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Bobcookite, $NaAl(UO_2)_2(SO_4)_4 \cdot 18H_2O$ and wetherillite, $Na_2Mg(UO_2)_2(SO_4)_4 \cdot 18H_2O$, two new uranyl sulfate minerals from the Blue Lizard mine, San Juan County, Utah, USA

Anthony R. Kampf[1,*], Jakub Plášil[2], Anatoly V. Kasatkin[3] and Joe Marty[4]

[1] Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA
[2] Institute of Physics ASCR, v.v.i., Na Slovance 1999/2, 18221 Prague 8, Czech Republic
[3] Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt, 18-2, 119071, Moscow, Russia
[4] 5199 East Silver Oak Road, Salt Lake City, UT 84108, USA

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ABSTRACT

The new minerals bobcookite (IMA 2014-030), $NaAl(UO_2)_2(SO_4)_4 \cdot 18H_2O$ and wetherillite (IMA 2014-044), $Na_2Mg(UO_2)_2(SO_4)_4 \cdot 18H_2O$, were found in the Blue Lizard mine, San Juan County, Utah, USA, where they occur together as secondary alteration phases in association with boyleite, chalcanthite, dietrichite, gypsum, hexahydrite, johannite, pickeringite and rozenite.

Bobcookite descriptive details: lime green to greenish-yellow massive veins and columnar crystals; transparent; vitreous lustre; bright greenish-white fluorescence; pale greenish yellow streak; hardness (Mohs) 2½; brittle; conchoidal fracture; no cleavage; moderately hygroscopic; easily soluble in cold H_2O; density$_{calc}$ = 2.669 g cm^{-3}. Optically, biaxial (–), α = 1.501(1), β = 1.523(1), γ = 1.536(1) (white light); $2V_{meas.}$ = 78(1)º; $2V_{calc.}$ = 74º; dispersion $r < v$, moderate. Pleochroism: X colourless, Y very pale yellow-green, Z pale yellow-green; $X < Y < Z$. EDS analyses yielded the empirical formula $Na_{0.97}Al_{1.09}(U_{1.02}O_2)_2(S_{0.98}O_4)_4(H_2O)_{18}$. Bobcookite is triclinic, $P\bar{1}$, a = 7.7912(2), b = 10.5491(3), c = 11.2451(8) Å, α = 68.961(5), β = 70.909(5), γ = 87.139(6)º, V = 812.79(8) Å^3 and Z = 1. The structure (R_1 = 1.65% for 3580 $F_o > 4\sigma F$) contains $[(UO_2)(SO_4)_2(H_2O)]$ chains linked by $NaO_4(H_2O)_2$ octahedra to form layers. Hydrogen bonds to insular $Al(H_2O)_6$ octahedra and isolated H_2O groups hold the structure together. The mineral is named for Dr Robert (Bob) B. Cook of Auburn University, Alabama, USA.

Wetherillite descriptive details: pale greenish-yellow blades; transparent; vitreous lustre; white streak; hardness (Mohs) 2; brittle; two cleavages, $\{10\bar{1}\}$ perfect and {010} fair; conchoidal or curved fracture; easily soluble in cold H_2O; density$_{calc}$ = 2.626 g cm^{-3}. Optically, biaxial (+), α = 1.498(1), β = 1.508(1), γ = 1.519(1) (white light); $2V_{meas.}$ = 88(1)º, $2V_{calc.}$ = 87.9º; dispersion is $r < v$, distinct; optical orientation: $Z = b$, $X \wedge a$ = 54º in obtuse β; pleochroism: X colourless, Y pale yellow-green, Z pale yellow-green; $X < Y \approx Z$. EDS analyses yielded the empirical formula $Na_{1.98}(Mg_{0.58}Zn_{0.24}Cu_{0.11}Fe^{2+}_{0.09})_{\Sigma 1.02}(U_{1.04}O_2)_2(S_{0.98}O_4)_4(H_2O)_{18}$. Wetherillite is monoclinic, $P2_1/c$, a = 20.367(1), b = 6.8329(1), c = 12.903(3) Å, β = 107.879(10)º, V = 1709.0(5) Å^3 and Z = 2. The structure (R_1 = 1.39% for 3625 $F_o > 4\sigma F$) contains $[(UO_2)(SO_4)_2(H_2O)]$ sheets parallel to {100}. Edge-sharing chains of $Na(H_2O)_5O$ polyhedra link adjacent uranyl sulfate sheets forming a weakly bonded three-layer sandwich. The sandwich layers are linked to one another by hydrogen bonds through insular $Mg(H_2O)_6$ octahedra and isolated H_2O groups. The mineral is named for John Wetherill (1866–1944) and George W. Wetherill (1925–2006).

* E-mail: akampf@nhm.org
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Keywords: bobcookite, wetherillite, new mineral, uranyl sulfate, crystal structure, Blue Lizard mine, Utah, USA.

Introduction

In most uranium deposits, the weathering of primary uranium minerals, mainly uraninite, by acidic solutions derived from the decomposition of associated sulfides yields secondary assemblages of uranyl sulfate minerals (Plášil, 2014). Our mineralogical investigations of the inactive Blue Lizard uranium mine in southeast Utah over the last several years have revealed an extensive array of uranyl sulfates, many of which are new to science. The descriptions of four of these, belakovskiite (Kampf *et al*., 2014), bluelizardite (Plášil *et al.*, 2014), meisserite (Plášil *et al.*, 2013) and plášilite (Kampf *et al*., 2015), have been published recently by our team. The fifth and sixth, bobcookite and wetherillite, are described herein. All of the new uranyl sulfates described from the Blue Lizard mine thus far contain essential Na, a remarkable fact considering that previously there was only one known uranyl sulfate mineral with essential Na – natrozippeite (Frondel *et al.*, 1976; Burns *et al.*, 2003). Bobcookite and wetherillite also contain essential Na, but each contains an additional cation, Al and Mg, respectively. Bobcookite is noteworthy for being the only known uranyl sulfate mineral with essential Al.

Bobcookite is named for Dr Robert (Bob) B. Cook (b. 1944). Dr Cook is a professor emeritus in the Department of Geology and Geography at Auburn University in Auburn, Alabama, USA, where he served for 35 years, 22 of them as department head, before retiring in 2007. He received his E.M. in mining engineering from the Colorado School of Mines and his M.S. and Ph.D. in geology from the University of Georgia. His professional specialties are exploration and environmental geology, and ore mineralogy and geochemistry. Dr Cook's past work has included several important contributions to the exploration for uranium deposits in the southeast United States. Besides his exceptional record as a scientist and educator, Dr Cook has served the amateur mineral community as an Executive Editor of *Rocks and Minerals* magazine for nearly 30 y, and since 1992 he has contributed a regular column to that publication. Dr Cook has agreed to the naming of this mineral in his honour.

Wetherillite (/ˈweðər il ait/) is named in honour of two noteworthy Wetherills: John Wetherill (1866–1944), who is responsible for the discovery of the deposit that would later be exploited as the Blue Lizard mine, and George W. Wetherill (1925–2006), whose seminal work on the spontaneous fission of uranium led to breakthrough research on the dating of rocks based on radioactive decay.

John Wetherill is perhaps best known as one of the discoverers of the ancient cliff dwellings at Mesa Verde, Colorado, in 1885. His passionate avocation for the remainder of his life was archeological exploration in the Four Corners region of the USA and he is credited with a variety of scientific discoveries. In the original description of the dinosaur *Megaloosaurus wetherilli* (later corrected to *Dilophosaurus wetherilli*), Welles (1954) states that the dinosaur was "Named in honor of the late John Wetherill of Kayenta, explorer, friend of scientists and trusted trader and counselor to the Navaho."

George W. Wetherill has been called one of the great scientists of the second half of the 20th Century (Allgre, 2009) and the father of modern theories of the formation of the Earth (Boss, 2006). During the last several decades of his career, he expanded his research focus to extraterrestrial materials – meteorite and lunar samples – and was at the forefront of research on the formation of the Solar System.

Although we have not been able to trace John Wetherill and George W. Wetherill to a common ancestor, their respective branches of the Wetherill family almost certainly do share a common origin. The Wetherill family is an ancient one in the north of England, variously spelled Wethereld, Weatherill or Witherhold. The family derived its name from the village of Wetheral, near Carlisle in the County of Cumbria near the border with Scotland. Among John Wetherill's ancestors was Richard Wetherill, an Irish Quaker, who immigrated to the United States from Rich Hill, County Armagh, Northern Ireland in 1812. Among George Wetherill's ancestors was Christopher Wetherill, who was born in ~1644 in Newcastle-upon-Tyne in Northumberland, England and died in 1711 in Mansfield Township, Burlington County, New Jersey, USA. Christopher's descendant, Samuel Wetherill (1736–1816), founded the "Society of Free Quakers" and the grandson of that Samuel

Wetherill, also Samuel Wetherill (1821–1890), was an inventor who pioneered the American zinc industry.

The new minerals and their names were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (bobcookite: IMA 2014-030; wetherillite: IMA 2014-044). The bobcookite description is based on one holotype and one cotype specimen. The holotype is deposited in the collections of the Natural History Museum of Los Angeles County, catalogue number 64164. A cotype specimen consisting of fragments removed from the holotype is housed in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4560/1. The description of wetherillite is based on three cotype specimens. Two cotypes are deposited in the collections of the Natural History Museum of Los Angeles County, catalogue numbers 64164 and 64172. Specimen 64164 is also the holotype for bobcookite. A cotype specimen consisting of fragments removed from cotype 64164 is housed in the collections of the Fersman Mineralogical Museum, registration number 4574/1.

Occurrence

Bobcookite and wetherillite were found underground in the Blue Lizard mine, Red Canyon, White Canyon district, San Juan County, Utah, USA (37º33′26″N 110º17′44″W). The Blue Lizard mine is located ~72 km west of the town of Blanding, Utah and ~22 km southeast of Good Hope Bay on Lake Powell. It is on the north side of Red Canyon and close to the Markey mine. Information on the history and geology of the deposit is taken largely from Chenoweth (1993).

The deposit was first recognized in the summer of 1898 by John Wetherill, while leading an archaeological expedition into Red Canyon. He noted yellow stains around a petrified tree. At that spot, he built a rock monument, in which he placed a piece of paper to claim the minerals.

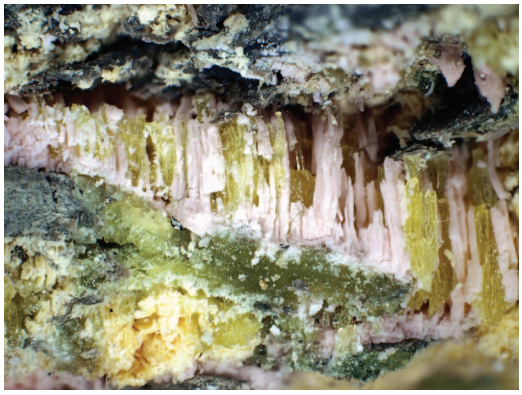

FIG. 1. Lime green bobcookite with pink boyleite; field of view = 6 mm.

