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CHARACTERIZATION OF PHOSPHATE-RICH METALODÈVITE FROM PŘÍBRAM, CZECH REPUBLIC

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Abstract

Phosphate-rich metalodèvite was found in the Jánská vein, in the Březové Hory deposit, Příbram ore district, Czech Republic. It occurs as coatings and centimeter-scale aggregates associated with metazeunerite in proximity to strongly altered uraninite in a vein of quartz and sphalerite. Powder X-ray-diffraction data for metalodèvite were indexed on the structure model reported for synthetic metakirchheimerite (space group $P\bar{1}$), in contrast to the tetragonal cell originally proposed for metalodèvite (space group $P4_2/m$). The refined unit-cell parameters are: *a* 7.193(5), *b* 9.771(8), *c* 13.24(1) Å, α 75.54(6), β 84.07(6), γ 81.68(6)° and *V* 889(1) Å^3. The results of electron-microprobe analyses show that metalodèvite from Březové Hory contains up to 40 mol.% of the phosphate component. Such extensive substitution has not been reported previously for metalodèvite and its related phases. The thermogravimetric curve of metalodèvite exhibits several dehydration steps in the range ~20–300°C, which can be assigned to the release of molecular water, with a total weight loss of 14.70 wt.%, corresponding to 8.43 H_2O *pfu*. The empirical formula of the metalodèvite studied is: $(Zn_{0.72}Fe_{0.10}Mg_{0.06}Al_{0.05})_{\Sigma 0.93}(UO_2)_{2.12}[(AsO_4)_{1.44}(PO_4)_{0.56}]_{\Sigma 2.00}•8.43H_2O$ (mean result of seven analyses, on the basis of As + P = 2 *apfu*). The observed content of H_2O is close to the ideal reported for the crystal structures of related octahydrates. Stretching and bending vibrations in the Raman and infrared spectra were tentatively assigned to the $(UO_2)^{2+}$, $(AsO_4)^{3-}$, $(PO_4)^{3-}$ and H_2O units.

Keywords: metalodèvite, uranyl arsenate, powder X-ray diffraction, electron-microprobe data, thermal analysis, infrared spectroscopy, Raman spectroscopy, hydrogen bonds, Příbram, Czech Republic.

Sommaire

Nous documentons la présence de métalodèvite phosphatée dans la veine de Jánská du gisement de Březové Hory, district de Příbram, en République Tchèque. Elle se présente sous forme de pellicule et en agrégats centimétriques en association avec la métazeunerite tout près de l'uraninite fortement altérée dans une veine de quartz et de sphalérite. Les données obtenues par diffraction X, méthode des poudres, ont été indexées selon le modèle structural de la métakirchheimerite synthétique (groupe spatial $P\bar{1}$) plutôt que la maille tétragonale originellement proposée (groupe spatial $P4_2/m$). Les paramètres réticulaires affinés sont: *a* 7.193(5), *b* 9.771(8), *c* 13.24(1) Å, α 75.54(6), β 84.07(6), γ 81.68(6)° et *V* 889(1) Å^3. Les résultats d'analyses effectuées avec une microsonde électronique montrent que la métalodèvite de Březové Hory contient jusqu'à 40% de la composante phosphatée. La possibilité d'un tel taux de substitution dans la métalodèvite et les phases connexes n'avait pas été signalée auparavant. La courbe thermogravimétrique fait preuve de plusieurs étapes de déshydratation dans l'intervalle ~20–300°C; elles seraient attribuables à la libération de molécules d'eau, la perte totale en poids étant de 14.70%, ce qui correspond à 8.43 H_2O par formule unitaire. La formule empirique de la métalodèvite ici étudiée est: $(Zn_{0.72}Fe_{0.10}Mg_{0.06}Al_{0.05})_{\Sigma 0.93}(UO_2)_{2.12}[(AsO_4)_{1.44}(PO_4)_{0.56}]_{\Sigma 2.00}•8.43H_2O$ (résultat moyen de sept analyses calculé sur une base de As + P = 2 *apfu*). La teneur observée en H_2O se

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rapproche de la valeur idéale décrite dans la structure d'octahydrates connexes. Les vibrations d'étirement et d'articulation des spectres de Raman et infrarouges ont été attribuées provisoirement dans le cas des groupes $(UO_2)^{2+}$, $(AsO_4)^{3-}$, $(PO_4)^{3-}$ et H_2O.

(Traduit par la Rédaction)

Mots-clés: métalodèvite, arsenate d'uranyle, diffraction X sur poudres, données de microsonde électronique, analyse thermique, spectroscopie infrarouge, spectroscopy Raman, liaisons hydrogène, Příbram, République Tchèque.

INTRODUCTION

Metalodèvite, a rare hydrated zinc uranyl arsenate, was found during research into the complex alteration-induced assemblages resulting from base-metal and uranium mineralization in the Jánská vein (Škácha *et al.* 2009). This is one of the less important veins at the famous base-metal deposit Březové Hory, near Příbram, central Bohemia, Czech Republic. Investigations have shown that this material exhibits rather extensive substitution of phosphate for arsenate and further interesting substitutions involving cations. The unusual composition and rarity of this mineral prompted us to examine it in detail, as reported below.

