Journal of Geosciences, 60 (2015), 259–267 DOI: 10.3190/jgeosci.203

Original paper

Ježekite, $Na_8[(UO_2)(CO_3)_3](SO_4)_2·3H_2O$, a new uranyl mineral from Jáchymov, Czech Republic

Jakub PLÁŠIL[1*], Jan HLOUŠEK[2,†], Anatoly V. KASATKIN[3], Dmitry I. BELAKOVSKIY[3], Jiří ČEJKA[4], Dmitry CHERNYSHOV[5]

[1] *Institute of Physics, Academy of Sciences of the Czech Republic v.v.i, Na Slovance 2, 182 21 Prague 8, Czech Republic; plasil@fzu.cz*
[2] *U Roháčových kasáren 24, 100 00 Prague 10, Czech Republic*
[3] *Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia*
[4] *Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00 Prague 9, Czech Republic*
[5] *Swiss–Norwegian Beamlines at the European Synchrotron Radiation Facility, 38000 Grenoble, France*
[†] *deceased on April 27, 2014*
**Corresponding author*

Ježekite (IMA2014-079), $Na_8[(UO_2)(CO_3)_3](SO_4)_2·3H_2O$, is a new uranyl carbonate-sulfate mineral from Jáchymov, Western Bohemia, Czech Republic. The new mineral was found on samples from the Geschieber vein in the Svornost mine. It occurs as a crystalline crust composed of thin, bladed prismatic crystals of yellow to sulfuric yellow color on a gangue along with andersonite, čejkaite, schröckingerite and ubiquitous gypsum. It is a supergene, low-temperature mineral formed by hydration–oxidation weathering of uraninite associated with post-mining processes. Ježekite is hexagonal, space group $P–62m$, with unit-cell parameters $a = 9.0664(11)$, $c = 6.9110(6)$ Å and $V = 491.97(12)$ Å^3, $Z = 1$. Crystals are thin blades elongated along [001]. Crystals exhibit the forms {001}, {1–11}, {100} and {010}, commonly forming twins/intergrowths with a twin plane parallel to [001]. Ježekite is light yellow to sulfuric yellow and has a very pale yellow streak. It exhibits a bright greenish white fluorescence under both long-wave and short-wave UV. It is transparent with a vitreous to pearly luster. The mineral has a Mohs hardness ~2; it is brittle, with uneven fracture and a perfect cleavage on {001} and along [010]. The calculated density based on the empirical formula is 2.966 g/cm^3. The mineral is optically uniaxial (+), with $\omega = 1.484(2)$ and $\varepsilon = 1.547(2)$ (589 nm). It is non-pleochroic. The chemical composition of ježekite (wt. %, electron-microprobe) is: Na_2O 27.92, SO_3 18.49, UO_3 32.85, CO_2 (calc.) 15.08, H_2O (calc.) 6.17, total 100.51, which yields the empirical formula $Na_{7.88}(UO_2)(CO_3)_3(S_{1.01}O_4)_2·3H_2O$ (based on 22 O *apfu*). Prominent features in the Raman spectrum include the O–H stretching vibrations, symmetric stretching vibrations of $(UO_2)^{2+}$ ions, and stretching and bending vibrations of symmetrically non-equivalent CO_3 groups and highly disordered SO_4 tetrahedra. The eight strongest powder X-ray diffraction lines for ježekite are [d_{obs} Å ($I_{rel.}$) (*hkl*)]: 7.861(59)(100), 6.925(20)(001), 5.193(100)(101), 4.534(44)(110), 3.415(23)(201), 2.751(17)(112), 2.728(20)(211), 2.618(25)(300). The crystal structure of ježekite ($R = 0.043$ for 444 reflections with $I_{obs} > 3\sigma[I]$) contains finite uranyl tricarbonate clusters linked through the Na–O bonds to form sheets of the composition $\{Na_2[(UO_2)(CO_3)_3]\}^{2-}$ parallel to (001). The adjacent sheets of polyhedra are also linked through Na–O bonds to the six Na2 atoms and highly disordered sheets of composition $\{[(SO_4)_2(H_2O)_3]\}^{4-}$ into a sandwich-like structure. The new mineral is named after Professor Bohuslav Ježek (1877–1950), a prominent Czech mineralogist and crystallographer.

Keywords: ježekite, new mineral, uranyl carbonate-sulfate, crystal structure, Jáchymov
Received: 17 September, 2015; accepted: 9 December, 2015; handling editor: J. Sejkora
The online version of this article (doi: 10.3190/jgeosci.203) contains supplementary electronic material.

1. Introduction

Uranyl carbonates are important alteration products of hydration–oxidation weathering of uraninite (Finch and Murakami 1999; Krivovichev and Plášil 2013; Plášil 2014), which are of great environmental importance due to the extensive thermodynamic stability of dissolved uranyl carbonate complexes in the solutions. Therefore, the uranyl carbonate complexes are often responsible for increased mobility of U (as U^{6+}, in the form of the uranyl ion, UO_2^{2+}), in particular under weakly acidic to alkaline conditions (Langmuir 1978). The increased activity of CO_2 in solution is due to dissolution of common gangue carbonates or from atmospheric CO_2 in descending/meteoric waters. Uranyl carbonates most frequently occur as efflorescence on mine walls, adits and tunnels, as characteristic minerals formed as recent or sub-recent phases due to post-mining weathering (Plášil 2014 and references therein). However, also "old" *in-situ* formed uranyl carbonates are known as constituents of massive aggregates of uranyl minerals called *gummites* (Plášil et al. 2006, 2010). Similarly, several well-known uranyl