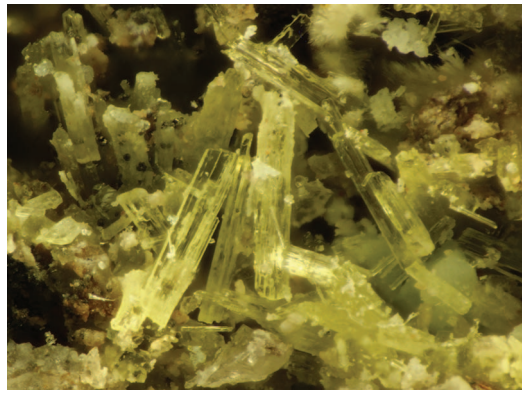

FIG. 2. Wetherillite prisms and blades; field of view = 3 mm.

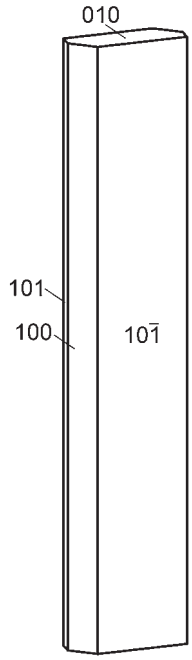

FIG. 3. Crystal drawing of wetherillite; clinographic projection in nonstandard orientation – [010] vertical.

Although he never officially recorded his claim, 45 years later, in 1943, he described the spot to Preston V. Redd of Blanding, Utah, who went to the site, found Wetherill's monument and claimed the area as the Blue Lizzard claim (note alternate spelling). Underground workings to mine uranium were not developed until the 1950s.

Mineralized channels are in the Shinarump member of the Chinle Formation. The Shinarump member consists of medium- to coarse-grained sandstone, conglomeratic sandstone beds and thick siltstone lenses. Ore minerals were deposited as replacements of wood and other organic material and as disseminations in the enclosing sandstone. Since the mine closed in 1978, oxidation of primary ores in the humid underground environment has produced a variety of secondary minerals, mainly sulfates, as efflorescent crusts on the surfaces of mine walls.

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.

Bobcookite and wetherillite are relatively rare minerals in the secondary uranyl sulfate mineral assemblage at the Blue Lizard mine. The two species occur together with other secondary minerals including boyleite, chalcanthite, dietrichite, gypsum, hexahydrite, johannite, pickeringite, rozenite and at least two other new uranyl sulfate minerals currently under study. The bulk of the matrix consists of subhedral to euhedral, equant quartz crystals that are recrystallized counterparts of the original grains of the

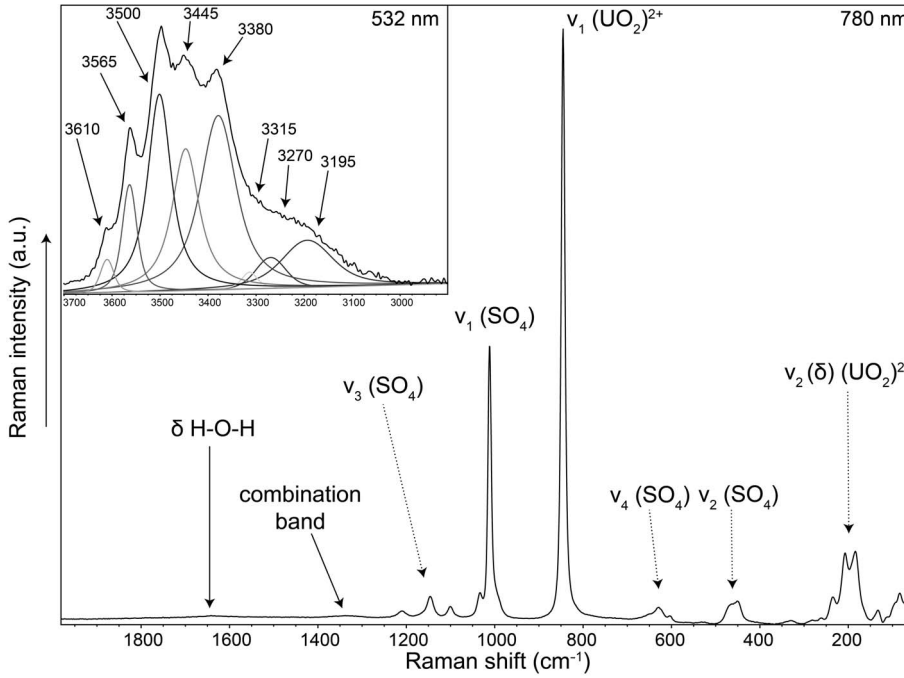

FIG. 4. The Raman spectrum of bobcookite measured with a 780 nm laser; the inset displays the region of O–H stretching frequencies (decomposed) measured with a 532 nm laser.

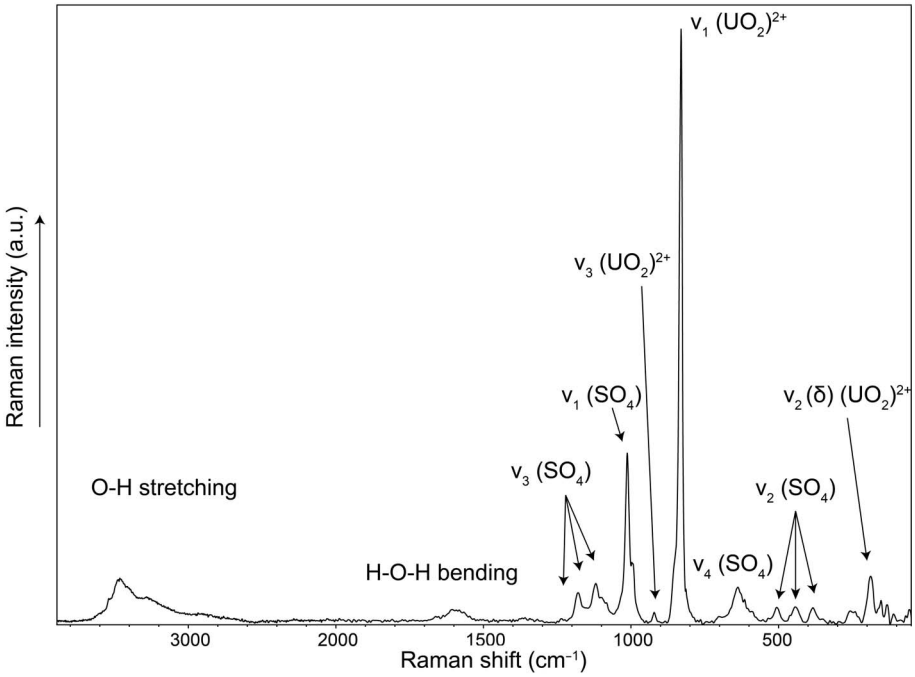

FIG. 5. The Raman spectrum of wetherillite measured with a 532 nm laser.

sandstone. Other minerals remaining from the original sandstone include feldspar, rare almandine and zircon. Minerals related to the ore deposition include baryte, bornite, chalcopyrite, covellite, pyrite and uraninite. Other secondary minerals in the general assemblage include

TABLE 1. Chemical analyses for bobcookite and wetherillite.

Constituent	Wt.%	Range	S.D.	Probe standard
Bobcookite				
Na_2O	2.29	2.03–2.57	0.19	Chkalovite
Al_2O_3	4.26	4.14–4.32	0.06	Al_2O_3 (syn.)
UO_3	44.47	44.08–44.92	0.27	UO_2 (syn.)
SO_3	23.96	23.48–24.63	0.40	ZnS (syn.)
H_2O*	24.75			
Total	99.73			
Wetherillite				
Na_2O	4.56	4.01–4.92	0.27	Chkalovite
MgO	1.75	1.28–2.04	0.22	Olivine
FeO	0.49	0–1.29	0.57	Ilmenite
CuO	0.62	0–2.01	0.88	Cu metal
ZnO	1.43	0.82–2.53	0.61	ZnO (syn.)
UO_3	44.24	42.29–45.39	1.03	UO_2 (syn.)
SO_3	23.35	22.54–24.11	0.59	$BaSO_4$ (syn.)
H_2O*	24.13			
Total	100.57			

* Calculated by stoichiometry on the basis of 38 O a.p.f.u.

aluminocoquimbite, atacamite, belakovskiite (Kampf *et al*., 2014), blödite, bluelizardite (Plášil *et al.*, 2014), brochantite, calcite, cobalto-blödite (Kasatkin *et al*., 2013), copiapite, coquimbite, cyanotrichite, d'ansite-(Mn), dickite, epsomite, fermiite (Kampf *et al*., 2015*a*), ferrinatrite, gerhardtite, gordaite, halite, kieserite, kröhnkite, lishizhenite, manganoblödite (Kasatkin *et al*., 2013), meisserite (Plášil *et al.*, 2013), metavoltine, natrozippeite, oppenheimite (Kampf *et al*., 2015*a*), plášilite (Kampf *et al*., 2015*b*), pseudojohannite, rhomboclase, römerite, sideronatrite, tamarugite and other new minerals currently under investigation.

Physical and optical properties

Bobcookite

Bobcookite commonly occurs in lime green to greenish-yellow massive veins and cavity fillings and as irregular columnar (crude prismatic) crystals, which are often more or less curved and sometimes composite (Fig. 1). Prisms are up to 2 mm long and are elongated on [10$\bar{1}$]. The terminations are irregular and the only forms observable are in the [10$\bar{1}$] zone: {010}, {101}, {111} and {1$\bar{1}$1}. No twinning was observed.

Crystals are transparent with a vitreous lustre. The mineral has very pale yellowish-green streak. The mineral fluoresces bright greenish white under both longwave and shortwave UV; stronger under shortwave. The Mohs hardness is ~2½. Crystals are brittle with no cleavage and conchoidal fracture. The mineral is moderately hygroscopic and is easily soluble in room temperature H_2O. Because it is also soluble in available aqueous density liquids, its density could not be measured. The calculated densities are 2.669 g cm^{-3} based on the empirical formula and 2.653 g cm^{-3} based on the ideal formula.

TABLE 2. Powder X-ray data for bobcookite and wetherillite. (Only calculated lines with $I \geq 2$ are shown.)

