences show that uranyl sulphate minerals easily alternate in other uranyl minerals having lower water solubility. Uranyl sulphates may also play a specific role in alteration and hydration-oxidation weathering of uranium dioxide, UO_2, and spent nuclear fuel. However, these problems remain unsolved and are not discussed here.

The chemistry of uranyl sulphate minerals has been studied for a long time (Larsen and Brown, 1917; Larsen and Berman, 1926; Peacock, 1935; Novácek, 1941; Traill, 1952; Ambartsumyan, 1957; Ambartsumyan *et al.*, 1961; Omori and Kerr, 1963; Anderson *et al.*, 1980) Of the mineral species approved by the International Mineralogical Association (IMA), XRD studies exist for deliensite (Vochten *et al.*, 1997), johannite (Frondel, 1958; Čejka *et al.*, 1988), rabejacite (Deliens and Piret, 1993; Sejkora *et al.*, 2000; Frost *et al.*, 2004*b*), uranopilite (Traill, 1952), jáchymovite (Čejka *et al.*, 1996), mare-cottite and some natural and synthetic zippeites (Frondel, 1952). Other minerals have been discovered in the uranyl sulphate group and their parameters elucidated (Donnay, 1955; Serezhkin, 1981; Čejka *et al.*, 1982; Mereiter, 1982; Vochten *et al.*, 1995; Halasyamani *et al.*, 1999; Burns, 2001; Brugger *et al.*, 2003; Burns *et al.*, 2003). Single-crystal structures of johannite (Mereiter, 1986), uranopilite (Burns *et al.*, 1997), marecottite and some natural or synthetic zippeites were determined. Novácek (1935, 1941) assumed that uranopilite, having the general formula $6UO_3.SO_3.xH_2O$ (x = 16 or 17), contains 16 or 17 H_2O. Frondel writes that the best formula for uranopilite is $(UO_2)_6(SO_4)(OH)_{10}.12 \; H_2O$ (Frondel, 1958; Frondel and Weeks, 1958). It is noted that in all these examples the U/S ratio is 6/1.

Novácek (1935, 1941) described a natural phase which he called β-uranopilite, $(UO_2)_6(SO_4)(OH)_{10}.5H_2O$, later named meta-uranopilite by Frondel (1952). Novácek (1935, 1941) assumed that this natural phase may be a product of partial dehydration of uranopilite. However, it was proved (Ondrus *et al.*, 1997*a,b*) that a phase corresponding to meta-uranopilite is not formed by dehydration of uranopilite. Uranopilite dehydration and dehydroxylation processes partly overlap and are related to the formation of X-ray amorphous phases. Partly dehydrated uranopilite, the composition of which corresponds to meta-uranopilite, is also X-ray amorphous. Thus, meta-uranopilite has continued as one of the insufficiently described uranyl minerals (Anthony *et al.*, 2003). Some new (not yet approved by the IMA or published) uranyl sulphate minerals have also been examined (Jensen *et al.*, 1997, 2000, 2002; Meisser *et al.*, 2000; Ondrus *et al.*, 2003).

Recently, Burns published a crystal structure for uranopilite and showed the formula to be $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6](H_2O)_8$ (Burns, 2001). The mineral is of space group P_1 and consists of six distinct U^{6+} cations forming part of a uranyl $(UO_2)^{2+}$ chain. Burns states that the uranyl ions are each coordinated by five ligands arranged at the equatorial vertices of pentagonal dipyramids and uranyl sulphate chains are linked to form the extended structure by hydrogen bonds bridging directly between the chains and to interstitial H_2O groups (Burns, 2001). It is therefore highly likely that as for other hydrated uranyl minerals the formula is a function of the moles of water which in turn is determined by the vapour pressure above the mineral. The mineral is monoclinic with an undetermined point group. The mineral consists of needles or laths elongated along [001] and flattened on the [010] direction (as may be observed in the SEM figures below). The mineral is very common and is found in many parts of the world. Thermal studies of uranium minerals including the uranyl sulphate minerals have been undertaken for some considerable time (Ambartsumyan, 1957; Čejka *et al.*, 1976; Čejka and Urbanec, 1979*a,b*; Urbanec and Čejka, 1980; Urbanec *et al.*, 1985). Čejka *et al.* (1996) reported exotherms for uranopilite at 623, 653 and 668ºC which corresponded to the crystallization of the new phases UO_3 and UO_2SO_4. Those authors also reported that both jachymovite and uranopilite dehydrate and dehydroxylate over several steps. Uranopilite lost seven moles of water in the 20−66ºC temperature range and 10.5 moles between 66 and 517ºC. These studies reported that the dehydration and dehydroxylation steps overlapped and that amorphous phases were formed. In this work we report the electron microscopy and thermal stability of a natural uranopilite from Australia.

