THE CRYSTAL STRUCTURE OF NATURAL ZIPPEITE, K$_{1.85}$H$^+_{0.15}$[(UO$_2$)$_4$O$_2$(SO$_4$)$_2$(OH)$_2$](H$_2$O)$_4$, FROM JÁCHYMOV, CZECH REPUBLIC[†]

Jakub PLÁŠIL[§]

Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, CZ–611 37 Brno, Czech Republic

Stuart J. MILLS

Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada, and Geosciences, Museum Victoria, GPO Box 666, Melbourne, Victoria 3001, Australia

Karla FEJFAROVÁ AND Michal DUŠEK

Institute of Physics ASCR, v.v.i., Na Slovance 2, CZ–18221 Praha, Czech Republic

Milan NOVÁK AND Radek ŠKODA

Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, CZ–611 37 Brno, Czech Republic

Jiří ČEJKA AND Jiří SEJKORA

Department of Mineralogy and Petrology, National Museum, Václavské nám. 68, CZ–118 79 Praha 1, Czech Republic

ABSTRACT

The crystal structure of natural zippeite, K$_{1.85}$H$^+_{0.15}$[(UO$_2$)$_4$O$_2$(SO$_4$)$_2$OH$_2$](H$_2$O)$_4$, from Jáchymov, Czech Republic, has been determined by single-crystal X-ray diffraction and refined to $R_1 = 0.0367$. Zippeite is monoclinic, space group $C2/m$, with a 8.7802(6), b 13.9903(12), c 8.8630(6) Å, β 104.524(7)°, V 1053.92(12) Å^3 and $Z = 2$. The structure consists of structural sheets of the zippeite uranyl anion topology and an interlayer, in which split K$^+$ atoms and disordered O atoms (of the H$_2$O groups) are located. The structure unit [(UO$_2$)$_4$O$_2$(SO$_4$)$_2$OH$_2$]$^{2-}$ is novel for both natural and synthetic compounds, but generally consistent with the known zippeite-type structures. The structural formula is in agreement with bond-valence analysis and the results of an electron-microprobe study. The composition of the zippeite specimen studied is assessed from the point of view of the bond-valence approach. Further, we comment on morphology of zippeite, its optical properties, and its relationship to the crystal structure.

Keywords: zippeite, single-crystal X-ray diffraction, crystal structure, chemical composition, mineral stability, Jáchymov, Czech Republic.

SOMMAIRE

Nous avons établi la structure cristalline d'un échantillon naturel de zippéite, K$_{1.85}$H$^+_{0.15}$[(UO$_2$)$_4$O$_2$(SO$_4$)$_2$OH$_2$](H$_2$O)$_4$, provenant de Jáchymov, République Tchèque, par diffraction X sur monocristal jusqu'à un résidu R_1 égal à 0.0367. La zippéite est monoclinique, groupe spatial $C2/m$, avec a 8.7802(6), b 13.9903(12), c 8.8630(6) Å, β 104.524(7)°, V 1053.92(12) Å^3 et $Z = 2$. La structure est faite de feuillets structuraux ayant la topologie uranyle anionique typique de la zippéite et un interfeuillet, dans lequel sont situés des atomes K$^+$ à position dédoublée et des atomes d'oxygène désordonnés (faisant partie des groupes H$_2$O). L'unité structurale [(UO$_2$)$_4$O$_2$(SO$_4$)$_2$OH$_2$]$^{2-}$ est non standard parmi les composés naturels et synthétiques, mais généralement concordante avec les structures connues de matériaux de type zippéite. La formule structurale concorde avec l'analyse des

[§] *Present address*: Mineralogical Crystallography, Institute of Geological Sciences, University Bern, Freiestrasse 3, CH–3012 Bern, Switzerland. *E-mail address*: jakub.plasil@krist.unibe.ch

[†] Dedicated to the memory of Radim Nováček (1905–1942), Professor of Mineralogy of the Charles University in Prague *in memoriam*, Czech mineralogist and a brave man, murdered by Nazis in the concentration camp of Mauthausen, Austria. The uranyl arsenate minerals nováčekite I, II and metanováčekite are named in his honor.

valences de liaison et les résultats de nos analyses avec une microsonde électronique. La composition de notre échantillon de zippéite est évaluée du point de vue des valences de liaison. De plus, nous évaluons la morphologie de la zippéite, ses propriétés optiques et la relation de celles-ci avec la structure cristalline.

(Traduit par la Rédaction)

Mots-clés: zippéite, diffraction X sur monocristal, structure cristalline, composition chimique, stabilité du minéral, Jáchymov, République Tchèque.

Introduction

Zippeite, $K_x[(UO_2)_4(SO_4)_2O_x(OH)_{4-x}](H_2O)_{6-x}$ (where $x \approx 2$), is a hydrated potassium uranyl sulfate, and the root name for a whole group of mineral species [note that there is currently no nomenclature approved by the CNMNC for the zippeite group that follows the nomenclature of Mills *et al.* (2009)]. Since the discovery of zippeite in 1845 by Haidinger, the mineralogy of this mineral, and the whole group in general, has attracted a lot of scientific work. However, despite the recent crystallographic research on synthetic analogues, the nature, chemical composition and the crystal structure of natural zippeite remain uncertain. The purpose of this study is to finally close the gaps in the knowledge of this natural mineral phase.

A Short Review of the Mineralogy of Zippeite

The discovery of the first uranyl sulfate, most probably of the zippeite group, was made by Austrian chemist F.J. John in 1821 during his study of uranium minerals from Jáchymov (St. Joachimsthal), Bohemia (John 1821). The mineral name *zippeite* was introduced later by Wilhelm Haidinger (1845) to honor Austrian mineralogist and geologist Franz Xaver Maxmilian Zippe (1791–1863), the first custodian of the mineral collection at the National Museum in Prague, and later professor of mineralogy at The University of Vienna. The first scientific study of "zippeites" was undertaken by Czech mineralogist Radim Nováček (1935). He demonstrated that the uranium-to-sulfur molar ratio for natural zippeite is equal to 2. Furthermore, he discovered that the molecular H_2O content in zippeite may be variable (he considered zippeite as a single species; the differences in their composition were revealed years later). Until 1976, it was accepted that zippeite is a hydrated uranyl sulfate mineral devoid of cations. Finally, Frondel *et al.* (1976) analyzed zippeite minerals and distinguished K^+, Na^+, Mg^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} members. The K^+-dominant member, nominally $K_4(UO_2)_6(SO_4)_3(OH)_{10}(H_2O)_4$, from a sample originating from Jáchymov, was used to establish zippeite and the root name for the group. Frondel *et al.* (1976) also prepared a NH_4^+-dominant member, discovered isomorphic trends in the mono- and divalent cation-containing groups, and inferred an orthorhombic symmetry for natrozippeite. Spitsyn *et al.* (1982)

reported a crystal structure for the synthetic compound containing zippeite-type uranyl sulfate sheets with Zn^{2+} cations in the interlayer space. The Zn^{2+} cations are octahedrally coordinated by four H_2O molecules and two uranyl oxygen atoms that belong to the uranyl pentagonal bipyramids of each adjacent sheet. Deliens & Piret (1993) described a new mineral, rabejacite from Lodèvois, Hérault (France), orthorhombic $Ca(UO_2)_4(SO_4)_2OH_6(H_2O)_6$. The crystal structure of rabejacite is unknown; the characteristic U:S ratio indicates, however, that rabejacite is probably a member of the zippeite group. Vochten *et al.* (1995) reported the crystal structure of a synthetic zippeite-like compound with a structural formula $K(UO_2)_2(SO_4)(OH)_3 \cdot H_2O$, and $Z = 8$, with the monoclinic space-group $C2/c$.