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*hkl*
Bobcookite				
100	9.82	9.8170	84	0 1 0
99	7.14	7.1373	100	1 0 1
55	6.33	6.3679	45	1 1 1
39	5.99	6.1076	21	$\bar{1}$ 1 0
		5.9711	23	0 $\bar{1}$ 1
		5.6745	3	1 1 0
83	5.25	5.3184	29	1 $\bar{1}$ 1
		5.2533	16	0 1 2
		5.2154	15	0 2 1
		5.1379	18	$\bar{1}$ 0 1
21	4.97	5.0857	6	$\bar{1}$ 1 1
		4.9507	5	0 0 2
		4.9323	9	1 0 2
12	4.328	4.3675	5	0 2 2
		4.2328	12	$\bar{1}$ 2 0
28	4.174	4.1894	5	1 2 2
		4.1576	7	$\bar{1}$ $\bar{1}$ 1
		4.0758	6	$\bar{1}$ 2 1
31	3.922	3.9433	16	1 2 0
		3.8890	2	0 $\bar{1}$ 2
		3.8736	8	0 $\bar{2}$ 1
21	3.689	3.6994	6	1 1 3
		3.6929	4	2 1 1
		3.6705	8	2 0 0
52	3.563	3.5896	9	$\bar{1}$ 0 2
		3.5759	11	2 1 2
		3.5686	21	2 0 2
		3.5406	3	2 $\bar{1}$ 1
		3.5278	3	$\bar{2}$ 1 0
		3.5098	8	0 3 1
49	3.441	3.4715	4	1 0 3
		3.4522	20	1 2 3
		3.4303	14	$\bar{1}$ 2 2
37	3.329	3.3618	10	0 2 3
		3.3549	12	2 1 0
		3.3452	2	0 3 2
		3.3005	12	0 0 3
31	3.213	3.2723	8	0 3 0
		3.2268	12	1 3 2
		3.2112	3	1 3 1
		3.1688	6	2 $\bar{1}$ 2
		3.1430	4	2 2 1
57	3.082	3.1208	3	$\bar{2}$ 0 1
		3.1086	2	2 1 3
		3.0854	23	$\bar{1}$ $\bar{1}$ 2
		3.0777	13	$\bar{1}$ 3 0
		3.0395	5	1 $\bar{2}$ 2
		2.9978	4	2 0 3
		2.9602	3	2 $\bar{2}$ 1
		2.9424	2	1 3 3
		2.9304	2	2 2 3
37	2.905	2.9117	5	0 3 3
		2.9072	8	1 3 0
		2.8892	10	$\bar{1}$ 3 2
		2.8779	6	$\bar{2}$ 2 1
25	2.821	2.8447	8	$\bar{1}$ 1 3
		2.8331	6	0 $\bar{1}$ 3
		2.8172	5	0 $\bar{3}$ 1
		2.7836	3	1 $\bar{3}$ 1
		2.7717	4	$\bar{1}$ 2 3
		2.7603	2	1 2 4
20	2.621	2.6471	7	$\bar{2}$ 1 2
		2.6380	4	0 1 4
		2.6267	3	0 2 4
		2.6238	4	1 0 4
		2.5892	4	2 1 4
		2.5829	5	2 3 1
23	2.541	2.5690	3	$\bar{2}$ 0 2
		2.5545	6	$\bar{1}$ $\bar{2}$ 2
		2.5429	4	$\bar{2}$ $\bar{2}$ 2
		2.5197	2	$\bar{1}$ 3 3
		2.5070	5	3 1 1
		2.4930	5	$\bar{2}$ 3 1
27	2.448	2.4673	2	1 4 1
		2.4542	8	0 4 0
		2.4475	2	0 3 4
		2.4425	2	$\bar{2}$ $\bar{2}$ 1
		2.4385	5	0 4 3
		2.4182	7	3 1 3
		2.4112	2	3 $\bar{1}$ 2
19	2.374	2.3879	5	$\bar{1}$ 4 2
		2.3791	3	3 0 3
		2.3741	2	3 2 2
		2.3694	5	0 $\bar{2}$ 3
		2.3635	3	0 $\bar{3}$ 2
		2.3511	2	2 3 4
		2.3351	3	1 $\bar{1}$ 4
		2.2996	2	2 2 3
		2.2601	4	$\bar{3}$ 2 0
8	2.205	2.2141	2	2 3 2
		2.2106	3	2 4 3
		2.1977	4	1 4 1
		2.1734	2	3 $\bar{2}$ 2
		2.1535	2	1 3 5
		2.1405	2	$\bar{1}$ 0 4
		2.1354	2	2 4 1
23	2.114	2.1285	4	3 3 2
		2.1260	2	3 2 0
		2.1232	3	$\bar{2}$ 4 1
		2.1215	2	$\bar{1}$ 3 2
		2.1164	4	$\bar{2}$ 4 0
		2.1058	4	0 5 2
		2.0942	4	0 1 5
		2.0929	4	$\bar{1}$ $\bar{2}$ 3
		2.0759	2	2 3 5
		2.0664	2	$\bar{2}$ 3 3
		2.0531	2	1 $\bar{3}$ 3
		2.0499	2	2 0 5
20	2.0355	2.0449	2	0 5 3
		2.0372	3	1 5 3
		2.0359	3	$\bar{3}$ 3 0
		2.0316	6	1 $\bar{2}$ 4
		2.0263	4	3 3 4
		2.0027	2	$\bar{1}$ 5 1
		1.9990	2	3 $\bar{2}$ 3
23	1.9715	1.9908	3	1 5 1
		1.9754	4	$\bar{1}$ 4 4
		1.9717	4	$\bar{2}$ 4 0
		1.9695	5	$\bar{2}$ $\bar{1}$ 3
		1.9634	3	0 5 0
12	1.9339	1.9437	9	4 0 2
		1.9368	4	0 $\bar{4}$ 2
		1.9294	2	4 1 2
		1.9188	2	0 4 5
		1.9088	2	$\bar{1}$ 5 3
18	1.8794	1.8915	2	3 3 0
		1.8893	2	$\bar{2}$ 4 3
		1.8849	2	2 $\bar{1}$ 5
		1.8840	4	$\bar{1}$ 2 5
		1.8776	3	$\bar{2}$ 2 4
		1.8677	2	$\bar{2}$ 1 4
		1.8656	2	$\bar{2}$ $\bar{4}$ 2
14	1.8352	1.8506	2	$\bar{3}$ 3 2
		1.8497	2	2 2 6
		1.8478	2	4 2 3
		1.8438	4	$\bar{1}$ 3 5
		1.8391	2	2 5 4
		1.8353	2	4 0 0
		1.8295	2	$\bar{4}$ 1 0
		1.8175	3	0 $\bar{1}$ 5
		1.8164	2	4 1 4
		1.8152	3	4 $\bar{1}$ 3
11	1.786	1.7843	3	4 0 4
		1.7818	2	$\bar{2}$ 5 2
		1.7800	2	$\bar{2}$ $\bar{2}$ 3
		1.7743	2	$\bar{1}$ 5 4
		1.7728	2	3 3 3
12	1.7478	1.7549	5	0 6 2
		1.7508	2	1 4 6
		1.7470	2	0 5 5
		1.7386	3	4 3 3
		1.7359	2	2 5 5
		1.7282	3	1 6 3
9	1.6962	1.6984	3	$\bar{3}$ $\bar{2}$ 2
		1.6939	2	4 $\bar{2}$ 3
		1.6881	2	4 1 5
		1.6787	2	2 5 0
2	1.6508	1.6646	3	4 $\bar{3}$ 1
		1.6573	2	$\bar{1}$ 6 3
		1.6441	2	$\bar{4}$ $\bar{1}$ 1
		1.6288	3	1 5 6
		1.6134	2	2 6 4
4	1.5973	1.6022	4	4 4 3
		1.5898	2	1 2 7
		1.5858	2	$\bar{4}$ 1 2
8	1.5686	1.5734	3	$\bar{1}$ 1 6
		1.5716	2	1 6 0
		1.5678	2	3 $\bar{4}$ 3
		1.5644	2	2 1 7
		1.5543	2	4 2 6
16	1.5411	1.5478	2	5 1 3
		1.5453	4	3 $\bar{1}$ 6
		1.5422	7	$\bar{2}$ 0 5
		1.5389	2	$\bar{2}$ 6 0
		1.5275	2	0 $\bar{6}$ 1
3	1.5056	1.5082	2	$\bar{1}$ 2 5
		1.5067	2	$\bar{1}$ 0 6
		1.4969	2	2 0 7
		1.4801	2	4 $\bar{4}$ 2
9	1.4606	1.4687	3	5 $\bar{2}$ 2
		1.4658	2	2 5 7
		1.4640	2	$\bar{1}$ 7 2
		1.4557	4	$\bar{2}$ 5 5
		1.4521	2	5 $\bar{1}$ 4
2	1.4208	1.4258	2	4 5 2
5	1.3867	1.3974	2	$\bar{1}$ 7 0
		1.3870	2	5 $\bar{3}$ 2
		1.3796	2	$\bar{5}$ 3 0

Optically, bobcookite is biaxial (−) with α = 1.501(1), β = 1.523(1) and γ = 1.536(1) (measured in white light). The 2V measured directly on a spindle stage is 78(1)º; the calculated 2V is 74º. Dispersion is $r < v$, moderate. Pleochroism is X colourless, Y very pale yellow-green, Z pale yellow-green; $X < Y < Z$. The partially determined optical orientation is Z ^ [10$\bar{1}$] ≈ 10º; note that [10$\bar{1}$] is the direction of prism elongation.

Wetherillite

Wetherillite commonly occurs as pale greenish-yellow prisms or blades with irregular termina-

TABLE 2 (*contd.*)