Experimental

Minerals

The uranopilite sample was obtained from Museum Victoria. The sample originated from The South Alligator River, Northern Territory, Australia (Threadgold, 1960).

X-ray diffraction

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-ray diffractometer, operating in step-scan mode, with Cu-*K*α radiation (1.54052 Å). Patterns were collected in the range 3−90º2θ with a step size of 0.02º2θ and a

rate of 30 s per step. Samples were prepared as a finely pressed powder into aluminium sample holders.

SEM

The uranopilite samples were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope. For X-ray micro-analysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25 kV accelerating voltage. Preliminary analyses of the uranopilite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. Standards used for the EDX analytical system included albite, olivine, diopside, sanidine, anhydrite, marcasite and uranium oxide (this is for the elements Na, Mg, Si, K, Ca, Fe and U, respectively). The uranopilite was analysed from six different spots on the mineral surface and an average value obtained.

Thermal analysis

Thermal decompositions of ~1.7 mg of the uranopilite were carried out in a TA® Instrument incorporating a high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). The sample was heated in an open platinum crucible at a rate of 2.0°C/min up to 1000°C. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The following gases were analysed according to their mass/charge ratios Cl, Cl_2, CO, CO_2, SO_2, SO_3 and H_2O.

Band-component analysis of the differential thermogravimetry (DTG) curves was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz

ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 >0.995.

Results and discussion

X-ray diffraction

The XRD patterns of the uranopilite from the South Alligator River, Northern Territory, Australia, together with the reference XRD pattern are shown in Fig. 1. The mineral corresponds precisely with the reference pattern and no impurities or other phases were observed. The XRD patterns of the products of the thermal analysis show that the end-product of uranopilite is compositionally and structurally $UO_{2.67}$, i.e. (U_3O_8).

It should be noted that partly dehydrated uranopilite, compositionally related to Novácek's β-uranopilite, however, is X-ray amorphous. This conclusion was made by Ondrus et al. (1997a,b) and Čejka et al. (1996). Meisser (2003) asserted that "chimiquement, l'uranopilite exposee à l'air sec se deshydrate facilement en se transformant en 'metauranopi-lite' sans modification du diagramme de poudre de diffraction-X. Nous avons pu tester ce phenomene de maniere spectaculaire...." ("chemi-cally, uranopilite exposed to dry air easily dehydrates and transforms in 'metauranopilite' without any modification of the X-ray powder pattern. We could test this spectacular phenom-enon..."). No mass changes were given for the uranopilite sample studied by Meisser. (Novácek's β(meta)-uranopilite was insufficiently described and the sample studied by him is not available. It was not found in the collections either of the National Museum or of the Faculty of Natural Sciences, Charles University.)

SEM analysis and in situ chemical analysis

Scanning electron microscopy images of the uranopilite are shown in Fig. 2a,b. The numbers indicate where the EDAX analyses were under-taken. The uranopilite crystals are up to 50 μm long and ~1 μm wide. The atomic analysis of uranopilite based on the formula $(UO_2)_6(SO_4)(OH)_{10}\cdot12H_2O$ would give U as 13.3%, S as 2.2% and O as 84.4%. The average of six analyses for the uranopilite gave U as 17.35, S as 1.65 and O as 80.0. The reduction in the S content from 2.2% (uranopilite) to 1.65% (the mineral phase studied), i.e. U/S/O molar ratio from
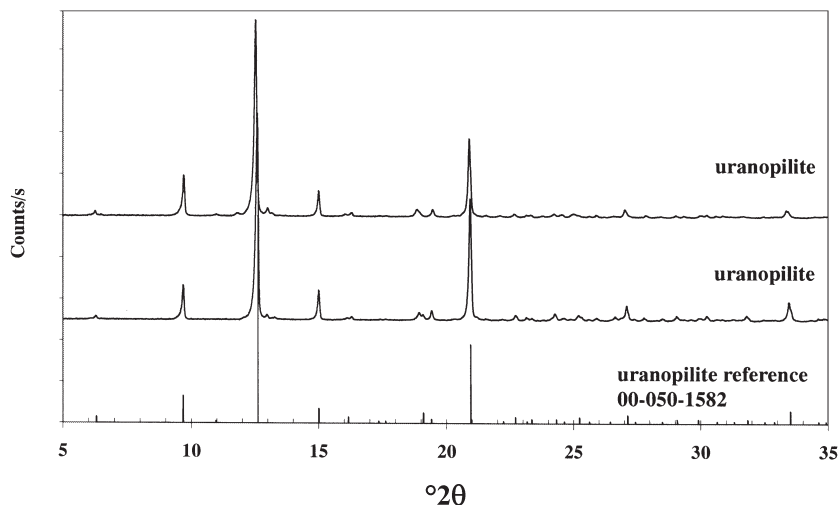
FIG. 1. XRD patterns for uranopilite and the standard mineral

