

Sejkoraite-(Y), a new member of the zippeite group containing trivalent cations from Jáchymov (St. Joachimsthal), Czech Republic: Description and crystal structure refinement

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ABSTRACT

Sejkoraite-(Y), the triclinic $(Y_{1.98}Dy_{0.24})_{\Sigma 2.22}H_{0.34}[(UO_2)_8O_{88}O_7OH(SO_4)_4](OH)(H_2O)_{26}$, is a new member of the zippeite group from the Červená vein, Jáchymov (Street Joachimsthal) ore district, Western Bohemia, Czech Republic. It grows on altered surface of relics of primary minerals: uraninite, chalcopyrite, and tennantite, and is associated with pseudojohannite, rabejacite, uranopilite, zippeite, and gypsum. Sejkoraite-(Y) forms crystalline aggregates consisting of yellow-orange to orange crystals, rarely up to 1 mm in diameter. The crystals have a strong vitreous luster and a pale yellow-to-yellow streak. The crystals are very brittle with perfect {100} cleavage and uneven fracture. The Mohs hardness is about 2. The mineral is not fluorescent either in short- or long-wavelength UV radiation. Sejkoraite-(Y) is yellow, with no visible pleochroism, biaxial negative with $\alpha' = 1.62(2)$, $\beta' = 1.662(3)$, $\gamma' = 1.73(1)$, $2V_{calc} = 79^\circ$. The empirical chemical formula (mean of 8 electron microprobe point analyses) was calculated on the basis of 12 (S + U) atoms: $(Y_{1.49}Dy_{0.17}Gd_{0.11}Er_{0.07}Yb_{0.05}Sm_{0.02})_{\Sigma 1.90}H_{0.54}[(UO_2)_{8.19}O_7OH(SO_4)_{3.81}](H_2O)_{26.00}$. Sejkoraite-(Y) is triclinic, space group $P\bar{1}$, $a = 14.0743(6)$, $b = 17.4174(7)$, $c = 17.7062(8)$ Å, $\alpha = 75.933(4)^\circ$, $\beta = 128.001(5)^\circ$, $\gamma = 74.419(4)^\circ$, $V = 2777.00(19)$ Å³, $Z = 2$, $D_{calc} = 4.04$ g/cm³. The seven strongest reflections in the X-ray powder diffraction pattern are [d_{obs} in Å (1) (hkl): 9.28 (100) (100), 4.64 (39) (200), 3.631 (6) ($\bar{1}42$), 3.451 (13) ($\bar{1}44$), 3.385 (10) ($\bar{2}\bar{4}2$), 3.292 (9) (044), 3.904(7) (300), 2.984 (10) ($\bar{1}\bar{4}2$). The crystal structure of sejkoraite-(Y) has been solved by the charge flipping method from single-crystal X-ray diffraction data and refined to $R_{obs} = 0.060$ with $GOF_{obs} = 2.38$, based on 6511 observed reflections. The crystal structure consists of uranyl sulfate sheets of zippeite anion topology, which alternate with an interlayer containing $Y^{3+}(H_2O)_n$ polyhedra and uncoordinated H_2O groups. Two yttrium atoms are linked to the sheet directly via uranyl oxygen atom, and the remaining one is bonded by hydrogen bonds only. In the Raman and infrared spectrum of sejkoraite-(Y) there are dominating stretching vibrations of SO_4 tetrahedra (~ 1200 – 1100 cm⁻¹), UO_5^{2+} stretching vibrations (~ 900 – 800 cm⁻¹), and O–H stretching (~ 3500 – 3200 cm⁻¹) and H–O–H bending modes (~ 1640 cm⁻¹). The new mineral is named to honor Jiří Sejkora, a Czech mineralogist of the National Museum in Prague.

Keywords: Sejkoraite-(Y), new mineral, uranyl, zippeite group, crystal structure, vibration spectroscopy, Jáchymov

INTRODUCTION

Uranyl sulfates are typical products of uraninite alteration in the acidic oxidizing environment (Ondruš et al. 1997a; Finch and Murakami 1999; Meisser et al. 2002; Brugger et al. 2003, 2006). The sulfate-rich solutions, resulting from the decomposition of primary sulfide minerals by oxidizing descending waters, are responsible for migration of the uranyl ion $(UO_2)^{2+}$ under low pH conditions (Fernandes et al. 1995; Brugger et al. 2003 and references therein).

Precipitation of uranyl sulfate minerals is connected with evaporation/precipitation from acid mine drainage waters (Finch and Murakami 1999). Zippeite-group minerals are typical products of supergene alteration processes of U-rich ores. Up to date,

the minerals of the zippeite group include (1) “zippeites” sensu stricto—zippeite, natrozippeite, magnesiozippeite, cobaltzippeite, nickelzippeite, and zinczippeite (Fron del et al. 1976; Burns et al. 2003); (2) triclinic members: marécottite (Brugger et al. 2003) and pseudojohannite (Brugger et al. 2006). Moreover, rabejacite (Deliens and Piret 1993) should be considered as an additional member of the zippeite group, based on many similar characteristics. Minerals of the zippeite group typically occur as powdery coatings and mixtures growing on the surface of uranium-bearing specimens. Gypsum usually covers the samples in rich crystalline coatings, and it is present as a fine-grained admixture in the aggregates of zippeite-group minerals; hence, the structural characterization of these minerals often becomes difficult. As a result, only structures of two minerals adhering to the zippeite-group have been reported up to date: marécottite

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(Brugger et al. 2003) and pseudojohannite (Brugger et al. 2006). The last one is only partially solved.

Sejkoraite-(Y) is a new member of the zippeite group, found in Jáchymov (St. Joachimsthal) ore district, Western Bohemia, Czech Republic. It has been approved by the CNMMN of IMA (2009-008). The holotype specimen is deposited in the Mineral collection of the Natural History Museum, National Museum in Prague, under the catalog number P1p6/2009. The name of the mineral is to honor Jiří Sejkora (National Museum, Prague) for his significant contribution to the study of uranyl-containing phases. Jiří Sejkora is the author of more than 270 papers including descriptions of new mineral species (e.g., smrkovecite, jáchymovite, zálesiite, phosphowalpurkite, šreinite, and metarauchite). The Levinson suffix modifier “-(Y)” is in line with the dominance of Y over REEs in the new mineral. Sejkoraite-(Y) is the first mineral of the zippeite group containing substantial amounts of trivalent cations in the crystal structure.

MINERAL AND ITS PROPERTIES

Occurrence

Sejkoraite-(Y), associated with pseudojohannite, rabejacite, uranopilite, zippeite, and ubiquitous gypsum, covers a surface of strongly altered gangue containing primary mineralization of uraninite, chalcopyrite, and tennantite, from the Červená vein, Rovnost mine (level of the Daniel adit), Jáchymov (St. Joachimsthal), Western Bohemia, Czech Republic. The Jáchymov ore district is a classic occurrence of Ag+As+Co+Ni±Bi and U mineralization, which was described in detail namely in the papers of Ondruš et al. (1997a, 1997b, 1997c, 2002, 2003a, 2003b, 2003c, 2003d). The Jáchymov ore district is known and famous for its mineral diversity (more than 400 minerals are known and for 35 of them Jáchymov is a type locality) and its history (Tvrdý and Plášil 2010).

Physical and optical properties

Extremely rare sejkoraite-(Y) occurs as well-formed crystals, which are multiply twinned. Yellow-orange to orange crystals and their aggregates, up to 1 mm across (Fig. 1), are transparent to translucent with a strong vitreous luster, locally pearly on a dominating pinacoidal face. The streak is pale yellow to yellow. Crystals are very brittle, with a perfect {100} cleavage and uneven fracture. Morphological observations are difficult due to the small size of the sejkoraite-(Y) crystals, multiple intergrowths and perfect cleavage that significantly modify the observable morphology. The Mohs hardness is about 2. The density of sejkoraite-(Y) was not determined directly because of the small size of crystals and their rarity on the studied samples. A density of 4.04 g/cm³ was calculated based on the refined structure from single-crystal data (unit-cell) and EPMA results. Sejkoraite-(Y) does not exhibit any fluorescence in both short- and long-wave ultraviolet radiation.

Sejkoraite-(Y) is yellow in small fragments with no visible pleochroism. It is biaxial (+) with $\alpha' = 1.62(2)$, $\beta' = 1.662(3)$, $\gamma' = 1.73(1)$, $2V_{\text{calc}} = 79^\circ$. Optical investigations were highly difficult due to the perfect cleavage of the crystals, which did not allow a more precise determination of refractive indices. Nevertheless, a Gladstone-Dale compatibility index, is 0.022, which is excellent (for a compatibility of 0.00 the mean N is 1.6855).