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*hkl*
Wetherillite				
14	19.84	19.3833	10	1 0 0
100	9.74	9.6917	100	2 0 0
50	6.46	6.4512	42	$\bar{1}$ 0 2
		6.1399	13	0 0 2
		6.1023	2	$\bar{2}$ 0 2
48	6.01	5.9708	31	0 1 1
		5.5845	4	2 1 0
		5.4807	3	1 1 1
		5.4606	3	$\bar{2}$ 1 1
40	5.41	5.3958	12	1 0 2
		5.3450	17	$\bar{3}$ 0 2
		4.8458	28	4 0 0
64	4.80	4.7751	19	2 1 1
		4.7530	14	$\bar{3}$ 1 1
		4.6946	6	3 1 0
		4.5888	2	2 0 2
12	4.60	4.5515	1	$\bar{2}$ 1 2
		4.5420	5	$\bar{4}$ 0 2
3	4.240	4.2347	1	1 1 2
		4.0912	1	3 1 1
		4.0717	3	$\bar{4}$ 1 1
4	4.036	3.9527	4	4 1 0
		3.8937	4	3 0 2
		3.8767	5	5 0 0
28	3.873	3.8556	17	$\bar{5}$ 0 2
		3.8094	1	2 1 2
		3.6268	8	$\bar{1}$ 1 3
10	3.640	3.6209	2	$\bar{2}$ 1 3
		3.5146	22	4 1 1
		3.5114	7	0 1 3
50	3.510	3.4987	4	$\bar{5}$ 1 1
		3.4956	14	$\bar{3}$ 1 3
		3.4165	8	0 2 0
15	3.385	3.3830	2	3 1 2
		3.3579	1	$\bar{5}$ 1 2
		3.3380	3	4 0 2
26	3.303	3.3059	9	1 1 3
		3.2914	10	0 2 1
		3.2306	2	6 0 0
		3.2256	5	$\bar{2}$ 0 4
		3.2221	5	2 2 0
47	3.202	3.2018	11	1 2 1
		3.1978	5	$\bar{2}$ 2 1
		3.1871	11	$\bar{1}$ 0 4
		3.1766	7	$\bar{3}$ 0 4
		3.0700	1	0 0 4
		3.0539	5	2 1 3
		3.0501	8	5 1 1
		3.0413	3	2 2 1
34	3.038	3.0356	2	$\bar{3}$ 2 1
		3.0296	4	$\bar{5}$ 1 3
		3.0192	6	$\bar{1}$ 2 2
		2.9992	1	4 1 2
		2.9854	2	0 2 2
		2.9811	1	$\bar{2}$ 2 2
		2.9774	1	$\bar{6}$ 1 2
		2.9206	2	6 1 0
		2.9169	3	$\bar{2}$ 1 4
		2.9005	1	5 0 2
23	2.892	2.8978	2	1 0 4
		2.8865	2	1 2 2
		2.8786	12	$\bar{3}$ 2 2
		2.8398	2	3 2 1
		2.8333	3	$\bar{4}$ 2 1
		2.8003	2	0 1 4
12	2.799	2.7923	2	4 2 0
		2.7860	2	$\bar{4}$ 1 4
		2.7690	4	7 0 0
		2.7403	1	2 2 2
		2.7303	1	$\bar{4}$ 2 2
		2.6789	6	6 1 1
19	2.673	2.6725	3	$\bar{6}$ 0 4
		2.6676	10	2 2 3
		2.6229	3	0 2 3
		2.6176	1	$\bar{5}$ 2 1
		2.5663	1	7 1 0
4	2.567	2.5570	3	$\bar{5}$ 2 2
		2.5541	1	6 0 2
		2.5429	3	4 1 3
		2.5338	2	1 2 3
13	2.529	2.5239	7	$\bar{4}$ 2 3
		2.5210	1	$\bar{7}$ 1 3
		2.5094	1	2 1 4
		2.4921	2	3 0 4
		2.4229	1	8 0 0
		2.4149	1	2 2 3
		2.4130	2	5 2 1
8	2.403	2.4108	1	$\bar{2}$ 1 5
		2.4080	4	$\bar{3}$ 1 5
		2.3876	1	4 2 2
		2.3801	1	7 1 1
		2.3771	4	$\bar{1}$ 1 5
6	2.368	2.3689	4	$\bar{4}$ 1 5
		2.3473	1	6 2 0
		2.3413	1	3 1 4
		2.3305	2	$\bar{1}$ 2 4
		2.3264	4	$\bar{3}$ 2 4
9	2.326	2.3205	1	$\bar{7}$ 1 4
		2.3166	1	5 1 3
		2.3112	1	0 1 5
		2.2987	1	$\bar{5}$ 1 5
		2.2970	1	$\bar{8}$ 1 3
		2.2790	1	3 2 3
		2.2759	1	7 0 2
9	2.267	2.2710	1	$\bar{8}$ 0 4
		2.2661	1	$\bar{6}$ 2 3
		2.2621	4	1 3 0
		2.2606	3	$\bar{9}$ 0 2
		2.2208	5	1 1 5
		2.2172	1	2 3 0
		2.2111	1	5 2 2
15	2.212	2.2099	2	1 2 4
		2.2052	5	$\bar{6}$ 1 5
		2.2006	2	$\bar{7}$ 2 2
		2.1994	1	$\bar{5}$ 2 4
		2.1593	1	7 1 2
		2.1537	3	9 0 0
		2.1512	1	7 2 0
		2.1481	3	3 3 0
		2.1462	1	$\bar{9}$ 1 2
27	2.140	2.1397	3	$\bar{2}$ 0 6
		2.1367	3	8 1 1
		2.1354	4	0 3 2
		2.1338	4	$\bar{2}$ 3 2
		2.1300	4	$\bar{9}$ 1 1
		2.1243	1	$\bar{7}$ 2 3
		2.1159	1	6 1 3
		2.1118	1	5 0 4
10	2.098	2.0984	7	1 3 2
		2.0776	1	$\bar{4}$ 3 1
		2.0613	2	4 3 0
		2.0571	2	$\bar{2}$ 2 5
		2.0553	1	$\bar{3}$ 2 5
		2.0512	1	$\bar{3}$ 1 6
		2.0492	3	8 0 2
		2.0466	2	0 0 6
		2.0456	1	6 2 2
20	2.044	2.0419	1	$\bar{2}$ 1 6
		2.0401	1	2 3 2
		2.0379	2	7 2 1
		2.0360	5	$\bar{4}$ 3 2
		2.0341	2	$\bar{6}$ 0 6
		2.0327	1	$\bar{8}$ 2 1
		2.0309	1	$\bar{4}$ 2 5
		2.0006	5	3 1 5
		1.9976	1	5 2 3
		1.9942	1	0 2 5
		1.9874	1	$\bar{3}$ 3 3
		1.9861	1	$\bar{5}$ 2 5
12	1.9934	1.9850	2	$\bar{8}$ 2 3
		1.9828	1	$\bar{8}$ 1 5
		1.9660	1	3 3 2
		1.9638	1	5 3 0
		1.9505	1	1 3 3
		1.9469	1	6 0 4
		1.9358	2	9 1 1
6	1.9423	1.9302	1	$\bar{10}$ 1 1
		1.9278	3	$\bar{10}$ 0 4
		1.9250	1	$\bar{10}$ 1 3
		1.9047	1	4 2 4
		1.8956	1	1 1 6
		1.8913	1	$\bar{8}$ 2 4
		1.8824	1	$\bar{7}$ 1 6
5	1.8841	1.8814	1	4 3 2
		1.8788	1	8 2 1
		1.8760	1	$\bar{6}$ 3 2
		1.8723	1	$\bar{8}$ 0 6
		1.8648	1	10 1 0
		1.8637	1	2 2 5
10	1.8576	1.8615	3	6 3 0
		1.8605	3	$\bar{2}$ 3 4
		1.8528	2	$\bar{9}$ 2 3
		1.8519	2	$\bar{7}$ 2 5
		1.8292	4	0 3 4
		1.8252	3	$\bar{4}$ 3 4
9	1.8178	1.8199	1	$\bar{3}$ 2 6
		1.8134	2	$\bar{2}$ 2 6
		1.8105	1	$\bar{4}$ 2 6
		1.7963	1	5 2 4
		1.7914	4	5 3 2
		1.7864	3	8 1 3
		1.7851	1	$\bar{5}$ 3 4
		1.7817	1	$\bar{9}$ 0 6
		1.7769	2	$\bar{4}$ 1 7
17	1.7761	1.7727	3	5 1 5
		1.7653	4	$\bar{2}$ 1 7
		1.7630	3	$\bar{11}$ 1 1
		1.7621	1	11 0 0
		1.7606	1	$\bar{5}$ 1 7
		1.7573	1	8 2 2
		1.7558	1	$\bar{10}$ 1 5
		1.7478	1	$\bar{6}$ 2 6
		1.7404	3	$\bar{2}$ 3 4
10	1.7461	1.7338	1	$\bar{10}$ 2 1
		1.7307	3	$\bar{6}$ 1 7
		1.7043	1	10 0 2
		1.7009	1	4 2 5
		1.6992	2	0 1 7
		1.6943	2	$\bar{8}$ 3 2
12	1.6892	1.6917	4	$\bar{1}$ 4 1
		1.6900	1	$\bar{10}$ 0 6
		1.6880	1	$\bar{9}$ 2 5
		1.6794	5	1 4 1
		1.6735	1	$\bar{7}$ 3 4
		1.6690	1	8 0 4
4	1.6577	1.6595	2	8 3 0
		1.6540	2	$\bar{3}$ 4 1
		1.6505	1	1 1 7
		1.6407	1	$\bar{12}$ 1 3
		1.6276	1	$\bar{11}$ 2 2
		1.6255	2	11 1 1
		1.6214	2	$\bar{3}$ 2 7
		1.6200	1	$\bar{3}$ 4 1
		1.6188	1	$\bar{4}$ 4 1
		1.6174	1	$\bar{11}$ 2 3
12	1.6163	1.6164	2	4 3 4
		1.6132	1	10 2 1
		1.6099	2	7 3 2
		1.6077	2	$\bar{5}$ 2 7
		1.6045	1	$\bar{9}$ 3 2
		1.6002	1	$\bar{11}$ 0 6
		1.5949	1	2 1 7
		1.5860	1	$\bar{2}$ 4 3
4	1.5800	1.5823	1	$\bar{9}$ 1 7
		1.5765	1	0 4 3
		1.5707	1	11 0 2
		1.5657	2	7 1 5
		1.5636	2	$\bar{3}$ 3 6
		1.5542	1	$\bar{4}$ 4 3
5	1.5558	1.5510	1	$\bar{12}$ 1 5
		1.5486	1	5 3 4
		1.5455	1	$\bar{1}$ 3 6
		1.5418	2	$\bar{5}$ 3 6
		1.5401	1	$\bar{9}$ 3 4
		1.5346	3	10 1 3
		1.5276	1	2 4 3
7	1.5296	1.5256	1	$\bar{6}$ 4 1
		1.5239	1	$\bar{9}$ 2 3
		1.5221	2	$\bar{11}$ 2 5
		1.5182	1	$\bar{10}$ 3 2
		1.5145	1	$\bar{9}$ 1 4
		1.5136	1	$\bar{8}$ 2 7
		1.4997	2	$\bar{12}$ 2 1
		1.4910	2	$\bar{13}$ 0 0
		1.4887	1	$\bar{12}$ 2 4
		1.4878	1	$\bar{6}$ 4 3
2	1.4849	1.4848	1	$\bar{7}$ 3 6
		1.4799	1	$\bar{6}$ 3 4
		1.4781	1	$\bar{12}$ 1 6
		1.4761	2	10 3 0
		1.4732	1	8 1 5
		1.4612	1	$\bar{5}$ 2 6
		1.4597	1	$\bar{13}$ 1 5
		1.4590	1	$\bar{11}$ 1 7
		1.4553	1	7 2 5
		1.4503	1	10 0 4
		1.4495	1	$\bar{14}$ 0 2
		1.4489	1	2 0 8
3	1.4446	1.4472	1	$\bar{7}$ 0 6
		1.4442	1	$\bar{2}$ 2 8
		1.4414	2	$\bar{9}$ 3 2
		1.4384	1	$\bar{14}$ 0 4
		1.4365	2	$\bar{11}$ 3 2
		1.4325	1	$\bar{13}$ 0 6
		1.4237	1	$\bar{2}$ 4 5
3	1.4211	1.4231	1	$\bar{3}$ 4 5
		1.4222	2	$\bar{14}$ 1 3
		1.4196	1	$\bar{10}$ 2 7
		1.4156	1	$\bar{8}$ 4 1
		1.4150	1	$\bar{4}$ 4 5
		1.4121	1	$\bar{7}$ 3 4
		1.4033	2	$\bar{9}$ 3 6
3	1.4033	1.4024	1	0 4 5
		1.4016	1	$\bar{5}$ 1 9
		1.3995	1	$\bar{5}$ 4 5
		1.3984	1	13 1 1

tions up to ~1 mm long (Figs 2 and 3) in subparallel intergrowths, divergent sprays and jackstraw aggregates. Crystals are elongated on [010], more or less flattened on $\{10\bar{1}\}$ and exhibit the forms {100}, {101} and $\{10\bar{1}\}$. Note that no terminal forms could be measured; the form {010} has been added to the crystal drawing in Fig. 3 to show the typical appearance of broken off blades. No twinning was observed.

Crystals are transparent with a vitreous lustre. The mineral has white streak. The Mohs hardness is ~2. Crystals are brittle with two cleavages: $\{10\bar{1}\}$ perfect and {010} fair. The fracture is conchoidal or curved. The mineral is easily soluble in room temperature H_2O. Because it is also soluble in available aqueous density liquids, its density could not be measured. The calculated densities are 2.626 g cm^{-3} based on the empirical formula and 2.563 g cm^{-3} based on the ideal formula.

