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Vysokýite, $U^{4+}[AsO_2(OH)_2]_4 \cdot 4H_2O$, a new mineral from Jáchymov, Czech Republic

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ABSTRACT

Vysokýite, $U^{4+}[(AsO_2(OH)_2]_4(H_2O)_4$ (IMA 2012−067), was found growing on an altered surface of massive native As in the Geschieber vein, Jáchymov ore district, Western Bohemia, Czech Republic. The new mineral was found in association with běhounekite, štěpite, kaatialaite, arsenolite, claudetite and gypsum. It forms extremely fibrous light-green crystals up to 8 mm long. Crystals have an alabaster lustre and a greenish-white to greyish streak. Vysokýite is brittle with uneven fracture and perfect cleavage along (100) and (001); the Mohs hardness is ~2. A density of 3.393 g/cm^3 was calculated using the empirical formula and unit-cell parameters obtained from a single-crystal diffraction experiment. Vysokýite is non-fluorescent under short or long wavelength UV radiation. It is colourless under the microscope, measured refractive indices are $\alpha' = 1.617(3)$, $\gamma' = 1.654(3)$; the estimated optical orientation is $\alpha' \sim X$, $\gamma' \sim Z$. The average of five spot wavelength dispersive spectroscopy (WDS) analyses is 29.44 UO_2, 1.03 SiO_2, 48.95 As_2O_5, 0.12 SO_3, 15.88 H_2O (calc.), total 95.42 wt.%. The empirical formula of vysokýite (based on 20 O a.p.f.u.) is $U_{1.00}[AsO_2(OH)_2]_{3.90}(SiO_4)_{0.16}(SO_4)_{0.01} \cdot 4H_2O$. The As−O−H and O−H vibrations dominate in the Raman spectrum. Vysokýite is triclinic, space group $P\bar{1}$, with $a = 10.749(2)$, $b = 5.044(3)$, $c = 19.1778(7)$ Å, $\alpha = 89.872(15)^o$, $\beta = 121.534(15)^o$, $\gamma = 76.508(15)^o$, and $V = 852.1(6)$ Å^3, $Z = 2$ and $D_{calc} = 3.34$ g·cm^{-3}. The strongest diffraction peaks in the X-ray powder diffraction pattern are [d_{obs} in Å($I_{rel.}$)(hkl)]: 8.872(100)(100), 8.067(50)(002), 6.399(7)(10$\bar{3}$), 4.773(6)(10$\bar{4}$), 3.411(10)(30$\bar{2}$), 3.197(18)(31$\bar{3}$). The crystal structure of vysokýite was solved from single-crystal X-ray diffraction data by the charge-flipping method and refined to $R_1 = 0.0595$ based on 2718 unique observed reflection, and to $wR_2 = 0.1160$ for all 4173 unique reflections. The structure of vysokýite consists of UO_8 square antiprisms sharing all of their vertices with 8 As-tetrahedra to form infinite chains parallel to [010]. These chains are linked by hydrogen bonds involving terminal (OH) groups of the double-protonated As-tetrahedra and molecules of H_2O located between the chains. The new mineral is named in honour of Arnošt Vysoký (1823−1872), the former chief of the Jáchymov mines and smelters, chemist and metallurgist.

Keywords: vysokýite, new mineral, uranium(IV) tetrakis[dihydrogen−arsenate] tetrahydrate, crystal structure, oxide zone, Jáchymov.

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Introduction

U-MINERALS represent one of the most chemically and structurally diverse mineral groups in nature. Particular interest in the paragenesis and crystal chemistry of U minerals arises, because of their role as weathering products of uraninite (UO_{2+x}) and other primary U minerals under oxidizing conditions (Frondel, 1958; Finch and Ewing, 1992; Finch and Murakami, 1999; Krivovichev and Plášil, 2013), as well as irradiated or spent nuclear fuel (Forsyth and Werme, 1992; Wronkiewicz *et al.*, 1996; Janeczek *et al.*, 1996) or modelling weathering and climate change (Birch *et al.*, 2011; Mills *et al.*, 2008; Göb *et al.*, 2013). Uranium occurs most typically in two common oxidation states, U^{4+} and U^{6+}, which control its geochemical behaviour: primary U^{4+} minerals (e.g. uraninite, coffinite, ningyoite) are mostly highly insoluble and occur typically as primary-ore in uranium deposits; U^{6+} is very mobile, compared to U^{4+}, under oxidizing conditions, and the uranyl ion, UO_2^{2+}, is characteristic of supergene phases (Langmuir, 1978; Finch and Murakami, 1999; Krivovichev and Plášil, 2013). Recently, an unusual association of U^{4+}-containing arsenate and sulfate minerals of supergene origin was described from the extreme As-rich acid-mine drainage (AMD) locality at the Geschieber vein in Jáchymov, Czech Republic (Plášil *et al.*, 2011*a*, 2013). Here we provide a description of the third new mineral found in this association, vysokýite. It has been approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2012-067). The mineral is named in honour of Ing. Arnošt Vysoký (1823−1872), the successor of Adolf Patera (after whom the mineral adolfpateraite is named; Plášil *et al.*, 2012*a*) as the chief of the State Mines and Smelters in Jáchymov (St Joachimsthal) from 1866. Vysoký followed the research of Patera in the field of technological processing of uranium and complex ores and he quickly invented several uranium colours, uranium black and also cobalt blue. Arnošt Vysoký published numerous scientific and popular articles, among which an important one describing the smelter production of uranium colours in Jáchymov (Vysoký, 1866), a paper about uranium, its minerals and production of uranium colours (Vysoký, 1860), and a paper on new minerals from Jáchymov (Vysoký, 1862). Prof. Dr Julius Stoklasa published an article in the *Prager Presse* newspaper on 11th February 1924, concerning the fact that Vysoký had, in 1861, formulated an idea that the fluorescence of glass stained by uranium colours is caused by the properties of U as an element itself, e.g. by the rays emitted by uranium.