Chemical composition

The chemical composition of sejkoraite-(Y) was studied using a Cameca SX100 electron microprobe operating in wavelength-dispersion mode. We applied an acceleration voltage of 15 kV, a current of 10 nA, and a beam diameter of 5 μm . The following X-ray lines and standards were selected to minimize line overlaps: $K\alpha$ lines: S (barite, detection limit 0.07 wt%), Ca (fluorapatite, 0.06 wt%), Si (sanidine, 0.03 wt%), Fe (andradite, 0.08 wt%); $L\alpha$ lines: Y (YAG, 0.09 wt%), Yb (YbP₅O₁₄, 0.20 wt%); $L\beta$ lines: Sm (SmF₃, 0.14 wt%), Gd (GdF₃, 0.15 wt%), Dy (DyPO₄, 0.20 wt%), Er (YErAG, 0.17 wt%); $M\beta$ lines: U (U metal, 0.30 wt%). Lanthanum, Ce, Pr, Nd, and Eu were also measured, but their contents were below the detection limit (0.15–0.30 wt%). Peak counting times (CT) were 10–20 s for major elements, 40–60 s for minor to trace elements and counting time on the background points was 1/2 CT. The measured intensities were converted to element concentrations using the PAP (Pouchou and Pichoir 1985) correction routine. High analytical totals are generally caused by water evaporation in high vacuum and continuous heating of the analyzed spot by the electron beam.

Sejkoraite-(Y) from Jáchymov is an yttrium-dominant member of the zippeite-group minerals. The cation positions are partially occupied by REEs, namely Dy (up to 0.21 Dy pfu) and Gd (up to 0.15 Gd pfu), besides dominant Y. The chondrite normalized REE pattern (Fig. 2) shows strong enrichment in MREE with a maximum at Dy and depletion of LREE and HREE. Electron microprobe analysis confirmed a relatively constant U/S molar ratio ~ 2 (range 2.09–2.25) characteristic for the minerals with the zippeite anion topology of the uranyl-sulfate structure sheets (Burns et al. 2003; Burns 2005). The empirical formula of sejkoraite-(Y) from Jáchymov calculated on the base of 12 apfu S+U (mean of 8 analyses see Table 1) is $(\text{Y}_{1.49}\text{Dy}_{0.17}\text{Gd}_{0.11}\text{Er}_{0.07}\text{Yb}_{0.05}\text{Sm}_{0.02})_{\Sigma 1.90}\text{H}_{0.54}[(\text{UO}_2)_{8.19}\text{O}_7\text{OH}(\text{SO}_4)_{3.81}](\text{H}_2\text{O})_{26}$.

Vibration spectroscopy

Raman spectrum of sejkoraite-(Y) was collected on a Labram HR dispersive Raman spectrometer (Jobin Yvon) with a confo-



FIGURE 1. The platy crystals of sejkoraite-(Y), growing on an altered gangue with cuprosklodowskite (green) and gypsum (colorless). FOV is 1.2 mm. Photo by J. Sejkora (Nikon SMZ1500).

cal Olympus microscope. The Raman signal was excited by a 732 nm laser and detected with a multichannel air-cooled CCD camera. As no visible damage of the sample connected with a thermal decomposition under the laser beam occurred during the acquisition of spectra, the power of the red laser was set unrestricted. Raman spectra were collected with a spectral resolution of 2 cm^{-1} in the range $200\text{--}1700\text{ cm}^{-1}$. The infrared spectrum of sejkoraite-(Y), mixed with KBr powder, was recorded by the DRIFTS method on a Nicolet Magna 760 FTIR spectrometer (range $600\text{--}4000\text{ cm}^{-1}$, resolution of 4 cm^{-1} , 128 scans, Happ-Genzel apodization) equipped with a Spectra Tech InspecIR micro-FTIR accessory. The spectral data were processed using Omnic spectral tools software.

Both spectra are shown on Figure 3. An infrared band at 3371 cm^{-1} with shoulders at 3491 and 3371 cm^{-1} is assigned to the ν O-H stretching vibrations of the molecular H_2O . These molecules are bonded within the crystal structure of sejkoraite-(Y) by a series of hydrogen bonds of a different strengths. The $\text{O-H}\cdots\text{O}$

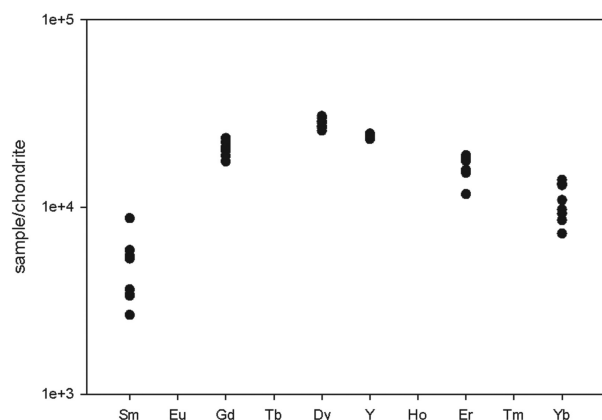


FIGURE 2. The chondrite-normalized REE pattern of sejkoraite-(Y). Data by Taylor and McLennan (1985) were used for normalization the EMP data.

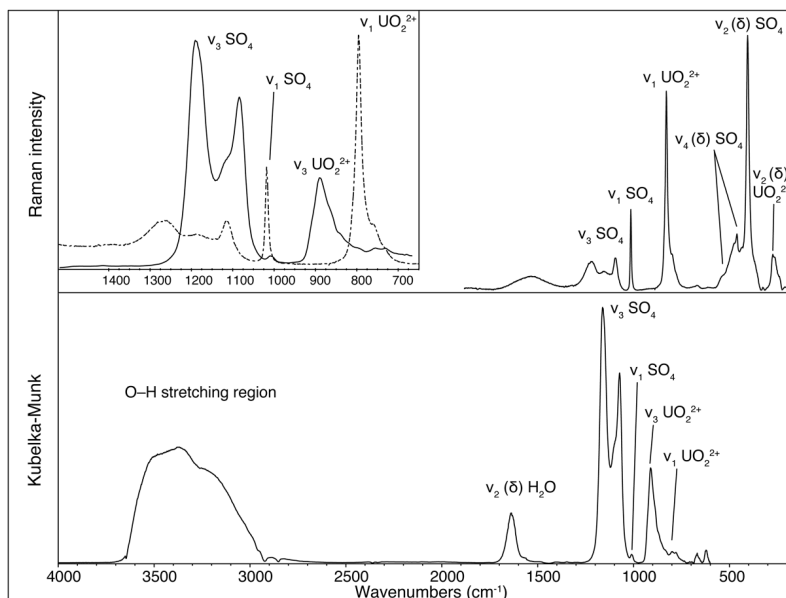
FIGURE 3. Raman (upper) and infrared (lower) spectrum of sejkoraite-(Y). The comparison of both spectra in the region of fundamental sulfate and uranyl vibrational modes is displayed in the left part. A broad band in Raman spectrum at 1500 cm^{-1} is a spectral artifact.

hydrogen bond lengths calculated using the correlation of Li-bowitzky (1999) are approximately in the range of $2.71\text{--}2.89\text{ Å}$. An infrared band at 1637 cm^{-1} with a shoulder at 1560 cm^{-1} and a weak broad Raman band at 1537 cm^{-1} are attributed to the ν_2 (δ) H_2O bending vibrations of water molecules. Infrared bands at 1158 (vs) and 1100 cm^{-1} (s-vs) with a shoulder at 1100 cm^{-1} and weak Raman bands at 1222 , 1157 , and 1095 cm^{-1} are assigned to the split triply degenerate ν_3 (SO_4) $^{2-}$ antisymmetric stretching vibrations. A weak infrared band at 1011 cm^{-1} and a Raman band at 1014 cm^{-1} , of medium intensity, are connected with ν_1

TABLE 1. Results of electron microprobe analyses (in wt%) of sejkoraite-(Y)