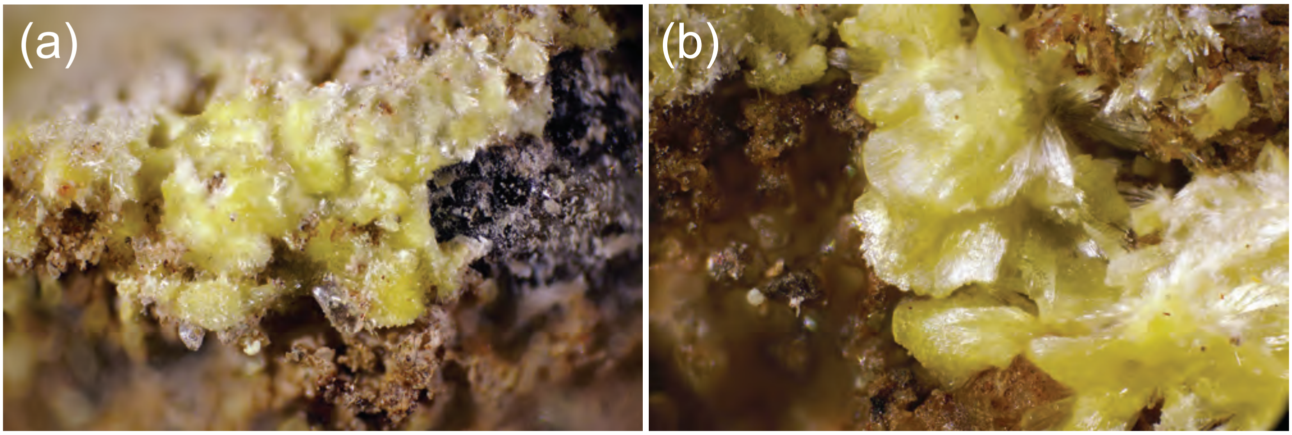

Fig. 1 Ježekite from Jáchymov. **a** – Typical massive crystalline crust on weathered gangue. Width of image is 4 mm. **b** – Detailed view of crystalline aggregates composed of thin, long hexagonal crystals. Width of image is 2.5 mm. (Both photographs by P. Škácha).

carbonates from U deposits of Democratic Republic of Congo such as wyartite, sharpite and roubaultite are most probably also of supergene *in-situ* (old) weathering origin, being associated with alteration of the U ore-bodies in the geological past.

Here we report on ježekite (pronounced 'ye zhe kait'; Cyrillic – ежекит), which is a new uranyl carbonate-sulfate mineral from Jáchymov (Joachimsthal), Czech Republic. The new mineral and name were approved by the Commission on the New Minerals, Names and Classification of the International Mineralogical Association (IMA2014-079). The new mineral is named after Professor Bohuslav Ježek (1877–1950), Czech crystallographer and mineralogist, professor of both Charles University in Prague and Technical University of Mining in Příbram. Bohuslav Ježek was a student of Professor Karel Vrba at the former Karl-Ferdinand University in Prague (later Charles University), after whom vrbaite is named (Ježek 1912). Professor Ježek obtained *venium-docendi* at the Charles University and started, for the first time in Czechia, experimenting with the diffraction of X-rays on crystals together with Dr. Karel Teige. They also began teaching crystallography at the University in 1922. Later, Professor Ježek moved on to the Technical University of Mining in Příbram, where he was appointed as a regular Professor of Mineralogy. Besides exceptional lecture texts and books (used by students long after his death), Professor Ježek translated Agricola's classical work "Twelve Books on Mining" from Latin to Czech (in 1933). Among his mineralogical works, a paper on johannite from Jáchymov (Ježek 1916) is of particular interest. It is noted that in 1914 another Czech mineralogist, Prof. František Slavík, had already named a phosphate from Greifenstein, Germany (Slavík 1914a, b) after Bohuslav Ježek. However, further analyses showed that "ježekite" of Slavík was the same as Na-rich morinite and, thus, the former mineral was discredited (Fischer 1962). Since more than fifty years have passed after that discrediting, re-use of the same name is allowed by CNMNC in accordance with its current rules (Nickel and Grice 1998).

The holotype specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, under the catalogue number 94620.

2. Occurrence

Ježekite was found on two specimens only collected during the 1990's by one of the authors (JH) at the Geschieber vein of the Svornost mine, Jáchymov, western Bohemia, Czech Republic. Unfortunately, there are no labels specifying the exact place where these specimens were collected. According to the mineral assemblage of these samples, we only infer that they came from the 10th level of the mine. A description of the locality of Jáchymov and its geological setting has been already given in detail elsewhere (e.g., Ondruš et al. 1997, 2003; Tvrdý and Plášil 2010; Hloušek et al. 2014). The Jáchymov ore district is a classic example of the Variscan hydrothermal vein type of deposit, the so-called "five-elements formation", Ag–Bi–Co–Ni–U. Jáchymov is the type locality for 45 minerals and more than 430 others have been identified there.

Minerals found in direct spatial association with ježekite include Na-rich uranyl carbonates: andersonite, čejkaite, schröckingerite and also natrozippeite. Minerals putty several fragments covering the footwall of an old mining adit. They are of supergene origin and formed due to alteration during post-mining processes.

3. Physical and optical properties

Ježekite forms markedly thin, fine, bladed to acicular crystals up to 0.2 mm long, tightly packed in isolated aggregates up to 0.5 mm across (Fig. 1) and/or massive veinlets consisting of these crystals. They were commonly found to be curved by torsion. Crystal forms {001},{1–11},{100},{010} were observed on crystals elongated on [001]. Common twinning is on (001) plane. Ježekite is pale to sulfur yellow in crystals and intensive sulfur yellow in larger aggregates with a pale yellow streak. Crystals are transparent with a vitreous to pearly luster. They are brittle, with a perfect cleavage on (001) and a good cleavage along (100), and have uneven fracture. The Mohs hardness is estimated at ~2. A density of 2.966 g/cm^3 was calculated using the empirical formula and unit-cell dimensions from single-crystal X-ray data. Ježekite shows bright greenish white fluorescence under both long- and short-wave UV; however, it is stronger under short-wave UV. The new mineral is optically uniaxial positive, with ω = 1.484(2) and ε = 1.547(2) (589 nm). It is non-pleochroic; however, it shows some pseudo-absorption effects due to the high birefringence. The elongation direction of the acicular crystals is negative; extinction is straight. The Gladstone-Dale compatibility, $1 - (K_p/K_c)$, is fair (0.069) for the empirical formula and the single-crystal unit-cell.

4. Chemical composition

The chemical composition of ježekite was determined using a CamScan4D scanning electron microscope (SEM) equipped with an Oxford Link ISIS energy-dispersive X-ray spectrometer. An operating voltage of 15 kV was used for the analysis with a beam current of 500 pA and a beam rasterizing area of 8 × 8 µm, since ježekite was found to be extremely unstable under the electron beam due to the presence of components that are volatilized readily (Na as well as CO_3 and H_2O). The molecular H_2O content was not determined directly, because of the paucity of pure material available for thermal analysis. The H_2O content was calculated from the stoichiometry in turn obtained from the structure model. The presence of H_2O was confirmed independently by Raman spectroscopy.