6:0.992 (~1):38.08 to 6:0.57:27.67 proves that some molecular water escaped during the preparation of the mineral sample for EDAX analysis, but any loss of sulphate ion cannot be inferred from these data.

If we use the following formula for uranopilite $(UO_2)_6(SO_4)(OH)_{10}.12 \ H_2O$ (corresponding to Frondel's formula and, in summary, to Burns's formula for uranopilite) we obtain a ratio of U/S/O (%) = 13.3:2.2:84.4, which in terms of six moles of uranium equals 6:0.992:38.08. The U content is 4% greater than expected, as calculated from Burn's formula, and the S and O contents are 0.55 and 4.4% less, respectively. For the uranopilite studied in this work, the ratio of U/S/O (%) = 17.35:1.65:80.0 which in terms of six moles of U is = 6:0.57:27.67. The difference between the Burns/Frondel formula and that calculated here, may be due to the intensity of the electron beam, 25 kV in our case. Uranyl minerals often show a less than desirable stability in the electron beam. There is an alternative explanation: the mineral phase studied does not correspond to uranopilite, but is one of the phases
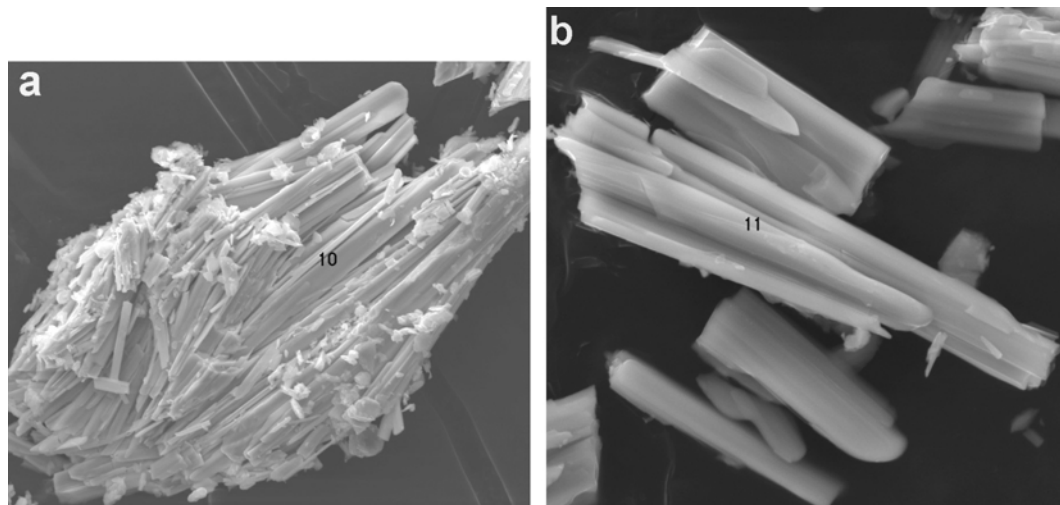

FIG. 2(*a,b*). SEM images of uranopilite from the South Alligator River, Northern Territory, Australia. (The positions of the numbers indicate where the EDAX analyses were undertaken.)

between uranopilite and schoepite as mentioned (e.g. by Jensen, 1998; Meisser *et al.*, 2000; Jensen *et al.*, 2002). However XRD clearly shows the mineral to be uranopilite with no other phases present, so the former explanation is preferred.