	Theor.	Mean	1	2	3	4	5	St.dev.	DetLim
Y_2O_3	9.94	5.20	4.98	5.32	5.27	5.27	5.09	0.13	0.10
Sm_2O_3		0.03	bdl	bdl	bdl	0.20	bdl	n/a	0.14
Gd_2O_3		0.61	0.70	0.60	0.74	0.56	0.66	0.07	0.15
Dy_2O_3		0.97	0.93	0.91	1.06	1.03	1.05	0.06	0.20
Er_2O_3		0.38	0.36	0.41	0.37	0.40	0.35	0.02	0.17
Yb_2O_3		0.27	0.33	0.27	0.38	0.21	0.18	0.07	0.17
SO_3	9.40	9.40	9.65	9.39	8.89	9.62	9.39	0.27	0.07
UO_3	67.17	72.28	72.22	73.06	71.43	72.42	71.85	0.55	0.30
H_2O^*	13.49	14.17	—	—	—	—	—	—	—
Total	100.00	103.39	89.30	90.08	88.15	89.71	88.65		
Y	3.000	1.494							
Sm		0.005							
Gd		0.109							
Dy		0.168							
Er		0.065							
Yb		0.044							
$\Sigma\text{M site}$	3.000	1.885							
SO_4^{2-}	4.000	3.808							
UO_2^{2+}	8.000	8.192							
OH^-	3.000	1.000							
H^+	0.000	0.578							
H_2O	24.00	26.00							
U:S	2.00	2.15							

Notes: Theor. = ideal composition for $\text{Y}_3(\text{OH})_2[(\text{UO}_2)_8\text{O}_7\text{OH}(\text{SO}_4)_4](\text{H}_2\text{O})_{24}$. Mean = mean of eight point analyses; the apfu coefficients are calculated on the basis of $(\text{U}+\text{S})=12$ atoms. 1–5 = representative point analyses of sejkoraite-(Y). St.dev. = standard deviation (in wt%). DetLim = detection limit (on mean of eight analyses, in wt%). bdl = measurement was below detection limit for measured element. * H_2O content is calculated based on theoretical content of H_2O + OH in the crystal structure.



(SO₄)²⁻ symmetric stretching vibrations. An infrared band at 911 cm⁻¹ (m-s) and a Raman band at 896 cm⁻¹ (vw) are attributed to ν_3 (UO₂)²⁺ antisymmetric stretching vibrations, corresponding to U-O (uranyl) bond lengths of 1.78 and 1.79 Å, respectively (Bartlett and Cooney 1989). An infrared shoulder at 833 cm⁻¹ and a Raman band at 829 cm⁻¹ (s-vs) are assigned to ν_1 (UO₂)²⁺ symmetric stretching vibrations. The bond length in U-O (uranyl) inferred from these bands is ~1.78 Å (Bartlett and Cooney 1989). This bond lengths obtained from the vibrational data are in an excellent agreement with those for uranyl pentagonal coordination polyhedra (Burns 2005 and references therein). The weak infrared bands at 796 and 778 cm⁻¹ and a Raman shoulder at 798 cm⁻¹ are connected with the libration modes of water molecules. The weak infrared bands at 668 and 623 cm⁻¹ and a weak Raman band at 670 cm⁻¹ with a shoulder at 546 cm⁻¹ are assigned to the split triply degenerate ν_4 (SO₄)²⁻ bending vibrations. Raman bands at 461 (m) and 404 cm⁻¹ (vs) with shoulders at 477 and 438 cm⁻¹ are attributed to the split doubly degenerate ν_2 (SO₄)²⁻ bending vibrations. A very weak Raman band at 326 cm⁻¹ with a shoulder at 369 cm⁻¹ is assigned to the ν U-O_{ligand} vibrations; Raman bands at 274 (w-m) and 262 cm⁻¹ (w-m) to the ν_2 (δ) (UO₂)²⁺ bending vibrations and those at 237 (sh) and 211 cm⁻¹ (w) to the lattice vibrations and molecular deformations.

Infrared and Raman spectra of sejkoraite-(Y) are in a good agreement with the infrared and Raman spectra of other, both natural and synthetic “zippeites” (e.g., Čejka 1999, 2007; Čejka and Sejkora 1994; Frost et al. 2005, 2007a, 2007b; Plášil et al. 2010).

X-ray powder diffraction

The X-ray powder diffraction data were collected on PANalytical X'Pert Pro powder diffractometer equipped with an X'Celerator detector, operating at 40 kV and 40 mA, using CuK α radiation. A very small amount of crushed sejkoraite-(Y) crystals was placed on a thin glass hair and mounted on a goniometric head. The Debye-Scherrer geometry was adopted for the diffraction experiment. The step size of 0.02° in the range of 4–55 °2 θ with the counting time of 2600 s per integrated step was used; the sample was rotated with the frequency of 2 s⁻¹. The positions of each diffraction maxima were found and refined by Xfit software (Cheary and Coelho 1996) using PearsonVII profile shape function. The unit-cell parameters were refined from the powder data by software Celref (LMGP Suite of Programs for the Interpretation of X-ray Experiments, by Jean Laugier and Bernard Bochu, ENSP Laboratoire des Matériaux et du Génie Physique, BP 46, F-38042 Saint Martin d'Hères, France, <http://www.inpg.fr/LMGP> and <http://www.ccp14.ac.uk/tutorial/lmgp/>). The advantage of the Debye-Scherrer geometry is that the preferential orientation is minimized. The powder diffraction pattern of the sejkoraite-(Y) sample is listed in Table 2. The relative intensities of the diffraction maxima are consistent with the theoretical values. The refined unit-cell parameters are in agreement with those obtained from the single-crystal measurement (Tables 3 and 6).

CRYSTAL STRUCTURE OF SEJKORAITE-(Y)

Experimental methods

A 0.11 × 0.09 × 0.05 mm tabular yellowish orange crystal of sejkoraite-(Y) was selected for the single-crystal X-ray diffrac-

tion experiment. A first data set was collected using an Enraf Nonius KappaCCD single-crystal diffractometer using monochromatic MoK α radiation (λ = 0.71073 Å) at ambient condi-

TABLE 2. Powder X-ray diffraction pattern of sejkoraite-(Y) from Jáchymov

d_{obs}	d_{calc}	l_{obs}	h	k	l
9.28	9.28	100	1	0	0
8.51	8.51	4	-1	0	2
6.73	6.73	4	-2	0	2
6.33	6.33	1	1	-1	0
5.90	5.89	2	0	0	2
4.99	4.99	3	0	-2	1
4.64	4.64	39	2	0	0
4.26	4.25	4	-2	0	4
4.13	4.13	3	1	4	0
4.00	4.00	1	-1	3	1
3.848	3.849	2	-2	2	1
3.731	3.732	3	-3	0	1
3.631	3.633	6	-1	4	2
3.451	3.450	13	-1	4	4
3.385	3.385	10	-2	-4	2
3.292	3.292	9	0	4	4
3.180	3.179	3	-2	4	4
3.094	3.093	7	3	0	0
3.059	3.059	6	-4	-4	2
2.984	2.984	10	-1	-4	2
2.836	2.836	3	-3	0	6
2.618	2.618	1	-5	2	2
2.578	2.577	4	-5	0	6
2.496	2.496	4	0	-4	2
2.368	2.367	2	2	4	4
2.320	2.320	2	4	0	0
2.295	2.297	2	-2	1	7
2.290	2.290	2	-5	2	7
2.141	2.141	3	1	8	2

Note: The mean square deviation on d_{obs} is 0.015 °2 θ (CuK α radiation).

