Mineralogical Magazine, June 2014, Vol. 78(3), pp. 639–649

Belakovskiite, $Na_7(UO_2)(SO_4)_4(SO_3OH)(H_2O)_3$, a new uranyl sulfate mineral from the Blue Lizard mine, San Juan County, Utah, USA

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[*Received 15 December 2013; Accepted 28 January 2014; Associate Editor: S. Krivovichev*]

ABSTRACT

The new mineral belakovskiite (IMA2013-075), $Na_7(UO_2)(SO_4)_4(SO_3OH)(H_2O)_3$, was found in the Blue Lizard mine, Red Canyon, White Canyon district, San Juan County, Utah, USA, where it occurs as a secondary alteration phase in association with blödite, ferrinatrite, kröhnkite, meisserite and metavoltine. Crystals of belakovskiite are very pale yellowish-green hair-like fibres up to 2 mm long and usually no more than a few μm in diameter. The fibres are elongated on [100] and slightly flattened on {021}. Crystals are transparent with a vitreous lustre. The mineral has a white streak and a probable Mohs hardness of ~2. Fibres are flexible and elastic, with brittle failure and irregular fracture. No cleavage was observed. The mineral is readily soluble in cold H_2O. The calculated density is 2.953 g cm^{-3}. Optically, belakovskiite is biaxial (+) with α = 1.500(1), β = 1.511(1) and γ = 1.523(1) (measured in white light). The measured 2V is 87.1(6)° and the calculated 2V is 88°. The mineral is non-pleochroic. The partially determined optical orientation is $X \approx$ **a**. Electron-microprobe analysis provided Na_2O 21.67, UO_3 30.48, SO_3 40.86, H_2O 6.45 (structure), total 99.46 wt.% yielding the empirical formula $Na_{6.83}(U_{1.04}O_2)(SO_4)_4(S_{0.99}O_3OH)(H_2O)_3$ based on 25 O a.p.f.u. Belakovskiite is triclinic, $P\bar{1}$, with a = 5.4581(3), b = 11.3288(6), c = 18.4163(13) Å, α = 104.786(7)°, β = 90.092(6)°, γ = 96.767(7)°, V = 1092.76(11) Å^3 and Z = 2. The eight strongest X-ray powder diffraction lines are [d_{obs} Å(I)(hkl)]: 8.96(35)(002), 8.46(29)(011), 5.19(100)($\bar{1}$01,101,$\bar{1}$10), 4.66(58)(013,$\bar{1}$02,$\bar{1}\bar{1}$0,110), 3.568(37)(120,023,005,0$\bar{3}$3), 3.057(59)(0$\bar{1}$6,1$\bar{1}$5,$\bar{1}$31), 2.930(27)(multiple) and 1.8320(29)(multiple). The structure, refined to R_1 = 5.39% for 3163 $F_o > 4\sigma F$ reflections, contains $[(UO_2)(SO_4)_4(H_2O)]^{6-}$ polyhedral clusters connected *via* an extensive network of Na–O bonds and H bonds involving eight Na sites, three other H_2O sites and an SO_3OH (hydrosulfate) group. The 3-D framework, thus defined, is unique among known uranyl sulfate structures. The mineral is named for Dmitry Ilych Belakovskiy, a prominent Russian mineralogist and Curator of the Fersman Mineralogical Museum.

Keywords: belakovskiite, new mineral, uranyl sulfate, hydrosulfate, crystal structure, Blue Lizard mine, Utah, USA.

Introduction

Uranyl sulfate minerals are found in most U deposits world-wide. They generally form by hydration-oxidation weathering of primary U minerals, mainly uraninite, by acidic solutions

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DOI: 10.1180/minmag.2014.078.3.12

derived from the decomposition of associated sulfides such as pyrite, marcasite and chalcopyrite (Finch and Murakami, 1999; Krivovichev and Plášil, 2013). Our mineralogical investigations of the Blue Lizard mine over the last three years have revealed a remarkable secondary assemblage of uranyl sulfates, the majority of which are new to science. Two of them, meisserite (Plášil *et al.*, 2013; IMA2013-039) and bluelizardite (Plášil *et al.*, 2014; IMA2013-062) were recently described by our team; a third one, belakovskiite, is described herein. In addition to these, seven other new uranyl sulfates from this mine are currently under study by our group. The discovery of such a wealth of new uranyl sulfates at a single mine is unprecedented. At least as many have been described from the classic Jáchymov deposit (Ondruš *et al*., 2003; Tvrdý and Plášil, 2010); however, they have been described from several mines and over a lengthy time period. The fact that seven of the ten new phases from the Blue Lizard mine contain only Na as the additional cation and only one contains no essential Na is similarly remarkable. Prior to the discovery of the Na-rich uranyl sulfate assemblage at the Blue Lizard mine, natrozippeite was the only known sodium uranyl sulfate.

The mineral is named for Dmitry Ilych Belakovskiy (born 1957), a prominent Russian mineralogist and Curator of the Fersman Mineralogical Museum, Russian Academy of Science, Moscow, Russia, since 1989. His research has included the descriptions of more than 40 new minerals, among them holfertite, a secondary U mineral from the Thomas Range in Utah (Belakovskiy *et al.*, 2006). It seems particularly appropriate that belakovskiite occurs in close association with meisserite, which is named in honour of Nicolas Meisser, the curator of another prominent European museum, the Geological Museum in Lausanne. Both Dmitry and Nicolas focus much of their efforts towards the preservation of rare mineral species in their collections. These two curators also represent their respective countries on the IMA Commission on Museums.