Burns (1999) introduced a new classification for uranyl minerals and compounds, which is based on polymerization of the polyhedra owing to higher bond-valence. The zippeite-type sheets involve chains of edge-sharing uranyl pentagonal bipyramids, two polyhedra wide, which are linked by sharing vertices with sulfate tetrahedra. This arrangement results in a U:S molar ratio of 2. Brugger *et al.* (2003) described the new mineral species *marécottite* from the La Creusaz deposit, Switzerland, nominally $Mg_3(H_2O)_{18}[(UO_2)_4O_3(OH)(SO_4)_2]_2(H_2O)_{10}$, with $Z = 1$. Marécottite contains zippeite-type sheets, but differs from magnesiozippeite in its interlayer configuration. Because of this, its symmetry is lower, triclinic, with the space group $P\bar{1}$. Brugger *et al.* (2003) also reported the redefinition of magnesiozippeite. Burns *et al.* (2003) provided a complete crystallographic study based on the synthetic analogues of the zippeite-group minerals. Zippeites (mono- and divalent) are of monoclinic symmetry, mostly belonging to the $C2/m$ space group (including those containing Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and one of the synthetic NH_4^+ zippeites), $P2_1/n$ (natrozippeite), $P2_1/c$ (a second synthetic magnesiozippeite) and orthorhombic $Cmca$ (a second synthetic NH_4^+ zippeite). Synthetic zippeite, according to Burns *et al.* (2003), has the nominal composition $K_3(H_2O)_3[(UO_2)_4(SO_4)_2O_3(OH)]$, with $Z = 4$, and has the space group $C2$. McCollam (2004) examined both synthetic and natural zippeites, encompassing the samples from the study of Burns *et al.* (2003). In her thesis, a few important features are discussed, namely the chemical composition of natural samples. Brugger *et al.* (2006) published crystallographic data for pseudo-

johannite, $Cu_{6.5}[(UO_2)_4O_4(SO_4)_2]_2(OH)_5(H_2O)_{25}$, with $Z = 1$, a new mineral species from Jáchymov (Ondruš *et al.* 2003). On the basis of a high-resolution powder synchrotron-diffraction data, Brugger *et al.* (2006) inferred a triclinic symmetry ($P1$ or $P\bar{1}$) and found the positions of heavy atoms (U and S). Peeters *et al.* (2008) reported crystallographic data for mixed cationic site zippeites (K^+ with Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) and introduced the important idea that potassium content in zippeite can be variable. They proposed a general formula, $K_x[(UO_2)_2(SO_4)O_x(OH)_{2-x}](H_2O)_{3-x}$. An important comment on the composition of zippeite was also made by Schindler & Hawthorne (2008) using a bond-valence approach. A chemical formula for zippeite, derived by such approach, should be $^{[7.33]}K_3(H_2^{[5]}O)[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5$. Seven-coordinated K^+ cations should bond to one inverse-transformer (H_2O) group, and an additional five non-transformer (H_2O) groups should be present in the crystal structure. A new mineral, sejkoraite-(Y) (IMA 2009–008), ideally triclinic $Y_3^{3+}(OH)_2[(UO_2)_8O_7OH(SO_4)_4](H_2O)_{24}$, with $Z = 2$, has structural sheets with the zippeite uranyl anion topology, and accommodates in the interlayer trivalent Y and REE (Plášil *et al.* 2011). Recently, Goss (2009) focused on the thermodynamics of zippeite compounds, giving the enthalpies of formation ΔH^0_f for zippeite, natrozippeite and magnesiozippeite, and Plášil *et al.* (2010) studied a well-characterized sample of zippeite (the same specimen used in the current study) by Raman spectroscopy, focusing namely on the low-wavenumber region.

From the history of zippeite research, we can conclude that a few important problems still need to be addressed. These problems were also outlined by Plášil *et al.* (2010). (1) Previous crystal-structure studies of zippeite *sensu stricto* were performed on samples synthesized under hydrothermal conditions, (2) there are nominal discrepancies in chemical composition between the natural and synthetic samples, (3) the reported H_2O content of natural zippeite species is variable, and (4) the cationic content within one mineral may be variable, which reflects the conditions of origin (pH–Eh and K^+ activity).

OCCURRENCE

The samples of zippeite that we studied originate from the type locality, Jáchymov, western Bohemia, Czech Republic. Samples containing an assemblage of secondary uranyl minerals including zippeite were found in the old mining works in the "Červená" vein (formerly known in German as the "Rottergang"), Daniel adit, Rovnost shaft (formerly Werner). A body of Tertiary basalt is found in proximity of the ore vein. This body of basalt contains notable phenocrysts of unanalyzed minerals from the mica group.

Zippeite is quite rare in the vein material, and occurs on the fracture surface and in small vugs in the vein gangue. Based on visual inspection, zippeite occurs in two generations (hence we designate them I and II); fine-grained zippeite II overgrows older zippeite I crystals (Fig. 1). The minerals observed in direct association with zippeite are gypsum in crystalline aggregates (Fig. 2), and mostly amorphous or poorly crystalline Cu (±) U sulfates and chalcophyllite. No additional uranyl minerals have been found in the proximity of the zippeite, except rabejacite (on one sample) and an inadequately characterized $Cu–UO_2–VO_4–H_2O$ phase overgrowing the surface of chalcopyrite grains in the gangue. The primary mineralogy is represented by strongly altered uraninite (which is primarily decomposed to the alteration products), chalcopyrite, tennantite and, locally, chalcocite.

EXPERIMENTAL

Single-crystal X-ray diffraction (SC–XRD), high-resolution synchrotron powder diffraction, crystal-structure solution and refinement

A $0.141 \times 0.126 \times 0.067$ mm tabular orange crystal of zippeite I was selected for the single-crystal X-ray diffraction experiment on Oxford diffraction Gemini single-crystal diffractometer with Atlas CCD detector, using monochromatic MoKα radiation, $\lambda = 0.71073$ Å, with fiber-optics Mo-Enhance collimator. For the entire measurement, a detector-to-crystal distance of 55 mm was set. The unit-cell parameters, a 8.7802(6), b 13.9903(12), c 8.8630(6) Å, β 104.524(7)° and V 1053.92(12) Å^3 were refined by a least-square refinement (CRYSALIS PRO package, Oxford Diffraction 2010) using 2292 reflections. Analyzing the diffraction pattern, it was found that a portion of unindexed reflections existed due to twinning. Omega scans were used (1° per step, with a counting time 80 s per °) for data collection. A total of 600 frames were acquired between 2.91 and 26.31 θ, which represents 99.84% of the Ewald sphere. A total number of 14987 measured reflections were integrated and corrected for Lorentz, polarization and background effects using Oxford Diffraction software CRYSALIS PRO package (Oxford Diffraction 2010). In all, 1125 of the reflections are considered unique, with 785 classified as observed [with $I_{obs}>3\sigma(I)$]. An analytical absorption correction, $\mu = 31.30$ mm^{-1}, taking into account a crystal shape modeled as a multifaceted plate (Clark & Reid 1995), was followed by a decrease of R_{int} factor from 24% to 7.9%. A summary of data collection, crystallographic data and refinement are listed in Table 1.