The empirical formula of ježekite, calculated as a mean of nine representative spot analyses (Tab. 1), is $Na_{7.88}[(UO_2)(CO_3)_3](S_{1.01}O_4)_2 \cdot 3H_2O$ (based on 22 O *apfu*). The simplified formula, $Na_8[(UO_2)(CO_3)_3](SO_4)_2 \cdot 3H_2O$, requires Na_2O 28.15, CO_2 14.98, SO_3 18.22, UO_3 32.51, H_2O 6.14, total 100 wt. %.

Tab. 1 Results of chemical analyses (in wt. %) of ježekite

	Mean (*n* = 9)	Range	SD	Standard
Na_2O	27.92	27.12–28.46	0.49	Albite
SO_3	18.49	17.62–19.47	0.59	$BaSO_4$ (synth.)
UO_3	32.85	32.38–33.63	0.44	UO_2 (synth.)
CO_2	15.08*			
H_2O	6.17*			
total	100.51			

* calculated from the structure
SD – standard deviation

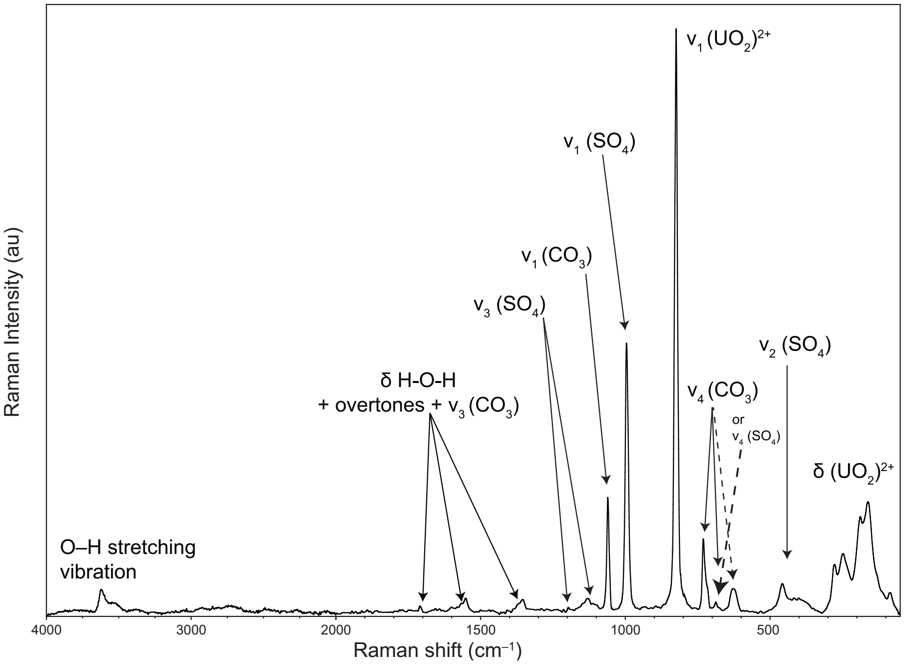

Fig. 2 The Raman spectrum of ježekite.

Ježekite is slightly soluble in a cold H_2O and readily soluble in 10% HCl acid.

5. Raman spectroscopy

A Raman spectrum of ježekite (Fig. 2) was collected in the range 50–4000 cm^{-1} using a DXR dispersive Raman spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope (100× objective). The Raman signal was excited by a 532 nm diode-pumped solid-state laser and detected by a CCD detector. The experimental parameters were: 5 s exposure time, 32 exposures, 400 lines/mm grating, 50 mm slit spectrograph aperture and 2.5 mW laser power level. The instrument was set up by a software-controlled calibration using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white-light sources (intensity calibration).

Spectral bands at 3620 and 3380 cm^{-1} are attributed to ν O–H vibrations of symmetrically non-equivalent H_2O molecules. According to the correlation published by Libowitzky (1999), the O–H···O hydrogen bond lengths vary between 3.20 and 2.90 Å. Bands at 2740 and 1710 cm^{-1} may be related to the overtones or combination bands. Bands at 1656 and 1600 cm^{-1} were assigned to the ν_2 (δ) bending vibrations of structurally non-equivalent H_2O molecules. Very weak bands in the region from 1300 to 1600 cm^{-1} are, however, related to the split doubly degenerate ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations. Bands at 1195, 1130 and 1110 cm^{-1} are attributed to the triply degenerate ν_3 (SO_4) antisymmetric stretching vibrations, and two bands at 1060 and 1050 cm^{-1} to the ν_1 (CO_3) symmetric stretching vibrations. According to Jolivet et al. (1980), the magnitude of the splitting of the doubly degenerate ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibrations (1550, 1375, 1355 cm^{-1}) supports conclusions of the X-ray crystal structure analysis: the carbonate planar groups are linked bidentately in the equatorial plane of the uranyl hexagonal bipyramids. A band at 996 cm^{-1} is attributed to the ν_1 (SO_4) symmetric stretching vibration. A very weak band at 896 cm^{-1} may be connected with the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration and the very intense band at 825 cm^{-1} to the ν_1 $(UO_2)^{2+}$ symmetric stretching mode. Anyway, the possibility of coincidence of the bands related to the ν_1 $(UO_2)^{2+}$ and the ν_2 (CO_3) cannot be excluded. According to the empirical relation given by Bartlett and Cooney (1989), the U–O bond lengths in the uranyl ion, inferred from the stretching wavenumbers of the ν_1 and ν_3 bands are approximately ~1.79 Å. The weak bands at 731 and 715 cm^{-1} are assigned to the ν_4 (δ) doubly degenerate (CO_3) in-plane bending vibrations. Bands at 688, 629 and 622 cm^{-1} are attributed to the triply degenerate ν_4 (δ) (SO_4) bending vibrations. Bands at 458 and 379 cm^{-1} may be connected with the doubly degenerate ν_2 (δ) (SO_4) bending vibrations, while those at 277 and 248 are due to the doubly degenerate ν_2 (δ) $(UO_2)^{2+}$ bending vibrations. The remaining bands at 188, 161 and 85 cm^{-1} may be assigned to ν $(U–O_{ligand})$ stretching and δ $(O_{ligand}UO_{ligand})$ and δ (OUO_{ligand}) bending vibrations (Volod'ko et al. 1981).