PREVIOUS STUDIES

Metalodèvite from Riviéral, Lodève, Hérault, in France, was first described by Agrinier *et al.* (1972). It is a rare mineral that has been reported to occur at only two other localities in the world: the Sterling mine, New Jersey, USA (Parker & Troy 1982) and Jáchymov (Joachimsthal), Czech Republic (Ondruš *et al.* 1997). The chemical formula given by Agrinier *et al.* (1972) is $Zn(UO_2)_2(AsO_4)_2 \bullet 8\text{–}12H_2O$, with unit-cell parameters *a* 7.16, *c* 17.20 Å, and *V* 881.8 Å^3 in the tetragonal system, space group $P4_2/m$. Anthony *et al.* (2000) and Back & Mandarino (2008) both listed metalodèvite as a decahydrate. Recently, new crystallographic data for some synthetic analogues of metalodèvite were reported by Locock *et al.* (2004). According to these results, there are three stable states of hydration for the hydrated uranyl arsenates and phosphates of divalent transition metals: the dodecahydrate, decahydrate and octahydrate. The symmetry of these phases depends on the hydration state: triclinic for 12 H_2O, monoclinic for 10 H_2O, and triclinic for 8 H_2O. The basal diffraction-maximum correlates with the hydration state of the phase: ~11 Å for the dodecahydrate, ~10 Å for the decahydrate, and ~8.5 Å for the octahydrate. Although Locock *et al.* (2004) were not able to synthesize the Zn-dominant species, one may hypothesize that metalodèvite (basal maximum ~8.6 Å) is of the same nature as the octahydrates studied by Locock *et al.* (2004) and should have triclinic symmetry. According to our investigations, the higher hydrates, the decahydrate and the dodecahydrate, the latter corresponding to "lodèvite" (which is not yet an approved mineral name), can change after pulverizing to a lower hydrated phase corresponding to "metalodèvite". Chernorukov *et al.* (2000) also studied synthetic analogues of this mineral group (including a Zn-containing phase) using powder X-ray diffraction, thermal analysis and infrared spectroscopy. The preparation and crystallographic characterization of Zn, Ni and Co uranyl arsenate octahydrates were described by Nabar & Iyer (1977). According to recent reviews on uranyl arsenates and phosphates (Locock 2007a, 2007b), metalodèvite is an octahydrate.

OCCURRENCE

We describe the presence of phosphate-rich metalodèvite at the Jánská vein, in the famous base-metal deposit Březové Hory, near Příbram, Czech Republic. The ore deposit is situated in Cambrian rocks of the Teplá–Barrandian zone of the Bohemian Massif. The vein has been intensively exploited for silver to depths of 450 m. The Jánská vein is noted for its uranium mineralization. Specimens of massive uraninite and "gummite", mostly amorphous Pb oxides and hydroxides of uranyl (Reuss 1863, Babánek 1872), have been found in this vein, along with cuprosklodowskite, metatorbernite, masuyite, wölsendorfite, anglesite (Ondruš & Hyršl 1989), kasolite (Škácha & Sejkora 2001), zinczippeite and other minerals of the zippeite group (Sejkora *et al.* 2003), compreignacite, uranopilite, uranophane (Plášil *et al.* 2005) and widenmannite (Plášil *et al.* 2010.).

Phosphate-rich metalodèvite forms accumulations of translucent to cloudy tabular crystals or crystalline aggregates up to 0.5 mm in length and 10 μm thick. These aggregates usually line cavities and fissures of the quartz–sphalerite gangue and surrounding rocks. Metalodèvite crystals are very brittle, yellow to dark yellow, locally pale yellow, and have a waxy luster. Most of crystals are multiply twinned and form rose-like aggregates (Fig. 1). Circular aggregates of bright yellow color that consist of hundreds of crystals are common; these aggregates cover up to several square centimeters in area. Metalodèvite does not exhibit fluorescence under either short-wave or long-wave ultraviolet radiation.

Metalodèvite occurs in association with metazeunerite near uraninite in a quartz–sphalerite gangue. Uraninite forms grains and aggregates up to 1 cm in diameter and has been strongly affected by supergene alteration. There are rich accumulations of As-bearing pyrite in the vicinity of the uraninite aggregates. The assemblage of supergene minerals includes metalodèvite, metazeunerite, beudantite, jarosite, and probably scorodite.

EXPERIMENT

Electron-microprobe analysis (EMPA) and thermal analysis

The metalodèvite samples were analyzed with a Cameca SX100 electron microprobe (Laboratory of Masaryk University and the Czech Geological Survey, Brno; operators R. Škoda and J. Sejkora). A crystal aggregate was mounted in an epoxy resin disc, polished, and the surface was coated with a carbon layer 250 Å thick. The wavelength-dispersion mode was used with an operating voltage of 15 kV, a current of a 4 nA, and a beam diameter of 10 μm. The following X-ray lines, crystals and standards were selected to minimize line overlap: $K\alpha$ lines: F [PC1, apatite-(CaF)], Mg (TAP, $MgAl_2O_4$), V (LLIF, vanadinite), P [LPET, apatite-(CaF)], Fe (LLIF, andradite), Zn (LLIF, ZnO), Al (TAP, sanidine), Si (TAP, sanidine), S (PET, barite), Ca (PET, andradite)], $L\alpha$ lines: Cu (TAP, dioptase), As (TAP, InAs), $L\beta$ lines: Ba (LPET, barite), $M\alpha$ lines: Pb (PET, vanadinite), $M\beta$ lines: Bi (LPET, Bi), U (LPET, U metal). Peak-counting times (CT) were 10–20 s for major elements, 40–60 s for minor to trace elements, and counting time on background was ½ CT. The measured intensities were converted to element concentrations using the PAP program (Pouchou & Pichoir 1985). Under the electron beam in vacuum, the samples are somewhat unstable. This, together with an imperfect surface of the samples, caused the experimentally determined oxide sums to be low (73.16–86.16 wt.%). The experimental sums do not correlate with the diameter of the electron beam. Table 1 lists the measured and recalculated analytical results, supplemented by the H_2O content derived from the thermogravimetric analysis.