Optically, wetherillite is biaxial (+) with α = 1.498(1), β = 1.508(1), γ = 1.519(1) (measured in white light). The 2V measured directly on a spindle stage is 88(1)º; the calculated 2V is 87.9º. Dispersion is $r < v$, distinct. Pleochroism is X colourless, Y pale yellow-green, Z pale yellow-green; $X < Y \approx Z$. The optical orientation is $Z = b$, $X \wedge a$ = 54º in obtuse β.

Raman spectroscopy

The Raman spectra of bobcookite and wetherillite were recorded on a Thermo-Scientific DXR Raman microscope interfaced to an Olympus microscope (objective 50×). The spectrometer was calibrated by a software-controlled calibration procedure (within *Omnic 8* software) using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white light sources (intensity calibration). Spectral manipulation such as background correction and band-component analysis was carried out with *Omnic 8* software.

Bobcookite

For bobcookite, due to sample fluorescence, a 532 nm laser was used only for obtaining information from the stretching O−H region. A 780 nm laser was used for the remainder of the spectrum. The Raman spectrum of bobcookite is shown in Fig. 4.

The bands of the highest energy, located in the spectral range ~3600−3000 cm^{-1} were assigned to the ν(O−H) stretching vibration of free or weakly hydrogen-bonded H_2O molecules. According to the empirical relation given by Libowitzky (1999), approximate O−H···O hydrogen bond lengths are in the range ~3.0−2.7 Å. A very weak band at 1640 cm^{-1} is connected with ν_2 (δ) H−O−H bending modes of water molecules.

Bands at 1210, 1145 and 1110 cm^{-1} belong to the split triply degenerate $\nu_3(SO_4^{2-})$ antisymmetric stretching vibrations, and a strong broad band, consisting of two overlapping vibrations at 1035 and 1010 cm^{-1}, belongs to the $\nu_1(SO_4^{2-})$ symmetric stretching vibration. A shoulder at 990 cm^{-1} may be assigned to δ(U−OH) bending or $\nu_1(SO_4^{2-})$.

There is no observable peak in the region of $\nu_3(UO_2)^{2+}$ antisymmetric stretching vibrations, which is possibly due to selection rules. A very strong band at 845 cm^{-1} belongs to the $\nu_1(UO_2^{2+})$ symmetric stretching vibration. According to the empirical relation (Bartlett and Cooney, 1989), U−O bond lengths in the uranyl ion, inferred from the stretching-vibration energies, are ~1.77 Å.

Bands at 630 and 600 cm^{-1} are related to split, triply degenerate $\nu_4(\delta)(SO_4^{2-})$ bending vibrations and bands at 470 and 450 cm^{-1} to the split doubly degenerate $\nu_2(\delta)(SO_4^{2-})$ bending vibrations. A band at 330 cm^{-1} can be probably assigned to $\nu(U-O_{equatorial})$ stretching vibrations or to Na−O stretching frequencies similarly to the assignments for K−O stretching frequencies observed for U^{6+} compounds (e.g. Volkovich *et al.*, 1998; Plášil *et al.*, 2010). The split doubly degenerate $\nu_2(\delta)(UO_2^{2+})$ bending vibration is represented by a medium intensity composite band at ~210 cm^{-1}. The low energy bands are related to lattice modes.

Wetherillite

The Raman spectrum of wetherillite, obtained using a green (532 nm) laser, is shown in Fig. 5. Bands of highest energy, located in the ~3600−3000 cm^{-1} range were assigned to the ν(O−H) stretching vibrations of free or weakly hydrogen bonded H_2O molecules. According to Libowitzky (1999), approximate O−H···O hydrogen bond lengths are in the range ~3.0−2.7 Å, which is in accordance with the structure data. A weak Raman splitting band at ~1610 cm^{-1} is attributed to the ν_2 (δ)H−O−H bending mode of H_2O molecules.

Bands at 1230, 1180, 1120, 1105 and 1080 cm^{-1} are attributed to the split triply

degenerate $\nu_3(SO_4)$ antisymmetric stretching vibrations of two symmetrically independent sulfate groups, and a strong band, consisting of two overlapping vibrations at 1010 and 995 cm^{-1}, belongs to the $\nu_1(SO_4)$ symmetric stretching vibration.

A weak band at 922 cm^{-1} is attributed to activated $\nu_3(UO_2)^{2+}$ antisymmetric stretching vibrations, and is possibly due to selection rules. A very strong band at ~830 cm^{-1} can be fitted by three band components, the most intensive of which is at ~830 cm^{-1}; two weaker component bands, at ~890 and 815 cm^{-1}, account for the asymmetry of the whole overlapping group. While the strong 830 cm^{-1} band is at a position expected for the $\nu_1(UO_2^{2+})$ symmetric stretching vibration, the two weaker bands are slightly higher and lower than one might expect. In the crystal structure, there is only one unique U atom, so the weak peaks cannot represent splitting due to symmetrically independent U atoms. Therefore, we conclude that these peaks are most likely a spectral artifact, possibly caused by some organic matter (C–C stretches; compare e.g. Quilès and Burneau, 1998, Unruh *et al.*, 2013) as a surface contaminant. Using empirical relations given by Bartlett and Cooney (1989), the U–O bond lengths in the uranyl ion are 1.78 Å (using ν_1) and 1.77 Å (using ν_3), in accordance with the structure data.

The band at 700 cm^{-1} can be attributed to the libration of water molecules. Bands at 640 and 615 (with a shoulder at 580 cm^{-1}) are related to split, triply degenerate $\nu_4(\delta)(SO_4)$ bending vibra-

TABLE 3. Data collection and structure-refinement details for bobcookite and wetherillite*.

Diffractometer	Rigaku R-Axis Rapid II	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo*K*α (λ = 0.71075 Å)	Mo*K*α (λ = 0.71075 Å)
X-ray power	50 kV, 40 mA	50 kV, 40 mA
Temperature	298(2) K	298(2) K
Structural formula	$NaAl(UO_2)_2(SO_4)_4 \cdot 18H_2O$	$Na_2(Mg_{0.775}Zn_{0.225})(UO_2)_2(SO_4)_4 \cdot 18H_2O$
Space group	$P\bar{1}$	$P2_1/c$
Unit-cell dimensions	a = 7.7912(2) Å	a = 20.3669(14) Å
	b = 10.5491(3) Å	b = 6.83288(12) Å
	c = 11.2451(8) Å	c = 12.903(3) Å
	α = 68.961(5)°	
	β = 70.909(5)°	β = 107.879(10)°
	γ = 87.139(6)°	
V	812.79(8) $Å^3$	1709.0(5) $Å^3$
Z	1	2
Density (for above formula)	2.653 g cm^{-3}	2.081 g cm^{-3}
Absorption coefficient	10.375 mm^{-1}	5.291 mm^{-1}
$F(000)$	612	1031.2
Crystal size (μm)	150 × 100 × 80	200 × 50 × 30
θ range	3.59 to 27.47°	3.34 to 27.47°
Index ranges	$-10 \leqslant h \leqslant 10$	$-26 \leqslant h \leqslant 26$
	$-13 \leqslant k \leqslant 13$	$-8 \leqslant k \leqslant 6$
	$-14 \leqslant l \leqslant 14$	$-16 \leqslant l \leqslant 16$
Reflections collected/unique	15,166/3705; R_{int} = 0.021	19,739/3889; R_{int} = 0.023
Reflections with $F > 4\sigma(F)$	3603	3625
Completeness to θ_{max}	99.4%	99.3%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters refined	265	269
Goof	1.209	1.100
Final R indices [$F_o > 4\sigma(F)$]	R_1 = 0.0165, wR_2 = 0.0412	R_1 = 0.0139, wR_2 = 0.0293
R indices (all data)	R_1 = 0.0172, wR_2 = 0.0414	R_1 = 0.0163, wR_2 = 0.0300
Largest diff. peak/hole	+1.27/−0.84 e $Å^{-3}$	+0.60/−0.46 e $Å^{-3}$

* $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. Goof = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for bobcookite a is 0.0233 and b is 0.4229; for wetherillite a is 0.0116 and b is 1.2638.