In addition, the high-resolution powder X-ray-diffraction data for zippeite I were collected at the bending magnet of the PDIFF beamline, ANKA synchrotron source (KIT, Karlsruhe, Germany) using monochromatic radiation (energy = 14.99 keV, λ = 0.82694 Å). The precise wavelength and the zero angle of the diffractometer were calibrated by using

Fɪɢ. 1. Two types of zippeite crystals. In the background, the older zippeite, studied by SC–XRD. The younger zippeite (right, focused part of the image) locally covers the massive crystalline aggregates. SE image, field of view 250 μm (JEOL JSM–6380).
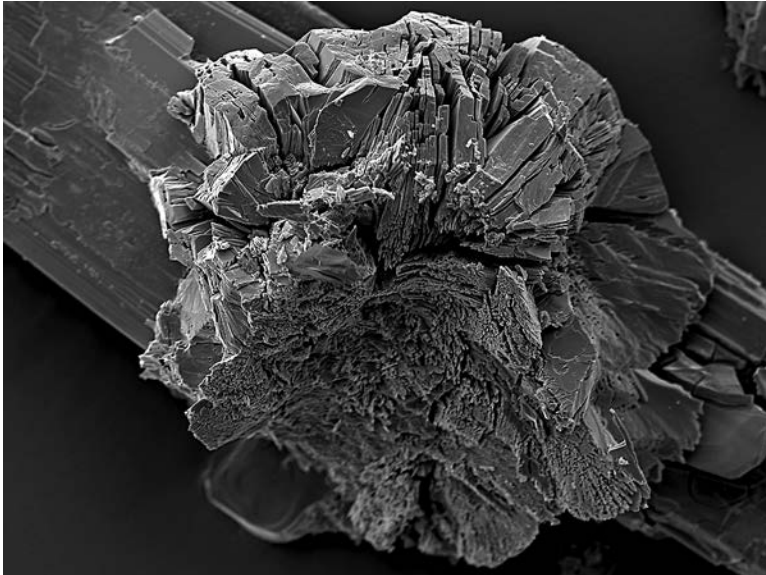

Fɪɢ. 2. Crystal aggregate of zippeite I growing on a gypsum crystal. Note the apparent cleavage of the crystals. SE image, field of view 450 μm (JEOL JSM–6380).

a silicon powder standard (NIST standard reference material 640). The zippeite sample was loaded into a 0.3 mm glass capillary, rotated about its axis during data collection. The intensity of the incoming beam was monitored during the data collection by an ion chamber, and the measured intensities of the diffracted beam were corrected for the decay and fluctuations of the primary beam. The XRD patterns were collected at room temperature with the scintillation counter and Ge (111) analyzer, over an angular range 4–35° 2θ, with the step of 0.005° 2θ and counting time of 2 s per point. The JANA2006 software (Petříček *et al.* 2006) was utilized for the Le Bail decomposition of the patterns to model differences between possible centrosymmetric and non-centrosymmetric space-groups and superstructure unit-cells. The Le Bail refinement followed the standard procedures (*e.g.*, Le Bail *et al.* 1988, Le Bail 2005). The background was modeled as Legendre polynomials of the 8th order, the zero shift was refined and the peak shapes were modeled as pseudo-Voigt profile functions (refined GW and LY parameters only). Asymmetry

was not taken into account, because the experimental settings of the beamline minimize that effect. Estimated standard uncertainties were corrected for local correlations after the procedure of Bérar & Lelann (1991). The statistical factors for both data sets are listed in Table 2.

Vochten *et al.* (1995) and Burns *et al.* (2003) reported the unit cell of synthetic zippeite with double the *c* dimension obtained for the currently investigated natural sample. Our data were carefully checked, and no reflections were observed to suggest that the *c* axis should be doubled. The reflections with *k* = odd are weak, but nevertheless present. These reflections are not connected with twinning. Systematic absences indicated that the unit cell is *C*-centered. The natural sample of zippeite was found to be crystallizing in the space group *C*2/*m*, which is different from those previously reported. However, the indexing of the single-crystal data is clear, the reflections connected with halving of the unit cell neither adhere to the second twin domain, nor to other artifacts.

The Le Bail refinements, based on the high-resolution synchrotron powder-diffraction data of natural zippeite, were performed for two possible models of zippeite structure: "ours" in *C*2/*m* and the model in *C*2 with a doubled *c* axis using a structural model proposed by Burns *et al.* (2003) for the synthetic zippeite obtained from the *American Mineralogist Crystal Structure Database* (Downs & Hall-Wallace 2003). The refinements for the two possibilities were carried out to see the fundamental differences, resulting namely from the absence of the mirror plane for the second choice. The results of the fits are summarized in Table 2, and the final plots with the highlighted beginning of the pattern with labeled peaks are displayed in Figures 3a, b. Statistical factors for both refinements showed similar values, even if the *C*2 model looks slightly better. We considered this as a result of presence of more peaks modeled, which can be modeled in the doubled *C*2 structure.

Furthermore, we tried the crystal-structure refinement from the single-crystal data in *C*2. That choice led to a significantly worse *R*-factors ($R_1 \approx 9\%$), strange

TABLE 1. SUMMARY OF DATA-COLLECTION CONDITIONS AND REFINEMENT PARAMETERS FOR NATURAL ZIPPEITE

Structural formula	$K_{1.85}[(UO_2)_4O_2(SO_4)_2(OH)_2](H_2O)_4$

Crystal data

Unit-cell parameters (based on 2292 reflections)	
a, *b* (Å)	8.7802(6), 13.9903(12)
c, β (Å, °)	8.8630(6), 104.524(7)
V (Å³)	1053.92(12)
Z	2
Space group	*C*2/*m*
Absorption correction (mm⁻¹), method	31.30, analytical
F_{000}	1260
D_{calc} (g cm⁻³)	4.66

Data collection

Temperature (K)	293
Wavelength	Mo*K*α, 0.7107 Å
Crystal dimensions (mm)	0.1410 × 0.1262 × 0.0666
Collection mode	ω scans to fill the Ewald sphere
Count time	80 s per °
Limiting 2θ angles	2.91–26.31°
Limiting Miller indices	−10 < *h* < 10, −17 < *k* < 17, −11 < *l* < 11
No. of reflections	14987
No. of unique reflections	1111
No. of observed reflections (criterion), R_{int}, coverage	773 [I_{obs}>3σ(*I*)], 0.079, 99.84%

Refinement by JANA2006 (full-matrix least squares) on F^2

Parameters refined, constraints	82,6
R_1	0.0367
wR_1	0.0707
R_2	0.0647
wR_2	0.0812
$GOF_{(obs)}$	1.10
Δσ_min, Δσ_max (e/Å³)	−2.99, 3.83
Twin matrix	$\begin{pmatrix} -0.82 & -0.04 & -0.41 \\ 0.01 & -1 & 0 \\ -0.81 & -0.04 & 0.82 \end{pmatrix}$

TABLE 2. RESULTS FROM THE Le Bail REFINEMENT OF THE HIGH-RESOLUTION SYNCHROTRON POWDER-DIFFRACTION DATA ON NATURAL ZIPPEITE AND FROM THE CELREF PROGRAM