Occurrence

The vysokýite samples were found in the internationally renowned Jáchymov ore district (St Joachimsthal), Krušné hory Mountains (Erzgebirge), located ~20 km north of Karlovy Vary, NW Bohemia (Czech Republic). The Jáchymov ore district is a classic example of a Ag-As-Bi-Co-Ni-U hydrothermal vein-type deposit (Ondruš *et al.*, 2003). The majority of the primary ore minerals crystallized during a Variscan mineralization phase from mesothermal hydrothermal fluids. More than 420 minerals have been described from there, including an extremely rich association of supergene minerals (e.g. Ondruš *et al.*, 1997, 2003, 2013; Sejkora *et al.*, 2010, 2011; Plášil *et al.*, 2010, 2011*a*,*b*, 2012*a*,*b*). A brief overview of the history of mining, geology and mineralogy of the locality was published recently by Tvrdý and Plášil (2010).

The new mineral was found at the 10th level of the Svornost (former 'Einigkeit') mine, located in the mining town of Jáchymov (GPS 50º22′21.47″N, 12º54′42.0″E). Vysokýite is spatially and genetically associated with an altered lens of native arsenic (with traces of arsenopyrite and pyrite) located at the intersection of the Geschieber and Geyer veins. This ore lens has been weathered by post-mining processes in the moist environment of an old mining adit for >40 years, and an interesting association of secondary alteration products has formed there. We found no evidence of uraninite in the mass of native arsenic and therefore the source of uranium is spatially separated from this site. We speculate that the solutions that moved U were acidic, and that they carried U in the form of uranyl ions and the reduction to U(IV) took place *in situ*, on the arsenic lens. The mineral association is quite simple with regard to its elemental composition. The phases found here include the abundant arsenolite, As_2O_3, and its dimorph claudetite, further kaatialaite, $Fe[AsO_2(OH)_2]_3 \cdot 5H_2O$, locally also scorodite, $FeAsO_4 \cdot 2H_2O$, parasymplesite, $Fe_3(AsO_4)_2 \cdot 8H_2O$, minor picropharmacolite, $Ca_4Mg(AsO_4)_2[AsO_3(OH)]_2 \cdot 12H_2O$, melanterite, $FeSO_4 \cdot 7H_2O$, and native sulfur. Vysokýite was found in association with prismatic green crystals

of běhounekite, $U^{4+}(SO_4)_2 \cdot 4H_2O$ (Plášil *et al.*, 2011*a*), green tabular crystals of štěpite, $U^{4+}(AsO_3OH)_2 \cdot 4H_2O$ (Plášil *et al.*, 2013), and an unnamed phase $(H_3O)_2^+(UO_2)_2(AsO_4)_2 \cdot nH_2O$, similar to UM1997-19-AsO:HU (Smith and Nickel, 2007) of Ondruš *et al.* (1997).