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

	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Bobcookite										
Na	½	0	0	0.0267(4)	0.0261(9)	0.0299(9)	0.0304(9)	−0.0130(8)	−0.0159(8)	0.0078(7)
Al	0	½	½	0.0158(2)	0.0153(5)	0.0160(5)	0.0158(5)	−0.0044(4)	−0.0062(4)	0.0004(4)
U	0.75913(2)	0.10395(2)	0.20753(2)	0.01335(4)	0.01330(6)	0.01394(6)	0.01106(6)	−0.00464(4)	−0.00158(4)	0.00029(4)
S1	0.14233(9)	0.18711(6)	−0.10530(6)	0.01463(13)	0.0154(3)	0.0136(3)	0.0116(3)	−0.0033(2)	−0.0019(2)	0.0022(2)
S2	0.55800(9)	0.16411(6)	0.52062(7)	0.01446(12)	0.0147(3)	0.0136(3)	0.0133(3)	−0.0053(2)	−0.0016(2)	−0.0002(2)
O1	0.2721(3)	0.1465(2)	−0.0338(2)	0.0302(5)	0.0311(12)	0.0348(12)	0.0332(13)	−0.0152(10)	−0.0203(10)	0.0147(10)
O2	0.2088(3)	0.3085(2)	−0.2270(2)	0.0215(4)	0.0247(10)	0.0163(9)	0.0154(10)	−0.0016(8)	−0.0003(8)	−0.0032(8)
O3	0.9680(3)	0.2161(2)	−0.0165(2)	0.0210(4)	0.0212(10)	0.0172(9)	0.0169(10)	−0.0057(8)	0.0024(8)	0.0042(8)
O4	0.0957(3)	0.0741(2)	−0.1437(2)	0.0200(4)	0.0224(10)	0.0162(9)	0.0195(10)	−0.0091(8)	−0.0014(8)	0.0008(8)
O5	0.7014(3)	0.0886(2)	0.5648(2)	0.0256(5)	0.0247(11)	0.0273(11)	0.0280(12)	−0.0113(9)	−0.0121(9)	0.0079(9)
O6	0.5756(3)	0.3075(2)	0.5062(2)	0.0233(4)	0.0236(10)	0.0154(9)	0.0309(12)	−0.0105(9)	−0.0062(9)	−0.0016(8)
O7	0.3748(3)	0.1048(2)	0.6174(2)	0.0214(4)	0.0200(10)	0.0198(10)	0.0168(10)	−0.0047(8)	0.0015(8)	−0.0015(8)
O8	0.5636(3)	0.1592(2)	0.3888(2)	0.0212(4)	0.0214(10)	0.0268(10)	0.0149(10)	−0.0102(8)	−0.0025(8)	0.0036(8)
O9	0.9378(3)	0.1093(2)	0.2704(2)	0.0258(5)	0.0195(10)	0.0353(12)	0.0238(11)	−0.0136(10)	−0.0050(9)	−0.0020(9)
O10	0.5839(3)	0.0999(2)	0.1403(2)	0.0244(5)	0.0214(11)	0.0319(12)	0.0222(11)	−0.0101(9)	−0.0102(9)	0.0054(9)
OW1	0.9077(3)	0.4216(2)	0.4072(2)	0.0214(4)	0.0208(10)	0.0256(10)	0.0175(10)	−0.0067(9)	−0.0062(9)	−0.0054(8)
H1A	0.806(4)	0.385(4)	0.441(3)	0.026						
H1B	0.946(4)	0.442(4)	0.330(2)	0.026						
OW2	0.8109(3)	0.4080(2)	0.6631(2)	0.0218(4)	0.0190(10)	0.0184(10)	0.0217(11)	−0.0027(8)	−0.0036(8)	0.0002(8)
H2A	0.804(5)	0.329(2)	0.702(4)	0.026						
H2B	0.713(4)	0.438(3)	0.679(4)	0.026						
OW3	0.1443(3)	0.3507(2)	0.5370(2)	0.0226(4)	0.0261(11)	0.0211(10)	0.0250(11)	−0.0093(9)	−0.0137(9)	0.0077(9)
H3A	0.185(5)	0.327(4)	0.601(3)	0.027						
H3B	0.151(5)	0.293(3)	0.510(4)	0.027						
OW4	0.7445(5)	0.3518(3)	0.1355(3)	0.0551(9)	0.071(2)	0.0202(12)	0.0370(15)	−0.0052(11)	0.0228(14)	0.0063(13)
H4A	0.658(5)	0.391(5)	0.172(5)	0.066						
H4B	0.826(5)	0.403(4)	0.087(5)	0.066						
OW5	0.7540(3)	0.1323(2)	−0.2133(3)	0.0295(5)	0.0297(12)	0.0288(12)	0.0320(13)	−0.0083(10)	−0.0162(10)	0.0060(10)
H5A	0.844(4)	0.105(4)	−0.199(4)	0.035						
H5B	0.750(5)	0.106(4)	−0.274(3)	0.035						
OW6	0.4843(3)	0.4973(2)	0.7182(3)	0.0300(5)	0.0253(12)	0.0246(11)	0.0336(13)	−0.0057(10)	−0.0064(10)	−0.0020(9)
H6A	0.473(6)	0.557(3)	0.656(3)	0.036						
H6B	0.413(5)	0.436(3)	0.738(4)	0.036						
OW7	0.0327(4)	0.4793(3)	0.1466(3)	0.0354(6)	0.0496(16)	0.0270(12)	0.0247(12)	−0.0082(10)	−0.0078(11)	0.0055(11)
H7A	0.129(4)	0.444(4)	0.131(4)	0.042						
H7B	0.050(6)	0.559(3)	0.108(4)	0.042						
OW8	0.1517(5)	0.1729(3)	0.4196(4)	0.0589(10)	0.071(2)	0.0510(18)	0.102(3)	−0.052(2)	−0.067(2)	0.0384(17)
H8A	0.204(6)	0.108(4)	0.427(6)	0.071						
H8B	0.047(4)	0.157(5)	0.430(6)	0.071						
OW9	0.3198(7)	0.3282(6)	0.1132(7)	0.0980(16)	0.069(3)	0.102(4)	0.150(5)	−0.074(4)	−0.044(3)	0.041(3)
H9A	0.344(11)	0.333(8)	0.179(5)	0.118						
H9B	0.386(10)	0.397(6)	0.048(5)	0.118						

Wetherillite										
Na	0.01145(6)	0.75512(16)	0.54927(9)	0.0390(3)	0.0570(7)	0.0268(6)	0.0317(6)	−0.0007(5)	0.0114(5)	0.0037(5)
Mg*	½	½	0	0.0230(3)	0.0215(5)	0.0232(5)	0.0247(5)	0.0029(4)	0.0078(3)	0.0010(3)
U1	0.22720(2)	0.06842(2)	0.56353(2)	0.01227(3)	0.01656(4)	0.00940(5)	0.01118(4)	0.00035(3)	0.00474(3)	0.00001(3)
S1	0.26943(3)	0.56850(8)	0.65091(4)	0.01581(11)	0.0221(3)	0.0117(3)	0.0155(3)	0.0001(2)	0.0085(2)	0.0003(2)
S2	0.18379(3)	0.14276(8)	0.81331(4)	0.01564(11)	0.0214(3)	0.0128(3)	0.0136(2)	−0.0014(2)	0.0066(2)	0.0011(2)
O1	0.32435(9)	0.5694(3)	0.60056(15)	0.0295(4)	0.0294(9)	0.0334(11)	0.0322(10)	0.0000(8)	0.0192(8)	0.0001(8)
O2	0.29785(9)	0.5651(3)	0.76948(14)	0.0303(4)	0.0322(10)	0.0408(12)	0.0162(8)	−0.0005(8)	0.0051(7)	0.0039(8)
O3	0.22416(9)	0.7417(2)	0.61678(14)	0.0224(4)	0.0328(9)	0.0095(8)	0.0278(9)	0.0019(7)	0.0136(7)	0.0020(7)
O4	0.22335(9)	0.3973(2)	0.61286(14)	0.0228(4)	0.0299(9)	0.0110(8)	0.0280(9)	−0.0013(7)	0.0096(7)	−0.0022(7)
O5	0.13027(9)	0.2723(3)	0.74780(14)	0.0259(4)	0.0267(9)	0.0215(9)	0.0264(9)	0.0003(8)	0.0038(7)	0.0070(7)
O6	0.15309(9)	0.9712(3)	0.84930(15)	0.0272(4)	0.0333(10)	0.0206(10)	0.0322(10)	0.0004(8)	0.0164(8)	−0.0048(8)
O7	0.22941(8)	0.2455(2)	0.90941(12)	0.0223(4)	0.0299(9)	0.0209(9)	0.0156(8)	−0.0067(7)	0.0060(7)	−0.0013(7)
O8	0.22929(9)	0.0725(2)	0.75019(13)	0.0201(3)	0.0289(9)	0.0196(9)	0.0135(7)	−0.0009(7)	0.0091(7)	0.0053(7)
O9	0.13589(8)	0.0649(2)	0.51841(14)	0.0241(4)	0.0185(8)	0.0263(10)	0.0256(9)	−0.0009(8)	0.0039(7)	−0.0008(7)
O10	0.31882(8)	0.0699(2)	0.61022(14)	0.0233(4)	0.0192(8)	0.0239(9)	0.0265(9)	0.0003(7)	0.0066(7)	0.0008(7)
OW1	0.47144(10)	0.7560(3)	0.91634(18)	0.0365(5)	0.0322(11)	0.0304(12)	0.0526(13)	0.0174(10)	0.0215(10)	0.0094(9)
H1A	0.4376(13)	0.821(5)	0.918(3)	0.044						
H1B	0.4925(14)	0.826(5)	0.891(3)	0.044						
OW2	0.41097(10)	0.3713(3)	0.90360(18)	0.0369(5)	0.0269(10)	0.0276(10)	0.0467(13)	0.0058(10)	−0.0029(9)	−0.0025(9)
H2A	0.3813(15)	0.432(4)	0.869(3)	0.044						
H2B	0.4018(17)	0.259(3)	0.904(3)	0.044						
OW3	0.45016(10)	0.5891(3)	0.11311(17)	0.0311(4)	0.0246(9)	0.0340(12)	0.0383(11)	−0.0057(9)	0.0147(8)	−0.0031(9)
H3A	0.4117(12)	0.551(4)	0.101(3)	0.037						
H3B	0.4509(15)	0.702(3)	0.135(2)	0.037						
OW4	0.23001(11)	0.6425(3)	0.91387(15)	0.0317(4)	0.0585(13)	0.0205(10)	0.0241(10)	0.0085(8)	0.0245(9)	0.0121(9)
H4A	0.2116(15)	0.746(4)	0.897(2)	0.038						
H4B	0.2461(15)	0.613(4)	0.867(2)	0.038						
OW5	0.01045(10)	0.0802(3)	0.62133(16)	0.0316(4)	0.0276(10)	0.0360(12)	0.0298(11)	−0.0050(9)	0.0068(8)	−0.0012(9)
H5A	−0.0164(13)	0.094(5)	0.656(2)	0.038						
H5B	0.0459(12)	0.122(5)	0.657(2)	0.038						
OW6	0.07625(10)	0.4957(4)	0.49966(18)	0.0366(5)	0.0286(11)	0.0458(12)	0.0376(12)	0.0020(11)	0.0136(9)	0.0075(10)
H6A	0.1053(15)	0.469(5)	0.551(2)	0.044						
H6B	0.0876(17)	0.515(5)	0.449(2)	0.044						
OW7	0.07056(11)	0.6505(3)	0.73349(17)	0.0354(5)	0.0380(11)	0.0255(11)	0.0381(12)	−0.0004(9)	0.0048(9)	0.0026(9)
H7A	0.0939(16)	0.554(4)	0.749(3)	0.042						
H7B	0.0941(15)	0.739(4)	0.763(3)	0.042						
OW8	0.36195(9)	0.9910(3)	0.91199(17)	0.0316(4)	0.0236(9)	0.0433(12)	0.0279(10)	0.0032(10)	0.0079(8)	0.0022(9)
H8A	0.3451(15)	0.985(5)	0.962(2)	0.038						
H8B	0.3312(14)	0.996(5)	0.8594(19)	0.038						
OW9	0.46151(11)	0.5225(4)	0.67522(17)	0.0368(5)	0.0292(10)	0.0507(13)	0.0303(10)	0.0011(10)	0.0089(9)	0.0055(10)
H9A	0.4229(11)	0.509(5)	0.669(3)	0.044						
H9B	0.4829(14)	0.518(5)	0.737(2)	0.044						

* Refined occupancy: 0.775(3) Mg, 0.225(3)Zn

tions, and bands at 506, 445 cm^{-1} to the split doubly degenerate $\nu_2(\delta)(SO_4)$ bending vibrations. A band at 385 cm^{-1} can be related to Na–O stretching frequencies (Volkovich *et al.*, 1998; Plášil *et al.*, 2010). The split, doubly degenerate $\nu_2(\delta)(UO_2)^{2+}$ bending vibration is represented by only a low intensity split band at ~240 cm^{-1}. The low-energy bands are related to the lattice modes.

Composition

The chemical compositions of bobcookite and wetherillite were determined using a CamScan4D scanning electron microscope (SEM) equipped with an Oxford Link ISIS energy-dispersive X-ray spectrometer. An operating voltage of 20 kV was used with a beam current of 1 nA and a 1 μm beam diameter. The energy dispersive spectroscopy mode on the SEM was chosen for the analyses instead of the wavelength dispersive spectroscopy (WDS) mode on the electron microprobe (EMP) because of the instability of the phases 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 minerals after several seconds under the electron beam. Due to some Zn admixture in wetherillite, special attention was paid to the accuracy of the resolution between the Na*K*α and Zn*L*α analytical lines during measurement of Na, while Zn content was measured using the Zn*K*α line. 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 38 O atoms per formula unit (a.p.f.u.), as indicated by the crystal-structure determinations of both minerals. No other elements with atomic numbers >8 were observed. Analytical data are given in Table 1.

The empirical formula of bobcookite, calculated as the mean of seven representative spot

TABLE 5. Selected bond distances (Å) and angles (º) for bobcookite and wetherillite.