The composition of the end-product of thermal decomposition of uranopilite, $[(UO_2)_6(SO_4)O_2 (OH)_6(H_2O)_6](H_2O)_8$, is close to $6UO_{2.67}$. This should correspond to the observed value 83.1 wt.% (theoretical molecular weight 1684.48 m.u.). With these measured data, it is possible to recalculate and infer the real molecular weight for the uranopilite sample studied. This is 2027.0565 m.u. The difference between this value and the theoretical value is $2102.478 - 2027.0565 = 75.4215$ m.u. This may correspond to 4.19 H_2O. The water content in the studied uranopilite sample is therefore lower than that expected from the theoretical point of view. This discrepancy may be attributed to the mineral being unstable under the vacuum in the SEM and EDX instrumentation. The vacuum may possibly result in the partial dehydration of loosely bound water molecules. Therefore the results from SEM may be different from that observed by XRD.

Thermal analysis

The TG analysis together with the DTG curves are shown in Fig. 3. The DTG curves are noisy but this is because only 1.7 mg of sample were used in the experiment. The reason for this minimal amount of sample is for reasons of health and safety. The smaller amounts mean less exposure to radiation. The experiment also represents a test to see how small an amount of sample could be used whilst still obtaining meaningful results. The evolved gas ion current curves are shown in Fig. 4.

A maximum in the DTG curve occurs at 31ºC, showing that dehydration of the uranopilite occurs at low temperatures. Indeed it is probable that the mineral converts to metauranopilite at this temperature. The first dehydration step, at 20−71ºC, corresponds to the decrease of 5.4 wt.%, i.e. 109.461 m.u. = 6.076 H_2O. The second dehydration step at 71−162.4ºC corresponds to a decrease of 4.7 wt.%, i.e. 95.272 m.u. = 5.288 H_2O, i.e. (6.076 + 5.288) = 11.364 H_2O, which is the total number of moles of water in the formula of uranopilite and approximates the 12 H_2O moles for uranopilite as proposed by Frondel (1952) and later by Čejka *et al.* (1996). However, the single-crystal structure analysis of uranopilite from Jáchymov (Czech Republic) leads to the conclusion that uranopilite contains 14 water molecules and 6 hydroxyls (Burns, 2001). However, our results show that the formula of uranopilite should be written as $(UO_2)_6(SO_4)(OH)_{10}\cdot12H_2O$. It is possible that some partial dehydration of the mineral could occur; this might be expected in hot climates such as that in Queensland. The
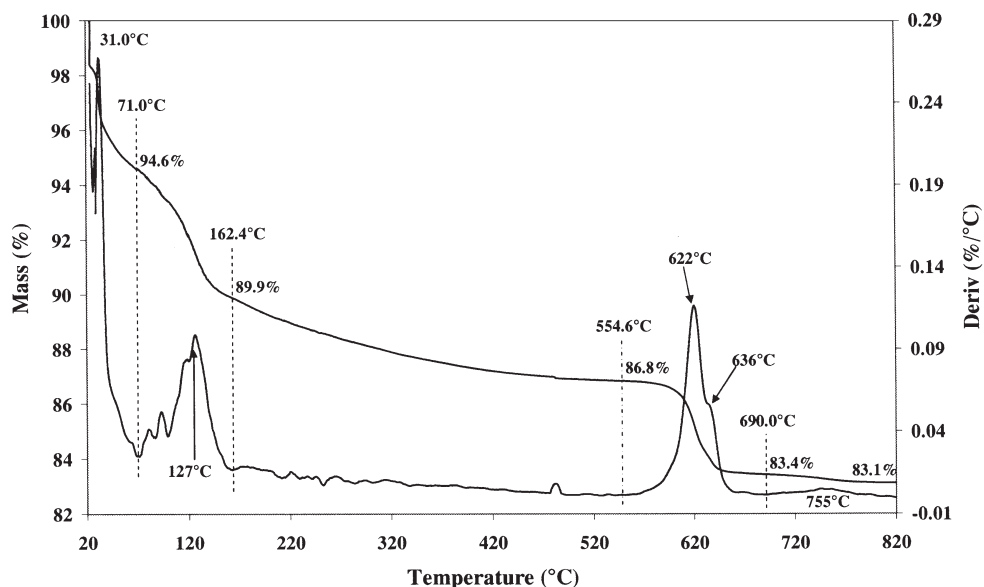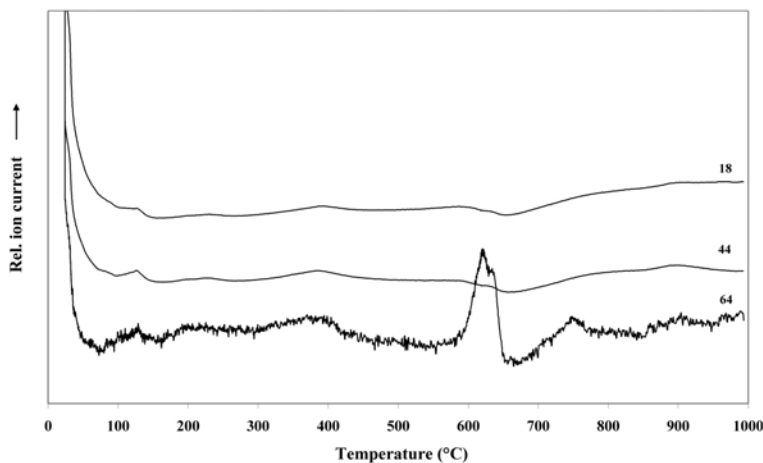