The new mineral and the name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2013-075). The description is based on two cotype specimens. One cotype specimen, deposited in the collections of the Natural History Museum of Los Angeles County, catalogue number 64055, is also one of the cotypes for meisserite. A crystal from this specimen was used for the structure determination and optical study. The second cotype specimen is housed in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4410/1 and it is also a cotype for meisserite. Crystals from that specimen were used for the electron-microprobe analysis.

Occurrence

Belakovskiite was found underground in the Blue Lizard mine, Red Canyon, White Canyon district, San Juan County, Utah, USA (37°33′26″N 110°17′44″W) by one of the authors (JM). Thaden *et al.* (1964) provided the most complete description of the mine and its geological setting and Chenoweth (1993) provided a more up-to-date report on the geology of the district. The mine was first claimed in 1943 and produced its first U ore in 1951. An extensive exploration program, begun in 1954, led to the discovery of high-grade U ore. The mine has been inactive since 1978.

The deposit is located in a channel cut into the Moenkopi Formation (Lower Triassic) and filled with sediments of the Shinarump Member of the Chinle Formation (Upper Triassic). The Shinarump Member consists of medium- to coarse-grained sandstone. Ore minerals (especially uraninite) and sulfides (pyrite, chalcopyrite, bornite and covellite) were deposited as replacements of wood and other organic material and as disseminations in the enclosing sandstone. The main ore body was interpreted by Thaden *et al.* (1964) as being related to ponding of ore solutions in permeable sandstone between less permeable siltstone and claystone. Since the mine closed in 1978, oxidation of primary ores in the relatively humid underground environment has produced a variety of secondary minerals, mainly sulfates, as efflorescent crusts on the surfaces of mine walls. The vast majority of the secondary minerals contain essential Na; however, there is nothing described in geological reports of the area to suggest a source for the Na enrichment in the secondary assemblage.

The Blue Lizard mine is the type locality for the recently described new minerals manganoblödite (Kasatkin *et al.*, 2013; IMA2012-029), cobaltoblödite (Kasatkin *et al.*, 2013; IMA2012-059), meisserite (Plášil *et al.* 2013; IMA2013-039) and bluelizardite (Plášil *et al.*

2014; IMA2013-062) and several other new uranyl sulfates and another new sulfate (without uranyl) are currently under study. These phases occur on tunnel walls as efflorescent crusts, which have resulted from post-mining oxidation of primary ores (uraninite, pyrite and chalcopyrite disseminated in lenses of organic matter) in the humid underground environment.

The matrix of the belakovskiite specimens is sandstone consisting of irregular quartz grains. Secondary minerals found in direct association with belakovskiite include blödite, ferrinatrite, kröhnkite, meisserite and metavoltine. Other secondary minerals in the general assemblage include atacamite, boyleite, brochantite, chalcanthite, cobaltoblödite, copiapite, coquimbite, cyanotrichite, d'ansite-(Mn), dickite, gerhardtite, gordaite, gypsum, halite, johannite, manganoblödite, natrochalcite, natrozippeite, pickeringite, pseudojohannite, rhomboclase, römerite, sideronatrite and tamarugite. Other minerals found associated with the host sandstone include baryte, calcite, feldspar and clays.

Physical and optical properties

Crystals of belakovskiite (Fig. 1) are very pale yellowish-green hair-like fibres up to 2 mm long and usually no more than a few μm in diameter. The fibres are elongated on [100], slightly flattened on {021} and exhibit several {0*kl*} forms, none of which could be measured. Crystals are transparent with a vitreous lustre. The mineral has a white streak. The Mohs hardness could not be tested, but is probably ~2. Fibres are flexible and elastic, with brittle failure and irregular fracture. No cleavage was observed. The mineral is readily soluble in cold H_2O and, because it is also soluble in available aqueous density liquids, its density could not be measured. The calculated densities are 2.953 g cm^{-3} based on the empirical formula and 2.936 g cm^{-3} based on the ideal formula.

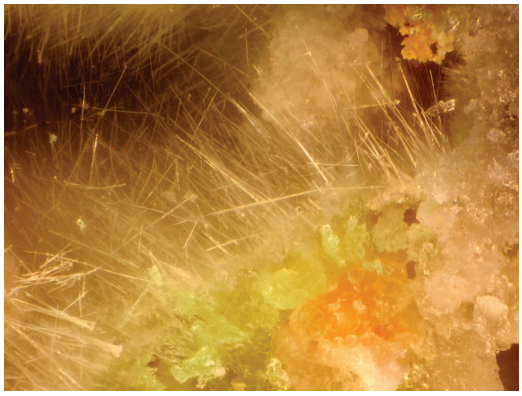

FIG. 1. Fibrous belakovskiite with light green meisserite crystals on blödite; field of view 2 mm.

Optically, belakovskiite is biaxial (+) with α = 1.500(1), β = 1.511(1) and γ = 1.523(1) (measured in white light). The measured 2V based on extinction data using *EXCALIBR* (Gunter *et al*., 2004) is 87.1(6)º and the calculated 2V is 88º. Dispersion could not be observed. The mineral is non-pleochroic. The partially determined optical orientation is $X \approx$ **a**.

