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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, scanning electron microscopy with EDAX attachment and thermogravimetry in conjunction with evolved gas mass spectrometry. X-ray diffraction shows the mineral is a pure uranopilite with little or no impurities. SEM images show the uranopilite to consist of long elongated crystals up to 50 μm in length and 5 μm in width. Thermogravimetry combined with mass spectrometry shows that dehydration occurs around 31 °C resulting in the formation of metauranopilite. The first dehydration step over 20 - 71 °C corresponds to the decrease of 5.4 wt %, equivalent to 6.076 H_2O. The second dehydration step over 71-162.4 °C 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 to 160 °C. The loss of sulphate occurs at higher temperatures in two steps at 622 and 636 °C. A mass loss also occurs at 755 °C accounted for by evolved oxygen.

Keywords: Keywords: uranopilite, johannite, zippeite, uranyl sulphate minerals, thermal analysis, dehydroxylation, dehydration, mass spectrometry

Introduction

With the potential increased use of uranium as an energy source comes a host of environmental problems. Among these problems 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 show significant solubility and therefore may be transported in ground waters. Among these secondary minerals of environmental importance are the sulphates including uranopilite.

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Uranyl sulphate minerals are in the main recent 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 precipitation 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 the zippeite-type minerals can be formed in the systems, where low valence cations M^+ and/or M^{2+} are in sufficient concentrations. 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 alterate 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 not discussed.

The chemistry of uranyl sulphate minerals has been undertaken over an extended period of time.(Larsen and Brown, 1917; Larsen and Berman, 1926; Peacock, 1935; Novacek, 1942a; Traill, 1952; Ambartsumyan, 1957; Ambartsumyan and et al., 1961; Omori and Kerr, 1963; Anderson *et al.*, 1980) Of the approved mineral species X-ray diffraction and other crystallochemical studies exist for deliensite (Vochten *et al.*, 1997), johannite (Frondel, 1958; Cejka *et al.*, 1988), rabejacite (Deliens and Piret, 1993; Sejkora *et al.*, 2000; Frost *et al.*, 2004b), uranopilite (Traill, 1952), jáchymovite (Cejka *et al.*, 1996), marecottite (Brugger et al. 2003) and some natural and synthetic zippeites (Vochten *et al.* 1995; Ondrus *et al.* 1997a, 1997b; Brugger *et al.* 2003; Burns *et al.* 2003). Single crystal structures of johannite (Mereiter, 1986), uranopilite (Burns 2001), marecottite (Brugger *et al.* 2003) and some natural or synthetic zippeites (Vochten *et al.* 1995; Burns *et al.* 2003) were determined. Nováček (Novácek, 1935; Novacek, 1942b) assumes 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.

Nováček (Novácek, 1935; Novacek, 1942b) described a natural phase which he called β-uranopilite, $(UO_2)_6(SO_4)(OH)_{10}.5H_2O$, later named meta-uranopilite by Frondel (Frondel, 1952). Nováček (Novacek, 1935; Novacek, 1942b) assumed that this natural phase may be a product of partial dehydration of uranopilite. However, it was proved (Ondrus *et al.*, 1997a; Ondrus *et al.*, 1997b) that a phase corresponding to meta-uranopilite is not formed by dehydration of uranopilite. Uranopilite dehydration and dehydroxylation processes partly overlap and are connected with 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 remained as one of the insufficiently described uranyl minerals (Anthony *et al.*, 2003). Some new not yet approved and published uranyl sulphate minerals have been also mentioned (Jensen *et al.*, 1997; Jensen *et al.*, 2000; Meisser *et al.*, 2000; Jensen *et al.*, 2002;). These natural phases may be compositionally related to the UO_3-SO_3-H_2O system.