TABLE 3. Summary of data collection conditions and refinement parameters for sejkoraite-(Y)

Structural formula		Y _{2.22} H _{0.34} [(UO ₂) ₆ O ₇ OH(SO ₄) ₄](H ₂ O) ₂₆	
Crystal data			
Unit-cell parameters (based on 12 314 reflections)		a = 14.0743(6) Å b = 17.4174(7) Å c = 17.7062(8) Å α = 75.933(4)° β = 128.001(5)° γ = 74.419(4)° V = 2777.0(2) Å ³	
Z		2	
Space group		P $\bar{1}$	
Data collection			
Temperature		293 K	
Wavelength		MoKα, 0.7107 Å	
Crystal dimensions		0.1124 × 0.0885 × 0.0529 mm	
Collection mode;			
crystal-to-detector distance		ω scans to fill Ewald sphere, 120 mm	
Count time		70 s per 0.5°	
Limiting 2θ angles		4.63–27.68°	
Limiting Miller indices		−18 < h < 17, −22 < k < 21, −23 < l < 23	
No. of reflections		38 805	
No. of unique reflections		11 644	
No. of observed reflections (criterion), R _{int} , coverage		6511 [I _{obs} > 3σ(I)], 0.067, 99.96%	
Absorption correction (mm ^{−1}), method		26.64, multiscan	
F ₀₀₀		2842	
Refinement by Jana2006 on F			
Parameters refined		404	
Reflections rejected by the refinement (twinning)		573	
R _{obs}		0.0599	
R _{all}		0.1049	
R _w (obs)		0.0600	
R _w (all)		0.0620	
GOF (obs), GOF (all)		2.38, 1.82	
Δσ _{min} , Δσ _{max} (e/Å ³)		−5.50, 8.71	

tions. The crystal structure of sejkoraite-(Y) was then solved by direct methods (SIR92; Altomare et al. 1994) and refined from these data to $R_1 = 7.6\%$ (SHELXL97; Sheldrick 1997, 2008). Due to the complex character of the structure, the second X-ray diffraction experiment on the same crystal was carried out using an Oxford Diffraction Gemini single-crystal diffractometer system equipped with an Atlas detector, using monochromatic $\text{MoK}\alpha$ radiation, with fiber-optics Mo-Enhance collimator. For the entire measurement, the detector-to-crystal distance of 120 mm was set to minimize overlapping of the reflections. For the unit-cell least-square refinement, 12 325 reflections were selected and used. Analyzing the diffraction pattern, it was found that a portion of unindexed reflections existed due to twinning realized as a 180° rotation around the reciprocal axis $[0.7254, -0.2337, 0.6474]$. Both twin domains could index 95% of the diffraction pattern. For the peak-extraction procedure and subsequent integration of the data, the smaller twin domain was neglected, the twinning matrix was used later on in structure refinement. Out of a total number of 38 805 diffractions integrated for the larger twin domain, 11 644 reflections were unique, and 6511 of the unique reflection were classified as observed $[I_{\text{obs}} > 3\sigma(I)]$. The analytical absorption correction ($\mu = 26.64 \text{ mm}^{-1}$) was implemented and was followed by a decrease of R_{int} factor from 10 to 6.7%. The crystallographic data pertinent to the data collection are listed in Table 3.

The crystal structure of sejkoraite-(Y) was solved by the charge-flipping method using the Superflip program (Palatinus and Chapuis 2007) and subsequently refined by the software JANA2006 (Petříček et al. 2006). The space group $P\bar{1}$ was suggested by the Superflip program and verified by the crystal-structure refinement. The refinement procedure took into account the twinning matrix for detection of fully overlapped, fully separated and partially overlapped reflections using user-defined limits on the diffraction angles. Therefore, 573 of partially overlapped reflections were discarded from the refinement. All heavy atoms were refined using anisotropic atomic displacement parameters (ADP); for the remaining atoms in the crystal structure of sejkoraite-(Y), isotropic parameters were used. Occupancies of the cation sites were refined, assuming that they are partially occupied (see Table 4). In case of the Y1 site, which exhibited electron excess, the sum of Y and Dy occupancies was restricted to the full occupation. All non-hydrogen atoms were found; the refinement converged with the final agreement indices $R_{\text{obs}} = 5.99\%$ and $\text{GOF}_{\text{obs}} = 2.39$. The software JANA2006 uses the weighting scheme based on the experimental expectations that do not force GOF to be one. Therefore, the values of GOF are usually larger than those from the SHELX program. Other data pertinent to the refinement are listed in Table 3. The atomic positions and displacement parameters are listed in Tables 4 and 5. For plotting the structure DIAMOND program (Crystal Impact; Brandenburg and Putz 2005) was used. The crystallographic information file is deposited¹.

Description of crystal structure

The crystal structure of sejkoraite-(Y) contains eight symmetrically unique uranium atoms, each strongly bonded to two O atoms forming nearly linear $(\text{UO}_2)^{2+}$ uranyl ions with U-O_{ax} bond-lengths ranging between 1.68 and 1.83 Å. Each ion is additionally coordinated by five anionic ligands designated as O_{eq} , located at the equatorial vertices of the pentagonal bipyramids. The U-O_{eq} bond-lengths for the UO_7 pentagonal bipyramids vary in the range from 2.21–2.51 Å. These values are consistently matching those reported by Burns et al. (1997a) and Burns (2005) for pentagonal uranyl bipyramidal coordination –2.37(9) Å. The bond-valence sums incident upon the uranyl sites, calculated with the parameters provided by Burns et al. (1997a), indicate that all uranium is acting as U^{6+} in the crystal structure of sejkoraite-(Y) (Table 4). There are four symmetrically unique S^{6+} sites (Table 4), where each S^{6+} atom is tetrahedrally coordinated O atoms. The S-O bond-lengths range between 1.44–1.52 Å. The bond-valence sums incident upon sulfur sites, calculated using the S^{6+} -O parameters given by Brown and Altermatt (1985), are consistent with the bond-valences sums expected for S^{6+} .

The structure contains three symmetrically unique M sites, occupied by trivalent cations, dominantly by yttrium. Cations are coordinated by H_2O groups and O atoms, forming distorted coordination polyhedra. The Y1 and Y3 polyhedra are bonded directly to the structural layer via a uranyl apical oxygen. The site Y2 is coordinated by H_2O groups only and bonded through hydrogen bonds to the Y3 (Fig. 4). The average cation to oxygen bond-lengths range from 2.11 to 2.66 Å. The site occupancies were refined following the results of chemical analyses, which showed the presence of REE (mostly Dy) besides dominant Y. The atomic site Y1, when occupancy is refined, exhibits an excess of electrons, giving unrealistically high refined occupancy of 1.22. Therefore, the sum of occupancies was restricted to be 1 and a Dy^{3+} atom was introduced into the fit on this site. The refinement returned quite reasonable values, 0.761(9) Y and 0.239(9) Dy^{3+} . The refinement of other M sites did not reveal presence of any Dy^{3+} , therefore, the occupancies were refined for Y^{3+} alone. Based on the refinement, the content of Dy^{3+} is 0.24 apfu ($Z = 2$), whereas the Dy^{3+} content, based on EPMA data, is lower, 0.17 apfu. The refined occupancy probably encompasses further REE's contributing to the final sum, which were not introduced to the refinement.

Structural formula

All atoms are located on general positions of the $P\bar{1}$ space group. Based on the bond-valence sums (Table 4) of the O atomic sites, all O atoms were designated as O^{2-} and H_2O except atom O28, owing to its low bond valence sum of 1.38(3) v.u. Therefore, the formula of sejkoraite-(Y) obtained from the crystal structure refinement is $(\text{Y}_{1.98}\text{Dy}_{0.24})_{\Sigma 2.22}[(\text{UO}_2)_8\text{O}_7\text{OH}(\text{SO}_4)_4](\text{H}_2\text{O})_{26}$, $Z = 2$, which is not electrically neutral, with an excess of negative charges. We can assume the presence of small quantities of H^+ ions, which may be hardly detected by X-ray diffraction and may be distributed over several H_2O sites in the crystal structure of sejkoraite-(Y). Hence, we may express the structural formula as $(\text{Y}_{1.98}\text{Dy}_{0.24})_{\Sigma 2.22}\text{H}_{0.34}^+[(\text{UO}_2)_8\text{O}_7\text{OH}(\text{SO}_4)_4](\text{H}_2\text{O})_{26.00}$, $Z = 2$. The assignment of the O28 atom as OH^- and the consequences of this assignment for the ideal chemical formula of sejkoraite-(Y) are

¹ Deposit item AM-11-038, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 4. Atomic positions, isotropic displacement parameters and bond-valence sums (Σ VB) for the crystal structure of sejkoraite-(Y)