Tab. 2 Powder diffraction data for ježekite

$I_{rel.}$	$d_{obs.}$	$d_{calc.}$	I_{calc}	*h*	*k*	*l*	$I_{rel.}$	$d_{obs.}$	$d_{calc.}$	I_{calc}	*h*	*k*	*l*
59	7.861	7.857	40	1	0	0	3	1.7147	1.7145	5	4	1	0
20	6.925	6.918	26	0	0	1	3	1.7089	1.7080	2	4	0	2
100	5.193	5.192	100	1	0	1	1	1.6897	1.6891	3	1	0	4
44	4.534	4.536	40	1	1	0	2	1.6644	1.6641	4	4	1	1
14	3.926	3.928	14	2	0	0	3	1.6173	1.6170	6	2	2	3
12	3.792	3.793	12	1	1	1	2	1.5989	1.5985	5	3	2	2
11	3.460	3.459	18	0	0	2	2	1.5841	1.5838	4	3	1	3
23	3.415	3.416	27	2	0	1	1	1.5712	1.5713	1	5	0	0
8	3.166	3.166	12	1	0	2	2	1.5362	1.5361	3	4	1	2
12	2.968	2.970	10	2	1	0	2	1.5324	1.5323	2	5	0	1
17	2.751	2.751	21	1	1	2	1	1.5119	1.5120	2	3	3	0
20	2.728	2.729	28	2	1	1	2	1.4949	1.4945	4	2	1	4
25	2.618	2.619	23	3	0	0	1	1.4847	1.4848	1	4	2	0
3	2.596	2.596	4	2	0	2	1	1.4772	1.4772	2	3	3	1
7	2.449	2.449	10	3	0	1	1	1.4521	1.4517	4	4	2	1
2	2.305	2.306	3	0	0	3	2	1.4438	1.4432	3	3	0	4
13	2.269	2.268	17	2	2	0	1	1.4205	1.4201	3	3	2	3
5	2.254	2.253	8	2	1	2	1	1.4108	1.4111	2	5	1	0
3	2.213	2.213	8	1	0	3	1	1.3855	1.3855	1	3	3	2
4	2.177	2.179	6	3	1	0	1	1.3828	1.3826	2	5	1	1
8	2.153	2.155	12	2	2	1	2	1.3760	1.3753	4	2	2	4
1	2.088	2.088	2	3	0	2	1	1.3646	1.3644	2	4	2	2
8	2.080	2.078	12	3	1	1	1	1.3614	1.3627	2	1	0	5
3	2.056	2.056	6	1	1	3	1	1.3552	1.3547	3	3	1	4
2	1.9895	1.9887	5	2	0	3	1	1.3099	1.3095	2	6	0	0
1	1.9647	1.9642	2	4	0	0	1	1.3064	1.3066	2	5	1	2
8	1.8973	1.8967	12	2	2	2	1	1.2984	1.2985	1	5	0	3
2	1.8841	1.8895	5	4	0	1	1	1.2863	1.2866	2	6	0	1
5	1.8440	1.8437	8	3	1	2	1	1.2697	1.2697	2	4	3	1
2	1.8220	1.8214	7	2	1	3	2	1.2479	1.2480	3	3	2	4
4	1.8026	1.8025	6	3	2	0	1	1.2376	1.2378	2	5	2	1
4	1.7444	1.7442	8	3	2	1	1	1.2245	1.2246	1	6	0	2
5	1.7310	1.7307	5	3	0	3	1	1.2179	1.2176	2	4	1	4
5	1.7283	1.7296	4	0	0	4							

d values quoted in Å

6. X-ray crystallography and structure determination

6.1. Powder diffraction

X-ray powder diffraction data (Tab. 2) were obtained from a hand-picked sample using a PANalytical Empyrean diffractometer equipped with a PIXcel^{3D} detector using CuK_α radiation (45 kV, 40 mA) and operating in Debye–Scherrer geometry provided by focusing Göbel mirror optics. Data were collected in the range 3–70° 2θ, with a step size of 0.01° and counting time of 2 s per step, using an accumulation of 40 scans to improve the intensity statistics. Positions and intensities of diffraction profiles were refined using a pseudo-Voigt shape function with the High-Score program (PANalytical, Almelo, B.V.). Unit-cell parameters were refined by least-squares with the Celref program (Laugier and Bochu 2003). The theoretical pattern, used for indexing the experimental dataset, was calculated from the structure data using PowderCell (Kraus and Nolze 1996). Refined unit-cell parameters of ježekite obtained from powder data are $a = 9.072(2)$, $c = 6.9182(1)$ Å, with $V = 493.1(1)$ Å^3 and $Z = 1$.

Tab. 3 Crystallographic data and refinement details for ježekite

Crystal data		
Formula	$Na_8[(UO_2)(CO_3)_3](SO_4)_2(H_2O)_3$	
Crystal system	hexagonal	
Space group	$P\bar{6}2m$	
Unit-cell parameters: a, c [Å]	9.0664(12), 6.9110(6)	9.08022(7), 6.92071(16)
Unit-cell volume [Å^3]	491.97(10)	494.168(12)
Z	1	
Calculated density [g/cm^3]	2.971	
Crystal size [mm]	0.10 × 0.03 × 0.02	
Data collection		
Diffractometer	Oxford Diffraction Gemini with Atlas detector	PILATUS@SNBL diffractometer, BM01A ESRF, Pilatus 2D detector
Temperature [K]	302	300
Radiation, wavelength [Å]	MoK_α, 0.71073 (50 kV, 30 mA)	Synchrotron, 0.68884
θ range for data collection [°]	2.95−29.18	2.51–31.37
Limiting Miller indices	$h = -11 \rightarrow 10$, $k = -12 \rightarrow 11$, $l = -8 \rightarrow 9$	$h = -13 \rightarrow 13$, $k = -13 \rightarrow 13$, $l = -6 \rightarrow 6$
Axis, frame width (°), time per frame (s)	ω, 0.9, 310	Φ, 1, 1
Total reflections collected	3392	4551
Unique reflections	444	539
Unique observed reflections, criterion	420, [$I > 3\sigma(I)$]	539, [$I > 3\sigma(I)$]
Absorption coefficient [mm^{-1}], type	8.75; Gaussian	8.75/multi-scan
T_{min}/T_{max}	0.526/15.533	0.898/1
R_{int}	0.116	0.046
F_{000}	406	395
Structure refinement by Jana2006	Full-matrix least-squares on F^2	
No. of ref. param., restraints, constraints	38, 0, 0	33, 0, 0
R, wR (obs)	0.0426, 0.0832	0.0431, 0.1051
R, wR (all)	0.0454, 0.0846	0.0431, 0.1051
GOF obs/all	1.43, 1.41	2.43, 2.43
Weighting scheme, weights	σ, $w = 1/(\sigma^2(I)+0.0004I^2)$	σ, $w = 1/(\sigma^2(I)+0.0016I^2)$
Largest diff. peak and hole (e$^-$/Å^3)	–1.37, 1.46	–3.18/4.31