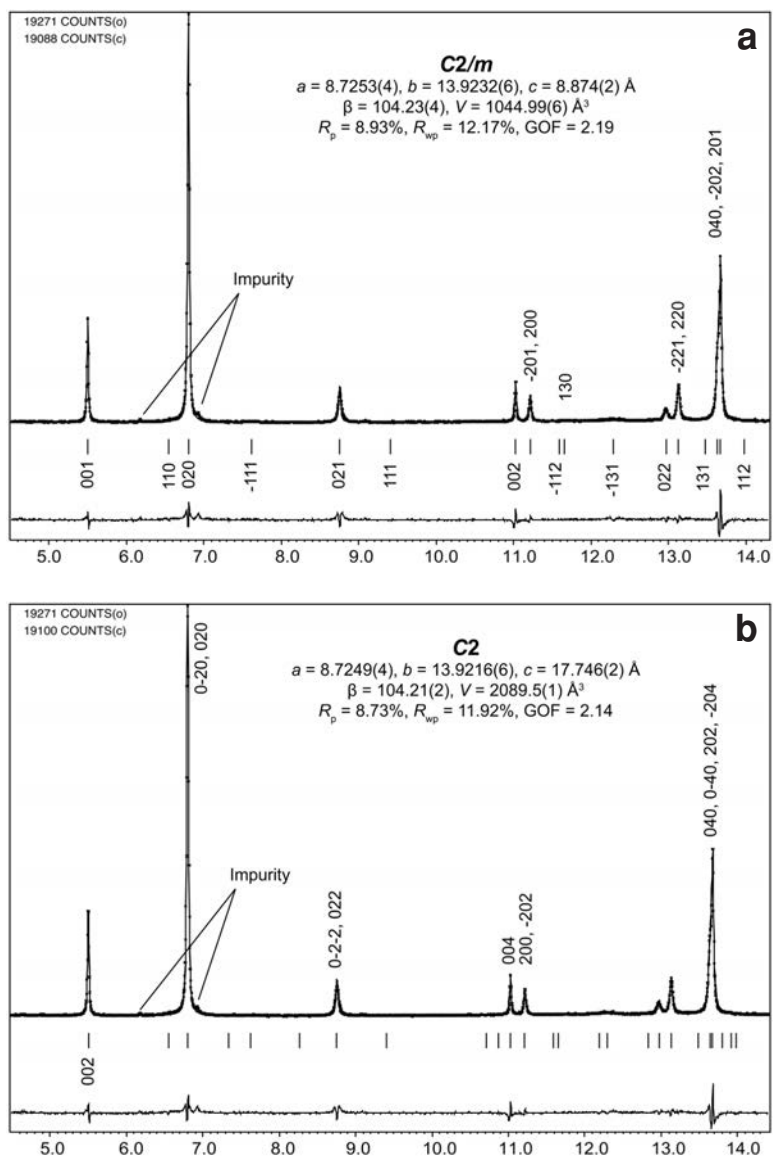|	Le Bail		CELREF
	*C*2/*m*	*C*2	*C*2/*m*
a [Å]	8.7253(4)	8.7249(4)	8.727(2)
b [Å]	13.9232(6)	13.9216(6)	13.925(3)
c [Å]	8.874(2)	17.746(2)	8.876(2)
β [°]	104.23(4)	104.21(2)	104.230(2)
V [Å³]	1044.99(6)	2089.5(1)	1045.4(4)
R_p (%)	8.93	8.73	-
R_{wp} (%)	12.17	11.92	-
GOF	2.19	2.14	-

FIG. 3. A, B. Final plots from the Le Bail refinement of the synchrotron powder-diffraction data of the zippeite studied, for the two space-group possibilities with no obvious differences, except higher number of calculated reflections in the case of the non-centrosymmetric group.

bond-lengths and coordinations, split positions and cigar-shaped atomic displacement parameters, which are all features commonly observed where the choice of space group is incorrect.

The crystal structure of zippeite (Table 3) was solved by the charge-flipping method from the single-crystal X-ray-diffraction data using the SUPERFLIP program

(Palatinus & Chapuis 2007) and subsequently refined with the software JANA2006 (Petříček *et al.* 2006). The space group $C2/m$ was suggested by the SUPERFLIP program and verified in the subsequent refinement. The structure was also independently solved using direct methods in SHELXL (Sheldrick 2008), which gave the same results as those from JANA2006. All

framework atoms were refined using harmonic atomic displacement parameters (*ADP*); atoms belonging to molecular H_2O were refined isotropically. The K and O atoms in the interlayer were found to be positionally disordered and split (long flat thermal ellipsoids). The refinement converged with the final agreement indices $R_1=3.67\%$, $wR_1= 7.07\%$ and a $GOF = 1.17$, taking into account the twinning matrix (Table 1) for detection of fully overlapped, fully separated and partially overlapped reflections, using user-defined limits on the diffraction angles. [Note that the software JANA2006 uses the weighting scheme based on the experimental expectations that do not force the *GOF* to be equal to one. Therefore, the values of *GOF* are usually larger than those from the SHELX program.] The second twin-fraction volume was refined to be 8%. The atomic positions and displacement parameters are listed in Tables 3 and 4. For plotting, the DIAMOND program (CRYSTAL IMPACT: Brandenburg & Putz 2005) was used. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the Mineralogical

Association of Canada website [document Zippeite CM49_1089].

Chemical study (EMPA)

The chemical composition of zippeite was determined by a Cameca SX100 electron microprobe (EMP) operating in the wavelength-dispersive mode with an acceleration voltage of 15 kV, specimen current of 2 nA, and 20 μm beam diameter. The following X-ray lines and standards were selected to minimize line overlaps: *K*α lines: S (barite), K (sanidine), Na (albite), Ca (andradite), Fe (andradite), Si (sanidine), Co (Co metal), *M*β lines: U (U metal). Peak counting times (CT) were 10–20 seconds for major elements, 40–60 seconds for minor to trace elements, and the counting time for background was 50% of the peak CT. The measured intensities were converted to element concentrations using the PAP program (Pouchou & Pichoir 1985).

RESULTS

Appearance of zippeite crystals

Zippeite appears on the samples as two types of aggregates of different appearance. The older zippeite I is represented by the thick platelets reaching up to 100 μm (Fig. 4), rarely up to 250 μm, forming crystal aggregates of orange to yellow-orange color. These aggregates reach up to 2 mm in size and younger crystals of sulfur-yellow zippeite II overgrow them. The crystals exhibit a prominent flattened face and a suite of additional faces and edges, which bound the shape. Commonly, an elongation along one axis occurs (for further description, see the Discussion).

Description of the crystal structure

The crystal structure of natural zippeite is, in general terms, of the same nature as that reported by Vochten *et al.* (1995), Burns *et al.* (2003), and also Peeters *et*

TABLE 3. POSITIONS AND DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN THE STRUCTURE OF NATURAL ZIPPEITE

	Site	x	y	z	U_{eq}
U1	8*j*	0.32998(6)	0.23438(4)	0.32576(6)	0.0279(2)
S1	4*g*	0.5	0.2579(3)	0	0.023(2)
K1*	4*i*	0.118(3)	0.5	0.353(4)	0.063(4)
K2*	4*i*	-0.067(1)	0.5	-0.233(1)	0.063(4)
O1	8*j*	0.1233(9)	0.1800(7)	0.096(1)	0.031(3)
O2	8*j*	0.435(1)	0.1961(7)	0.103(1)	0.032(3)
O3	8*j*	0.303(1)	0.3556(7)	0.275(1)	0.041(4)
O4	8*j*	0.353(1)	0.1107(6)	0.363(1)	0.039(4)
O5	8*j*	0.102(1)	0.2369(8)	0.410(1)	0.055(4)
O6a (Wa)#	4*i*	0.061(4)	0	0.300(5)	0.047(6)
O6b (Wa)#	4*i*	0.074(3)	0	0.399(5)	0.047(6)
O7a (Wa)#	4*i*	0.225(3)	0.5	-0.011(3)	0.055(7)
O7b (Wa)#	4*i*	0.334(9)	0.5	0.015(8)	0.055(7)

* refined occupancies of K1 = 0.24(1), K2 = 0.68(1).
# refined occupancies of Wa sites are: 0.47(2) O6a, 0.53(2) O6b, 0.75(2) O7a, 0.25(2) O7b. Note that U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR ATOMS IN THE STRUCTURE OF NATURAL ZIPPEITE

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U1	0.0216(3)	0.0443(4)	0.0175(3)	-0.0068(2)	0.0046(2)	-0.0001(3)
S1	0.013(2)	0.039(3)	0.018(2)	0	0.007(2)	0
K1	0.043(5)	0.053(5)	0.099(8)	0	0.031(6)	0
K2	0.043(5)	0.053(5)	0.099(8)	0	0.031(6)	0
O1	0.018(5)	0.055(6)	0.017(5)	-0.007(4)	0.000(4)	-0.010(4)
O2	0.028(5)	0.057(6)	0.013(5)	-0.007(4)	0.009(4)	-0.007(4)
O3	0.025(6)	0.060(7)	0.036(6)	-0.007(4)	0.008(5)	-0.016(5)
O4	0.028(6)	0.036(6)	0.046(7)	-0.004(4)	-0.003(5)	0.008(5)
O5	0.016(5)	0.12(1)	0.029(6)	0.001(5)	0.005(4)	0.005(6)

The exponent of the anisotropic displacement factor takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

al. (2008) for the synthetic analogues. The structural unit $[(UO_2)_4O_2(SO_4)_2(OH)_2]^{2-}$ builds up the uranyl – sulfate sheets of the zippeite uranyl anion topology (Fig. 5), with the nominal U:S ratio equal to 2:1. These sheets consist of pentagonal UO_2O_5 bipyramids that are linked to two others by sharing the equatorial vertices only, forming chains that are two polyhedra wide. Each pentagonal bipyramid shares three of its equatorial ligands within the chain. The remaining two vertices are linked to sulfate tetrahedra that cross-link these chains. Each sulfate tetrahedron shares all of its vertices with a different uranyl bipyramid. The only anions within the sheets that are not bonded to at least two cations are the uranyl oxygen atoms, as was previously reported by Burns et al. (2003).