Thermal analysis was performed on a Stanton Redcroft thermobalance TG 750 with a heating rate of 10°C/min, a dynamic air atmosphere, a flow rate of 10 mL/min and a sample weight of 0.741 mg.

Single-crystal and powder X-ray diffraction

A thin tabular fragment of metalodèvite was measured using an Oxford Diffraction XCalibur–2 single-crystal diffractometer equipped with a Sapphire–2 area detector, a graphite monochromator, and Mo$K\alpha$ radiation emitted from a fine-focus sealed tube.

A hand-picked sample was used for the powder X-ray-diffraction experiment. The continuous mode of the PANalytical X'Pert Pro powder diffractometer operating at 40 kV and 30 mA with an X'Celerator detector was used. A very small amount of powdered sample was mounted on a thin glass fiber on a goniometer head and scanned in Debye–Scherrer geometry. For the refinement of the unit-cell parameters, the powder X-ray-diffraction pattern was collected in the range 5–100°2θ Cu$K\alpha$ radiation (Ni filter, with integrated

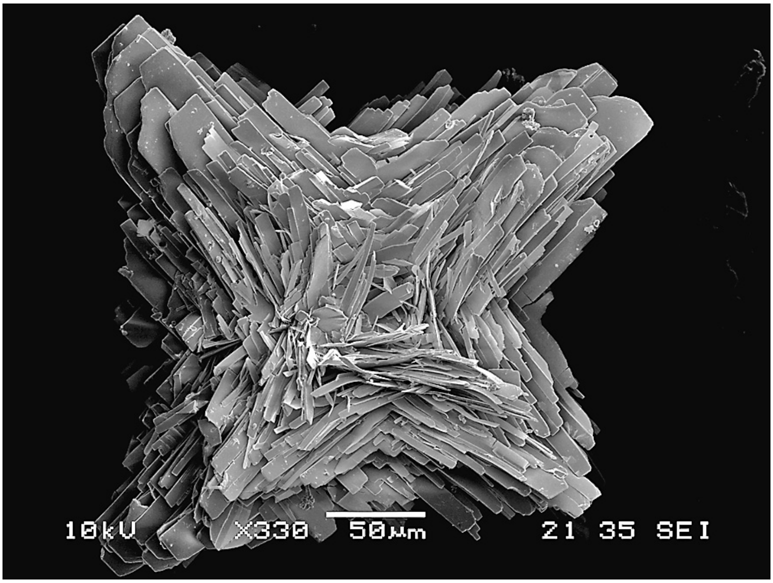

FIG. 1. Rose-like aggregates of metalodèvite from Příbram. Secondary electron image (JEOL JSM–6380).

step size 0.05°/2500 s, sample rotated at a frequency of one cycle per second). The position of each diffraction maximum was refined using a Pearson VII profile-shape function with XFIT software (Coelho & Cheary 1997), and these data were used for the refinement of the unit-cell parameters with the program CELREF (Laugier & Bochu 2002), based on the least-squares method.

The material that remained after thermal analysis was also investigated by powder X-ray diffraction. In this case, a Bragg–Brentano geometry was used with a PANalytical X'Pert Pro powder diffractometer operating at 40 kV and 30 mA with an X'Celerator detector and a secondary monochromator. The pattern was obtained with an integrated step-width of 0.02° and count time of 800 s over the range 4–70° 2θ Cu$K\alpha$. The sample was rotated at a frequency of one cycle per two seconds.

Infrared and Raman spectroscopy

The infrared spectrum of the sample, mixed with KBr powder, was recorded by the microdiffuse reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range 600–4000 cm^{-1}, resolution 4 cm^{-1}, 128 scans, Happ–Genzel apodization) equipped with a Spectra Tech InspectIR micro-FTIR accessory. The Raman spectrum of metalodèvite in the range 200–4000 cm^{-1} was collected with a Labram HR dispersive Raman spectrometer (Jobin Yvon) with a confocal Olympus microscope. The Raman signal was excited by a 532.2 nm laser and detected with a multichannel air-cooled CCD camera. The laser power was restricted to 5 mW to limit possible thermal damage to the sample. Data processing was performed using OMNIC SPECTRA software. A digital version of the spectra is available in the Depository of Unpublished Data, MAC website [document Metalodèvite CM48_113].

TABLE 1. COMPOSITION OF METALODÈVITE FROM PŘÍBRAM

	mean*	mean	range		*apfu*
FeO wt.%	0.67	0.62	0.40 - 0.85	Fe	0.097
MgO	0.21	0.20	0.08 - 0.30	Mg	0.055
ZnO	5.66	5.23	4.67 - 6.34	Zn	0.719
Al_2O_3	0.26	0.24	0.05 - 0.63	ΣM^{2+}	0.871
As_2O_5	15.97	14.75	10.71 - 16.17		
P_2O_5	3.87	3.57	2.83 - 4.44	Al	0.052
UO_3	58.65	54.17	51.89 - 58.86	ΣM^{3+}	0.052
H_2O	14.70	-			
				Σ*A* site	0.922
Total	99.99	78.78	73.16 - 86.16		
				As	1.437
				P	0.563
				Σ*T* site	2.000
				U	2.119
				H_2O	8.43

* Recalculated to 100 wt.% with H_2O from TGA. The elements F, Si, S, Ca, V, Cu, Ba, Pb, and Bi were sought but not detected. The range refers to results of seven point-analyses. In the column at right, the mean composition is expressed in terms of atoms per formula unit (*apfu*).