Physical and optical properties

Vysokýite forms rich, radial aggregates on the surface of altered arsenic, consisting of very fine, extremely fibrous crystals elongated on [010] (Fig. 1). Crystal aggregates consist of individual, exceptionally long fibres up to 8 mm, covering usually just a few cm^2 of matrix. Crystals of vysokýite are occasionally covered by small aggregates of štěpite (Fig. 2). From visual observations of the paragenetic sequence, it appears that vysokýite is older than štěpite, and it is older, or of the same age as, běhounekite. Vysokýite crystals are light-green in colour with an alabaster lustre and greenish-white to greyish streak. The mineral is brittle with an uneven fracture. Vysokýite has perfect cleavage along (100) and also along (001). The Mohs hardness of vysokýite is ~2. A density of 3.393 g/cm^3 was calculated using the empirical formula and unit-cell parameters obtained from a single-crystal diffraction experiment. Direct density measurements were not done due to the scarcity of appropriate specimens. Vysokýite is non-fluorescent under short or long wavelength UV-radiation. Optical properties were measured from very fine vysokýite fibrous crystals (using 589 nm light). Vysokýite is, as a triclinic mineral, expected to be biaxial; however, the optical measurements were extremely difficult due to the nature of the aggregates consisting of extremely fine fibres. As such the β refractive index could not been measured. In thin section, vysokýite is colourless, refractive indices are $\alpha' = 1.617(3)$, $\gamma' = 1.654(3)$, the birefringence is 0.016, and the indices were measured roughly perpendicular and parallel to the elongation of the fibres. The orientation is estimated as $\alpha' \sim X$, $\gamma' \sim Z$. Due to the incomplete optical data, the Gladstone-Dale compatibility index (Mandarino, 1981) could not be calculated.

Chemical composition (WDS)

The chemical composition of vysokýite was determined using a Cameca SX100 electron microprobe (WDS mode, 15 kV, 4 nA and 8 μm beam diameter) from 5 point analyses. The following X-ray lines and standards were selected to minimize line overlaps: $K\alpha$ lines: Si (sanidine), As (lammerite), S ($SrSO_4$), $M\beta$ lines: U (metallic U). Peak counting times (CT) were 10–20 s and the background counting time was 50% of the peak CT. The measured intensities were converted to element concentrations using the *PAP* program (Pouchou and Pichoir, 1985).

The chemical composition obtained from electron-microprobe analysis is given in Table 1. The empirical formula of vysokýite (based on 20 O a.p.f.u.) is $U_{1.00}[AsO_2(OH)_2]_{3.90}(SiO_4)_{0.16}(SO_4)_{0.01} \cdot 4H_2O$ (H_2O content calculated by stoichiometry obtained from the crystal structure). The ideal formula, $U^{4+}[AsO_2(OH)_2)]_4 \cdot 4H_2O$ requires UO_2 30.90, As_2O_5 52.60, H_2O 16.50, total 100.00 wt.%.

FIG. 1. Vysokýite from Jáchymov. Acicular crystals growing on corroded native As covered mostly by a mixture of arsenolite and kaatialaite (fine grained in the matrix). Field of view 3.0 mm. Photo: P. Škácha.

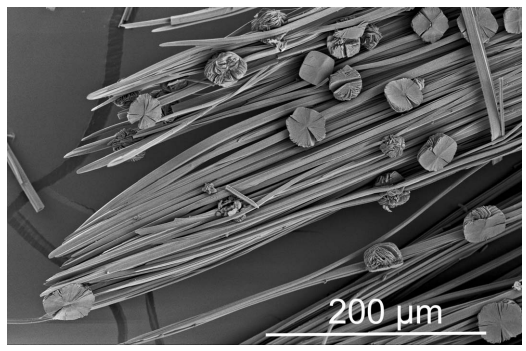

FIG. 2. Long prismatic crystals of vysokýite with overgrowing hemispherical aggregates of štěpite. BSE image by Hitachi S3700N.

TABLE 1. Chemical composition of vysokýite.

	Mean (n = 5)	Range	Std. dev.
SiO_2	1.03	0.70–1.05	0.17
UO_2	29.44	24.50–32.05	3.07
As_2O_5	48.95	46.29–50.99	1.92
SO_3	0.12	0.00–0.48	0.21
H_2O	15.88*		
Total	95.42		
Calculated on basis of 20 O a.p.f.u.			
Si	0.16		
U	0.99		
As	3.87		
S	0.01		
H_2O	8.00		

* calculated by stoichiometry (4 H_2O + 8 OH) obtained from the crystal structure.

Raman spectroscopy

A Raman spectrum of vysokýite (Fig. 3) covering the range 50–3150 cm^{-1} (with spectral resolution of 2 cm^{-1}) was collected using a DXR dispersive Raman spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by a 780 nm diode-pumped solid-state laser and detected by a CCD detector. Experimental parameters – exposure time: 20 s; number of exposures: 50; spectrograph aperture: 50 mm slit; laser power level: 5.0 mW. The instrument was calibrated by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white-light sources (intensity calibration). Spectral data were processed using the OMNIC Spectral tool software v.7.3 (ThermoElectron Corp.).