The crystal structure of the natural zippeite (Fig. 6) contains one symmetrically unique ($4i$) positionally disordered K^+ site. The K1 site is seven-coordinated by six O_{Ur} atoms (O3 and O4) and one oxygen atom belonging to the split site of the H_2O (O6b) (Table 5). The K2 site is nine-fold coordinated to four O_{Ur} atoms (O3 and O4), three O atoms of the H_2O sites (O7a and O7b) and weakly to two O atoms of the sulfate groups (O2). The refined site-occupancy for K atoms are 0.68 (K1) and 0.24 (K2), respectively, which give a total of 1.85 K^+ in the asymmetric unit per unit cell, if Z is equal to 2.

Selected interatomic distances and other geometrical information for the crystal structure of zippeite are listed in Table 5.

The bond-valence analysis and structural formula

The bond-valence analysis for the crystal structure of natural zippeite is listed in Table 6. The bond-valence sum of the U site [calculated using the parameters of Burns et al. (1997)] is 6.13 vu, in agreement with the assignment of U as being hexavalent; the site is slightly oversaturated, however. The bond valence for the S site is 5.94 vu, which is consistent with the formal valence of S^{6+}. Inspection of the bond valences show that the O5 atom has some OH character. In this case, the bond-valence incident to U^{6+} will be slightly lower and, therefore, closer to six. If we consider that the ratio between O^{2-} and OH^- on the site is 1:1, we obtain two oxygen atoms and two hydroxyl groups per formula unit, which equates to the structural unit $[(UO_2)_4O_2(SO_4)_2(OH)_2]^{2-}$. Therefore, the formula of the natural zippeite based on the refinement is: $K_{1.85}H^+_{0.15}[(UO_2)_4O_2(SO_4)_2(OH)_2]$ $(H_2O)_4$. The presence of H^+ is based only on charge-balance considerations and cannot be proved or discarded with the results of the current refinement.

Chemical composition of studied crystals (EPMA)

The chemical composition (Table 7) of zippeite I can be expressed by the empirical formula (mean results of four spot-analyses, based on K + Na + Ca + Fe + Co + S + Si + U = 8 apfu): $(K_{1.73}Fe_{0.04}Ca_{0.02}Na_{0.02}Co_{0.01})_{\Sigma1.82}$ $[(UO_2)_{4.16}O_2(OH)_{1.91}((SO_4)_{1.90}(SiO_4)_{0.13})_{\Sigma2.03}](H_2O)_4.$
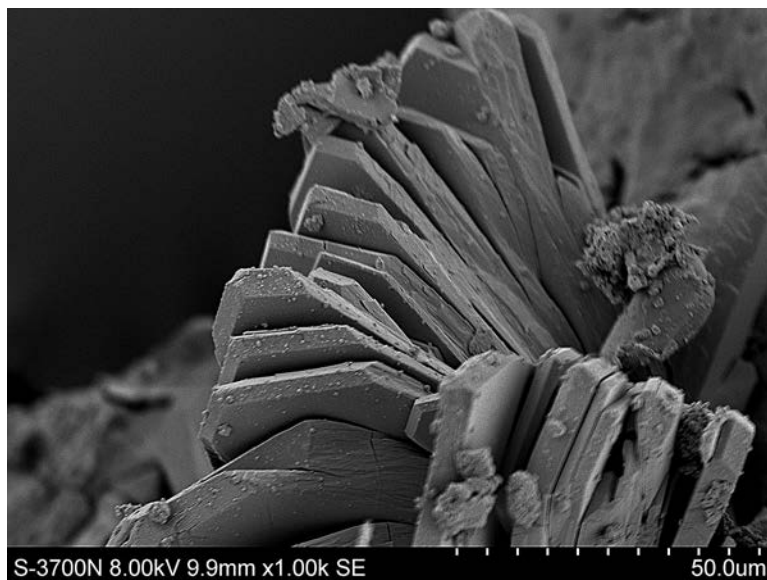

S-3700N 8.00kV 9.9mm x1.00k SE   50.0um

FIG. 4. Perfect platy crystals of zippeite I with prominent (010) basal face. Note the elongation, the (100) edge. The oblique terminations, such as the (101) edge, are not usually such apparent in the morphology of other zippeite crystals, mainly more fine-grained (powder) (cf. similar nature of crystals in the paper of Vochten et al. 1995). SE image (Hitachi S3700N).

FIG. 5. Uranyl sulfate sheet of zippeite anion topology found in natural zippeite from Jáchymov. Uranyl pentagonal bipyramids of the sheets are shown in blue, the sulfate tetrahedra in yellow, whereas the oxygen atoms are shown in red. The mixed O,OH site O5 is displayed in pink.
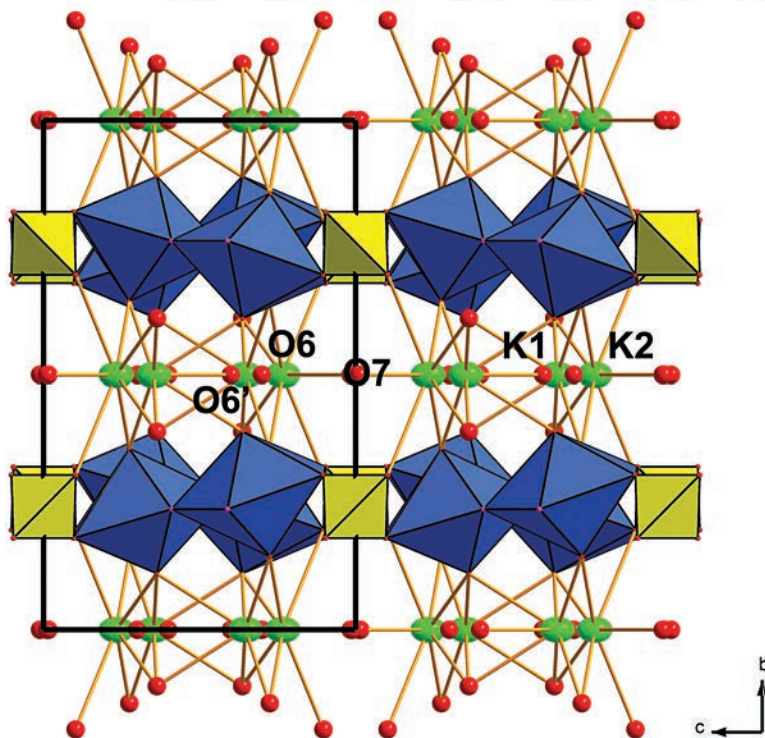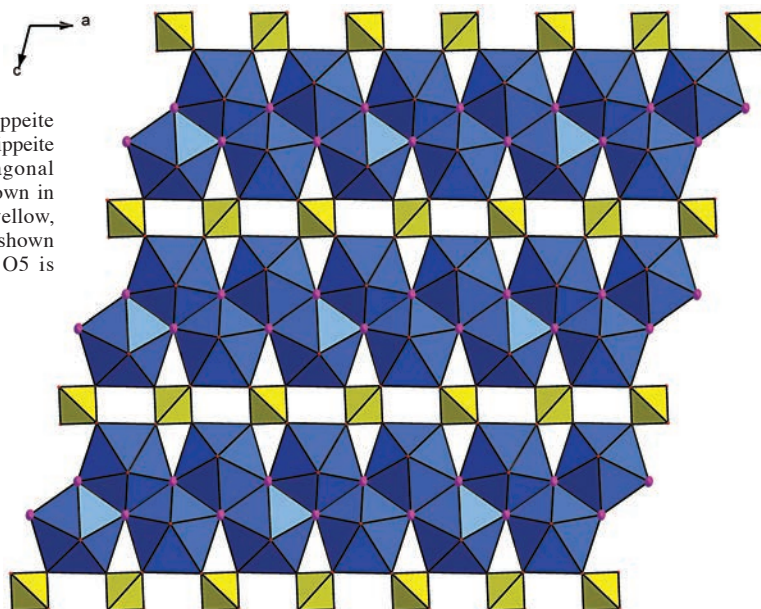