RESULTS AND DISCUSSION

EMPA and thermal analysis

The empirical formula, calculated from the average results of seven spot-analyses and based on As + P = 2 *apfu*, is $(Zn_{0.72}Fe_{0.10}Mg_{0.06}Al_{0.05})_{\Sigma0.93}(UO_2)_{2.12}[(AsO_4)_{1.44}(PO_4)_{0.56}]_{\Sigma2.00}\bullet8.43H_2O$ (Table 1). In addition to the dominant Zn (0.63–0.78 *apfu*), there is mostly Fe (0.07–0.12 *apfu*) at the *A* position. We assume that iron is present in the analyzed samples only as Fe^{2+}, as it is in metakahlerite, $Fe^{2+}[(UO_2)(AsO_4)]_2\bullet8H_2O$ (Locock *et al.* 2004). The presence of Al in our samples is somewhat surprising, but similar contents were found in all grains analyzed (Table 1). In the related Al-dominant member of the autunite group, chistyakovaite, $Al(UO_2)_2(AsO_4)_2(F,OH)\bullet6.5H_2O$, the Al content is charge-balanced mainly by the presence of F (Chukanov *et al.* 2006). However, in our analyses of metalodèvite, fluorine was not found at concentrations above the limit of detection, possibly as a result of the analytical conditions used. The tetrahedral sites are occupied by As, which is dominant (1.19–1.55 *apfu*), with P incorporated (0.45–0.81 *apfu*). This appears to indicate solid solution between metalodèvite and an as-yet unnamed hydrated zinc uranyl phosphate (Pozas-Tormo *et al.* 1986, Chernorukov *et al.* 2000). Isotypy of uranyl phosphates and arsenates is quite common (Locock *et al.* 2004, Locock 2007b).

The dehydration of metalodèvite in the range ~20–300°C can be expressed as follows: $8H_2O \rightarrow 5H_2O \rightarrow 3H_2O \rightarrow$ dehydrated phase (Fig. 2, Table 2). The total loss in weight below 300°C, 14.70 wt.%, corresponds to 8.43 mol of H_2O. Thermal decomposition takes place at higher temperatures (300–800°C) where overlapping solid-state reactions proceed, probably connected with the release of about half of the arsenic content. The material that remained after heating was checked by powder X-ray diffraction to determine the products of thermal decomposition. The X-ray-diffraction pattern (Table 3) exhibits the presence of an unknown crystalline phase. In contrast, Chernorukov *et al.* (2000)

TABLE 2. RESULTS OF THERMAL ANALYSIS OF METALODÈVITE

temperature [°C]	weight loss [%]	interpretation
20 – 90	4.40	2.53 H_2O
90 – 110	3.70	2.12 H_2O
110 – 240	5.60	3.21 H_2O
240 – 300	1.00	0.57 H_2O
20 – 300	Σ 14.70	8.43 H_2O
300 – 800	Σ 7.30	release of As_2O_3 and O_2

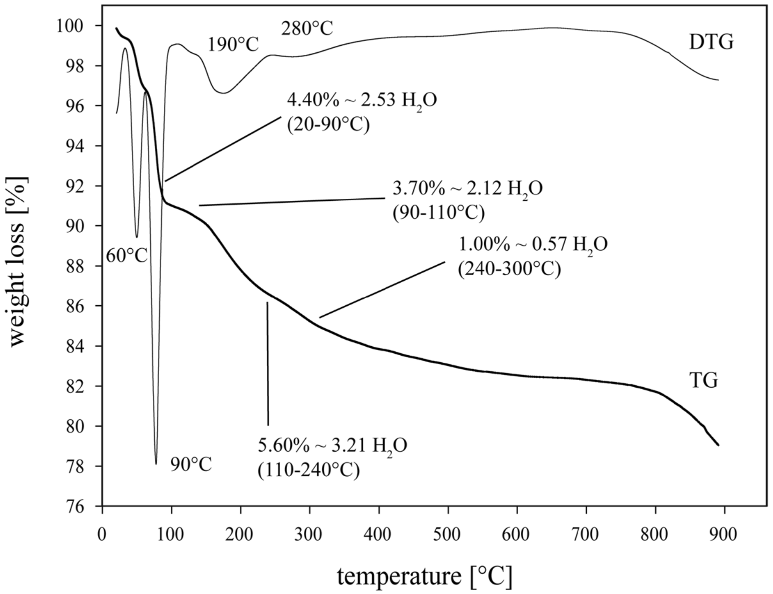

FIG. 2. Annotated diagram of the differential thermal analysis (DTG) and thermogravimetric analysis (TGA) of metalodèvite.

TABLE 3. POWDER XRD OF MATERIAL REMAINING AFTER THERMAL ANALYSIS

d_obs	I_rel	d_obs^1	I_rel^1	d_obs	I_rel	d_obs^1	I_rel^1
8.70	100	-	-	3.260	19	-	-
7.92	60	-	-	-	-	3.038	16
5.33	5	5.505	100	-	-	2.867	16
4.31	57	4.848	9	-	-	2.747	23
4.04	25	4.058	9	2.694	5	-	-
3.947	12	3.900	16	2.623	7	-	-
3.563	16	3.562	20	2.531	6	2.553	6
3.403	8	3.382	16	2.439	5	2.386	3
3.343	15	-	-	2.131	6	2.217	6

[1] Chernorukov *et al.* (2000). The values of *d* are quoted in Å.

reported powder X-ray-diffraction data for an anhydrous phase corresponding to $Zn(UO_2)_2(AsO_4)_2$, which differs from our results, despite some similarities in the patterns (Table 3).