Bobcookite					
U–O9	1.767(2)	Na–O1(×2)	2.330(2)	Al–OW1(×2)	1.860(2)
U–O10	1.772(2)	Na–O10(×2)	2.443(2)	Al–OW2(×2)	1.891(2)
U–O4	2.355(2)	Na–OW5(×2)	2.527(2)	Al–OW3(×2)	1.891(2)
U–O8	2.356(2)	<Na–O>	2.433	<Al–O>	1.881
U–O7	2.364(2)				
U–O3	2.401(2)	S1–O1	1.447(2)	S2–O5	1.456(2)
U–OW4	2.452(2)	S1–O2	1.458(2)	S2–O6	1.471(2)
$<U–O_{ap}>$	1.770	S1–O3	1.492(2)	S2–O7	1.483(2)
$<U–O_{eq}>$	2.386	S1–O4	1.501(2)	S2–O8	1.488(2)
		<S1–O>	1.475	<S2–O>	1.475
Hydrogen bonds					
D–H···*A*	*D*–H	H···*A*	*D*···*A*	<*D*H*A*	
OW1–H1A···O6	0.81(2)	1.81(2)	2.617(3)	176(4)	
OW1–H1B···OW7	0.77(2)	1.84(2)	2.611(3)	176(4)	
OW2–H2A···OW5	0.79(2)	1.94(2)	2.721(3)	170(4)	
OW2–H2B···OW6	0.80(2)	1.82(2)	2.626(3)	177(4)	
OW3–H3A···O2	0.83(2)	1.94(2)	2.738(3)	159(4)	
OW3–H3B···OW8	0.77(2)	1.88(2)	2.642(4)	170(4)	
OW4–H4A···OW6	0.84(3)	2.04(3)	2.845(4)	161(5)	
OW4–H4B···OW7	0.77(3)	2.21(5)	2.733(5)	126(5)	
OW5–H5A···O4	0.79(2)	2.22(2)	2.989(3)	166(4)	
OW5–H5B···O5	0.83(2)	2.04(3)	2.850(3)	164(3)	
OW6–H6A···O6	0.78(2)	2.01(3)	2.787(3)	172(4)	
OW6–H6B···O2	0.79(2)	1.98(3)	2.763(3)	170(4)	
OW7–H7A···OW9	0.82(2)	1.88(2)	2.684(5)	168(4)	
OW7–H7B···O3	0.79(2)	2.24(2)	3.016(3)	167(4)	
OW8–H8A···O5	0.77(3)	2.14(3)	2.902(3)	166(5)	
OW8–H8B···O9	0.80(3)	2.42(5)	2.965(4)	126(5)	
OW9–H9A···OW8	0.84(3)	2.60(7)	3.078(8)	118(6)	
OW9–H9B (no evident recipient of a hydrogen bond)					

analyses, is $Na_{0.97}Al_{1.09}U_{2.04}S_{3.92}O_{38.00}H_{36.00}$, or $Na_{0.97}Al_{1.09}(U_{1.02}O_2)_2(S_{0.98}O_4)_4(H_2O)_{18}$ (based on 38 O a.p.f.u.). The simplified formula is $NaAl(UO_2)_2(SO_4)_4{\cdot}18H_2O$ which requires Na_2O 2.39, Al_2O_3 3.92, UO_3 44.07, SO_3 24.65, H_2O 24.97, total 100 wt.%.

The empirical formula of wetherillite, calculated as the mean of eight representative spot analyses, is $Na_{1.98}Mg_{0.58}Zn_{0.24}Cu_{0.11}Fe^{2+}_{0.09}U_{2.08}S_{3.92}O_{38.00}H_{36.00}$, or $Na_{1.98}(Mg_{0.58}Zn_{0.24}Cu_{0.11}Fe^{2+}_{0.09})_{\Sigma 1.02}(U_{1.04}O_2)_2(S_{0.98}O_4)_4(H_2O)_{18}$ (based on 38 O a.p.f.u.). The simplified formula is $Na_2Mg(UO_2)_2(SO_4)_4(H_2O)_{18}$, which requires Na_2O 4.70, MgO 3.06, UO_3 43.38, SO_3 24.28, H_2O 24.59, total 100 wt.%.

The Gladstone-Dale compatibility index $1 - (K_P/K_C)$ for the empirical formulas of bobcookite and wetherillite are −0.002 and −0.012, respectively, in both cases in the range of superior compatibility (Mandarino, 2007). As noted by Kampf *et al*. (2015), Gladstone-Dale calculations for uranyl sulfates should utilize $k(UO_3) = 0.118$, as provided by Mandarino (1976).

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 patterns calculated from the structure determinations. Unit-

TABLE 5 (*contd.*)

Wetherillite					
Na−OW5	2.389(2)	U−O9	1.7702(16)	S1−O1	1.4558(18)
Na−OW5	2.411(2)	U−O10	1.7760(16)	S1−O2	1.4604(18)
Na−OW6	2.411(2)	U−O3	2.3425(16)	S1−O3	1.4814(17)
Na−OW6	2.415(3)	U−O4	2.3434(16)	S1−O4	1.4858(17)
Na−OW7	2.420(2)	U−O7	2.3723(16)	<S1−O>	1.475
Na−O9	3.110(2)	U−O8	2.3960(17)		
<Na−O>	2.526	U−OW4	2.4245(18)	S2−O5	1.4561(17)
		<U−O_{ap}>	1.773	S2−O6	1.4692(18)
Mg−OW1(×2)	2.0438(19)	<U−O_{eq}>	2.376	S2−O7	1.4787(16)
Mg−OW2(×2)	2.0552(19)			S2−O8	1.4887(16)
Mg−OW3(×2)	2.1072(19)			<S2−O>	1.475
<Mg−O>	2.069				

Hydrogen bonds				
D−H···*A*	*D*−H	H···*A*	*D*···*A*	<*D*H*A*
OW1−H1A···OW8	0.82(2)	1.91(2)	2.735(3)	174(3)
OW1−H1B···OW9	0.78(2)	1.97(2)	2.751(3)	175(3)
OW2−H2A···O2	0.76(2)	2.00(2)	2.758(3)	174(3)
OW2−H2B···OW8	0.79(2)	2.02(2)	2.798(3)	169(3)
OW3−H3A···O10	0.79(2)	2.10(2)	2.877(3)	165(3)
OW3−H3B···OW9	0.82(2)	1.95(2)	2.762(3)	172(3)
OW4−H4A···O6	0.80(2)	1.93(2)	2.719(3)	171(3)
OW4−H4B···O2	0.80(2)	1.90(2)	2.691(3)	170(3)
OW5−H5A···OW7	0.81(2)	2.09(2)	2.891(3)	170(3)
OW5−H5B···O5	0.78(2)	2.03(2)	2.810(3)	171(3)
OW6−H6A···O4	0.76(2)	2.34(3)	2.979(3)	143(3)
OW6−H6B···O6	0.76(2)	2.12(3)	2.851(3)	159(3)
OW7−H7A···O5	0.80(2)	2.06(2)	2.838(3)	162(3)
OW7−H7B···O6	0.79(2)	2.09(2)	2.884(3)	176(3)
OW8−H8A···O1	0.82(2)	1.99(2)	2.797(3)	166(3)
OW8−H8B···O8	0.77(2)	2.18(2)	2.916(3)	159(3)
OW9−H9A···O1	0.77(2)	1.97(2)	2.680(3)	153(4)
OW9−H9B···OW3	0.78(2)	2.12(2)	2.874(3)	160(4)

cell parameters refined from the powder data using *JADE 2010* with whole pattern fitting are for bobcookite: a = 7.784(2), b = 10.567(2), c = 11.230(2) Å, α = 68.884(7), β = 70.909(7), γ = 87.056(6)º and V = 812.0(3) Å^3; and for wetherillite: a = 20.364(4), b = 6.817(4), c = 12.908(4) Å, β = 107.994(5)º and V = 1704(1) 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 structures were solved by direct methods using *SIR2004* (Burla *et al*., 2005). *SHELXL-2013* (Sheldrick, 2008) was used for the refinements of the structures. For the wetherillite structure, the Mg site was refined with joint occupancy by only Mg and Zn, providing $Mg_{0.78}Zn_{0.22}$ (scattering power: 16.0 *e*), although it is worth noting that the empirical formula is consistent with this site being occupied by $Mg_{0.58}Zn_{0.24}Cu_{0.11}Fe^{2+}_{0.09}$ (scattering power: 19.7 *e*). For each structure, difference Fourier syntheses located all H atom positions, which were then refined with soft restraints of 0.82(3) Å on the O−H distances and 1.30(3) Å on the H−H distances and with the U_{eq} of each H set to 1.2 times that of the donor O atom. 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 bond-valence analyses in Table 6.

Description and discussion of the structures

In the structures of bobcookite and wetherillite, the U sites are surrounded by seven O atom sites forming squat pentagonal bipyramids. This is the most typical coordination for U^{6+}, particularly in uranyl sulfates (Krivovichev, 2010, 2013), where the two short apical bonds of the bipyramid constitute the uranyl group. The bond lengths in U^{6+}-coordination polyhedra in both structures (bobcookite: $\langle U-O_{ap}\rangle$ = 1.770, $\langle U-O_{eq}\rangle$ = 2.386; wetherillite: $\langle U-O_{ap}\rangle$ = 1.773, $\langle U-O_{eq}\rangle$ = 2.376Å) are consistent with the most typical lengths observed for [7]-coordinated U^{6+} (Burns *et al*., 1997). In both structures, four of the five equatorial O atoms also participate in SO_4 tetrahedra and the fifth is a H_2O group. Also in both structures, adjacent pentagonal bipyramids are linked to one another *via* two bridging SO_4 groups, although in bobcookite the linkage results in chains, while in wetherillite it results in sheets. A final similarity is that uranyl sulfate compo-

TABLE 6. Bond-valence analysis for bobcookite and wetherillite. Values are expressed in valence units*.