FIG. 6. The crystal structure of natural zippeite projected along [100]. Blue polyhedra represent UO$_7$ pentagonal bipyramids linked by sulfate tetrahedra (yellow) into sheets of the zippeite uranyl-anion topology with molar ratio U:S = 2:1. In the interlayer, two (K1 and K2) K$^+$ positions (green) are coordinated to the adjacent sheets and to each other *via* a H$_2$O molecule (O7 atom). The unit-cell edges are sketched, and the thermal ellipsoids representing anisotropic atomic displacements are drawn at the 50% probability level.

The OH content that was calculated on the basis of charge balance (with fixed two O atoms in the structural sheet) is in accordance to the value obtained from the refinement, as well as the content derived from the ideal formula proposed by Peeters *et al.* (2008). The U:S ratio varies only slightly from the ideal value of 2. The average is represented by 2.06, with a range from 1.99 to 2.16. Some beam damage of the crystals may account for these slightly high values. The EPMA results proved that our sample is K⁺-dominant and contains only minor concentrations of additional cations. The substitution trend involving univalent and divalent elements at the cationic position in the zippeite studied can be expressed as $M^+ \leftrightarrow 0.5\ M^{2+}$.

TABLE 6. BOND-VALENCE ANALYSIS FOR ZIPPEITE

	U	K1	K2	S1	ΣBV
O1	0.43			1.45 ×2↓	1.88
O2	0.46		0.15 ×2↓	1.52 ×2↓	2.05
O3	1.76	0.17 ×2↓	0.29 ×2↓		2.07
O4	1.73	0.32 ×2↓, 0.24 ×2↓	0.26 ×2↓		2.15
O5	1.75				1.75
O6a					0.00
O6b		0.09			0.09
O7a			0.16, 0.14		0.30
O7b			0.03		0.03
ΣBV	6.13	0.99	0.96	5.94	

Values are expressed in valence units (*vu*). Multiplicity is indicated by ×↓; the U⁶⁺–O bond strengths (r_0 = 2.045, b = 0.51) are taken from Burns *et al.* (1997); the S⁶⁺–O and K–O bond strengths are taken from Brown & Altermatt (1985).

TABLE 5. SELECTED BOND-DISTANCES AND INTERATOMIC DISTANCES [Å], BOND ANGLES [°], AND DISTORTION INDICES§ IN THE CRYSTAL STRUCTURE OF NATURAL ZIPPEITE

U1–O1	2.479(7)	S1–O1ⁱˣ	1.481(8)	×2
U1–O2	2.442(9)	S1–O2	1.470(10)	×2
U1–O3	1.757(10)	<S–O>	1.48	
U1–O4	1.764(9)	Δ	0.004	
U1–O5	2.307(10)	O1–S1–O2	111.3(2)	×2
U1–O5ⁱ	2.299(10)	O1–S1–O2	109.1(3)	
U1–O5ⁱⁱ	2.351(9)	O2–S1–O2	108.0(3)	
<O_Ur–U–O_Ur>	176.1(3)	O2–S1–O1	108.6(3)	
<U–O_Ur>	1.76	O1–S1–O1	108.2(3)	
<U-O_eq>	2.38	<O–S–O>	109.42	
		σ²	2.23	
		ECoN	4.00	
K1–O3	2.79(2)	K2–O2ᵛⁱⁱⁱ	3.087(10)	
K1–O3ⁱᵛ	2.79(2)	K2–O2ⁱˣ	3.087(10)	
K1–O4ᵛ	2.81(3)	K2–O3ⁱˣ	2.849(11)	
K1–O4ᵛⁱⁱ	2.81(3)	K2–O3ˣ	2.849(11)	
K1–O4ᵛⁱ	2.91(3)	K2–O4ᵛⁱⁱⁱ	2.887(14)	
K1–O4ⁱ	2.91(3)	K2–O4ⁱˣ	2.887(14)	
K–O6bᵛⁱ	3.02(4)	K2–O7a	2.85(3)	
<K–O>	2.86	K2–O7aⁱⁱⁱ	2.81(2)	
V_K1	27.70 Å³	K2–O7bⁱⁱⁱ	3.39(9)	
Δ	0.026	<K–O>	2.98	
ECoN	6.79	V_K2	39.23 Å³	
		Δ	0.050	
		ECoN	8.00	
O1–O1ⁱⁱⁱ	2.399(10)	O3–O7a	3.18(2)	
O1–O2	2.735(12)	O3–O7b	3.12(6)	
O1–O2ⁱˣ	2.437(12)	O4–O4ˣⁱᵛ	3.064(12)	
O1–O2ᵛⁱⁱ	2.404(13)	O4–O4ˣᵛ	3.100(13)	
O1–O3	3.125(12)	O4–O5	2.935(14)	
O1–O4	2.863(11)	O4–O5ⁱ	2.887(14)	
O1–O5	2.942(14)	O4–O5ⁱⁱ	3.006(14)	
O1–O6a	3.23(3)	O4–O6a	2.93(3)	
O1–O7aⁱˣ	3.032(18)	O4–O6b	2.98(3)	
O1–O7bˣⁱ	2.77(3)	O4–O7aˣⁱ	3.39(2)	
O2–O2ˣⁱⁱ	2.379(14)	O5–O5ˣᵛⁱ	2.677(15)	
O2–O3	3.091(14)	O5–O5ⁱ	2.708(12)	
O2–O3ⁱⁱ	3.283(12)	O5–O6a	3.324(11)	
O2–O4	2.846(14)	O6a–O6b	0.85(6)	
O2–O5ⁱⁱ	2.906(12)	O6a–O6bˣᵛⁱ	3.17(6)	
O2–O7aˣⁱ	3.099(14)	O6a–O7bˣᵛⁱⁱ	2.80(7)	
O3–O5	2.892(15)	O6a–O7bˣⁱ	3.16(9)	
O3–O5ⁱ	2.997(14)	O6b–O6bˣᵛⁱ	2.46(6)	
O3–O5ⁱⁱ	2.905(12)	O7a–O7b	0.92(8)	
O3–O6aˣⁱⁱⁱ	3.00(3)	O7b–O7bˣⁱⁱ	3.00(12)	
O3–O6bˣⁱⁱⁱ	3.11(2)			

§ Δ: Bond-length distorsion after Brown & Shannon (1973); σ²: bond-angle distorsion after Robinson *et al.* (1971). ECoN: an effective coordination-number after Hoppe (1979).
Symmetry codes: (i) –x + 1/2, –y + 1/2, –z; (ii) –x + 1/2, –y + 1/2, –z + 1; (iii) x + 1/2, –y + 1/2, z; (iv) –x, y, –z; (v) –x, –y + 1, –z; (vi) x, –y + 1, z; (vii) x – 1/2, y + 1/2, z; (viii) x – 1/2, –y + 1/2, z; (ix) –x + 1/2, y + 1/2, –z + 1; (x) –x + 1/2, y – 1/2, –z; (xi) x + 1/2, y + 1/2, z; (xii) –x + 1, y, –z + 1; (xiii) x, –y, z; (xiv) –x, y, –z + 1; (xv) x – 1/2, y – 1/2, z; (xvi) –x + 1/2, y + 1/2, –z; (xvii) –x + 1, y, –z.