Crystallography

Attempts to solve and refine the crystal structure of metalodèvite from single-crystal X-ray-diffraction data were unsuccessful; nine crystals were tested, but they were found to exhibit weak diffraction and broad diffraction-profiles. For the best fragment, a set of 943 unique reflections were collected, but the results were of poor quality, with mean $F^2/\sigma I = 2.61$. The unit-cell parameters refined from these single-crystal data are *a* 7.108(3), *b* 7.117(3), *c* 9.175(5) Å, α 98.68(4), β 107.36(5), γ 90.13(4)° and *V* 437.4(4) Å^3. The cell is about the half the volume of that reported for synthetic metakirchheimerite by Locock *et al.* (2004) and is probably a subcell.

The unit-cell parameters were therefore refined from powder X-ray-diffraction data (Table 4) on the basis of positions of 52 reflections. The pattern was indexed with the diffraction pattern calculated for synthetic metakirchheimerite (Locock *et al.* 2004) as the ionic radii of Zn and Co are similar (Shannon 1976). The refined unit-cell parameters of metalodèvite from Příbram (Table 5) are: *a* 7.193(5), *b* 9.771(8), *c* 13.24(1) Å, α 75.54(6), β 84.07(6), γ 81.68(6)° and *V* 889(1) Å^3 (with mean squared deviation of the refined positions 0.057° 2θ). The refined parameters are similar to those of synthetic metakirchheimerite (Locock *et al.* 2004), and the unit-cell volume is close to that reported by Agrinier *et al.* (1972).

IR and Raman spectroscopy

The Raman band at 3418 cm^{-1} (Fig. 3) and three infrared bands at 3568, 3366 and 3235 cm^{-1} (Fig. 4) are attributed to the ν OH stretching vibrations of H_2O molecules (Čejka 1999). From the features of both spectra, the presence of hydrogen bonds in the crystal structure of metalodèvite can be inferred, in which H_2O molecules from the interlayer and some uranyl oxygen, as well as oxygen atoms of $[(As, P)O_4]$ tetrahedra from the sheets may participate. The O–H…O bond lengths, determined with the empirical relation of Libowitzky (1999), are in the range 3.08 to 2.72 Å. An infrared band at 1636 cm^{-1} (Fig. 4) is attributed to the ν_2 (δ) bending vibration of H_2O molecules. No band was observed in the Raman spectrum of this region (Fig. 3). Infrared bands at 742 and 688 cm^{-1} (Fig. 4) are connected with the libration modes of H_2O molecules (Čejka 1999).

TABLE 4. POWDER XRD DATA FOR METALODÈVITE

metalodèvite Příbram space group $P\bar{1}$						metalodèvite Agrinier *et al.* (1972) space group $P4_2/m$				
I_{meas}	*h*	*k*	*l*	d_{obs}	d_{calc}	*h*	*k*	*l*	I_{meas}	d_{obs}
10	0	$\bar{1}$	0	9.29	9.39					
100	0	1	1	8.67	8.61	0	0	2	70	8.66
2	1	1	1	5.97	5.97					
35	$\bar{1}$	$\bar{1}$	1	5.03	5.06	1	1	0	40	5.09
15	1	0	2	4.88	4.92	1	1	1	10	4.92
19	0	2	0	4.74	4.69					
25	0	2	2	4.32	4.31	0	0	4	5	4.33
10	0	1	3	4.28	4.28					
14	1	2	2	3.98	3.97					
12	1	$\bar{1}$	2	3.93	3.95					
80	$\bar{2}$	0	0	3.55	3.55	2	0	0	100	3.59
50	2	1	1	3.49	3.48	2	0	1	30	3.50
40	$\bar{1}$	2	2	3.45	3.44					
11	0	0	4	3.20	3.20					
26	0	2	4	2.995	2.995	2	1	2	60	2.98
6	$\bar{1}$	0	4	2.837	2.841					
3	1	3	3	2.817	2.823					
1	$\bar{1}$	$\bar{3}$	1	2.771	2.769					
1	2	2	3	2.754	2.754					
<1	2	$\bar{2}$	0	2.674	2.677					
8	1	$\bar{3}$	1	2.587	2.586	2	1	4	15	2.58
16	2	$\bar{1}$	3	2.539	2.533	2	2	0	30	2.55
18	$\bar{2}$	$\bar{2}$	2	2.525	2.528	3	0	2	30	2.29
20	$\bar{2}$	$\bar{1}$	3	2.506	2.503					
5	$\bar{1}$	1	5	2.383	2.386					
25	1	3	5	2.254	2.256	1	3	1	5	2.24
20	1	$\bar{1}$	5	2.237	2.236					
15	$\bar{1}$	4	2	2.172	2.172	3	0	3	5	2.19
13	0	4	4	2.154	2.153	2	2	4	25	2.17
11	2	4	2	2.139	2.143					
1	3	3	3	1.9924	1.9893					
3	1	5	3	1.9020	1.9044					
2	0	1	7	1.8802	1.8786					
3	2	$\bar{3}$	3	1.8696	1.8723					
5	3	4	2	1.8281	1.8288					
16	$\bar{2}$	0	6	1.7732	1.7728	4	0	0	20	1.79
5	2	1	7	1.7318	1.7311					
4	$\bar{1}$	4	6	1.6910	1.6895	3	3	0	10	1.69
5	$\bar{3}$	$\bar{3}$	3	1.6852	1.6895					
4	$\bar{2}$	$\bar{5}$	1	1.6876	1.6874					
13	4	0	4	1.5989	1.6000	3	3	3	15	1.61
11	$\bar{2}$	$\bar{2}$	6	1.5896	1.5882					
8	$\bar{4}$	$\bar{3}$	1	1.5830	1.5825					
10	1	6	0	1.5701	1.5694					
4	$\bar{3}$	5	3	1.3774	1.3774					
4	4	1	7	1.3567	1.3574					
2	$\bar{3}$	2	8	1.2786	1.2790					
2	3	7	1	1.2594	1.2596					
3	6	1	5	1.1257	1.1250					