6.2. Single-crystal X-ray diffraction and structure solution

A prismatic crystal of ježekite, with dimensions 0.10 × 0.03 × 0.02 mm, was selected under the microscope and examined using an Oxford Diffraction Gemini single-crystal diffractometer with an Atlas CCD detector using monochromatized MoK_α radiation, with a fibre-optic Mo-Enhance collimator. According to single-crystal X-ray data, ježekite is hexagonal with $a = 9.0664(11)$, $c = 6.9110(6)$ Å, $V = 491.97(12)$ Å^3 and $Z = 1$. Of the 3392 collected reflections, 444 were unique and 404 were classified as observed based on the criterion [$I_{obs} > 3\sigma(I)$]. Data were corrected for the Lorentz effect, polarization factor and background; also Gaussian correction for absorption was applied in Jana2006 program (Petříček et al. 2014). In order to obtain a better dataset, the same crystal was investigated at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) at room temperature using the PILATUS@SNBL diffractometer at the BM01A end station of the Swiss–Norwegian Beamlines; the wavelength of the synchrotron radiation was set to 0.70135 Å. The data were collected with a single Φ scan with an angular step of 0.1° in a shutter-free mode with the Pilatus2M detector. The raw data were pre-processed with SNBL TOOLBOX and the integral intensities were extracted from the frames with the CrysAlisPro software (Rigaku). However, the dataset provided results very similar to the laboratory data in terms of the refined structure and the indices of agreement. The dataset from ESRF, with better intensity statistics, clearly demonstrated that the crystal investigated is a multi-domain split crystal. Nevertheless, introduction of a split crystal (modelled as a non-crystallographic rotational twin) into the refinement did not lead either to a substantial improvement of the fit or a more acceptable model. The data were checked for twinning by merohedry or pseudomerohedry (reticular), but again the fit did not provide reasonable results (negative values of twin fractions etc.). Due to the similar results provided by both datasets we decided to base our interpretation and discussion of the structure on the results from the laboratory diffractometer. The details of the data collection and refinement for both datasets are given in Tab. 3.

The crystal structure of ježekite was solved by the charge-flipping algorithm implemented in the Superflip program (Palatinus and Chapuis 2007) and subsequently refined using the software Jana2006 (Petříček et al. 2006,

Tab. 4 Atom coordinates, displacement parameters and bond-valence sums for the crystal structure of ježekite

Atom	*Occ.*	*BV*	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso} (Å^2)	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}
U1		6.02(7)	0	0	0.5	0.0204(2)	0.0115(3)	0.0115(3)	0.0106(5)	0.00574(17)	0
Na1		1.00(2)	0.666667	0.333333	0.5	0.0221(18)	0.097(5)	0.097(5)	0.010(5)	0.048(2)	0
Na2		0.81(1)	–0.3631(8)	0	0.7532(13)	0.022(3)	0.083(4)	0.248(13)	0.016(5)	0.124(7)	0.000(3)
C1		4.1(1)	0	0.3173(18)	0.5	0.026(4)	0.034(10)	0.016(6)	0.010(11)	0.017(5)	0
S1	0.333	6.3(2)	0.6736(9)	0.4041(9)	0	0.0228(15)					
O1		2.42(4)	0.666667	0.333333	0.176(2)	0.048(2)					
O2		2.08(5)	–0.1394(15)	0.1730(16)	0.5	0.090(8)					
O3		1.64(4)	0	0	0.2404(19)	0.031(4)					
O4		1.97(8)	0	0.4556(12)	0.5	0.085(7)					
O5	0.5	1.24(4)	0.599(3)	0.494(3)	0	0.023(3)					
O6	0.5	0.244(4)	0.819(3)	0.700(3)	0	0.030(4)					
O7	0.1667	1.92(6)	0.814(3)	0.532(3)	0	0.022(3)					

Occ. – occupancy; BV – bond-valence sum (in *vu*)

2014) with the full-matrix least-squares refinement based on F^2. Superflip output suggested a solution in the hexagonal highest space-group $P6/mmm$. However, the structure has lower symmetry, $P\overline{6}2m$, as documented by the refinement; even though the real symmetry can be lower still (see below). The hexagonal symmetry is consistent with the point group of the sub-lattice in ježekite, represented by the U and Na atoms in the structure. We note that the ježekite structure as presented here is an average one, containing highly positionally and occupationally disordered SO_4 groups in the interlayer. Nevertheless, a structure refinement in lower symmetry space groups did not lead to any improvement in the fit to the data. Therefore, we decided to present the model with the disordered SO_4, since refined values for all other atoms turned out to make physical sense. We also note that the diffraction intensities are affected 1) by the dominant contributions from the U atoms and 2) the presence of rotational twin domains from the split crystal.

The heavy atoms were found in the structure solution readily and the lighter ones were localized by the difference Fourier syntheses. An attempt to use the rigid-body approach for the refinement of the disordered (SO_4) led to significantly worse results than a simple less-constrained refinement. The refinement converged with the final indices of agreement R = 0.0426 and wR = 0.0832 for 420 observed reflections with GOF = 1.43 (Tab. 3). The atom coordinates, the displacement parameters and bond-valence sums are given in Tab. 4 and selected interatomic distances in Tab. 5. The bond-valence sums were calculated according to Brown (2002), using bond-valence parameters of Burns et al. (1997) and Brown and Altermatt (1985).