Composition

The chemical composition of belakovskiite was determined using a CamScan4D scanning electron microscope (SEM) equipped with an Oxford Link ISIS energy-dispersive X-ray spectrometer (EDS). An operating voltage of 20 kV was used with a beam current of 1 nA and a 1 μm beam diameter. The EDS mode on the SEM was chosen for the analysis instead of the wavelength-dispersive spectrometer (WDS) mode on the electron microprobe because of the extreme thinness of the fibres and instability of belakovskiite under the electron beam caused by the high contents of both Na and H_2O. Attempts to use the WDS mode were unsuccessful because of significant decomposition of the mineral after several seconds under the electron beam with a current of 15 nA. The H_2O content was not determined directly because of the scarcity of pure material. Instead, the H_2O content was calculated by stoichiometry on the basis of 25 O a.p.f.u. (atoms per formula unit), as indicated by the crystal-structure determination. No other elements with atomic numbers higher than 8 were observed. Analytical data are given in Table 1.

The empirical formula of belakovskiite, calculated as the mean of nine representative spot analyses (Table 1), is $Na_{6.83}U_{1.04}S_{4.99}O_{25.00}H_{7.00}$, or $Na_{6.83}(U_{1.04}O_2)(SO_4)_4(S_{0.99}O_3OH)(H_2O)_3$ (based on 25 O a.p.f.u.). The simplified formula is $Na_7(UO_2)(SO_4)_4(SO_3OH)(H_2O)_3$ which requires Na_2O 22.45, UO_3 29.60, SO_3 41.43 and H_2O 6.53, total 100 wt.%. The Gladstone-Dale compatibility index $1 - (K_P/K_C)$ is 0.023 for the empirical formula, in the range of superior compatibility (Mandarino, 2007).

TABLE 1. Chemical analyses for belakovskiite.

Constituent	Wt.%	Range	SD	Probe standard
Na_2O	21.67	20.78–22.60	0.57	chkalovite
UO_3	30.48	27.83–33.54	1.67	syn. UO_2
SO_3	40.86	36.95–43.50	1.89	syn. ZnS
H_2O*	6.45			
Total	99.46			

* Calculated by stoichiometry on the basis of 25 O a.p.f.u.

X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized Mo*K*α radiation. For the powder-diffraction study, a Gandolfi-like motion on the φ and ω axes was used to randomize the sample and observed *d* spacings and intensities were derived by profile fitting using *JADE 2010* software (Materials Data, Inc.). The powder data presented in Table 2 show good agreement with the pattern calculated from the structure determination. Unit-cell parameters refined from the powder data using *JADE 2010* with whole-pattern fitting are a = 5.454(4), b = 11.308(4), c = 18.340(4) Å, α = 104.76(2), β = 89.83(3), γ = 96.77(2)° and V = 1085.7(9) Å^3.

The Rigaku *CrystalClear* software package was used for processing structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). The structure was solved by direct methods using *SIR2004* (Burla *et al*., 2005). *SHELXL-2013* (Sheldrick, 2008) was used for the refinement of the structure. Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond-valence analysis in Table 6.

Description and discussion of the structure

The structure of belakovskiite is shown in Fig. 2. The *U* site is surrounded by seven O atom sites forming a squat pentagonal bipyramid. This is a

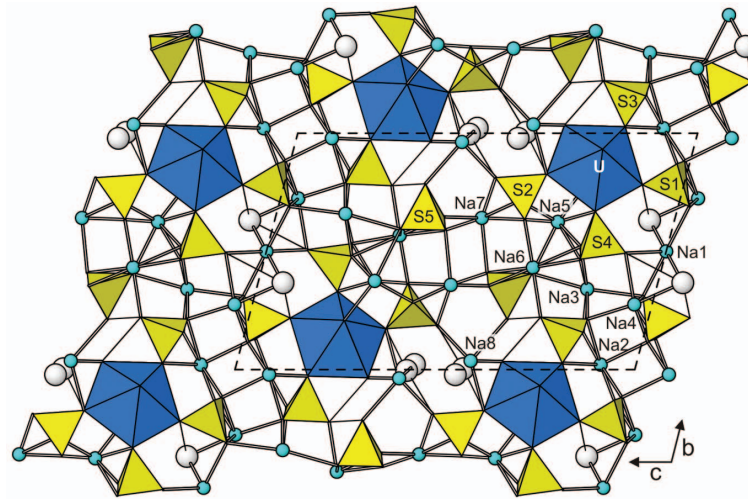

FIG. 2. The crystal structure of belakovskiite viewed down [100]. The unit cell is shown by dashed lines. Na–O bonds are shown as sticks. Hydrogen bonds are shown as thin lines.