The values of *d* are quoted in Å.

A lowering of the $D_{\infty h}$ symmetry of $(UO_2)^{2+}$ and the T_d symmetry of $(AsO_4)^{2-}$ and $(PO_4)^{3-}$ can cause infrared and Raman activation of these units and a splitting of degenerate vibrations. In the case of phosphate-rich metalodèvite, Raman bands at 994 and 977 cm^{-1} (Fig. 3) and infrared bands at 1027 and 942 cm^{-1} (Fig. 4) are attributed to the triply degenerate ν_3 $(PO_4)^{3-}$ antisymmetric stretching vibrations and the ν_1 $(PO_4)^{3-}$ symmetric stretching vibration, respectively. A coincidence of the ν_1 $(PO_4)^{3-}$ vibration and the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration in the infrared spectrum is possible.

The Raman band at 892 cm^{-1} (Fig. 3) is assigned to the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration; similarly, an infrared band at 891 cm^{-1} (Fig. 4) is connected with this vibration. According to the empirical relation of Bartlett & Cooney (1989), the wavenumbers of these two bands correspond to U–O bond lengths in the uranyl ion, 1.790 and 1.791 Å, respectively. These values are in agreement with U–O bond lengths for uranyl square bipyramidal polyhedra tabulated by Burns (1999, 2005) and Burns *et al.* (1996, 1997), and with related structures that contain the autunite-type sheet (*e.g.*, Locock *et al.* 2004). As mentioned, coincidence of the ν_3 $(UO_2)^{2+}$ band and especially the ν_1 $(PO_4)^{3-}$ vibration may be expected. A Raman band at 977 cm^{-1} (Fig. 3) and an infrared band at 943 cm^{-1} (Fig. 4) could also be related to the ν_3 $(UO_2)^{2+}$ vibration, but the calculated U–O bond lengths from these two bands are rather

TABLE 5. UNIT-CELL PARAMETERS OF METALODÈVITE FROM PŘÍBRAM AND RELATED PHASES

formula	$Zn(UO_2)_2[(As,P)O_4]_2\cdot 8H_2O$	$Zn(UO_2)_2(AsO_4)_2\cdot 8–12H_2O$	$Co(UO_2)_2(AsO_4)_2\cdot 8H_2O$
provenance	Příbram, Czech Republic	Lodève, France	synthetic
reference	this work	Agrinier *et al.* (1972)	Locock *et al.* (2004)
d_{011} (tricl.); d_{002} (tetr.) [Å]	8.67	8.66	8.61
space group	$P\bar{1}$	$P4_2/m$	$P\bar{1}$
a [Å]	7.193(5)	7.16	7.1955(3)
b [Å]	9.771(8)	-	9.7715(4)
c [Å]	13.24(1)	17.20	13.2319(6)
α [°]	75.54(6)	-	75.525(1)
β [°]	84.07(6)	-	84.052(1)
γ [°]	81.68(6)	-	81.661(1)
V [Å^3]	889(1)	882	889.08(7)
formula	$Zn(UO_2)_2(PO_4)_2\cdot 7H_2O$	$Zn(UO_2)_2(AsO_4)_2\cdot 8H_2O$	$Zn(UO_2)_2(PO_4)_2\cdot 9.5H_2O$
provenance	synthetic	synthetic	synthetic
reference	Chernorukov *et al.* (2000)	Nabar & Iyer (1977)	Pozas *et al.* (1986)
d_{002} [Å]	8.588	8.35	10.01
space group	-	$P4_2/m$	$P4_2/m$
a [Å]	-	7.226	7.050(7)
c [Å]	-	17.12	20.08(7)
V [Å^3]	-	894	998(4)