6.3. Description of the crystal structure

The single U site in the structure of ježekite is surrounded by eight O atom sites forming a squat hexagonal bipyra-

Tab. 5 Selected interatomic distances (Å) in the structure of ježekite

U1–O2	2.458(17)	S1–O1	1.361(15)
U1–O2^{i}	2.458(16)	S1–O1^{xi}	1.361(15)
U1–O2^{ii}	2.458(18)	S1–O5	1.29(3)
U1–O2^{iii}	2.458(17)	S1–O7	1.22(6)
U1–O2^{iv}	2.458(16)	<S1–O>	1.31
U1–O2^{v}	2.458(18)		
U1–O3	1.794(13)	C1–O2	1.287(13)
U1–O3^{vi}	1.794(13)	C1–O2^{v}	1.287(13)
<U–O$_{Ur}$>	1.794	C1–O4	1.25(2)
<U–O$_{eq}$>	2.458	<C1–O>	1.28
Na1–O1	2.240(17)	Na2–O2	2.541(10)
Na1–O1^{vi}	2.240(17)	Na2–O2^{vi}	2.541(10)
Na1–O2^{vii}	2.786(17)	Na2–O4^{xxi}	2.401(11)
Na1–O2^{viii}	2.786(18)	Na2–O5^{xxii}	2.52(3)
Na1–O2^{ii}	2.786(16)	Na2–O5^{v}	2.522(18)
Na1–O4^{vii}	2.6481(19)	Na2–O6^{xxiii}	2.62(2)
Na1–O4^{viii}	2.648(13)	Na2–O6^{xxiv}	2.62(3)
Na1–O4^{ii}	2.648(13)	Na2–O7^{xxiii}	2.249(19)
<Na1–O>	2.59	Na2–O7^{xxiv}	2.249(17)
		<Na2–O>	2.47
O1–O1^{xi}	2.43(2)	O3–O6^{xix}	2.90(2)
O1–O5	2.21(3)	O3–O6^{xx}	2.90(3)
O1–O5^{ix}	2.21(2)	O5–O5^{xii}	1.65(4)
O1–O5^{x}	2.21(3)	O5–O6	1.93(3)
O1–O7	2.02(2)	O5–O6^{xii}	2.61(4)
O1–O7^{ix}	2.02(3)	O5–O7	1.80(4)
O1–O7^{x}	2.02(3)	O5–O7^{ix}	1.68(4)
O2–O2^{iv}	2.717(18)	O5–O7^{xix}	2.76(5)
O2–O2^{v}	2.189(16)	O6–O6^{xii}	1.88(5)
O2–O4	2.218(16)	O6–O6^{xxv}	2.84(3)
O3–O6^{xvi}	2.898(18)	O6–O7	1.50(4)
O3–O6^{ix}	2.90(2)	O7–O7^{ix}	2.80(3)
O3–O6^{xvii}	2.90(3)	O7–O7^{x}	2.80(4)
O3–O6^{xviii}	2.898(18)	O7–O7^{xxv}	2.92(4)

Symmetry codes: (i) *–y*, *x–y*, *z*; (ii) *–x+y*, *–x*, *z*; (iii) *y*, *x*, *–z*+1; (iv) *x–y*, *–y*, *–z*+1; (v) *–x*, *–x+y*, *–z*+1; (vi) *x*, *y*, *–z*+1; (vii) *x*+1, *y*, *z*; (viii) *–y*+1, *x–y*+1, *z*; (ix) *–y*+1, *x–y*, *z*; (x) *–x+y*+1, *–x*+1, *z*; (xi) *x*, *y*, *–z*; (xii) *y*, *x*, *–z*; (xiii) *x*+1, *y*, *–z*+1; (xiv) *–y*+1, *x–y*+1, *–z*+1; (xv) *–x+y*, *–x*, *–z*+1; (xvi) *x*–1, *y*–1, *z*; (xvii) *–x+y*, *–x*+1, *z*; (xviii) *y*–1, *x*–1, *–z*; (xix) *x–y*, *–y*+1, *–z*; (xx) *–x*+1, *–x+y*, *–z*; (xxi) *–x+y*–1, *–x*, *z*; (xxii) *–y*, *x–y*, *z*+1; (xxiii) *–x+y*, *–x*+1, *z*+1; (xxiv) *y*–1, *x*–1, *–z*+1; (xxv) *–x*+2, *–x+y*+1, *–z*.

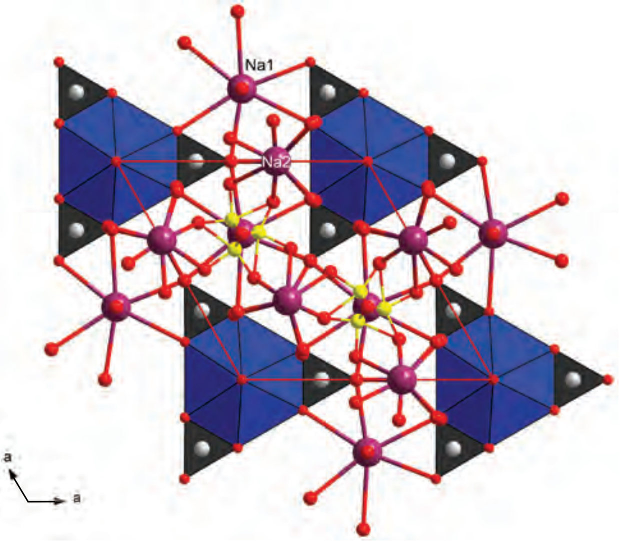

Fig. 3 The structure of ježekite viewed down [001]. The unit cell is shown by red solid lines. The UO_8 hexagonal bipyramids are blue, CO_3 planar groups chelating UO_8 are black. Sodium atoms are violet, S atoms yellow, O atoms shown as small red spheres.

mid. This is one of the typical coordinations for U^{6+} in the solid state in which the two short apical bonds of the bipyramid constitute the uranyl, UO_2^{2+} ion. Observed bond lengths for the polyhedra (Tab. 5) are consistent with those most frequently observed for [8]-coordinated U^{6+} (Burns et al. 1997). The uranyl bipyramid is chelated by three planar CO_3 groups (one symmetrically unique C site) forming a typical uranyl tricarbonate cluster (UTC) $[(UO_2)(CO_3)_3]^{4-}$. These clusters are linked to the Na1 atoms, occupying 2*d* sites, to form sheets of composition $\{Na_2[(UO_2)(CO_3)_3]\}^{2-}$. The Na1 site is [8]-coordinated by six O atoms within the sheet and two O atoms that are the vertices of the disordered SO_4 tetrahedron. The coordination environment around the second Na site (Na2) in the structure is much more complicated. The Na2 site is [9]-coordinated, but some of these nine bonds belong to occupationally disordered O atoms (of the SO_4 group) and one O atom (O6) clearly belongs to an H_2O group, according to the bond-valence analysis (Tab. 3). This H_2O is an inverse-transformer group with a [4]-coordinated O atom, with it linked to two Na atoms and two hydrogen atoms (the H atoms are not present in the current structure model). There are three positionally disordered SO_4 groups in the structure (generated by the six-fold axis). The coordination environment of these SO_4 groups is quite complicated and is displayed in Fig. 3; in an average structure they are represented by three mutually exclusive positions. The structure of ježekite can be viewed as a three-storey sandwich-like structure (Fig. 4) with firm, ordered $\{Na_2[(UO_2)(CO_3)_3]\}^{2-}$ sheets, an alternating interlayer with six $(Na2)^+$ ions plus highly disordered sheets of composition $\{[(SO_4)_2(H_2O)_3]\}^{4-}$. The structural formula of ježekite obtained from the refinement is $Na_8[(UO_2)(CO_3)_3](SO_4)_2(H_2O)_3$, $Z = 1$.