TABLE 2. Powder X-ray data for belakovskiite.*

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
11	17.91	17.7968	20	0 0 1
11	10.76	10.8714	6	0 1 0
		10.5646	8	0 $\bar{1}$ 1
35	8.96	8.8984	55	0 0 2
29	8.46	8.3691	44	0 1 1
		7.9624	7	0 $\bar{1}$ 2
		6.1537	5	0 1 2
		5.8822	3	0 $\bar{1}$ 3
12	5.62	5.6179	15	0 $\bar{2}$ 1
		5.4357	4	0 2 0
		5.4171	3	1 0 0
100	5.19	5.2307	46	$\bar{1}$ 0 1
		5.1354	28	1 0 1
		5.1041	26	$\bar{1}$ 1 0
		5.0272	3	1 $\bar{1}$ 1
		4.8611	14	0 2 1
		4.7937	5	$\bar{1}$ 1 1
58	4.66	4.7218	9	0 1 3
		4.6965	11	$\bar{1}$ 0 2
		4.6371	11	$\bar{1}$ $\bar{1}$ 1
		4.6279	16	1 1 0
		4.6094	2	1 $\bar{1}$ 2
		4.5608	2	1 0 2
		4.5481	9	0 $\bar{1}$ 4
		4.4492	7	0 0 4
8	4.36	4.3588	3	$\bar{1}$ $\bar{1}$ 2
		4.3359	10	1 1 1
		4.2655	2	$\bar{1}$ 1 2
4	4.07	4.0956	6	$\bar{1}$ 2 0
		4.0676	6	$\bar{1}$ 0 3
		4.0529	3	1 $\bar{1}$ 3
		3.9848	4	1 $\bar{2}$ 2
17	3.937	3.9361	16	1 0 3
		3.9200	3	$\bar{1}$ $\bar{1}$ 3
		3.7901	2	0 1 4
10	3.722	3.7442	10	0 $\bar{3}$ 1
		3.7082	10	$\bar{1}$ 1 3
		3.6736	6	0 $\bar{1}$ 5
37	3.568	3.6220	13	1 2 0
		3.5757	5	0 2 3
		3.5594	18	0 0 5
		3.5215	13	0 $\bar{3}$ 3
		3.5026	2	$\bar{1}$ 2 2
		3.4952	4	$\bar{1}$ 0 4
10	3.395	3.4272	2	1 1 3
		3.4062	14	0 $\bar{2}$ 5
		3.3839	3	1 0 4
23	3.272	3.3041	6	1 $\bar{2}$ 4
		3.2680	12	1 $\bar{3}$ 1
		3.2485	8	0 $\bar{3}$ 4
		3.2306	6	1 $\bar{3}$ 2
		3.1515	12	0 1 5
		3.1199	10	$\bar{1}$ $\bar{2}$ 4
		3.0900	15	0 3 2
59	3.057	3.0690	7	0 $\bar{1}$ 6
		3.0507	13	1 $\bar{1}$ 5
		3.0399	23	$\bar{1}$ 3 1
		3.0302	9	$\bar{1}$ $\bar{1}$ 5
27	2.930	2.9462	6	0 $\bar{3}$ 5
		2.9439	6	1 $\bar{2}$ 5
		2.9411	2	0 $\bar{2}$ 6
		2.9306	3	1 0 5
		2.9212	7	$\bar{1}$ $\bar{3}$ 1
		2.9112	6	$\bar{1}$ $\bar{3}$ 2
		2.8974	4	1 $\bar{3}$ 4
		2.8554	4	1 2 3
7	2.812	2.8267	3	$\bar{1}$ $\bar{2}$ 5
		2.8090	5	0 $\bar{4}$ 2
		2.7879	7	$\bar{1}$ 2 4
17	2.707	2.7267	8	1 3 1
		2.7179	3	0 4 0
		2.7086	13	2 0 0
		2.6910	4	$\bar{2}$ 0 1
		2.6864	3	$\bar{1}$ $\bar{3}$ 4
		2.6787	2	0 2 5
		2.6703	2	1 $\bar{3}$ 5
17	2.635	2.6411	3	0 $\bar{4}$ 4
		2.6386	4	$\bar{1}$ 0 6
		2.6218	4	1 $\bar{2}$ 6
		2.6153	5	$\bar{2}$ 0 2
		2.5989	2	$\bar{1}$ 3 3
16	2.563	2.5755	5	1 2 4
		2.5700	8	1 $\bar{4}$ 3
		2.5662	6	1 0 6
		2.5579	4	$\bar{1}$ 4 0
		2.5520	2	$\bar{2}$ 2 0
		2.5424	3	0 0 7
11	2.516	2.5186	4	$\bar{2}$ $\bar{1}$ 2
		2.5112	4	0 3 4
		2.4867	2	$\bar{1}$ 2 5