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 $(UO_2)^{2+}$ chains. 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 a 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; Cejka *et al.*, 1976; Cejka and Urbanec, 1979a, b; Urbanec and Cejka, 1980; Urbanec *et al.*, 1985). Cejka reported exotherms for uranopilite at 623, 653 and 668 °C which corresponded to the crystallization of new phases UO_3 and UO_2SO_4 (Cejka *et al.*, 1996). Cejka et al. reported that both jachymovite and uranopilite dehydrate and dehydroxylate over several steps (Cejka *et al.*, 1996). Uranopilite lost 7 moles of water in the 20 to 66 °C temperature range and 10.5 moles between 66 and 517 °C. 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 mineral 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 to 90° 2θ with a step size of 0.02° and a rate of 30s per step. Samples were prepared as a finely pressed powder into aluminium sample holders.

SEM

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 (SEM). For X-ray microanalysis (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 25kV 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 carried out in a TA® Instruments incorporated 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 analyzed according to their mass/charge ratios Cl, Cl_2, CO, CO_2, SO_2, SO_3, and H_2O.

Band component analysis of the 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 done 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 greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 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 Figure 1. The mineral corresponds precisely with the reference pattern and no impurities or other phases could be observed. XRD of the products of the thermal analysis showed the endproduct 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 Novacek´s beta-uranopilite, however, is X-ray amorphous. This conclusion is made by Ondrus et al. (1997) and Cejka et al. (1996). Meisser (2003) assumes that "*chimiquement, l'uranopilite exposee a l'air sec se deshydrate facilement en se transformant en "metauranopilite" sans modification du diagramme de poudre de diffraction-X. Nous avons pu tester ce phenomene de maniere spectaculaire....*". No mass changes were given for the uranopilite sample studied by Meisser. (Novacek´s beta(meta)-uranopilite was insufficiently described and the sample studied by Novacek is not available. It was not found in the collections either of the National Museum or of the Faculty of Natural Sciences, Charles University [Jiri Cejka, private communication].)

SEM analysis and in-situ chemical analysis

The SEM images of the uranopilite are shown in Figures 2a and 2b. The numbers indicate where the EDAX analyses were undertaken. The uranopilite crystals are elongated up to 50 μm in length and about 1 micron in width. The atomic analysis of uranopilite based upon the formula $(UO_2)_6(SO_4)(OH)_{10}\cdot 12H_2O$ would give the 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 lowering of the S content from 2.2 % (uranopilite) to 1.65 % (the mineral phase studied), i. e. U/S/O molar ratio from 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 sulfate ion cannot be inferred from these data.

If we use the following formula for uranopilite of $(UO_2)_6(SO_4)(OH)_{10}.12\ H_2O$ (corresponding to Frondel's formula of uranopilite, in summary corresponding also with Burns's formula of 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% higher than expected as calculated from Burn's formula and the S and O contents are 0.55 and 4.4 % lower. For the uranopilite studied in this work the ratio U/S/O (%) = 17.35 : 1.65 : 80.0 which in terms of six mole of **U** is = 6 : 0.57 : 27.67. The difference between the Burns/Frondel formula and that calculated here, may be due to intensity of the electron beam of 25 kV. Uranyl minerals often show a less than desirable stability in the electron beam. An alternative explanation could be made: the mineral phase studied does not correspond to uranopilite, but is one of the phases between uranopilite and schoepite as mentioned e.g. by Jensen, Meisser and others (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 6 $UO_{2.67}$. This should correspond to the observed value 83.1 w.% (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 the SEM may be different from that observed by XRD.

Thermal analysis

The thermogravimetric analysis together with the DTG curves is shown in Figure 3. The DTG curves are noisy but this is because only 1.7 mg of sample was 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 that could be used and still obtain meaningful results. The evolved gas ion current curves are shown in Figure 4.