7. Discussion

7.1. Structure topology, structure relations

The structure of ježekite is unique, but there are several similarities to other known uranyl minerals and compounds. There is only one known uranyl tricarbonate

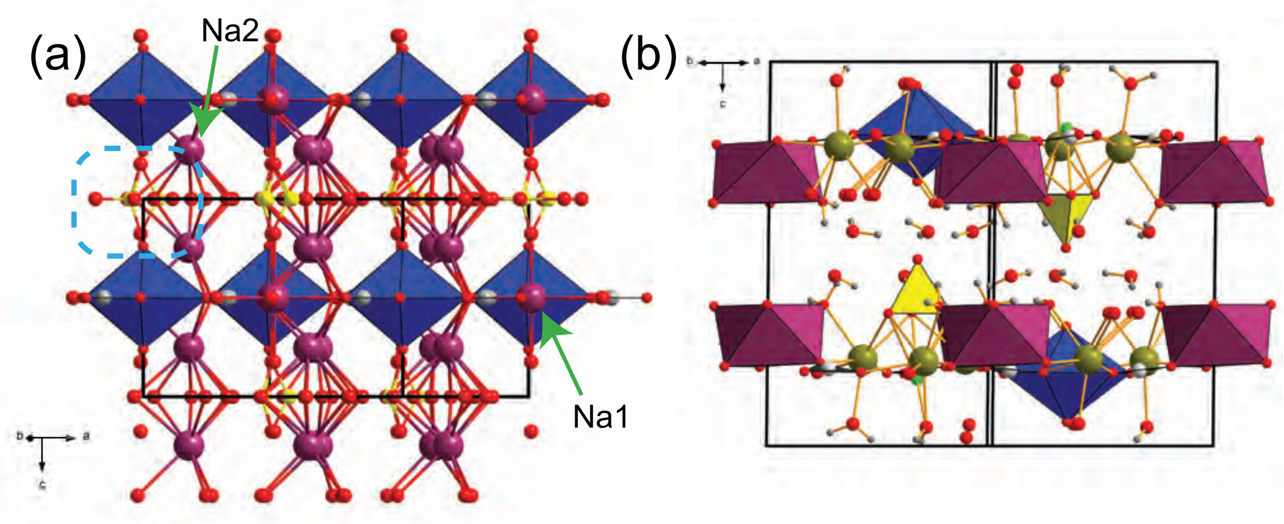

Fig. 4 a – The sandwich-like structure of ježekite (left) viewed perpendicular to [001]. The unit cell is shown by black solid lines. The sheets of UO_8 bipyramids and Na1-polyhedra alternate with an interstitial layer containing disordered SO_4 groups and Na2-polyhedra. The stacking sequence corresponds to the unit-cell parameter **c**. **b –** The structure of schröckingerite (Mereiter 1986) showing linkage of SO_4 groups. UO_8 bipyramids are blue, NaO_6 polyhedra are violet, Ca atoms are displayed in green. In schröckingerite the interstitial complex consists of H-bonded H_2O groups only.

mineral containing $(SO_4)^{2-}$ anions in the crystal structure, schröckingerite (Mereiter 1986). The way how the sulfate tetrahedron is linked in the structure differs from that in ježekite. In the structure of schröckingerite, the SO_4 tetrahedron is shared between three Ca atoms within the structural sheet, with one non-bridging vertex staggered towards the interlayer (Fig. 4). Interestingly, the structure of ježekite is somewhat related to that of synthetic trigonal $Na_4[(UO_2)(CO_3)_3]$ (Císařová et al. 2001; Li et al. 2001), in terms of the unit cell metrics. This compound is a dimorph of monoclinic čejkaite (Plášil et al. 2013) and has not been found in Nature. Hexagonal ježekite has an **a** parameter that is similar to the synthetic compound and also to schröckingerite, and a halved **c** parameter. The latter, which represents the stacking of the layers in the structure, is very close to the stacking in čejkaite, but the two structures are essentially different. The columnar stacking of NaO_x (most commonly $x = 6$) polyhedra is, however, a well-known feature from the structures of Na-containing uranyl carbonates (Císařová et al. 2001; Li et al. 2001; Li and Burns 2001; Plášil et al. 2012, 2013).

7.2. Note on occurrence

Uranyl carbonates that contain alkali metals such as Na^+ or K^+ are fairly common in Jáchymov, occurring in various places, where the appropriate conditions occur. Their origins have been connected with post-mining weathering processes in the old mining adits with stable humidity and temperature. The most common Na^+-bearing uranyl carbonate mineral in Jáchymov is schröckingerite, $NaCa_3[(UO_2)(CO_3)_3](SO_4)F(H_2O)_{10}$ (Ondruš et al. 1997; Mereiter 1986), which also contains S^{6+} in the structure, as ježekite does. However, ježekite is by far rarer, most probably due to the very high molar proportion of the Na^+ in the structure.

Acknowledgements. We appreciate kind cooperation of Pavel Škácha, who provided microphotographs of ježekite. We thank Ivan Němec (Faculty of Science, Charles University in Prague) for providing us access to the Raman microspectrometer. We thank Martin Števko and an anonymous referee for their comments that greatly helped improving the manuscript. This research was financially supported by the post-doctoral grant of the GAČR no. 13-31276P to JP and by the long-term project DKRVO 2015-02 of the Ministry of Culture of the Czech Republic (National Museum 00023272) to J.Č.

Electronic supplementary material. Supplementary crystallographic data for this paper are available online at the Journal web site (*http://dx.doi.org/10.3190/jgeosci.203*).