Few detailed publications exist related to interpretation of the spectra of $AsO_2(OH)_2$-containing compounds in the solid state. For

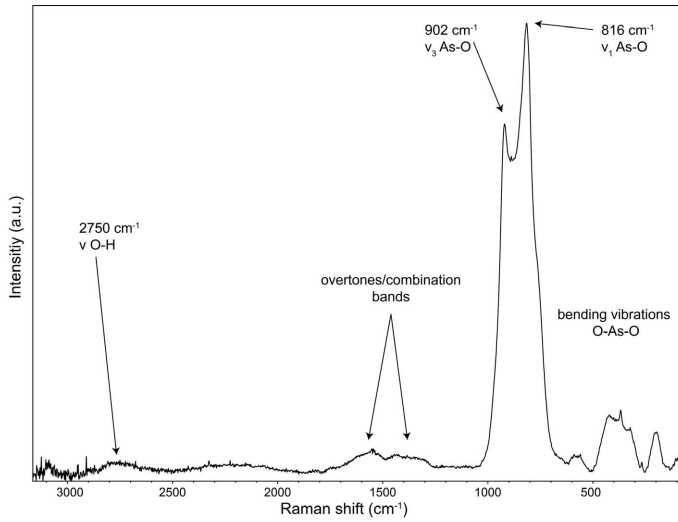

FIG. 3. Raman spectrum of vysokýite.

tentative assignment and interpretation of the experimentally derived Raman spectrum of vysokýite, the papers of Nakamoto (1986), Keller (1971), Vansant *et al.* (1973), Mielke and Ratajczak (1972), Myneni *et al.* (1998), Libowitzky (1999) and Ondruš *et al.* (2013) (plus references therein) were followed.

The Raman vibration bands at 2750 and 2230 cm^{-1} were assigned to the ν O–H stretching vibrations of (As–OH) in the $[AsO_2(OH)_2]^-$ units and of hydrogen-bonded H_2O molecules. According to the correlation of Libowitzky (1999), the corresponding approximate O–H···O hydrogen bond lengths are in the range 2.6–2.55 Å. The combination bands and/or overtones were observed at 1545 and 1425 cm^{-1}. The bands of the highest intensity, at 920 and 816 cm^{-1}, were assigned to the ν_3 antisymmetric and ν_1 symmetric As–O stretching vibrations. A band at 769 cm^{-1} may be related to the ν_3 antisymmetric or ν_1 symmetric stretching As–OH vibrations. Bands at 595 and 559 cm^{-1} are then attributed to the δ As–OH out-of-plane bending vibrations; bands at 427 and 368 cm^{-1} to the ν_4 (δ) O–As–O bending vibrations, and that at 324 cm^{-1} to the ν_2 (δ) bending vibration. Bands with the lowest energies (at 200, 184, 99 and 61 cm^{-1}) are lattice modes.

Powder diffraction

Powder X-ray diffraction (XRD) data were obtained using a Bruker D8 Advance powder diffractometer with a LynxEye detector operating in Bragg-Brentano geometry (Table 2). Positions of diffraction maxima were obtained by profile-shape fitting performed with the ZDS software (Ondruš, 1995) using the Pearson VII peak-shape function. The experimental powder pattern was indexed in accordance with the calculated values

TABLE 2. Powder XRD data (d_{hkl} in Å) for vysokýite.