Atom	x	y	z	U_{iso}	Σ VB
U1	0.50569(10)	0.70517(6)	0.16924(7)	0.0166(8)	6.14(8)
U2	0.49937(10)	0.04323(6)	0.33362(7)	0.0183(9)	5.98(5)
U3	0.48709(11)	0.54890(6)	0.32956(8)	0.0220(9)	6.02(7)
U4	0.51220(10)	0.78842(6)	0.34152(7)	0.0167(8)	5.99(7)
U5	0.50218(10)	0.45656(6)	0.16629(8)	0.0185(8)	6.03(10)
U6	0.42522(11)	0.81105(6)	0.79490(7)	0.0202(9)	6.59(8)
U7	0.46742(10)	0.96710(6)	0.14252(8)	0.0204(9)	6.05(9)
U8	0.57213(10)	0.26032(6)	0.37918(7)	0.0192(9)	6.26(10)
Y1*	0.94661(19)	0.13274(12)	0.11257(15)	0.0259(18)	3.10(6)
Y2*	0.94661(19)	0.13274(12)	0.11257(15)	0.0259(18)	2.95(6)
Y3*	0.0013(4)	0.4481(3)	0.8098(3)	0.048(4)	3.04(13)
Y1*	0.0544(5)	0.6227(4)	0.3662(4)	0.029(5)	2.59(12)
S1	0.5182(6)	0.3699(4)	0.0075(5)	0.015(5)	5.84(14)
S2	0.5083(6)	0.1205(4)	0.5053(5)	0.013(5)	5.93(14)
S3	0.5340(7)	0.1131(4)	0.0220(5)	0.019(6)	5.95(15)
S4	0.4739(7)	0.6348(4)	0.4857(5)	0.024(6)	5.95(14)
O1	0.7588(15)	0.1924(9)	0.4767(11)	0.023(3)	1.80(4)
O2	0.3186(15)	0.1234(9)	0.1959(11)	0.024(3)	1.69(2)
O3	0.2996(14)	0.6029(9)	0.2046(11)	0.020(3)	1.65(3)
O4	0.6722(15)	0.4881(10)	0.4675(12)	0.028(4)	1.67(4)
O5	0.3215(15)	0.5064(10)	0.0944(12)	0.027(4)	1.73(8)
O6	0.6796(15)	0.4109(10)	0.2311(11)	0.026(3)	1.68(5)
O7	0.6928(15)	0.6445(10)	0.2903(12)	0.027(4)	1.73(6)
O8	0.3911(16)	0.3275(10)	0.2970(12)	0.031(4)	1.85(8)
O9	0.3149(14)	0.7695(9)	0.0364(11)	0.022(3)	1.86(3)
O10	0.5891(14)	0.0265(9)	0.6025(11)	0.022(3)	1.95(6)
O11	0.2845(15)	1.0478(10)	0.0550(12)	0.026(3)	1.76(4)
O12	0.2426(15)	0.8742(9)	0.6794(11)	0.024(3)	1.94(3)
O13	0.6017(16)	0.7508(10)	0.9199(12)	0.029(4)	1.97(6)
O14	0.3883(14)	0.6290(9)	0.3853(11)	0.022(3)	1.95(7)
O15	0.6497(14)	0.8926(9)	0.2190(11)	0.022(3)	1.65(4)
O16	0.3253(14)	0.8522(9)	0.2646(11)	0.020(3)	1.55(4)
O17	0.6994(15)	0.7216(9)	0.4295(11)	0.023(3)	1.71(4)
O18	0.6252(14)	0.2737(9)	0.1155(11)	0.023(3)	1.81(5)
O19	0.5642(15)	0.5442(9)	0.5910(11)	0.023(3)	1.99(6)
O20	0.6771(14)	-0.0379(9)	0.4730(11)	0.022(3)	1.70(3)
O21	0.6314(15)	0.1137(9)	0.1251(12)	0.025(3)	1.97(7)
O22	0.6208(14)	0.0413(9)	0.0253(11)	0.023(3)	1.98(9)
O23	0.5759(14)	0.4018(9)	0.3405(11)	0.017(3)	1.50(3)
O24	0.5684(15)	0.6608(9)	0.4890(11)	0.023(3)	1.89(8)
O25	0.6194(14)	0.1372(9)	0.5261(11)	0.022(3)	1.82(7)
O26	0.4265(14)	0.3655(9)	-0.0922(11)	0.022(3)	2.03(8)
O27	0.5462(14)	0.1577(9)	0.3192(11)	0.019(3)	1.93(4)
O28	0.5767(14)	0.0436(9)	0.2448(11)	0.019(3)	1.38(3)
O29	0.4518(14)	0.8382(9)	0.1787(11)	0.016(3)	1.87(4)
O30	0.5442(14)	0.3096(9)	0.2330(11)	0.017(3)	1.97(4)
O31	0.4193(15)	0.1278(9)	0.3960(11)	0.023(3)	1.97(7)
O32	0.3717(14)	0.7079(9)	0.4720(11)	0.020(3)	1.89(8)
O33	0.4139(14)	0.1906(9)	0.4999(11)	0.017(3)	1.90(8)
O34	0.5138(14)	0.5687(9)	0.2163(11)	0.017(3)	1.93(4)
O35	0.4804(14)	0.6827(9)	0.2838(11)	0.020(3)	1.97(4)
O36	0.4459(14)	0.2062(9)	-0.0836(11)	0.022(3)	1.86(5)
O37	0.4349(15)	0.0945(9)	0.0169(11)	0.025(3)	1.99(9)
O38	0.5043(14)	-0.0743(9)	0.2929(11)	0.019(3)	1.89(4)
O39	0.6008(14)	0.4040(9)	0.0023(11)	0.023(3)	1.88(8)
O40	0.4273(14)	0.4314(9)	0.0110(11)	0.022(3)	1.90(8)
OW1	0.075(2)	0.0190(13)	0.4302(15)	0.059(5)	0.00
OW2	0.8792(19)	0.2873(12)	0.0812(15)	0.057(5)	0.36(1)
OW3	0.8817(16)	0.1349(10)	0.2038(12)	0.033(4)	0.46(3)
OW4	0.8595(17)	0.0572(11)	0.0190(13)	0.041(4)	0.42(2)
OW5	0.112(3)	0.317(2)	0.140(2)	0.126(10)	0.00
OW6	0.0605(19)	0.8622(12)	0.1358(15)	0.055(5)	0.00
OW7	0.884(2)	0.9194(15)	0.4089(18)	0.084(7)	0.00
OW8	0.1416(16)	0.1227(11)	0.2702(13)	0.038(4)	0.42(2)
OW9	0.1408(16)	0.0439(10)	0.1425(12)	0.032(4)	0.42(2)
OW10	1.0875(17)	-0.0297(11)	0.2639(13)	0.039(4)	0.37(2)
OW11	0.9153(17)	0.2175(11)	-0.0350(14)	0.045(4)	0.39(2)
OW12	-0.143(2)	0.3930(16)	0.7186(19)	0.094(7)	0.46(3)
OW13	-0.149(2)	0.4847(16)	0.8350(19)	0.091(7)	0.30(3)
OW14	-0.154(3)	0.615(2)	0.705(2)	0.136(10)	0.30(2)
OW15	0.161(4)	0.339(2)	0.828(3)	0.160(12)	0.47(6)
OW16	0.134(3)	0.506(2)	0.819(2)	0.137(10)	0.38(5)
OW17	0.099(3)	0.2938(19)	0.961(2)	0.124(9)	0.22(2)
OW18	0.130(3)	0.6792(18)	0.503(2)	0.112(9)	0.10(1)

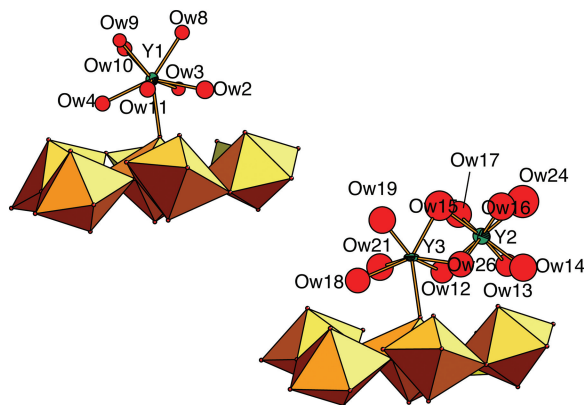
TABLE 4.—CONTINUED

Atom	x	y	z	U_{iso}	Σ VB
OW19	-0.130(3)	0.715(2)	0.320(2)	0.130(10)	0.31(3)
OW20	0.9124(19)	-0.0803(12)	0.2614(15)	0.055(5)	0.00
OW21	0.095(3)	0.753(2)	0.302(2)	0.130(10)	0.08(1)
OW22	-0.116(3)	0.7579(19)	0.651(2)	0.123(9)	0.00
OW23	0.906(4)	0.447(3)	0.375(3)	0.184(14)	0.00
OW24	0.133(4)	0.450(3)	0.985(3)	0.190(14)	0.24(3)
OW25	0.077(4)	0.777(2)	0.633(3)	0.174(13)	0.00
OW26	0.105(3)	0.4894(19)	0.378(2)	0.119(9)	0.00

* Refined occupancies for interlayer M-sites are: Y1 = 0.761(9), Dy1 = 0.239(9), Y2 = 0.801(9), Y3 = 0.418(8).