		2.4701	3	$\bar{1}$ 1 6
		2.4421	5	1 $\bar{3}$ 6
		2.3764	2	1 3 3
		2.3609	3	0 2 6
8	2.351	2.3543	5	1 1 6
		2.3455	6	0 1 7
		2.3439	2	1 $\bar{4}$ 5
		2.3361	5	$\bar{2}$ $\bar{2}$ 1
8	2.326	2.3288	2	$\bar{1}$ $\bar{3}$ 6
		2.3235	2	0 $\bar{4}$ 6
		2.3128	2	2 $\bar{3}$ 2
		2.3095	2	$\bar{2}$ $\bar{1}$ 4
4	2.279	2.2986	4	0 $\bar{1}$ 8
		2.2729	3	2 1 3
		2.2301	2	$\bar{1}$ 2 6
7	2.168	2.1764	2	$\bar{1}$ 4 3
		2.1706	2	1 $\bar{5}$ 2
		2.1660	3	$\bar{1}$ 3 5
		2.1648	3	$\bar{2}$ 3 2
5	2.121	2.1231	4	$\bar{2}$ 1 5
		2.1098	5	1 $\bar{1}$ 8
		2.0944	3	0 5 1
		2.0923	2	0 4 4
19	2.074	2.0749	4	$\bar{2}$ $\bar{2}$ 5
		2.0736	5	2 $\bar{4}$ 2
		2.0697	2	2 $\bar{3}$ 5
		2.0618	2	2 2 3
		2.0502	6	1 $\bar{4}$ 7
		2.0349	3	1 $\bar{3}$ 8
		2.0304	2	$\bar{2}$ $\bar{1}$ 6
		2.0279	2	$\bar{1}$ 4 4
		2.0206	2	1 3 5
12	2.000	2.0131	2	$\bar{1}$ 2 7
		2.0063	2	1 4 3
		1.9958	2	$\bar{1}$ $\bar{5}$ 2
		1.9924	4	2 $\bar{4}$ 4
		1.9755	2	$\bar{1}$ 1 8
8	1.9567	1.9607	7	0 $\bar{3}$ 9
		1.9553	2	2 $\bar{3}$ 6
		1.9511	4	$\bar{1}$ 5 2
		1.9260	3	$\bar{2}$ $\bar{3}$ 5
16	1.9096	1.9162	3	$\bar{1}$ $\bar{1}$ 9
		1.9141	2	1 2 7
		1.9055	5	$\bar{1}$ $\bar{5}$ 5
		1.9022	2	1 $\bar{1}$ 9
		1.8951	2	0 2 8
		1.8904	2	0 5 3
		1.8878	2	2 $\bar{2}$ 7
		1.8850	2	$\bar{2}$ 0 7
		1.8726	2	0 $\bar{6}$ 3
		1.8630	2	0 1 9
		1.8528	2	1 $\bar{5}$ 7
		1.8512	2	0 $\bar{6}$ 1
		1.8457	3	$\bar{2}$ $\bar{4}$ 2
29	1.8320	1.8385	3	1 $\bar{6}$ 2
		1.8364	5	2 $\bar{4}$ 6
		1.8340	3	$\bar{2}$ $\bar{4}$ 3
		1.8331	4	0 $\bar{1}$ 10
		1.8251	2	$\bar{2}$ 1 7
		1.8161	2	1 $\bar{6}$ 4
		1.8041	4	0 $\bar{5}$ 8
		1.7811	2	0 5 4
14	1.7517	1.7513	7	$\bar{3}$ $\bar{1}$ 1
		1.7434	2	1 $\bar{2}$ 10
		1.7256	2	1 $\bar{6}$ 6
		1.7215	2	0 2 9
12	1.7090	1.7136	2	2 2 6
		1.7102	2	$\bar{3}$ $\bar{1}$ 3
		1.7082	6	3 $\bar{3}$ 1
10	1.6836	1.6962	4	$\bar{1}$ $\bar{6}$ 4
		1.6794	2	$\bar{3}$ 3 1
		1.6738	5	0 5 5
		1.6590	2	$\bar{3}$ $\bar{2}$ 2
		1.6542	2	3 2 0
12	1.6321	1.6429	2	$\bar{2}$ 5 3
		1.6383	2	$\bar{2}$ $\bar{1}$ 9
		1.6314	3	2 $\bar{6}$ 3
7	1.5964	1.6055	2	$\bar{1}$ 6 3
		1.5999	2	1 $\bar{2}$ 11
		1.5911	2	$\bar{2}$ $\bar{5}$ 5
11	1.5702	1.5757	3	0 2 10
		1.5717	2	1 $\bar{7}$ 1
		1.5564	2	$\bar{3}$ $\bar{3}$ 2
		1.5431	2	$\bar{3}$ 1 6
		1.5327	2	1 $\bar{7}$ 6
12	1.5144	1.5170	2	$\bar{1}$ 4 8
		1.5013	3	2 $\bar{6}$ 7
		1.4993	2	$\bar{2}$ 5 5