I_{rel}	d_{obs}	$d_{calc.}$	$I_{calc.}$	h	k	l	I_{rel}	d_{obs}	$d_{calc.}$	$I_{calc.}$	h	k	l
100	8.782	8.800	100	1	0	0	1	2.890	2.891	7	2	$\bar{1}$	$\bar{5}$
50	8.067	8.070	54	0	0	2	1	2.710	2.708	9	2	1	3
7	6.399	6.375	<1	1	0	$\bar{3}$	<1	2.693	2.694	8	1	$\bar{1}$	3
2	5.230	5.232	2	2	0	$\bar{2}$	2	2.689	2.690	2	0	0	6
<1	4.864	4.867	1	0	1	1	1	2.613	2.616	2	4	0	$\bar{4}$
<1	4.842	4.844	<1	1	1	$\bar{1}$	<1	2.569	2.570	2	3	$\bar{1}$	$\bar{4}$
6	4.773	4.775	9	1	0	$\bar{4}$	1	2.496	2.500	4	1	2	1
<1	4.478	4.485	<1	0	1	2	3	2.492	2.492	5	4	0	$\bar{2}$
<1	4.466	4.460	2	0	1	$\bar{1}$	1	2.396	2.397	2	2	0	4
<1	4.456	4.449	<1	1	1	$\bar{2}$	1	2.385	2.388	3	2	0	$\bar{8}$
4	4.400	4.400	7	2	0	0	<1	2.374	2.375	1	3	0	2
<1	4.068	4.071	5	1	$\bar{1}$	$\bar{2}$	<1	2.356	2.357	<1	0	2	3
1	4.050	4.056	4	2	1	$\bar{1}$	2	2.251	2.251	1	3	$\bar{1}$	$\bar{7}$
3	4.032	4.035	2	0	0	4	<1	2.203	2.200	2	4	0	0
<1	3.924	3.925	5	1	1	2	<1	2.191	2.190	2	4	0	$\bar{8}$
<1	3.890	3.889	4	1	1	$\bar{3}$	1	2.132	2.131	1	2	1	5
1	3.839	3.838	13	1	$\bar{1}$	$\bar{3}$	<1	2.108	2.107	4	0	2	5
1	3.828	3.831	2	2	1	0	<1	2.096	2.094	<1	3	$\bar{1}$	$\bar{8}$
<1	3.809	3.805	18	2	1	$\bar{3}$	1	2.075	2.077	1	5	0	$\bar{4}$
3	3.459	3.467	9	2	1	1	<1	2.016	2.018	1	0	0	8
10	3.411	3.413	11	3	0	$\bar{2}$	<1	1.985	1.986	5	2	$\bar{2}$	$\bar{1}$
3	3.376	3.377	18	1	1	3	2	1.955	1.954	1	5	0	$\bar{2}$
1	3.354	3.352	19	0	1	$\bar{3}$	2	1.938	1.937	2	3	$\bar{1}$	$\bar{9}$
4	3.348	3.344	<1	1	1	$\bar{4}$	<1	1.917	1.915	1	4	2	0
6	3.220	3.214	1	2	$\bar{1}$	$\bar{2}$	1	1.887	1.886	5	2	0	6
18	3.197	3.197	15	3	1	$\bar{3}$	<1	1.824	1.822	3	0	2	7
11	3.189	3.188	7	2	0	$\bar{6}$	<1	1.775	1.777	1	1	1	8
11	3.076	3.080	13	1	0	$\bar{6}$	<1	1.760	1.760	1	5	$\bar{1}$	$\bar{4}$
5	2.935	2.933	10	3	0	0	1	1.722	1.724	2	3	$\bar{2}$	$\bar{1}$

of intensities obtained from the crystal-structure refinement (Yvon *et al*., 1977). The unit cell was refined based on the positions of 58 reflections utilizing the Burnham software (Burnham, 1962).

Structure determination

A long prismatic crystal of vysokýite, with dimensions 0.19 mm × 0.02 mm × 0.01 mm, was mounted on a glass fibre and examined by an Oxford Diffraction Gemini single-crystal four-circle diffractometer. The graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) from the sealed X-ray tube, collimated with a fibre optics Mo-Enhance collimator and detected with an Atlas CCD detector, was used for the diffraction experiment. Vysokýite is triclinic, $P\bar{1}$, with a = 10.749(2), b = 5.044(3), c = 19.1778(7) Å, α = 89.872(15)º, β = 121.534(15)º, γ = 76.508(15)º, and V = 852.1(6) Å^3. The unit cell was refined from 12402 reflections by the least-squares algorithm with the *CrysalisPro* package (Agilent Technologies, 2012). The ω-rotational scans (1º frame width, 240 s per frame) were adopted to assemble the set of three-dimensional intensity data, covering the full sphere. A total of 12402 reflections were kept, of them 4173 were unique and 2721 were classified as observed with the criterion [I_{obs}>3σ(I)]. An empirical correction for absorption (multi-scan in *ABSPACK3*, *CrysAlis RED*; Agilent Technologies, 2012) led to an R_{int} of 0.0703. The relatively large internal agreement factor is caused by the weak data and twin (split crystal) overlaps. Reduction of the data was performed using the *Crysalis* package (*CrysAlis RED*; Agilent Technologies, 2012). Details of the data collection and refinement are given in Table 3.

The structure of vysokýite was solved by the charge-flipping algorithm from the single-crystal XRD data using the *Superflip* program (Palatinus and Chapuis, 2007) and subsequently refined

TABLE 3. Summary of data-collection conditions and refinement parameters for vysokýite.