TABLE 5. Anisotropic atomic displacement parameters for crystal structure of sejkoraite-(Y)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U1	0.0330(6)	0.0195(5)	0.0216(5)	-0.0186(5)	0.0257(5)	-0.0153(4)
U2	0.0387(6)	0.0208(5)	0.0240(5)	-0.0216(5)	0.0295(5)	-0.0172(4)
U3	0.0475(7)	0.0254(5)	0.0274(5)	-0.0271(5)	0.0351(6)	-0.0201(4)
U4	0.0325(6)	0.0195(5)	0.0208(5)	-0.0182(5)	0.0249(5)	-0.0145(4)
U5	0.0367(6)	0.0205(5)	0.0237(5)	-0.0200(5)	0.0281(5)	-0.0164(4)
U6	0.0418(6)	0.0234(5)	0.0263(5)	-0.0230(5)	0.0323(5)	-0.0185(4)
U7	0.0438(7)	0.0246(5)	0.0280(5)	-0.0259(5)	0.0341(6)	-0.0206(5)
U8	0.0381(6)	0.0246(5)	0.0241(5)	-0.0226(5)	0.0295(5)	-0.0184(4)
Y1	0.0305(13)	0.0312(12)	0.0239(12)	-0.0162(10)	0.0228(11)	-0.0151(9)
Dy1	0.0305(13)	0.0312(12)	0.0239(12)	-0.0162(10)	0.0228(11)	-0.0151(9)
Y2	0.047(3)	0.071(3)	0.047(2)	-0.033(2)	0.040(2)	-0.037(2)
Y3	0.012(3)	0.027(3)	0.018(3)	-0.006(3)	0.004(3)	-0.004(3)
S1	0.028(4)	0.011(3)	0.017(3)	-0.013(3)	0.019(3)	-0.010(3)
S2	0.013(3)	0.015(3)	0.015(3)	-0.009(3)	0.010(3)	-0.009(3)
S3	0.038(4)	0.015(3)	0.028(3)	-0.019(3)	0.029(4)	-0.018(3)
S4	0.054(5)	0.022(3)	0.033(4)	-0.030(3)	0.039(4)	-0.023(3)

**FIGURE 4.** Yttrium coordination polyhedra in the crystal structure of sejkoraite-(Y). UO₂ bipyramids are orange, SO₄ tetrahedra are yellow, Y atoms are green, and O atoms are red. Thermal ellipsoids represent anisotropic displacement parameters (50% probability level).

not fully straightforward (Fig. 5) and shall therefore be discussed a little further. The bond-valence sum for the O28 atom, when compared to the -valence sums for the other oxygen atoms of the structural sheet, suggests that this oxygen atom is involved in the hydrogen bonding. The sum 1.38(3) v.u. is similar with those assigned to an OH⁻ species in many crystallographic studies of minerals and inorganic compounds (e.g., Burns et al. 1997b, 2003; Li and Burns 2000; Brugger et al. 2003, 2007; Finch et al. 2006; Nagashima et al. 2010). Hence the structural sheets is most likely of the composition [(UO₂)₈O₇OH(SO₄)₄]⁷⁻. The ideal formula of sejkoraite-(Y) is therefore open to question. If we assume as ideal three fully ordered occupied M³⁺ sites, the formula

may be expressed as $Y_3^{3+}(OH)_2[(UO_2)O_7OH(SO_4)_4](H_2O)_{24}$, $Z = 2$. However, there are no indications for OH^- to be present in the interlayer space from the current structure refinement. In the current case, where M^{3+} displays some occupational disorder, it can be expected that a hydrogen-bonding network maintains the stability of the structure via a small portion of H^+ ions distributed

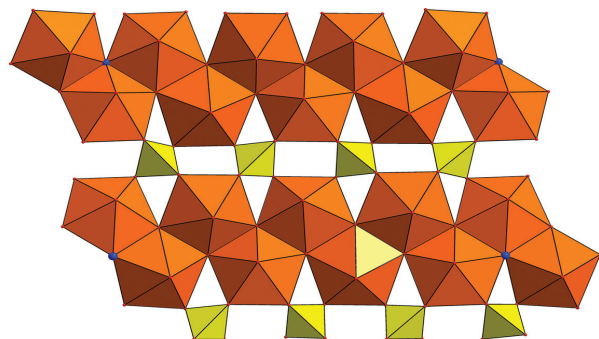


FIGURE 5. An uranyl sulfate sheet of the zippeite anion topology in the crystal structure of sejkoraite-(Y). Sheets consist of chains of edge-sharing uranyl pentagonal bipyramids (orange) linked by vertices of sulfate tetrahedra (yellow). The position of oxygen atom corresponding to OH^- species on the sheet is marked with dark blue circles.

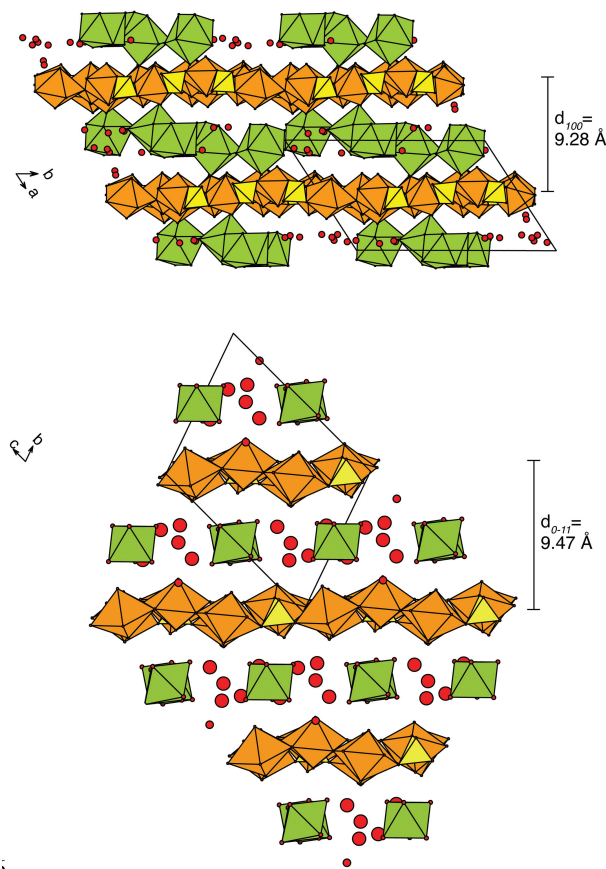


FIGURE 6. The crystal structure of sejkoraite-(Y) (**upper**) and marécottite (**lower**; after Brugger et al. 2003). Main differences are in the interlayers of both structures (interplanar d_{100} distance is shown).

over the H_2O sites in the structure, although their presence cannot be proven from the current refinement.

Structural connectivity

The eight symmetrically distinct uranyl pentagonal bipyramids share equatorial edges, forming chains that are two polyhedra wide (Fig. 5). Adjacent chains of uranyl polyhedra are linked by the sharing of equatorial vertices of the uranyl pentagonal bipyramids with sulfate tetrahedral and form two-dimensional sheets in that way. Each sulfate tetrahedron is, therefore, linked to four different uranyl pentagonal bipyramids. This arrangement results in the structural uranyl-sulfate sheets of the zippeite topology found in the synthetic zippeite (Vochten et al. 1995; Burns et al. 2003), in synthetic zippeite-group phases (Burns et al. 2003), in synthetic zippeite phases with mixed univalent and divalent cations (Peeters et al. 2008), and in marécottite (Brugger et al. 2003). The $M(H_2O)_7O$ and $M(H_2O)_9$ polyhedra are located in the interlayer between uranyl-sulfate sheets. The perfect cleavage parallel (100) is caused by the fact that the M^{3+} coordination polyhedra are not connected to each other in the interlayer (only Y2 and Y3, not with Y1), therefore the interaction between the sheets is weak.