A maximum in the DTG curve occurs at 31 °C, 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 20 - 71 °C corresponds to the decrease of 5.4 w.%, i. e. 109.461 m.u. = 6.076 H_2O. The second dehydration step 71-162.4 °C corresponds to a decrease of 4.7 w.%, 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 and later by Cejka et al. (Frondel, 1952; Cejka *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 $(UO_2)_6(SO_4)(OH)_{10}\cdot 12H_2O$. It is possible that some partial dehydration of the mineral could occur as might be expected in hot climates as in Queensland. The 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, 162.4 - 554.6 °C, 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. = 3 H_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 3 H_2O is 18.015 x 3 = 54.045 m.u. The fourth mass decrease, 554.6-690 °C, 3.4 w.%, 68.919 m.u., which can be attributed to SO_3, 68.919: 80.061 = 0.861 SO_3. At higher temperatures SO_3 may decompose in SO_2 and O_2 The fifth mass decrease, 690-820 °C, 0.3 w.%, 6.08 m.u. = 0.19 O_2. Some overlapping of the steps may be possible. A high temperature mass loss occurs at 755 °C which is accounted for by the loss of oxygen. The sum of mass decrease (w.%): 5.4 + 4.7 + 3.1 + 3.4 + 0.3 = 16.9 w.%, may be compared with the theoretical mass decrease 18.46 w.%. 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 substantially differs from theoretical data for uranopilite as mentioned above.

Conclusions

The natural uranopilite from the uranium mines at the South Alligator River, Northern Territory, Australia showed the classic powder XRD pattern for uranopilite. The mineral was analysed by SEM and shown to be laths and needles elongated along the [001] axis and were up to several mm in length. 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 was used. Thermal decomposition takes place in three steps (a) up to 71 °C where water is lost (b) from 70 ° up to 175 °C for dehydroxylation and (c) from 500 °C up to 690 °C for the loss of sulphate.

Molecular water content in the uranopilite sample studied is lower that 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, $[(UO_2)_8O_2(OH)_{12}].12\ H_2O$ and its partial dehydration to metaschoepite (Finch *et al.*, 1996; Miller *et al.*, 1996). However, chemistry of this partly spontaneously dehydrated uranopilite to its lower hydrate could not be proved because of very low amounts of sample available for the study. Structural relation of uranopilite and its partial dehydration 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 nonequivalent water molecules. This supports conclusion from X-ray single crystal structure analysis, infrared and Raman spectroscopy (Frost *et al.*, 2004a). Thermal decomposition of uranopilite proceeds in a set of partly overlapping steps, dehydration, dehydroxylation, and decomposition of anhydrous intermediates. Formation of 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).

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References

Ambartsumyan, T.L. (1957) Thermal studies of some uranium minerals. *Atomnaya Energ., Voprosy Geol. Urana, Suppl.*, 86-125.

Ambartsumyan, T.L., and et al. (1961) *Termicheskie issledovaniya uranovykh i uransoderzhashchikh mineralov (thermal studies of the uranium-containing minerals).* 146 pp p.

Anderson, A., Chieh, C., Irish, D.E., and Tong, J.P.K. (1980) An x-ray crystallographic, raman, and infrared spectral study of crystalline potassium uranyl carbonate, k4uo2(co3)3. *Canadian Journal of Chemistry*, **58**, 1651-8.

Anthony, J.W., Bideaux, R.A., Bladh, K.W., and Nichols, M.C. (2003) Handbook of mineralogy vol.V. Borates, carbonates, sulfates. - mineral data publishing, tucson, arizona.

Burns, P.C. (2001) A new uranyl sulfate chain in the structure of uranopilite. *Canadian Mineralogist*, **39**, 1139-46.

Cejka, J., Sejkora, J., Mrazek, Z., Urbanec, Z., and Jarchovsky, T. (1996) Jachymovite, (uo2)8(so4)(oh)14. 13 h2o, a new uranyl mineral from jachymov, the krusne hory mts., czech republic, and its comparison with uranopilite. *Neues Jahrbuch fuer Mineralogie, Abhandlungen*, **170**, 155-70.