Ideal structural formula	$U[AsO_2(OH)_2]_4(H_2O)_4$
a, b, c (Å)	10.749(2), 5.044(3), 19.1778(7)
α, β, γ (º)	89.872(15), 121.534(15), 76.508(15)
V (Å^3)	852.1(6)
Space group	$P\bar{1}$
Z	2
$D_{calc.}$ [g.cm^{-3}] for the formula above	3.342
Temperature (K)	293
Wavelength (Å)	MoK_α, 0.71073
Crystal dimensions (mm)	0.19 × 0.02 × 0.01
Collection mode, frame width, count. time	ω scans, 1.0º, 240 s
Limiting θ angles	3.18−29.21º
Limiting Miller indices	$-14 \leqslant h \leqslant 14$, $-6 \leqslant k \leqslant 6$, $-24 \leqslant l \leqslant 23$
No. of reflections measured	12402
No. of unique reflections	4173
No. of observed reflections (criterion)	2718 [I_{obs}>3σ(I)]
Completeness, R_{int}	0.9986, 0.0703
Absorption correction (mm^{-1}), T_{min}/T_{max}	17.33 (multi-scan), 0.824/1.000
F_{000}	769
Refinement by *Jana2006* on F^2	
Parameters refined, restraints, constraints	127, 0, 0
R_1, wR_2 (obs)	0.0595, 0.1054
R_1,wR_2 (all)	0.1001, 0.1160
GOF obs/all	1.71/1.51
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−5.82, 9.9
Weighting scheme, weights	σ, $w = 1/(\sigma^2(F) + 0.0001F^2)$
Domain fractions 1, 2	0.512(2), 0.488(2)
Domain matrix	$\begin{pmatrix} -1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

TABLE 4. Atomic positions and displacement parameters (U_{iso}/U_{eq}, in Å^2) for vysokýite.

	x/a	y/b	z/c	U_{iso}/U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U	0.00510(13)	0.66047(14)	0.24632(7)	0.0187(3)	0.0167(3)	0.0105(3)	0.0245(3)	−0.0039(5)	0.0081(2)	−0.0023(5)
As1	−0.0509(3)	1.1957(10)	0.08990(15)	0.0210(12)	0.0217(13)	0.0147(13)	0.0225(12)	−0.0036(12)	0.0098(11)	−0.0037(13)
As2	0.3065(3)	1.0069(9)	0.30774(14)	0.0190(11)	0.0150(12)	0.0113(13)	0.0261(13)	−0.0027(12)	0.0083(11)	−0.0026(12)
As3	0.0594(3)	0.1341(10)	0.40248(15)	0.0228(12)	0.0267(14)	0.0160(14)	0.0245(13)	−0.0069(13)	0.0126(12)	−0.0013(13)
As4	−0.2935(3)	0.3031(9)	0.18781(15)	0.0201(12)	0.0133(12)	0.0169(14)	0.0280(13)	−0.0030(12)	0.0101(11)	−0.0014(13)
O1	0.4505(18)	1.067(4)	0.3988(9)	0.031(4)*						
O2	0.0619(18)	1.273(4)	0.0600(10)	0.034(4)*						
O3	−0.390(2)	0.831(6)	−0.0091(11)	0.051(5)*						
O4	−0.205(2)	1.170(4)	−0.0031(11)	0.041(5)*						
O5	0.2264(17)	0.795(3)	0.3278(9)	0.023(4)*						
O6	−0.4446(18)	0.506(4)	0.0964(9)	0.029(4)*						
O7	−0.1875(17)	0.494(3)	0.2453(9)	0.020(4)*						
O8	0.1943(18)	0.311(3)	0.2470(9)	0.026(4)*						
O9	0.384(2)	0.442(6)	0.5048(11)	0.045(5)*						
O10	−0.0324(18)	−0.068(3)	0.3362(9)	0.027(4)*						
O11	0.0404(16)	0.895(2)	0.1524(8)	0.018(3)*						
O12	−0.3828(17)	0.205(3)	0.2337(9)	0.028(4)*						
O13	−0.1127(16)	0.465(3)	0.1251(8)	0.019(4)*						
O14	−0.0517(19)	0.313(4)	0.4343(10)	0.038(5)*						
O15	−0.2088(18)	0.028(3)	0.1665(9)	0.028(4)*						
O16	0.1278(18)	0.334(3)	0.3715(9)	0.033(4)*						
O17	0.4049(19)	0.854(3)	0.2661(10)	0.036(4)*						
O18	0.2109(19)	−0.055(3)	0.4952(10)	0.033(4)*						
O19	0.7310(19)	0.805(4)	0.3674(10)	0.056(5)*						
O20	0.3174(17)	0.499(4)	0.1553(9)	0.041(4)*						

* refined with U_{iso}.

TABLE 5. Selected interatomic distances (Å) for vysokýite.