* Only calculated lines with intensities $\geqslant 2$ are shown.

TABLE 3. Data collection and structure refinement details for belakovskiite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo$K\alpha$ (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	298(2) K
Structural Formula	$Na_7(UO_2)(SO_4)_4(SO_3OH)(H_2O)_3$
Space group	$P\bar{1}$
Unit-cell dimensions	a = 5.4581(3) Å
	b = 11.3288(6) Å
	c = 18.4163(13) Å
	α = 104.786(7)°
	β = 90.092(6)°
	γ = 96.767(7) °
V	1092.76(11) Å^3
Z	2
Density (for above formula)	2.936 g cm^{-3}
Absorption coefficient	8.161 mm^{-1}
F(000)	912
Crystal size (μm)	300 × 10 × 5
θ range	3.31–25.02°
Index ranges	$-5 \leqslant h \leqslant 6$, $-13 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 21$
Reflections collected/unique	16,376/3854; R_{int} = 0.093
Reflections with $F_o > 4\sigma(F)$	3163
Completeness to θ = 25.02°	99.5%
Max. and min. transmission	0.960 and 0.193
Refinement method	Full-matrix least-squares on F^2
Parameters refined	358
GoF	1.083
Final R indices [$F_o > 4\sigma(F)$]	R_1 = 0.0539, wR_2 = 0.1084
R indices (all data)	R_1 = 0.0718, wR_2 = 0.1162
Largest diff. peak/hole	+2.21/−2.63 e·A^{-3}

* $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0, b is 27.0359 and P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

typical coordination for U^{6+} in which the two short apical bonds of the bipyramid (1.728 and 1.760Å in belakovskiite) constitute the UO_2^{2+} uranyl group. Four of the five equatorial vertices of the bipyramid link to four distinct SO_4 tetrahedra and the fifth equatorial vertex is an H_2O group, yielding a $[(UO_2)(SO_4)_4(H_2O)]^{6-}$ polyhedral cluster. Bond-valence analysis indicates that a fifth sulfate tetrahedron, which is not part of the cluster, is an SO_3OH (hydrosulfate) group. The $[(UO_2)(SO_4)_4(H_2O)]^{6-}$ clusters do not link directly to one another, but rather are connected via an extensive network of Na–O bonds and H bonds involving eight *Na* sites, three other H_2O sites and the SO_3OH group. One *Na* site (Na8) and two H_2O sites (OW25 and OW26), in relatively close proximity, refined to approximately half occupancy and they were assigned exactly half occupancy in the final structure refinement. Bond lengths and bond-valence calculations indicate that OW25 is coordinated to Na8, while OW26 takes the place of both Na8 and OW25 when those sites are not occupied.