TABLE 7. CHEMICAL COMPOSITION OF NATURAL ZIPPEITE FROM JÁCHYMOV

	Mean	1	2	3	4
Na₂O wt.%	0.03	0.01	0.00	0.11	0.02
K₂O	5.48	5.80	6.02	5.12	4.97
CaO	0.09	0.04	0.00	0.10	0.21
CoO	0.07	0.18	0.02	0.37	0.07
FeO	0.19	0.16	0.00	0.00	0.23
SO₃	10.24	10.24	11.08	10.26	9.37
SiO₂	0.51	0.56	0.00	0.78	0.7
UO₃	80.12	80.21	80.56	80.26	79.47
H₂O*	6.01	6.08	6.21	5.85	5.92
Total	102.74	103.27	103.89	102.85	100.96
Na *apfu*	0.016	0.002	0.000	0.051	0.010
K	1.726	1.803	1.865	1.607	1.621
Sum M^+	1.742	1.805	1.865	1.658	1.631
Ca	0.024	0.011	0.000	0.027	0.058
Co	0.013	0.035	0.004	0.000	0.014
Fe	0.04	0.032	0.000	0.077	0.050
Sum M^{2+}	0.077	0.078	0.004	0.034	0.122
Sum cations	1.819	1.883	1.869	1.692	1.753
S	1.898	1.873	2.020	1.896	1.798
Si	0.126	0.137	0.000	0.192	0.180
Sum *T* site	2.024	2.010	2.020	2.088	1.978
U	4.158	4.107	4.111	4.151	4.270
OH⁻	1.910	1.883	2.054	1.607	2.101
H₂O	4.001	4.001	4.004	4.000	4.000
U/(S + Si)	2.056	2.044	2.035	1.988	2.160

Mean: based on the mean result of analyses 1–4. *: The H₂O content (wt.%) was calculated on the basis of theoretical 4 H₂O derived from the structural refinement plus OH content from the charge balance.

DISCUSSION

The compositional properties of the crystal structure of natural zippeite in view of the "bond-valence" approach

The different roles of (H_2O) groups in crystal structures in which a strong distinction exists between (H_2O) as part of the structural unit and (H_2O) as an interstitial species were explained by Hawthorne (1992). The "bond-valence approach" applied to the stereochemistry and the chemical composition of the interstitial complexes of hydrated oxy-hydroxy minerals and compounds was developed and described in papers of Hawthorne (1983, 1985, 1986, 1990, 1994, 1997), Schindler & Hawthorne (2001a, 2001b, 2001c, 2004) and Schindler et al. (2000). On the basis of the bond-valence approach, Schindler et al. (2004a) developed a new approach to calculate the stability of edges on basal surfaces of uranyl sheet minerals, which helped to understand the dissolution and growth processes in hydrated uranyl minerals (see also Schindler et al. 2004b, Schindler & Putnis 2004, Schindler et al. 2004c, 2006a, 2006b, 2007a, 2007b, 2009). The papers of Hawthorne & Schindler (2008), and Schindler & Hawthorne (2008) review the "bond-valence approach" issue in detail. This topic was assessed also by Brown (2009) in a review of the bond-valence method.

Here, we have two (H_2O) groups per unit cell of zippeite, where $Z = 2$. [Note that we will consider below the split atomic sites as unsplit.] The O6 (Wa1) atom can be designated as a non-transformer (H_2O) group. It is not bonded to any interstitial cation, and the O...O distance to the nearest neighbor O atom (O4) is 2.91 Å; therefore, it is held in the structure only by weak hydrogen bonding. The O7 (Wa2) atom can be designated as non-transformer (H_2O) group also. It is bonded to two K^+ cations and forms two additional bonds *via* H^+ atoms. The real nature of these bonds and the precise coordination could not be obtained accurately (as mentioned above), owing to the difficult mesh in the coordination environment of positionally disordered O atoms.

As was discussed by Schindler & Hawthorne (2008), the crystal structures of zippeite-group minerals contain topologically identical sheets, but with varying chemical composition (see Burns et al. 2003). Schindler & Hawthorne (2008) mentioned three sheet structural units with the same range of Lewis basicity: 1) $[(UO_2)_4(SO_4)_2O_3(OH)]^{3-}$ (0.14–0.25 *vu*), occurring in synthetic zippeite, [7.33]$K_3[(UO_2)_4(SO_4)O_3(OH)](H_2O)_3$ (Burns et al. 2003), and marécottite, [6]$Mg_3[(UO_2)_4(SO_4)_2O_3(OH)]_2(H_2O)_{28}$ (Brugger et al. 2003). 2) $[(UO_2)_8(SO_4)_4O_5(OH)_3]^{5-}$ (0.14–0.25 *vu*), which occurs in synthetic natrozippeite, [6.6]$Na_5[(UO_2)_8(SO_4)_4O_5(OH)_3](H_2O)_{12}$ (Burns et al. 2003), and 3) $[(UO_2)_2(SO_4)O_2]^{2-}$ (0.15–0.25 *vu*), which occurs in synthetic

magnesiozippeite, cobaltzippeite and zinczippeite (Burns et al. 2003).

As a result of the crystal-structure refinement of natural zippeite, we obtained the sheet structural unit $[(UO_2)_4O_2(SO_4)_2(OH)_2]^{2-}$. It differs slightly from all known compositions of the zippeite-like compounds with the structural sheets of zippeite uranyl-anion topology. Hence, the bond-valence characteristic values, according to Schindler & Hawthorne (2008), were calculated. The structural unit of the natural zippeite has a "charge deficiency per anion" (*CDA*) value of 0.12 *vu*; thus the minimal and maximal number of bonds emanating from the structural unit is 10 and 19, respectively. The Lewis basicity range of the structural unit is therefore 0.13 to 0.25 *vu*, which is consistent with above-mentioned basicities of the sheet units of zippeite uranyl-anion topology. We know that the *CDA* value correlates with the mean number of bonds from the interstitial complex to the O atoms of the structural unit, and that defines a band allowing prediction of the range in average number of bonds to the O atoms of the structural unit. By varying the number of such bonds, the structural unit maintains its stability as the pH of the environment changes (Hawthorne & Schindler 2008, Schindler & Hawthorne 2008). Such an idea was pointed out by Hawthorne & Schindler (2008) and displayed for the case of a relationship between the *CDA* value of boron-containing aqueous species and the pH of the solution. When the pH of the solution increases, the *CDA* increases, as a non-linear function. The Lewis acidity value of an interstitial complex $[K_{1.85}^{[4]}(H_2O)_4]^{1.85-}$ was calculated taking into account of two different coordinations of split K1 and K2 atoms. The interstitial complex has a *CDA* of 0.13 *vu*; this value closely matches the range of Lewis basicity calculated above; therefore the structure will occur and will be stable. The number of bonds required by the structural unit reflecting its Lewis basicity is between 10 and 19 bonds for a total of 20 oxygen atoms. The number of bonds emanating from the interstitial complex in zippeite I is 16 bonds from K atoms and two additional hydrogen bonds to the OH^- groups. We can further derive the bond-valence distribution factor (*D*), which is 1.11 for our structure. According to the empirical relations given by Schindler & Hawthorne (2008), we are now able to calculate the total number of H_2O groups per cation, the number of transformer H_2O groups per cation, and then deduce the number of the inverse-transformer and non-transformer H_2O groups. This results in three H_2O groups per cation; one transformer H_2O group and two non-transformer H_2O groups. Hence we obtained from the bond-valence calculations a total of six H_2O groups. In contrast, Schindler & Hawthorne (2008) obtained for synthetic zippeite $\{^{[7.33]}K_3(H_2^{[5]}O)[(UO_2)_4(SO_4)_2O_3(OH)](H_2O)_5\}$ one inverse-transformer and five non-transformer H_2O groups for the three monovalent cations present in interlayer.