References

Bartlett JR, Cooney RP (1989) On the determination of uranium–oxygen bond lengths in dioxouranium(VI) compounds by Raman spectroscopy. J Mol Struct 193: 295–300

Brown ID (2002) The Chemical Bond in Inorganic Chemistry. International Union of Crystallography Monographs on Crystallography 12. Oxford University Press, Oxford, pp 1–292

Brown ID, Altermatt D (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Cryst B41: 244–248

Burns PC, Ewing RC, Hawthorne FC (1997) The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. Canad Mineral 35: 1551–1570

Císařová I, Skála R, Ondruš P, Drábek M (2001) Trigonal $Na_4[UO_2(CO_3)_3]$. Acta Cryst E57: i32–i34

Finch RJ, Murakami T (1999) Systematics and paragenesis of uranium minerals. In: Burns PC, Finch RJ (eds) Uranium: Mineralogy, Geochemistry and the Environment. Mineralogical Society of America and Geochemical Society Reviews in Mineralogy and Geochemistry 38, Washington, pp 91–179

Fischer DJ (1962) Ježekite is morinite. Amer Miner 47: 398–400

Hloušek J, Plášil J, Sejkora J, Škácha P (2014) News and new minerals from Jáchymov, Czech Republic (2003–2014). Bull mineral-petrolog Odd Nár Muz (Praha) 22: 155–181

Ježek B (1912) Vrbait, ein neues Thalliummineral von Allchar in Macedonien. Z Krystall Miner 51: 365–378

Ježek B (1916) Über den Johannit von Joachimsthal. Acad Sci Empereur Francois Joseph Bull, internat, Cl sci math nat 200: 358–376

Jolivet JP, Thomas Y, Taravel B (1980) Vibrational study of coordinated CO_3^{2-} ions. J Mol Struct 60: 93–98

Kraus W, Nolze G (1996) POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J Appl Cryst 29: 301–303

Krivovichev SV, Plášil J (2013) Mineralogy and crystallography of uranium. In: Burns PC, Sigmon GE (eds) Uranium: From Cradle to Grave. Mineralogical Association of Canada Short Courses 43: pp 15–119

Langmuir D (1978) Uranium solution–mineral equilibria at low temperatures with applications to sedimentary ore. Geochim Cosmochim Acta 42: 547–569

Laugier J, Bochu B (2003) CELREF: Unit Cell Refinement Program from Powder Diffraction Diagram. Laboratoires des Matériaux et du Génie Physique, Ecole Nationale Supérieure de Physique de Grenoble (INPG), Grenoble, France. Accessed on September

15, 2014, at *http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/*

Li Y, Burns PC (2001) The crystal structure of synthetic grimselite, $K_3Na[(UO_2)(CO_3)_3](H_2O)$. Canad Mineral 39: 1147–1151

Li Y, Krivovichev SV, Burns PC (2001) The crystal structure of $Na_4(UO_2)(CO_3)_3$ and its relationship to schröckingerite. Mineral Mag 65: 297–304

Libowitzky E (1999) Correlation of O–H stretching frequencies and O–H…O hydrogen bond lengths in minerals. Monatsh Chem 130: 1047–1059

Mereiter K (1986) Crystal structure and crystallographic properties of a schröckingerite from Joachimsthal. Tschermaks Mineral Petrogr Mitt 35: 1–18

Nickel EH, Grice JD (1998) The IMA Commission on New Minerals and Mineral Names: procedures and guidelines on mineral nomenclature, 1998. Canad Mineral 36: 913–926

Ondruš P, Veselovský F, Hloušek J, Skála R, Vavřín I, Frýda J, Čejka J, Gabašová A (1997) Secondary minerals of the Jáchymov (Joachimsthal) ore district. J Czech Geol Soc 42: 3–76

Ondruš P, Veselovský F, Gabašová A, Drábek M, Dobeš P, Malý K, Hloušek J, Sejkora J (2003) Ore-forming processes and mineral parageneses of the Jáchymov ore district. J Czech Geol Soc 48: 157–192

Palatinus L, Chapuis G (2007) Superflip – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J Appl Cryst 40: 451–456

Petříček V, Dušek M, Palatinus L (2006) Jana2006. The crystallographic computing system. Institute of Physics, Prague, Czech Republic. Accessed on March 24, 2015, at *http://jana.fzu.cz*

Petříček V, Dušek M, Palatinus L (2014) Crystallographic computing system Jana 2006: general features. Z Kristallogr 229: 345–352

Plášil J (2014) Oxidation–hydration weathering of uraninite: the current state-of-knowledge. J Geosci 59: 99–114

Plášil J, Sejkora J, Ondruš P, Veselovský F, Beran P, Goliáš V (2006) Supergene minerals in the Horní Slavkov uranium ore district, Czech Republic. J Czech Geol Soc 51: 149–158

Plášil J, Čejka J, Sejkora J, Škácha P, Goliáš V, Jarka P, Laufek F, Jehlička J, Němec I, Strnad L (2010) Widenmannite, a rare uranyl lead carbonate: occurrence, formation and characterization. Mineral Mag 74: 97–110

Plášil J, Fejfarová K, Skála R, Škoda R, Meisser N, Hloušek J, Císařová I, Dušek M, Veselovský F, Čejka J, Sejkora J, Ondruš P (2012) The crystal chemistry of the uranyl carbonate mineral grimselite, $(K,Na)_3Na[(UO_2)(CO_3)_3](H_2O)$, from Jáchymov, Czech Republic. Mineral Mag 76: 446–453

Plášil J, Fejfarová K, Dušek M, Škoda R, Rohlíček J (2013) Revision of the symmetry and the crystal structure of čejkaite, $Na_4(UO_2)(CO_3)_3$. Amer Miner 98: 549–553

Slavík F (1914a) Neue Phosphate vom Greifenstein bei Ehrenfriedersdorf. Bull Internation Res Trav Prés Cl Sci Mat Natur Méd 19: 108–123

Slavík F (1914b) Sur les fluorophosphates ternaires de Al^2O^3, RO et R^2O (morinite, ježekite, lacroixite). Bull Soc Fr Min Cristallogr 37: 152–162

Tvrdý J, Plášil J (2010) Jáchymov – Reiche Erzlagerstätte und Radonbad im böhmischen Westerzgebirge. Aufschluss 61: 277–292

Volod'ko LV, Komyak AI, Umreyko DS (1981) Uranyl Compounds, Spectra and Structure. Izdatel'stvo BGU, Minsk Volume 1, pp 1–620