Like the other newly described uranyl sulfates from the Blue Lizard mine, meisserite and bluelizardite and several others still under study, belakovskiite possesses a complicated 3-D framework structure; however, its structure is unique among known uranyl sulfates. The $[(UO_2)(SO_4)_4(H_2O)]^{6-}$ cluster is somewhat similar, regarding the U:S stoichiometry, to the clusters found in the synthetic Na-uranyl sulfates (Burns and Hayden, 2002; Hayden and Burns, 2002*a*,*b*); however, these contain no H_2O as an equatorial ligand and contain a bidentately linked SO_4 tetrahedron.

TABLE 4. Atom coordinates and displacement parameters (Å^2) for belakovskiite.

	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
U	0.72620(9)	0.13824(4)	0.76828(3)	0.02036(15)	0.0252(3)	0.0147(2)	0.0209(3)	0.00376(18)	−0.00275(18)	0.00340(18)
*S*1	0.7486(5)	0.1927(3)	0.97103(17)	0.0190(6)	0.0187(15)	0.0143(14)	0.0228(15)	0.0027(12)	−0.0009(12)	0.0010(12)
*S*2	0.6798(6)	0.2541(3)	0.59870(17)	0.0221(7)	0.0262(17)	0.0210(16)	0.0189(15)	0.0026(13)	−0.0017(12)	0.0073(13)
*S*3	0.7264(5)	0.8436(3)	0.81019(16)	0.0177(6)	0.0191(15)	0.0131(14)	0.0206(15)	0.0036(12)	−0.0023(12)	0.0024(12)
*S*4	0.6868(5)	0.4643(3)	0.81836(16)	0.0168(6)	0.0168(14)	0.0120(14)	0.0204(15)	0.0027(12)	−0.0024(12)	0.0005(11)
*S*5	0.2053(6)	0.6464(3)	0.61504(18)	0.0240(7)	0.0203(16)	0.0240(17)	0.0281(17)	0.0077(14)	−0.0036(13)	0.0027(13)
*Na*1	0.0000	0.5000	0.0000	0.0292(16)	0.031(4)	0.034(4)	0.027(4)	0.010(3)	0.005(3)	0.015(3)
*Na*2	0.1971(9)	0.9789(5)	0.9114(3)	0.0305(12)	0.029(3)	0.024(3)	0.033(3)	−0.004(2)	−0.003(2)	0.004(2)
*Na*3	0.2080(9)	0.6594(4)	0.8272(3)	0.0293(12)	0.025(3)	0.021(3)	0.038(3)	−0.002(2)	0.002(2)	0.006(2)
*Na*4	0.7221(9)	0.7243(4)	0.9555(3)	0.0275(11)	0.032(3)	0.020(3)	0.028(3)	0.002(2)	0.003(2)	0.003(2)
*Na*5	0.2182(9)	0.3752(5)	0.7094(3)	0.0298(12)	0.029(3)	0.026(3)	0.029(3)	0.000(2)	0.005(2)	−0.002(2)
*Na*6	0.7158(10)	0.5679(5)	0.6773(3)	0.0342(13)	0.041(3)	0.026(3)	0.033(3)	0.003(2)	0.007(2)	0.002(2)
*Na*7	0.2966(10)	0.3584(5)	0.5166(3)	0.0371(13)	0.039(3)	0.045(3)	0.028(3)	0.011(3)	−0.008(2)	0.005(3)
*Na*8*	0.428(3)	0.9629(14)	0.5835(9)	0.078(5)	0.106(14)	0.050(9)	0.070(10)	0.001(8)	−0.013(9)	0.010(9)
*O*1	0.9311(16)	0.1177(8)	0.9862(5)	0.028(2)	0.033(5)	0.035(5)	0.020(5)	0.005(4)	−0.005(4)	0.020(4)
*O*2	0.2278(16)	0.6904(8)	0.9720(4)	0.028(2)	0.039(5)	0.021(5)	0.015(4)	−0.008(4)	0.002(4)	0.002(4)
*O*3	0.4989(15)	0.1294(8)	0.9689(5)	0.031(2)	0.017(4)	0.029(5)	0.042(6)	−0.001(4)	0.002(4)	−0.002(4)
*O*4	0.8013(16)	0.2181(7)	0.8963(4)	0.026(2)	0.046(6)	0.016(4)	0.012(4)	−0.001(3)	−0.010(4)	0.001(4)
*O*5	0.5768(18)	0.1880(9)	0.5242(5)	0.038(2)	0.051(6)	0.038(6)	0.017(5)	−0.006(4)	−0.010(4)	0.005(5)
*O*6	0.5566(16)	0.3650(7)	0.6248(5)	0.028(2)	0.038(5)	0.018(5)	0.028(5)	0.005(4)	0.000(4)	0.010(4)
*O*7	0.9488(15)	0.2849(9)	0.5989(5)	0.034(2)	0.015(5)	0.049(6)	0.035(5)	0.009(5)	−0.002(4)	0.002(4)
*O*8	0.6150(18)	0.1730(8)	0.6497(5)	0.034(2)	0.054(6)	0.027(5)	0.022(5)	0.006(4)	−0.015(4)	0.008(4)
*O*9	0.4892(15)	0.8426(7)	0.8456(5)	0.027(2)	0.022(5)	0.019(5)	0.039(5)	0.007(4)	0.008(4)	0.002(4)
*O*10	0.8985(14)	0.7866(7)	0.8476(5)	0.0218(19)	0.019(4)	0.013(4)	0.037(5)	0.012(4)	−0.004(4)	0.002(3)
*O*11	0.6946(16)	0.7782(7)	0.7296(5)	0.026(2)	0.035(5)	0.017(4)	0.021(4)	−0.005(4)	−0.004(4)	0.004(4)
*O*12	0.8415(14)	0.9725(7)	0.8144(4)	0.0191(18)	0.021(4)	0.008(4)	0.026(4)	0.001(3)	−0.005(3)	−0.001(3)
*O*13	0.7148(15)	0.5072(8)	0.8998(4)	0.0246(19)	0.033(5)	0.025(5)	0.011(4)	−0.002(4)	−0.002(4)	0.001(4)
*O*14	0.9237(15)	0.4797(8)	0.7831(5)	0.031(2)	0.020(5)	0.025(5)	0.042(6)	−0.005(4)	0.002(4)	0.007(4)
*O*15	0.5115(15)	0.5331(7)	0.7901(5)	0.0235(19)	0.028(5)	0.012(4)	0.032(5)	0.008(4)	−0.001(4)	0.004(4)
*O*16	0.5758(15)	0.3306(7)	0.7955(5)	0.0211(19)	0.025(5)	0.007(4)	0.035(5)	0.011(4)	0.010(4)	0.006(3)
*O*17	0.9743(17)	0.6458(10)	0.5781(5)	0.043(3)	0.032(6)	0.061(7)	0.036(6)	0.011(5)	−0.014(4)	0.009(5)
*O*18	0.3921(17)	0.5905(8)	0.5664(5)	0.035(2)	0.032(5)	0.031(5)	0.047(6)	0.014(5)	0.017(4)	0.018(4)
*O*19	0.1757(17)	0.5936(9)	0.6793(5)	0.036(2)	0.040(6)	0.037(6)	0.037(6)	0.021(5)	0.001(4)	0.004(5)
*OH*20	0.3015(19)	0.7862(8)	0.6472(6)	0.041(2)	0.051(7)	0.027(5)	0.045(6)	0.010(5)	−0.007(5)	0.002(5)
*O*21	0.0256(17)	0.2089(8)	0.7595(5)	0.031(2)	0.041(6)	0.019(5)	0.032(5)	0.006(4)	−0.002(4)	−0.002(4)
*O*22	0.4308(17)	0.0673(8)	0.7731(6)	0.036(2)	0.039(6)	0.017(5)	0.053(6)	0.016(4)	−0.014(5)	−0.014(4)
*OW*23	0.8171(19)	0.9655(8)	0.6618(5)	0.037(2)	0.067(7)	0.016(5)	0.028(5)	0.002(4)	0.010(5)	0.009(5)
*OW*24	0.2701(16)	0.3674(8)	0.9376(5)	0.033(2)	0.027(5)	0.037(6)	0.037(5)	0.014(5)	0.009(4)	0.003(4)
*OW*25*	0.083(6)	0.022(3)	0.5546(17)	0.072(8)	0.07(2)	0.07(2)	0.076(19)	0.022(16)	0.002(17)	0.012(17)
*OW*26*	0.208(4)	0.996(2)	0.5701(17)	0.052(8)	0.009(11)	0.028(12)	0.12(2)	0.015(13)	0.011(12)	0.010(9)