DISCUSSION

Comparison to marécottite

Brugger et al. (2003) published the description and crystal-structure refinement of marécottite from La Creusaz deposit (Switzerland), a triclinic member of the zippeite group with the nominal chemical composition $Mg_3(H_2O)_{18}[(UO_2)_4O_3(OH)(SO_4)_2](H_2O)_{10}$. Since sejkoraite-(Y) is triclinic as well, the question of their similarity has to be addressed. Both structures are depicted on Figure 6, and as can be readily seen, the distance between the structure sheets of the zippeite-topology is different for marécottite (9.47 Å) and sejkoraite-(Y) (9.28 Å), respectively. The distance in the marécottite structure is the largest found within the zippeite-type compounds, because the interlayer cations are only bonded via hydrogen bonds to the structural sheets, whereas in sejkoraite-(Y), two yttrium atoms are bonded via uranyl apical oxygen to the structural sheets. The occupancy disorder of interlayer atoms in marécottite (Mg) seems to be less important relative to sejkoraite-(Y), where the refined values of M-site occupancies are significantly lower. Moreover, notable displacement parameters of yttrium (Y2, Y3) and coordinating oxygen atoms indicate small positional disorder, which has not been found in marécottite. However, the above-mentioned disorder cannot be described in detail based on the present data because the analysis of difference Fourier maps did not show a significant split of electron density for the oxygen atoms. The unit-cell volume of sejkoraite-(Y) (~2800 Å³) is twice as large than that of marécottite (~1400 Å³) (Table 6).

The relations to other zippeite-group minerals

Sejkoraite-(Y) is the third known triclinic mineral of the zippeite group along with marécottite (Brugger et al. 2003) and pseudojohannite (Brugger et al. 2006; unpublished data). Moreover, it is the first mineral/compound of the zippeite topology containing trivalent cations. Based on the EPMA results of sejkoraite-(Y), no other cations in addition to REE were

TABLE 6. Summary of the important physical and chemical properties of selected members of the zippeite-group

Mineral	Sejkoraite-(Y)		Marécottite
Locality	Jáchymov (Czech Republic)		La Creusaz, Switzerland
Reference	This paper		Brugger et al. (2003)
A site (Ideal)	Y _{3.00}		Mg _{3.00}
<i>n</i> H ₂ O	25		28
Crystal syst.	triclinic		triclinic
Space group	<i>P</i> $\bar{1}$		<i>P</i> $\bar{1}$
Unit cell	Single crystal	Powder	Single crystal
<i>a</i> (Å)	14.0743(6)	14.032(9)	10.815(4)
<i>b</i> (Å)	17.4174(7)	17.367(9)	11.249(4)
<i>c</i> (Å)	17.7062(8)	17.703(11)	13.851(6)
α°	75.933(4)	75.93(5)	66.224(7)
β°	128.001(5)	127.91(3)	72.412(7)
γ°	74.419(4)	74.46(5)	69.95(2)
<i>V</i> (Å ³)	2777.0(2)	2768(5)	1422.1(9)
<i>Z</i>	2		1

Mineral	Magnesiozippeite		Zippeite
Locality	Lucky Strike no. 2, U.S.A.	synt.	synt.
Reference	Brugger et al. (2003)	Burns et al. (2003)	Burns et al. (2003)
A site (Ideal)	Mg _{1.00}	Mg _{1.00}	K _{3.00}
<i>n</i> H ₂ O	3.5	3.5	3
Crystal syst.	monoclinic	monoclinic	monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2</i>
Unit cell	Powder	Single crystal	Single crystal
<i>a</i> (Å)	8.654(3)	8.6514(4)	8.7524(4)
<i>b</i> (Å)	14.182(6)	14.1938(7)	13.9197(7)
<i>c</i> (Å)	17.714(7)	17.7211(9)	17.6972(8)
α°	90	90	90
β°	103.92	104.131(1)	104.178(1)
γ°	90	90	90
<i>V</i>	2110.21	2110.25(2)	2090.4(2)
<i>Z</i>	8	8	4

present above the detection limits of the EMPA (~0.06 wt%) at the conditions used. The ionic radius of Y³⁺ (0.96 Å for CN = 7; 1.02 for CN = 8) is similar e.g., to that of Ca²⁺ (1.06 Å for CN = 7; 1.12 Å for CN = 8), and Sr²⁺ (1.21 Å for CN = 7; 1.26 Å for CN = 8) (Shannon 1976). The hydrated uranyl sulfate containing Sr²⁺ is not known. The Ca²⁺ dominant hydrated uranyl sulfate is represented by rabejacite (Deliens and Piret 1993). Disregarding the fact that the crystal structure of rabejacite is not known, its pertinence to the zippeite group is apparent enough, because its molar uranium-to-sulfur ratio corresponds to 2:1, a characteristic for the zippeite uranyl anion topology (Deliens and Piret 1993; Sejkora et al. 2000). During the reinvestigation of rabejacite, a specimen containing up to 1 wt% Y₂O₃ in addition to dominant CaO was found (unpublished data). Surprisingly, Ca was below the detection limit of EMPA analyses of sejkoraite-(Y) (see Table 1). The reason why sejkoraite-(Y) does not contain Ca, in an environment where this element is significantly present in rich coatings of gypsum and in rabejacite, has yet to be addressed.

The influence of the sulfate complexes in the shape of REE pattern in the strongly acidic solutions is not clear; pH, fluid-rock interaction, and precipitation of Fe hydroxides may have played a role (see Verplanck et al. 2004; Merten et al. 2005; Zhao et al. 2007). Consequently we can only speculate about the REE pattern of the solution from which sejkoraite-(Y) precipitated, and its influence on the REE pattern of sejkoraite-(Y). It shows maxima of the REE and Y pattern around Gd-Dy-Y and the sharp depletion of LREE and medium depletion of HREE (see the Fig. 2). These suggest that the Y-site strongly prefers ions with a radius close to 1.02 Å. The size of Ca²⁺ (1.12 Å for CN = 8) is similar to that of Pr³⁺ (1.13 Å for CN = 8), whose chondrite-

normalized concentrations is 1 to 2 orders of magnitude lower than Y or Dy. Hence, the size of the M site may be the principal factor in controlling the site occupancy.

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REFERENCES CITED

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, C.M., Polidori, G., and Camalli, M. (1994) SIRPOW 92—a program for automatic solution of crystal structures by direct methods. *Journal of Applied Crystallography*, 27, 435–436.
- Bartlett, J.R. and Cooney, R.P. (1989) On the determination of uranium-oxygen bond lengths in dioxouranium(VI) compounds by Raman spectroscopy. *Journal of Molecular Structure*, 193, 295–300.
- Brandenburg, K. and Putz, H. (2005) DIAMOND Version 3. Crystal Impact GbR, Postfach 1251, D-53002 Bonn, Germany.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, B41, 244–248.
- Brugger, J., Burns, P.C., and Meisser, N. (2003) Contribution to the mineralogy of acid drainage of uranium minerals: Marécottite and the zippeite group. *American Mineralogist*, 88, 676–685.
- Brugger, J., Wallwork, K.S., Meisser, N., Pring, A., Ondruš, P., and Čejka, J. (2006) Pseudojohannite from Jáchymov, Musonoi, and La Creusaz: A new member of the zippeite-group. *American Mineralogist*, 91, 929–936.
- Brugger, J., Meisser, N., Krivovichev, S., Armbruster, T., and Favreau, G. (2007) Mineralogy and crystal structure of bouazzerite from Bou Azzer, Anti-Atlas, Morocco: Bi-As-Fe nanoclusters containing Fe³⁺ in trigonal prismatic coordination. *American Mineralogist*, 92, 1630–1639.
- Burns, P.C. (2005) U⁶⁺ minerals and inorganic compounds: Insights into an expanded structural hierarchy of crystal structures. *Canadian Mineralogist*, 43, 1839–1894.
- Burns, P.C., Ewing, R.C., and Hawthorne, F.C. (1997a) The crystal chemistry of hexavalent uranium: Polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Canadian Mineralogist*, 35, 1551–1570.
- Burns, P.C., Ewing, R.C., and Miller, M.L. (1997b) Incorporation mechanisms of actinide elements into the structures of U⁶⁺ phases formed during the oxidation of spent nuclear fuel. *Journal of Nuclear Materials*, 245, 1–9.
- Burns, P.C., Deely, K.M., and Hayden, L.A. (2003) The crystal chemistry of the zippeite group. *Canadian Mineralogist*, 41, 687–706.
- Čejka, J. (1999) Infrared spectroscopy and thermal analysis of the uranyl minerals. In P.C. Burns and R. Finch, Eds., *Uranium: Mineralogy, Geochemistry and the Environment*, vol. 38, p. 521–622. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- (2007) Vibrational spectroscopy of uranyl minerals—Infrared and Raman spectroscopy of the uranyl minerals III. Uranyl sulfates. *Bulletin mineralogicko-petrologického oddělení Národního muzea (Praha)*, 14–15, 40–46 (in Czech).
- Čejka, J. and Sejkora, J. (1994) Minerals of the zippeite group. In conference proceedings: Mineralogy, Geochemistry and the Environment, p. 28–30, Ostrava-Poruba (in Czech).
- Cheary, R.W. and Coelho, A.A. (1996) Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England, U.K. (<http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm>).
- Deliens, M. and Piret, P. (1993) La rabejacite, Ca(UO₂)₄(SO₄)₂(OH)₆·6H₂O, nouveau sulfate d'uranyle et de calcium des gites du Lodévois, Hérault, France. *Canadian Mineralogist*, 5, 873–877.
- Fernandes, H.M., Veiga, L.H.S., Franklin, M.R., Prado, V.C.S., and Taddei, J.F. (1995) Environmental impact assessment of uranium mining and milling facilities: a study case at the Pocos de Caldas uranium mining and milling site, Brazil. In R.J. Allan and W. Salomons, Eds., *Heavy metal aspects of mining pollution and its remediation*, 52 p. 161–173. Elsevier, Amsterdam.