FIG. 3. TG and DTA analysis of uranopilite.

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FIG. 4. Ion current curves for the evolved gases from the thermal decomposition of uranopilite.

difference in the formula as proposed by Burns and Frondel and confirmed in this work may be a result of the water-vapour pressure.

The dehydroxylation step, at 162.4−554.6ºC, corresponds to the decrease of 3.1 wt.%, i.e. 62.839 m.u. = 3.5 H_2O or may be [54.045 m.u. = 3H_2O, and 8.794 m.u. = 0.275 O_2]. This should be attributed to the dehydroxylation and probably also partial decomposition of UO_3. The theoretical value for 3H_2O is 18.015 × 3 = 54.045 m.u. The fourth mass decrease, at 554.6−690ºC, 3.4 wt.% or 68.919 m.u., can be attributed to SO_3, 68.919:80.061 = 0.861 SO_3. At higher temperatures, SO_3 may decompose into SO_2 and O_2. The fifth mass decrease, at 690−820ºC, 0.3 wt.% or 6.08 m.u. = 0.19 O_2. Some overlapping of the steps is possible. A high-temperature mass loss occurs at 755ºC which is accounted for by the loss of oxygen. The sum of mass decrease (wt.%): 5.4 + 4.7 + 3.1 + 3.4 + 0.3 = 16.9 wt.%, may be compared with the theoretical mass decrease 18.46 wt.%. The sum of mass decrease for $[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$ $(H_2O)_8$ is 417.994 m.u. The observed difference is 75.42 m.u. It may be inferred that the water content in the studied uranopilite sample is lower and differs substantially from theoretical data for uranopilite as mentioned above.

Conclusions

The natural uranopilite from the uranium mines at the South Alligator River, Northern Territory, Australia, shows the classic powder XRD pattern for uranopilite. The mineral was analysed by SEM and comprised laths and needles elongated along the [001] axis and up to several mm long. Thermogravimetry in conjunction with evolved gas mass spectrometry has been used to study the thermal decomposition of natural uranopilite. In this case only ~1.7 mg of sample were used. Thermal decomposition takes place over three steps: (1) up to 71ºC where water is lost; (2) from 70 to 175ºC for dehydroxylation; and (3) from 500 up to 690ºC for the loss of sulphate.

The molecular water content in the uranopilite sample studied is less than that expected for fully hydrated uranopilite. This may be caused by spontaneous partial dehydration of uranopilite at room temperature and low relative humidity as observed, e.g. in the case of schoepite, $[(UO_2)_8O_2(OH)_{12}].12H_2O$, and its partial dehydration to metaschoepite (Finch *et al.*, 1996; Miller *et al.*, 1996). However, the chemistry of this part-dehydrated (spontaneously) uranopilite to its lower hydrate could not be proved because of the very small amount of sample available for the study. A structural relationship of uranopilite with its partially-dehydrated intermediate could not be established. The results of this work could not clearly elucidate the true water content of the uranopilite. Indications are that the water content as given by the Burns formula is correct. From the TG curve of uranopilite it may be inferred that uranopilite contains structurally non-equivalent water molecules. This supports conclusions from X-ray single-crystal structure analysis, and from infrared and Raman spectroscopy (Frost *et al.*, 2004*a*). The thermal decomposition of uranopilite proceeds in a set of partly overlapping steps,

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dehydration, dehydroxylation, and decomposition of anhydrous intermediates. The formation of an amorphous intermediate during dehydration of uranopilite is assumed. Decomposition of SO_3 released from the anhydrous intermediate to SO_2 + 1/2 O_2 may be expected. The endproduct of uranopilite is compositionally and structurally $UO_{2.67}$, i.e. (U_3O_8).

Acknowledgements

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