* *Na*8, *OW*25 and *OW*26 sites are half occupied.

TABLE 5. Selected bond distances (Å) for belakovskiite.

U−O22	1.728(9)	S1−O1	1.452(8)	S2−O5	1.461(9)	S3−O9	1.451(9)	S4−O13	1.456(8)	S5−O17	1.430(9)
U−O21	1.760(9)	S1−O2	1.457(8)	S2−O6	1.468(9)	S3−O10	1.463(8)	S4−O14	1.460(9)	S5−O18	1.451(9)
U−O4	2.317(8)	S1−O3	1.459(9)	S2−O7	1.469(9)	S3−O11	1.479(8)	S4−O15	1.474(8)	S5−O19	1.456(9)
U−O16	2.353(7)	S1−O4	1.497(9)	S2−O8	1.488(10)	S3−O12	1.503(8)	S4−O16	1.516(8)	S5−OH20	1.568(10)
U−O12	2.395(8)	<S1−O>	1.466	<S2−O>	1.472	<S3−O>	1.474	<S4−O>	1.477	<S5−O>	1.476
U−O8	2.406(8)										
U−OW23	2.489(8)	Na2−O3	2.270(10)	Na3−O15	2.308(9)	Na4−O3	2.333(10)	Hydrogen bonds			
<U−O>	2.287	Na2−O1	2.432(9)	Na3−O10	2.317(9)	Na4−O13	2.406(9)	OH20−O11	2.650(13)		
		Na2−O9	2.455(9)	Na3−O14	2.371(10)	Na4−O10	2.436(10)	OW23−O11	2.744(13)		
Na1−OW24 (′2)	2.323(9)	Na2−O1	2.475(10)	Na3−O9	2.380(10)	Na4−OW24	2.452(10)	OW23−OW25	2.62(3)		
Na1−O13 (′2)	2.435(8)	Na2−O10	2.576(9)	Na3−O2	2.599(10)	Na4−O1	2.481(10)	OW23−OW26	2.77(3)		
Na1−O2 (′2)	2.530(9)	Na2−O12	2.617(9)	Na3−O19	2.635(11)	Na4−O2	2.709(10)	OW24−O4	2.881(12)		
<Na1−O>	2.429	<Na2−O>	2.471	<Na3−O>	2.435	Na4−O2	2.857(10)	OW24−O13	2.964(12)		
						<Na4−O>	2.525	OW25−OW26	2.74(5)		
Na5−O14	2.338(10)	Na6−O6	2.316(10)	Na7−O17	2.272(10)			OW25−O7	3.06(3)		
Na5−O6	2.411(10)	Na6−O11	2.347(9)	Na7−O18	2.405(11)	Na8−OW25	2.18(4)	OW26−O5	2.74(2)		
Na5−O7	2.433(10)	Na6−O15	2.457(10)	Na7−O6	2.426(10)	Na8−O5	2.262(17)	OW26−O8	2.92(3)		
Na5−O21	2.435(10)	Na6−O19	2.491(11)	Na7−O18	2.544(11)	Na8−O8	2.477(17)				
Na5−O15	2.435(9)	Na6−O17	2.577(12)	Na7−O7	2.622(11)	Na8−OW23	2.56(2)				
Na5−O16	2.686(10)	Na6−O14	2.708(11)	Na7−O5	2.630(11)	Na8−OH20	2.596(19)				
Na5−O19	2.706(10)	Na6−O18	2.779(11)	<Na7−O>	2.483	<Na8−O>	2.415				
<Na5−O>	2.492	<Na6−O>	2.525								

TABLE 6. Bond-valence analysis for belakovskiite. Values are expressed in valence units.*

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	O15	O16	O17	O18	O19	OH20	O21	O22	OW23	OW24	OW25	OW26	Σ_c
U				0.60				0.50				0.52				0.56					1.75	1.86	0.43				6.22
Na1		0.12 ×2→												0.16 ×2→										0.22 ×2→			1.00
Na2	0.16 0.14		0.25						0.15	0.11		0.10															0.91
Na3		0.10							0.19	0.22			0.19		0.22				0.09								1.01
Na4	0.14	0.08 0.05	0.21							0.16				0.17										0.15			0.96
Na5						0.17	0.16						0.21		0.16	0.08			0.08		0.16						1.02
Na6						0.22					0.20		0.08		0.15		0.11	0.06	0.14								0.96
Na7					0.09	0.16	0.10										0.25	0.17 0.12									0.89
Na8					0.13 ×2→			0.07 ×2→												0.05 ×2→			0.06 ×2→		0.16 ×2→		0.94
S1	1.59	1.57	1.56	1.41																							6.13
S2					1.55	1.52	1.52	1.44																			6.04
S3									1.60	1.55	1.48	1.39															6.01
S4													1.57	1.56	1.50	1.34											5.97
S5																	1.69	1.60	1.57	1.16							6.02
H20											0.22									0.78							1.00
H23a											0.19												0.81				1.00
H23b																							0.78		0.24 ×½→	0.20 ×½→	1.00
H24a				0.16																				0.84			1.00
H24b													0.12											0.88			1.00
H25a							0.04 ×2→																		0.92		1.00
H25b																									0.80	0.10 ×2→	1.00
H26a					0.10 ×2→																					0.80	1.00
H26b								0.07 ×2→																		0.86	1.00
Σ_a	2.03	1.92	2.02	2.17	1.87	2.07	1.82	2.08	1.94	2.04	2.09	2.01	2.17	1.89	2.03	1.98	2.05	1.95	1.88	1.99	1.91	1.86	2.08	2.09	2.12	1.95	

* S^{6+}–O bond strength from Brown and Altermatt (1985); Na^{+}–O bond strength from Wood and Palenik (1999); U^{6+}–O bond strength from Burns *et al*. (1997); H-bond strengths based on O···O bond lengths from Brown and Altermatt (1985).

In the structure of belakovskiite, the SO_3OH group links to the $[(UO_2)(SO_4)_4(H_2O)]^{6-}$ clusters *via* relatively weak Na−O bonds only. The only other known uranyl mineral structure containing a protonated sulfate tetrahedron is that of meisserite (Plášil *et al.*, 2013) and in this structure, as well, the SO_3OH group is linked through relatively weak Na−O bonds to the uranyl sulfate clusters. Protonated sulfate (hydrosulfate) tetrahedra are quite rare in mineral structures and are indicative of formation at low pH, as has been noted to be the case for the secondary uranyl sulfate mineral assemblages in the Blue Lizard mine.

Acknowledgements

Reviewers Stuart J. Mills and Igor V. Pekov are thanked for their constructive comments on the manuscript. Ken Krahulec of the Utah Geological Survey is thanked for providing information about the genesis of the U deposits in the area. A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County. JP acknowledges funding through the post-doctoral grant project 13-31276P of the Grant Agency of the Czech Republic.

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