Cejka, J., Tobola, K., and Urbanec, Z. (1976) Thermal analysis of some uranium minerals and related synthetic compounds. *Proc. Eur. Symp. Therm. Anal., 1st*, 353-4.

Cejka, J., and Urbanec, Z. (1979a) Thermal analysis of natural uranium sulfates. *Zb. Celostatnej Konf. Term. Anal., 8th*, 177-80.

-. (1979b) Use of thermal analysis for determining uranium secondary minerals in collections at the national museum in prague. *Casopis Narodniho Muzea v Praze, Rada Prirodovedna*, **146**, 114-25.

Cejka, J., Urbanec, Z., Cejka, J., Jr., and Mrazek, Z. (1988) Contribution to the thermal analysis and crystal chemistry of johannite cu[(uo2)2(so4)2(oh)2].8h2o. *Neues Jahrbuch fuer Mineralogie, Abhandlungen*, **159**, 297-309.

Deliens, M., and Piret, P. (1993) Rabejacite, ca(uo2)4(so4)2(oh)6.6h2o, a new uranyl sulfate of calcium from the lodevois ore deposit, herault, france. *European Journal of Mineralogy*, **5**, 873-7.

Finch, R., and Murakami, T. (1999) Systematics and paragenesis of uranium minerals. *Reviews in Mineralogy*, **38**, 91-179.

Finch, R.J., Cooper, M.A., Hawthorne, F.C., and Ewing, R.C. (1996) The crystal structure of schoepite, [(uo2)8o2(oh)12](h2o)12. *Canadian Mineralogist*, **34**, 1071-88.

Frondel, C. (1952) Uranium minerals. X. Uranopilite. *American Mineralogist*, **37**, 950-9.

-. (1958) Systematic mineralogy of uranium and thorium. *U.S. Geological Survey Bulletin*, **No. 1064**, 400 pp.

Frondel, C., and Weeks, A.D. (1958) Recent progress in the descriptive mineralogy of uranium. *Proc. UN Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958*, **2**, 277-85.

Frost, R.L., Carmody, O., Erickson, K.L., Weier, M.L., Henry, D.O., and Cejka, J. (2004a) Molecular structure of the uranyl mineral uranopilite-a raman spectroscopic study. *Journal of Molecular Structure*, **733**, 203-10.

Frost, R.L., D. O, H., and Erickson, K. (2004b) Raman spectroscopic detection of wyartite in the presence of rabejacite. *Journal of Raman Spectroscopy*, **35**, 255-60.

Jensen, K.A. (1998) Petrography and chemistry of the uraninites and uraninite alteration phases from the uranium ore-deposit at bangomé. *Nuclear Scince and Technology*, **EUR 18314 EN**, 139-59.

Jensen, K.A., Ewing, R.C., and Gauthier-Lafaye, F. (1997) Uraninite: A 2 ga spent nuclear fuel from the natural fission reactor at bangombe in gabon, west africa. *Materials Research Society Symposium Proceedings*, **465**, 1209-18.

Jensen, K.A., Janeczek, J., Ewing, R.C., Stille, P., Gauthier-Lafaye, F., and Salah, S. (2000) Crandallites and coffinite: Retardation of nuclear reaction products at the bangombe natural fission reactor. *Materials Research Society Symposium Proceedings*, **608**, 525-32.

Jensen, K.A., Palenik, C.S., and Ewing, R.C. (2002) U6+ phases in the weathering zone of the bangombe u-deposit: Observed and predicted mineralogy. *Radiochimica Acta*, **90**, 761-9.

Larsen, E.S., and Berman, H. (1926) The identity of gilpinite and johannite. *American Mineralogist*, **11**, 1-5.

Larsen, E.S., and Brown, G.V. (1917) Gilpinite, a new uranium mineral from colorado. *American Mineralogist*, **2**, 75-9.