	U−O5		2.327(18)
	U−O7		2.40(2)
	U−O8		2.352(19)
	U−O10^{i}		2.341(19)
	U−O11		2.39(2)
	U−O13		2.344(14)
	U−O15^{i}		2.321(13)
	U−O16		2.423(15)
	<U−O>		2.36
As1−O2	1.70(3)	As2−O1	1.710(15)
As1−O4	1.718(16)	As2−O5	1.68(2)
As1−O11	1.665(11)	As2−O8i	1.681(13)
As1−O13^{i}	1.672(18)	As2−O17	1.69(2)
<As1−O>	1.69	*<As2−O>*	1.69
As3−O10	1.669(16)	As4−O6	1.732(13)
As3−O14	1.69(2)	As4−O7	1.629(17)
As3−O16	1.65(2)	As4−O12	1.75(2)
As3−O18	1.719(13)	As4−O15	1.649(18)
<As3−O>	1.68	*<As4−O>*	1.69
O1−O5	2.77(3)	O7−O15	2.79(2)
O1−O8^{i}	2.754(18)	O7−O15^{i}	2.98(3)
O1−O9^{ii}	2.75(3)	O7−O16	2.85(2)
O1−O17	2.62(3)	O20−O8	2.96(3)
O2−O2^{iii}	2.77(3)	O20−O12^{vii}	2.75(2)
O2−O4	2.65(3)	O20−O17	2.70(2)
O2−O4^{iv}	2.95(3)	O8−O11^{viii}	2.99(2)
O2−O20^{i}	2.89(3)	O8−O13	2.77(2)
O2−O11	2.73(3)	O8−O16	2.82(3)
O2−O13^{i}	2.77(3)	O8−O17^{viii}	2.70(2)
O3−O3^{v}	2.76(3)	O9−O9^{ii}	2.79(4)
O3−O4	2.87(4)	O9−O16	2.79(2)
O3−O6	2.97(4)	O9−O18^{i}	2.71(3)
O3−O6^{vi}	2.67(3)	O10−O14	2.74(3)
O3−O13	2.88(2)	O10−O15	2.74(2)
O4−O20^{iv}	2.85(3)	O10−O16^{viii}	2.98(2)
O4−O11	2.794(17)	O10−O16	2.82(3)
O4−O13^{i}	2.72(2)	O10−O18	2.80(2)
O5−O8	2.89(2)	O11−O13	2.91(3)
O5−O8^{i}	2.88(2)	O11−O13^{i}	2.852(18)
O5−O10^{i}	2.79(3)	O11−O15^{i}	2.76(3)
O5−O11	2.838(19)	O12−O15	2.78(3)
O5−O16^{i}	2.97(2)	O12−O19^{ix}	2.77(2)
O5−O17	2.80(4)	O13−O15	2.91(3)
O6−O7	2.74(2)	O14−O16	2.78(4)
O6−O12	2.71(3)	O14−O18	2.62(2)
O6−O15	2.76(2)	O14−O19^{x}	2.72(2)
O7−O10	2.93(2)	O16−O18	2.68(2)
O7−O12	2.75(3)	O17−O19	2.93(3)
O7−O13	2.80(3)	O18−O19^{ii}	2.76(3)

Symmetry codes: (i) x, y+1, z; (ii) −x+1, -y+1, −z+1; (iii) −x, -y+3, −z; (iv) −x, −y+2, −z; (v) −x-1, -y+2, −z; (vi) −x−1, −y+1, −z; (vii) x+1, y, z; (viii) x, y−1, z; (ix) x−1, y−1, z; (x) x−1, y, z.

using the software *Jana2006* (Petříček *et al.*, 2006) the full-matrix least-squares methods based on F^2. The structure solution obtained from *Superflip* confirmed the chosen space group $P\bar{1}$. The twin matrix was introduced into the refinement to account for fully overlapped and fully separated reflections. The twin matrix as well as the ratio of particular twin domains are given in Table 2. The U and As atoms were refined with anisotropic displacement parameters. Refinement including 133 parameters converged quickly to the final $R_1 = 0.0594$ for 2718 observed reflections (Table 3). The slightly larger values of the residual difference Fourier electron density (maximal density of 9.9 eÅ^{-3}; the highest peak of the charge of 1.85 e$^-$, 0.07 Å from U1) are probably due to the unresolved twinning features. The final atomic coordinates and the displacement parameters are given in Table 4. Selected interatomic distances are listed in Table 5. The bond-valence analysis was carried out following the procedure of Brown (1981, 2002), using parameters for the U^{4+}–O pair given by Brese and O'Keeffe (1991), and for As^{5+}–O by Brown and Altermatt (1985), and is given in Table 6.