- Finch, R. and Murakami, T. (1999) Systematics and paragenesis of uranium minerals. In P.C. Burns and R. Finch, Eds., *Uranium: Mineralogy, Geochemistry and the Environment*, vol. 38, p. 91–179. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.
- Finch, R.J., Burns, P.C., Hawthorne, F.C., and Ewing, R.C. (2006) Refinement of the crystal structure of billietite, $\text{Ba}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_8$. *Canadian Mineralogist*, 44, 1197–1205.
- Fronzel, C., Ito, J., Honea, R.M., and Weeks, A.M. (1976) Mineralogy of the zippeite-group. *Canadian Mineralogist*, 14, 429–436.
- Frost, R.L., Weier, M.L., Borstrom, T., Čejka, J., and Martens, W. (2005) Molecular structure of the uranyl mineral zippeite—An XRD, SEM and Raman spectroscopic study. *Neues Jahrbuch für Mineralogie Abhandlungen*, 181, 271–279.
- Frost, R.L., Čejka, J., Ayoko, G.A., and Weier, M.L. (2007a) Raman spectroscopic and SEM analysis of sodium-zippeite. *Journal of Raman Spectroscopy*, 38, 1311–1319.
- Frost, R.L., Čejka, J., Bostrom, T., Weier, M., and Martens, W. (2007b) Raman spectroscopic study of molecular structure of the uranyl mineral zippeite from Jáchymov (Joachimsthal), Czech Republic. *Spectrochimica Acta A*, 67, 1220–1227.
- Li, Y. and Burns, P.C. (2000) Synthesis and crystal structure of a new Pb uranyl oxide hydrate with a framework structure that contains channels. *Canadian Mineralogist*, 38, 1433–1441.
- Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, 130, 1047–1059.
- Meisser, N., Brugger, J., and Lahaye, Y. (2002) Mineralogy and acid-mine drainage of La Creusaz uranium prospect, Switzerland. In B. Kribek and J. Zeman, Eds., *International Workshop Uranium Deposits: from their Genesis to their Environmental Aspects*, p. 147–150. Czech Geological Survey, Prague.
- Merten, D., Geletneký, J., Bergmann, H., Haferburg, G., Koth, E., and Büchel, G. (2005) Rare earth element patterns: A tool for understanding processes in remediation of acid mine drainage. *Chemie der Erde*, 65, 97–114.
- Nagashima, M., Armbruster, T., and Libowitzky, E. (2010) The hydrogen-bond system in pumpellyite. *European Journal of Mineralogy*, 22, 333–342.
- Ondruš, P., Veselovský, F., and Hloušek, J. (1997a) A review of mineral associations and paragenetic groups of secondary minerals of the Jáchymov (Joachimsthal) ore district. *Journal of the Czech Geological Society*, 42, 109–114.
- Ondruš, P., Veselovský, F., Hloušek, J., Skála, R., Vavřín, I., Frýda, J., Čejka, J., and Gabašová, A. (1997b) Secondary minerals of the Jáchymov (Joachimsthal). *Journal of the Czech Geological Society*, 42, 3–76.
- Ondruš, P., Veselovský, F., Skála, R., Cisařová, I., Hloušek, J., Frýda, J., Vavřín, I., Čejka, J., and Gabašová, A. (1997c) New naturally occurring phases of secondary origin from Jáchymov (Joachimsthal). *Journal of the Czech Geological Society*, 42, 77–107.
- Ondruš, P., Skála, R., Cisařová, I., Veselovský, F., Frýda, J., and Čejka, J. (2002) Description and crystal structure of vajdakite, $[(\text{Mo}^{6+}\text{O}_2)_2(\text{H}_2\text{O})_2\text{As}_2^{3+}\text{O}_3]\cdot\text{H}_2\text{O}$ —A new mineral from Jáchymov, Czech Republic. *American Mineralogist*, 87, 983–990.
- Ondruš, P., Veselovský, F., Gabašová, A., Hloušek, J., and Šrein, V. (2003a) Geology and hydrothermal vein system of the Jáchymov (Joachimsthal) ore district. *Journal of the Czech Geological Society*, 48, 3–18.
- Ondruš, P., Veselovský, F., Gabašová, A., Hloušek, J., Šrein, V., Vavřín, I., Skála, R., Sejkora, J., and Drábek, M. (2003b) Primary minerals of the Jáchymov ore district. *Journal of the Czech Geological Society*, 48, 19–147.
- Ondruš, P., Veselovský, F., Gabašová, A., Hloušek, J., and Šrein, V. (2003c) Supplement to secondary and rock-forming minerals of the Jáchymov ore district. *Journal of the Czech Geological Society*, 48, 149–155.
- Ondruš, P., Veselovský, F., Gabašová, A., Drábek, M., Dobeš, P., Malý, K., Hloušek, J., and Sejkora, J. (2003d) Ore-forming processes and mineral parageneses of the Jáchymov ore district. *Journal of the Czech Geological Society*, 48, 157–192.
- Palatinus, L. and Chapuis, G. (2007) Superflip—A computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied Crystallography*, 40, 451–456.
- Peeters, M.O., Vochten, R., and Bleton, N. (2008) The crystal structures of synthetic potassium-transition metal zippeite-group phases. *Canadian Mineralogist*, 46, 173–182.
- Petříček, V., Dušek, M., and Palatinus, L. (2006) Jana2006. The crystallographic computing system. Institute of Physics, Praha, Czech Republic.
- Plášil, J., Buixaderas, E., Čejka, J., Sejkora, J., Jehlička, J., and Novák, M. (2010) Raman spectroscopic study of the uranyl sulfate mineral zippeite: low wave-number and U-O stretching regions. *Analytical and Bioanalytical Chemistry*, 397, 2703–2715, DOI: 10.1007/s00216-010-3577-z.
- Pouchou, J.L. and Pichoir, F. (1985) “PAP” (ϕρZ) procedure for improved quantitative microanalysis. In J.T. Armstrong, Ed., *Microbeam Analysis*, p. 104–106. San Francisco Press, California.
- Sejkora, J., Čejka, J., and Ondruš, P. (2000) New data of rabejacite (Jáchymov, the Krušné Hory Mts., Czech Republic). *Neues Jahrbuch für Mineralogie Monatshefte*, 7, 289–301.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sheldrick, G.M. (1997) SHELXL97, Program for the refinement of crystal structures. Institut für Anorganische Chemie, Universität Göttingen, Germany.
- (2008) A short history of *SHELX*. *Acta Crystallographica*, A64, 112–122.
- Taylor, S.R. and McLennan, S.M. (1985) *The continental crust: Its composition and evolution*, 328 p. Blackwell, Oxford.
- Tvrđý, J. and Plášil, J. (2010) Jáchymov-Reiche Erzlagerstätte und Radonbad im böhmischen Westetagebirge. *Aufschluss*, 61, 277–292.
- Verplanck, P.L., Nordstrom, D.K., Taylor, H.E., and Kimball, B.A. (2004) Rare earth element partitioning between hydrous ferric oxides and acid mine water during iron oxidation. *Applied Geochemistry*, 19, 1339–1354.
- Vochten, R., Van Haverbeke, L., and Van Springel, K. (1995) The structural and physicochemical characteristics of synthetic zippeite. *Canadian Mineralogist*, 33, 1091–1101.
- Zhao, F., Cong, Z., Sun, H., and Ren, D. (2007) The geochemistry of rare earth elements (REE) in acid mine drainage from the Sitai coal mine, Shanxi Province, North China. *International Journal of Coal Geology*, 70, 184–192.

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