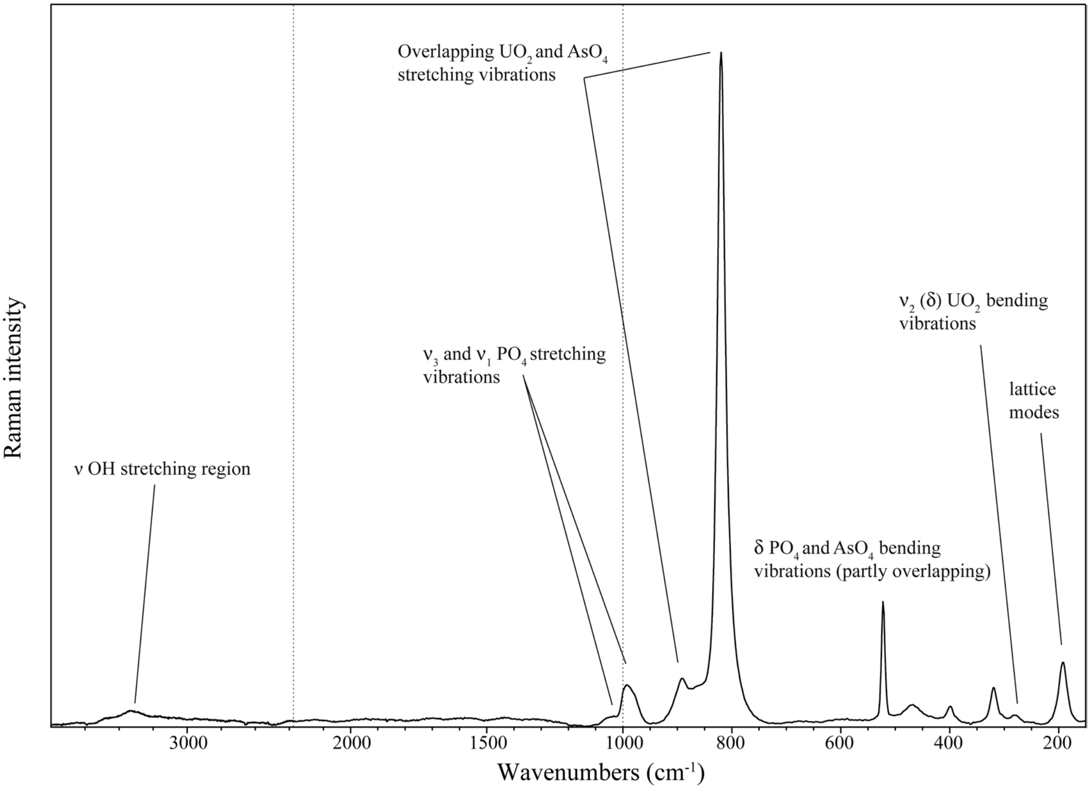

FIG. 3. Raman spectrum of metalodèvite from Příbram. The x axis was rescaled at 2300 and 1000 cm^{-1} to emphasize selected features in the spectrum.

short (1.732 and 1.755 Å, respectively), and thus such an assignment seems improbable.

The Raman band at 866 cm^{-1} (Fig. 3) is probably connected with the triply degenerate ν_3 $(AsO_4)^{3-}$ antisymmetric stretching vibration, and the band at 819 cm^{-1} (Fig. 3), together with an infrared band at 816 cm^{-1} (Fig. 4), can be assigned to the ν_1 $(AsO_4)^{3-}$ symmetric stretching vibration, coinciding with the ν_1 $(UO_2)^{2+}$ symmetric stretching vibration. The Raman band at 522 cm^{-1} (Fig. 3) and an infrared band at 620 cm^{-1} (Fig. 4) are assigned to the triply degenerate $(PO_4)^{3-}$ bending vibrations, and the Raman bands at 469, 447 and 399 cm^{-1} (Fig. 3) are assigned to the split triply degenerate ν_4 $(AsO_4)^{3-}$ bending vibrations, coinciding with the doubly degenerate ν_2 $(PO_4)^{3-}$ bending vibrations, whereas the band at 319 cm^{-1} (Fig. 3) corresponds to the ν_2 $(AsO_4)^{3-}$ bending vibration (Nakamoto 1986, Čejka 1999). The split doubly degenerate ν_2 (δ) $(UO_2)^{2+}$ vibrations may be connected with the Raman bands at 303 and 280 cm^{-1} and a Raman band at 191 cm^{-1} (Fig. 3) assigned to lattice vibrations (Čejka 1999).

Comparison of current results to the original description of metalodèvite

Metalodèvite was described by Agrinier *et al.* (1972) as a mineral species containing 8–12 H_2O. From our investigations, we can state that metalodèvite has the ideal chemical formula $Zn[(UO_2)(AsO_4)_2]•8H_2O$. This hydration state is supported by the results of a thermogravimetric analysis. The most intense *d*-value in the powder-diffraction pattern is at ~8.6 Å. This value, together with the refined unit-cell parameters, correspond to the data given by Locock *et al.* (2004) for synthetic uranyl arsenate octahydrates. The unit-cell volume, 882 Å^3, reported by Agrinier *et al.* (1972) is close to the volume determined for metalodèvite from Příbram, 889 Å^3, but the powder-diffraction pattern of metalodèvite is better described by a triclinic unit-cell (Fig. 5), with parameters similar to those given by Locock *et al.* (2004) for synthetic metakirchheimerite (Table 5). The triclinic symmetry is also in agreement with the biaxial optical properties reported by Agrinier