The crystal structure of vysokýite

The structure of vysokýite contains one unique U atom, four As and 19 O atoms in the asymmetric unit. The U atom is coordinated by eight ligands, at an average distance of 2.36 Å (Table 5), forming a slightly distorted tetragonal square antiprism, a very typical coordination polyhedron for U^{4+} in solids (Krivovichev and Plášil, 2013). The U^{4+} ligands are eight O atoms, all of them bridging the central U^{4+} cation and one of the four neighbouring As^{5+} cations. All As^{5+} cations are the central ions of $AsO_2(OH)_2$ units, hence, each As tetrahedron shares two of its apical O atoms with adjacent U polyhedra (Fig. 4*a*). This results in infinite chains (rods) extending along [010] (Fig. 4). Each of the two remaining O atoms of the As tetrahedra are protonated. The attempts to localize and refine hydrogen atoms belonging to these arsenate groups were not successful. There are four independent O atoms (O3, O9, O19, O20) in the interstitial space between the chains, and all of them belong, according to the bond-valence analysis (Table 6), to H_2O groups. These four independent H_2O molecules connect to the

TABLE 6. Bond-valence analysis for vysokýite.

	U	As1	As2	As3	As4	Σ BV	Anion
O1			1.14			1.14	OH
O2		1.23				1.23	OH
O3						0.00	H_2O
O4		1.14				1.14	OH
O5	0.54		1.28			1.82	O
O6					1.11	1.11	OH
O7	0.45				1.48	1.93	O
O8	0.53		1.26			1.79	O
O9						0.00	H_2O
O10	0.54			1.25		1.79	O
O11	0.48	1.34				1.82	O
O12					1.08	1.08	OH
O13	0.57	1.28				1.85	O
O14				1.17		1.17	OH
O15	0.59				1.36	1.95	O
O16	0.40			1.41		1.81	O
O17			1.20			1.20	OH
O18				1.14		1.14	OH
O19						0.00	H_2O
O20						0.00	H_2O
Σ BV	4.10	4.99	4.98	4.97	5.03		

All values are in valence units (vu). U^{4+}–O bond strength from Brese and O'Keeffe (1991), As^{5+}–O bond strengths from Brown and Altermatt (1985).

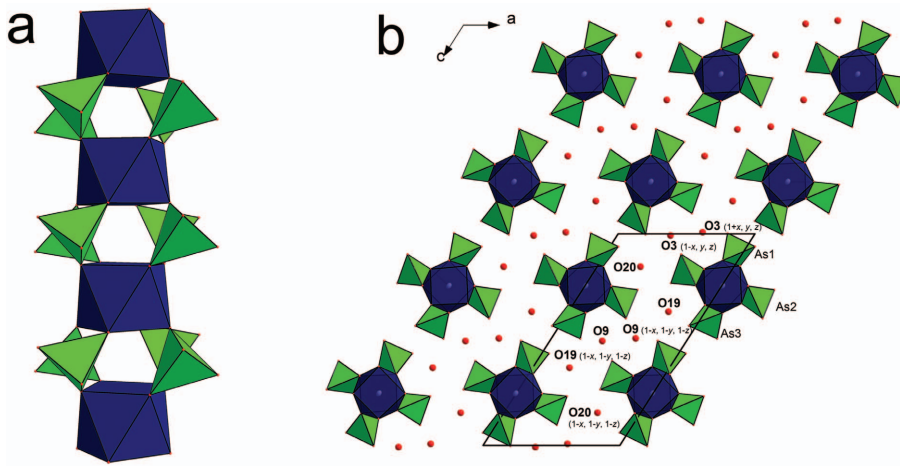

FIG. 4. (*a*) The inter-chain linkage in the structure of vysokýite. The UO_8 polyhedra (blue) are connected by $AsO_2(OH)_2$ groups (green); each arsenate group shares two of its vertices with neighbouring U-polyhedra. (*b*) The structure with infinite chains viewed along [010]. Adjacent chains are linked by the network of H bonds to the H_2O molecules located between them (O3, O9, O19, O20).

infinite chains and to each other only by hydrogen bonds. These H_2O molecules in the structure are transformer groups (Hawthorne and Schindler, 2008), since the central O atoms are [4]-coordinated (donating two bonds to two H atoms plus each receiving two H-bonds from the $AsO_2(OH)_2$ groups) in order to satisfy their bond-valence requirements, $2 \times \sim 0.8$ vu + $2 \times \sim 0.2$ vu = 2 vu (Brown, 1981, 2002; Hawthorne, 1992). The prominent morphological feature – an elongation of the crystals along [010], arises from the infinite polyhedral chains in the structure. The perfect cleavage along (100) and also along (001) is probably due to the weak bonding interactions of the hydrogen bonds (Fig. 4*b*).

The structure of vysokýite is topologically unique. However, a similar chain structure linked together by hydrogen bonds is present in the structure of the acid iron(III) arsenate kaatialaite, $Fe[As(OH)_2]_3(H_2O)_5$ (Raade *et al.*, 1984), which was found in close association with vysokýite at the site studied.

According to the bond-valence analysis (Table 6) and the structure refinement, the structural formula of vysokýite is $U^{4+}[AsO_2(OH)_2]_4(H_2O)_4$, $Z = 2$.

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