*Morphology and optical properties
of the zippeite crystals*

The morphological aspects of uranyl hydrated hydroxy-oxysalts are discussed with regard to the dissolution and growth of these phases by Schindler *et al.* (2004a), who introduced a modified method of Hartman & Perdok (1955a, 1955b, 1955c), the periodic bond-chain (PBC). The modification of Schindler *et al.* (2004a) is based on the bond-valence approach and more mechanistic. This approach was utilized by Schindler *et al.* (2004b, 2004c, 2006a, 2006b, 2007a, 2007b, 2009, 2011) and by Schindler & Putnis (2004) to predict the morphology of the etch pits on the surface and explain the dissolution processes in uranyl oxysalts. The following paragraph is based on theoretical predictions given in the above-mentioned papers and are discussed with regard to the results of Schindler *et al.* (2011).

The dominant morphology of all the zippeite crystals is the (010) basal face (Fig. 3), which is parallel to the uranyl sulfate layers (an F face in PBC terminology). This face is bounded by a suite of edges, forming the characteristic habits of the crystals. The chains of uranyl polyhedra in the uranyl sulfate sheets are parallel to the [100] direction; hence we observe the elongation of the crystals along **a** and the corresponding edge [100] (Fig. 7). The edges [201] or [101] represent transversal directions over the structural sheets and may be present in the morphology (see the oblique shape of the crystal termination). Twinning may also occur along [100] edges along the basal surface of the crystals where the lowest bond-valence deficiency of the chains exists. Schindler *et al.* (2011) showed that the relative stability of an edge along the basal surface of synthetic zippeite increases in the sequence [010] < [100] < [201], corresponding to decreasing bond-valence deficiencies of the chains of polyhedra.

Nováček (1935) reported on the optical properties of zippeite(s) from Jáchymov. He indicated indices of refraction α (1.575–1.616) perpendicular to the flat face of the mineral, which was later designated as (010) face in accordance with Larsen (1921). Pleochroism is developed perpendicular to that face. The index of refraction γ bisects the acute angle of the crystals, therefore in the direction of the crystal elongation and in accordance with the orientation of the uranyl chain direction (100). Nováček (1935) labeled this direction parallel to **c**, but according to the structure refinement and above-mentioned reasons, it should be the (100) face. Frondel *et al.* (1976) gave the following optical properties for the natural sample of zippeite from Jáchymov as α 1.655, β 1.716 and γ 1.768, optically negative with large 2*V*, and pleochroic, where *X* is colorless, *Y* is pale yellow and *Z* is yellow. We can conclude that these optical measurements are in agreement with the relationship between crystal structure of zippeite and its morphology, mentioned above. However, the index of

refraction α given by Nováček (1935) (α in the range 1.575–1.616) is distinct from that given by Frondel *et al.* (1976) (α = 1.655). Such a large difference suggests that they studied different "zippeites", and the indices of refraction given by Nováček (1935) are among the lowest ever reported for the zippeite group [see Frondel *et al.* (1976) and references therein]. Disregarding these discrepancies, the optical properties of minerals of zippeite group (indices of refraction, 2*V*, pleochroism) may be a useful tool for the study of zippeite-group minerals; nevertheless, it is significantly limited by the quality of crystals, as demonstrated for triclinic "zippeites" by Plášil *et al.* (2011).

*Comparison of current results to the original
definition by Frondel et al. (1976) and the study
of synthetic compounds by Burns et al. (2003)*

The definition of zippeite as a mineral was given by Frondel *et al.* (1976) on the basis of the re-examination of material from Jáchymov that was previously studied by Nováček (1935) and its identity to the synthetic hydrated potassium uranyl sulfate. As mentioned by Frondel *et al.* (1976), an identical mineral was found also on the old specimen labeled as "Uranochre" from Jáchymov, deposited at Harvard (acquired in 1821), and that is probably contemporaneous with the material studied by John (1821). This material was designated as a neotype of zippeite by Frondel. The chemical composition of zippeite, the K-dominant member, based on wet-chemical analytical data, corresponds to $K_4[(UO_2)_6(SO_4)_3(OH)_{10}](H_2O)_4$. Clearly this formula is at odds with all other analyses. Burns *et al.* (2003) synthesized and later determined the structure of synthetic zippeite-like phase with the composition $K_3[(UO_2)_4(SO_4)_2O_3OH](H_2O)_3$, Z = 4. They inferred, on the basis of the calculated powder-diffraction pattern from the refined crystal-structure, that their synthetic zippeite and both synthetic and natural zippeite studied by Frondel *et al.* (1976) are identical. As one is able to see from the different structure determinations, the composition of zippeite is variable. According to the current results, we may take the ideal formula of zippeite proposed by Peeters *et al.* (2008), $K_x[(UO_2)_2(SO_4)O_x(OH)_{2-x}](H_2O)_{3-x}$, Z = 4, as the most representative for minerals of the zippeite group and compounds that are like zippeite (*sensu stricto*), as it also takes into account the variability in OH,O. The ideal structural formula (taking account of full occupancies of K⁺ positions) for zippeite is $K_2[(UO_2)_4O_2(SO_4)_2(OH)_2](H_2O)_4$. The theoretical H_2O content in wt.%, deduced from the formula written above (calculation on sum of 100 wt.%) is 6.05 wt.%. Frondel *et al.* (1976) reported for their synthetic zippeite (their analysis no. 2) a weight loss of 4.92 wt.%; however, their calculated formula containing 4 H_2O molecules and 10 OH^- groups requires ~7 wt.% H_2O. Why is there such a discrepancy between the analyzed material and the proposed formula
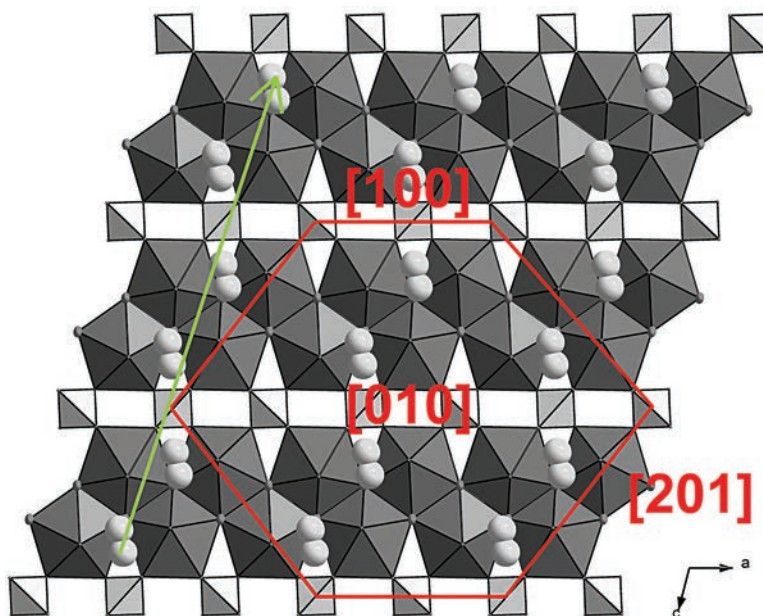
FIG. 7. Uranyl sulfate sheet found in natural zippeite with schematically outlined edges occurring on the crystal shapes and the basal (010) face. The interlayer K atoms are displayed with outlined direction ~[101] that may occur on the morphology.

is not clear from their text. A chemical admixture is one plausible explanation. The third composition presented by Frondel *et al.* (1976) also pertains to natural material from Jáchymov, with a thermally dependent weight-loss at 500°C equal to 10.70 wt.%. This unprecedented high value may be caused by admixtures of gypsum, which commonly forms intergrowths with zippeite. Regarding the variability in the chemical composition of zippeite, a re-examination of the composition of available samples of zippeite, including the neotype specimen, would contribute to this study of natural zippeite and would be of high importance.

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