Meisser, N. (2003) Thesis. Faculty of sciences, lausanne university.

Meisser, N., Brugger, J., and Lahaye, Y. (2000) Mineralogy and acid-mine drainage of la creusaz uranium prospect, switzerland, in uranium deposits. *B. Kríbek & J. Zeman, eds.*, 147-50.

Mereiter, K. (1986) Neue kristallographische daten ueber das uranmineral andersonit. - anzeiger der oesterreichischen akademie der wissenschaften. *Mathematisch-Naturwissenschaftliche Klasse*, **3**, 39-41.

Miller, M.L., Finch, R.J., Burns, P.C., and Ewing, R.C. (1996) Description and classification of uranium oxide hydrate sheet anion topologies. *Journal of Materials Research*, **11**, 3048-56.

Novacek, R. (1935) Some secondary uranium minerals. *Vestnik Kral. Ceske Spol. Nauk*, **Cl. 2**, 36 pp.

-. (1942a) The chemical formula of uranopilite and .Beta.-uranopilite. *Vestnik Kral. Ceske Spol. Nauk*, 13 pp.

-. (1942b) The chemical formula of uranopilite and b-uranopilite. *Vestnik Kral. Ceske Spol. Nauk*, 13 pp.

Novácek, R. (1935) Study on some secondary uranium minerals. *V?stník Královské ?eské Spole?nosti Nauk, T?ída II*, 35.

Omori, K., and Kerr, P.F. (1963) Infrared studies of saline sulfate minerals. *Geological Society of America Bulletin*, **74**, 709-34.

Ondrus, P., Skala, R., Veselovsky, F., Sejkora, J., and Vitti, C. (2003) Cejkaite, the triclinic polymorph of na4(uo2)(co3)3 - a new mineral from jachymov, czech republic. *American Mineralogist*, **88**, 686-93.

Ondrus, P., Veselovsky, F., and Hlousek, J. (1997a) A review of mineral associations and paragenetic groups of secondary minerals of the jachymov (joachimsthal) ore district, czech republic. *Journal of the Czech Geological Society*, **42**, 109-14.

Ondrus, P., Veselovsky, F., Skala, R., Cisarova, I., Hlousek, J., Fryda, J., Vavrin, I., Cejka, J., and Gabasova, A. (1997b) New naturally occurring phases of secondary origin from jachymov (joachimsthal), czech republic. *Journal of the Czech Geological Society*, **42**, 77-108.

Peacock, M.A. (1935) Johannite from joachimsthal and colorado. *Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie*, **90**, 112-19.

Sejkora, J., Cejka, J., and Ondrus, P. (2000) New data of rabejacite (jachymov, the krusne hory mts., czech republic). *Neues Jahrbuch fuer Mineralogie, Monatshefte*, 289-301.

Threadgold, I.M. (1960) The mineral composition of some uranium ores from the south alligator river area, northern territory. *Australian, C.S.I.R.O., Mineragraphic Invest. Tech. Paper*, **No. 2**, 53 pp.

Traill, R.J. (1952) Synthesis and x-ray study of uranium sulfate minerals. *American Mineralogist*, **37**, 394-406.

Urbanec, Z., and Cejka, J. (1980) Thermal and infrared spectrum analyses of uranopilite. *Therm. Anal., [Proc. Int. Conf. Therm. Anal.], 6th*, **2**, 359-64.

Urbanec, Z., Mrazek, Z., and Cejka, J. (1985) Thermal, x-ray and infrared absorption spectrum analyses of a new uranyl sulfate mineral. *Thermochimica Acta*, **86**, 383-6.

Vochten, R., Blaton, N., and Peeters, O. (1997) Deliensite, fe(uo2)2(so4)2(oh)2.3h2o, a new ferrous uranyl sulfate hydroxyl hydrate from mas d'alary, lodeve, herault, france. Canadian Mineralogist, 35, 1021-5.