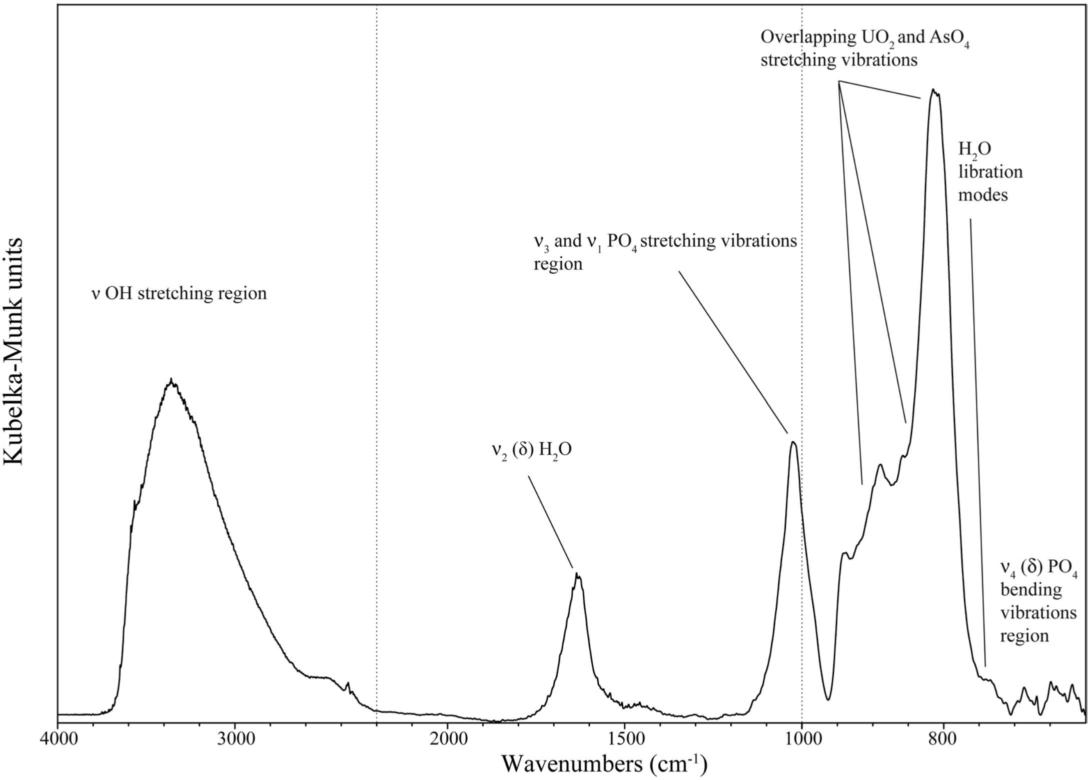

Fig. 4. Micro-DRIFTS spectrum of metalodèvite from Příbram. The x axis was rescaled at 2300 and 1000 cm^{-1} to emphasize selected features in the spectrum.

et al. (1972). The electron-microprobe results show the presence of minor amounts of other interlayer cations (Fe^{2+}, Mg^{2+} and Al^{3+}), whereas the wet-chemical data of Agrinier *et al.* (1972) show a small proportion of Fe^{2+} as a substituent. These results are interpreted to represent solid solution, and are expected on the basis of the similar ionic radii of these cations (Shannon 1976). The substitution of P for As is expected from the literature on other uranyl arsenate and phosphate compounds, and from the analysis of Agrinier *et al.* (1972), who also reported minor P. The content of H_2O in the analysis of Agrinier *et al.* (1972), 15.70 wt.%, corresponds to ~10 H_2O molecules (on the basis of 2 U atoms per formula unit). In our preliminary investigations, a few of the powder-diffraction patterns showed an intense maximum at about 10 Å. In agreement with Locock *et al.* (2004), this can be interpreted to represent a decahydrate phase, $Zn[(UO_2)(AsO_4)_2]\bullet 10H_2O$. Such a phase would correspond to the as-yet unnamed mineral "lodèvite". It is possible that the presence of "lodèvite" may be responsible for the higher weight-loss reported by Agrinier *et al.* (1972).

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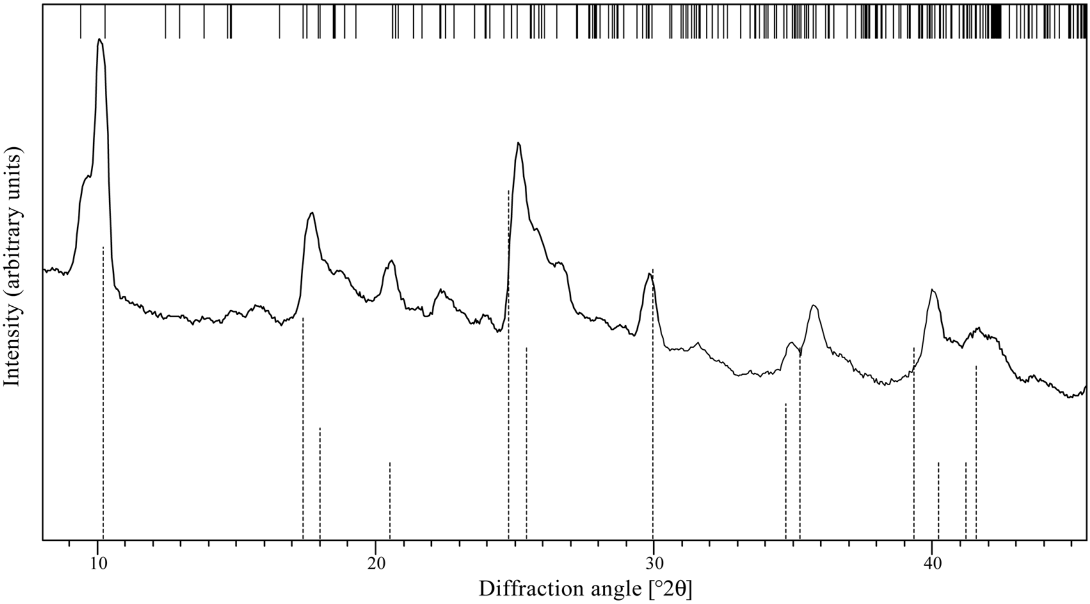

FIG. 5. Powder-diffraction pattern of metalodèvite from Příbram (displayed between 10 and 46°2θ, Cu*K*α radiation). The line positions from Agrinier *et al.* (1972) are represented by dashed lines beneath the profile. The positions calculated for the refined triclinic unit-cell related are shown at the top of the diagram.

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