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	OW1	OW2	OW3	OW4	OW5	OW6	OW7	OW8	OW9	Σ
Bobcookite																				
Na	0.21									0.16					0.12					0.99
Al											0.57	0.52	0.52							3.23
U			0.51	0.56			0.55	0.56	1.73	1.71				0.46						6.07
S1	1.61	1.57	1.43	1.39																6.00
S2					1.57	1.51	1.46	1.44												5.99
H1A						0.19					0.81									1.00
H1B											0.82						0.18			1.00
H2A												0.86			0.14					1.00
H2B												0.82				0.18				1.00
H3A		0.14											0.86							1.00
H3B													0.84					0.16		1.00
H4A														0.89		0.11				1.00
H4B														0.92			0.08			1.00
H5A				0.08											0.92					1.00

H5B					0.11										0.89					1.00
H6A						0.12										0.88				1.00
H6B		0.13														0.87				1.00
H7A																	0.84		0.16	1.00
H7B			0.08														0.92			1.00
H8A					0.10													0.90		1.00
H8B									0.06									0.94		1.00
H9A																		0.04	0.96	1.00
H9B																			1.00	1.00
Σ	1.83	1.84	2.02	2.03	1.78	1.82	2.01	2.00	1.79	1.87	2.20	2.20	2.22	2.27	2.07	2.04	2.02	2.04	2.12	
Wetherillite																				
Na									0.03						0.18	0.17	0.17			0.89
															0.17	0.17				
Mg											0.39	0.38	0.33							2.20
											×2→	×2→	×2→							
U			0.57	0.57			0.54	0.51	1.72	1.70				0.49						6.10
S1	1.61	1.57	1.43	1.39																6.00
S2					1.57	1.51	1.46	1.44												5.98
H1A											0.85							0.15		1.00
H1B											0.86								0.14	1.00
H2A		0.13										0.87								1.00
H2B												0.88						0.12		1.00
H3A										0.10			0.90							1.00
H3B													0.86						0.14	1.00
H4A						0.15								0.85						1.00
H4B		0.15												0.85						1.00
H5A															0.90		0.10			1.00
H5B					0.12										0.88					1.00
H6A				0.07												0.93				1.00
H6B						0.10										0.90				1.00
H7A					0.11												0.89			1.00
H7B						0.10											0.90			1.00
H8A	0.13																	0.87		1.00
H8B								0.09										0.91		1.00
H9A	0.14																		0.86	1.00
H9B													0.10						0.90	1.00
Σ	1.88	1.85	2.00	2.03	1.80	1.86	2.00	2.04	1.75	1.80	2.10	2.13	2.19	2.19	2.13	2.17	2.06	2.05	2.04	

* Multiplicities indicated by ×2→; S^{6+}–O, Al^{3+}–O, Mg^{2+}–O and Zn^{2+}–O bond-valence parameters from Brown and Altermatt (1985); Na^{+}–O from Wood and Palenik (1999); U^{6+}–O from Burns *et al*. (1997); hydrogen-bond strengths based on O–H···O bond lengths from Brown and Altermatt (1985).

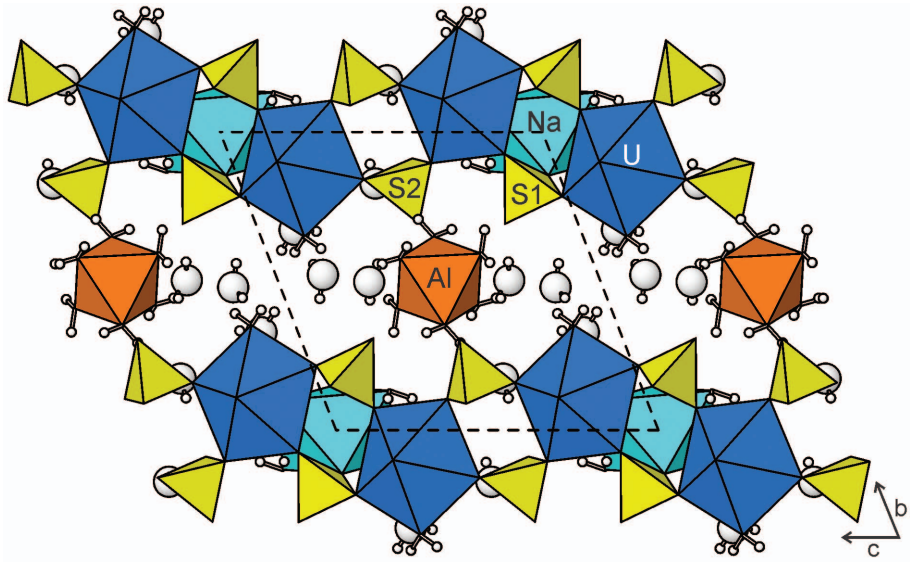

FIG. 6. The structure of bobcookite viewed down [100]. The unit is cell shown by dashed lines. O atoms of isolated H_2O groups are shown as large white spheres. H atoms are shown as small white spheres.

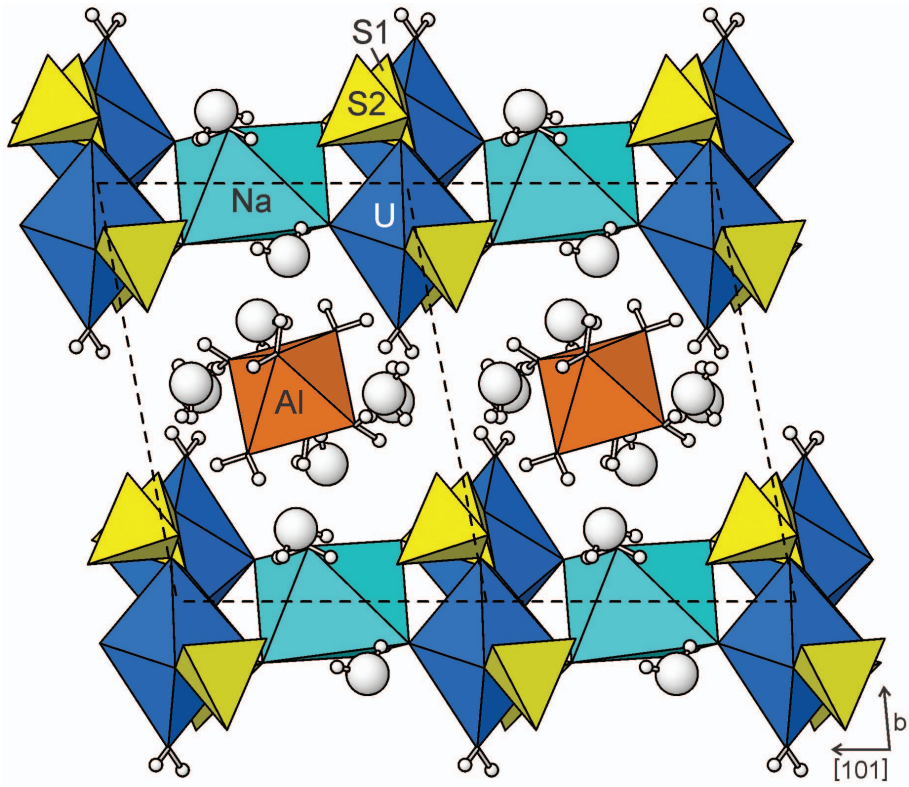

FIG. 7. The structure of bobcookite viewed down [10$\bar{1}$]. The unit is cell shown by dashed lines. O atoms of isolated H_2O groups are shown as large white spheres. H atoms are shown as small white spheres.

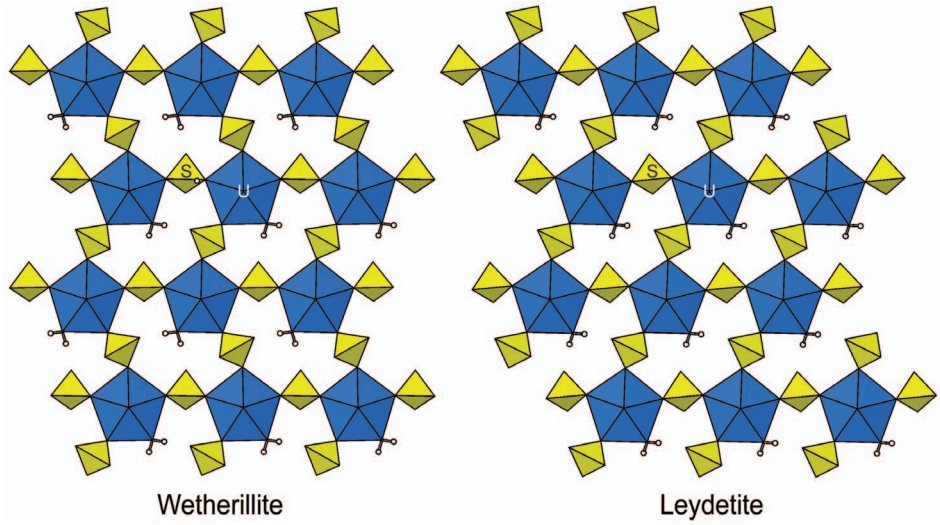

FIG. 8. The $[(UO_2)(SO_4)_2(H_2O)]$ sheets in wetherillite (viewed down a^*) and leydetite. H atoms of H_2O groups are shown as small white spheres.

nents in both minerals are connected through NaO_6 polyhedra to form layers that constitute the structural units and these units are linked *via* hydrogen bonds to isolated H_2O groups and to $Al(H_2O)_6$ (in bobcookite) or $Mg(H_2O)_6$ (in wetherillite) octahedra in their interstitial complexes (Schindler and Hawthorne, 2001). The structures are described in more detail below.

Bobcookite

In the structure of bobcookite (Figs 6 and 7), the linkages of pentagonal bipyramids and tetrahedra form an infinite $[(UO_2)(SO_4)_2(H_2O)]$ chain along $[10\bar{1}]$. (Note that $[10\bar{1}]$ is also the direction of elongation of bobcookite crystals.) Similar infinite uranyl sulfate chains are found in the structures of synthetic $K_2[(UO_2)(SO_4)_2(H_2O)](H_2O)$ (Ling *et al.*, 2010) and synthetic $Mn(UO_2)(SO_4)_2(H_2O)_5$ (Tabachenko *et al.*, 1979).

In bobcookite, the $[(UO_2)(SO_4)_2(H_2O)]$ chains are linked by sharing vertices with $NaO_4(H_2O)_2$ octahedra yielding a layer parallel to {010} of composition $[Na(UO_2)_2(SO_4)_4(H_2O)_4]^{3-}$. This layer constitutes the structural unit. An $Al(H_2O)_6$ octahedron, located between the layers, and isolated H_2O groups, located both between the sheets and in cavities in the sheets, constitute the $[Al(H_2O)_6{\cdot}8(H_2O)]^{3+}$ interstitial complex. An extensive system of hydrogen bonds holds the structural components together.

Wetherillite

In the structure of wetherillite, the linkages of pentagonal bipyramids and tetrahedra form a $[(UO_2)(SO_4)_2(H_2O)]$ sheet parallel to {100}. Sheets similar to that in wetherillite are found in the minerals leydetite, $Fe(UO_2)(SO_4)_2(H_2O)_{11}$ (Plášil *et al.*, 2013) and geschieberite, $K_2(UO_2)(SO_4)_2{\cdot}2H_2O$ (Plášil *et al.*, 2015); however, the sheet in wetherillite is topologically distinct, in that alternate rows of bipyramids are flipped in orientation (Fig. 8).

The entire structure is shown in Fig. 9. Between adjacent $[(UO_2)(SO_4)_2(H_2O)]$ sheets in the wetherillite structure are edge-sharing chains of $Na(H_2O)_5O$ polyhedra. Each polyhedron has five normal (2.389–2.420 Å) Na–O bonds to H_2O groups, including those participating in the shared edge, and one very long bond (3.110 Å) to an apical O atom of the UO_7 bipyramid. Alternate $Na(H_2O)_5O$ polyhedra in the chains link to alternate sheets, forming a weakly bonded three-layer sandwich. This sandwich of composition $[Na_2(UO_2)_2(SO_4)_4(H_2O)_8]^{2-}$ constitutes the structural unit in wetherillite. A $Mg(H_2O)_6$ octahedron and isolated H_2O groups located between the three-layer sandwiches constitute the $[Mg(H_2O)_6{\cdot}4(H_2O)]^{2+}$ interstitial complex. An extensive system of hydrogen bonds holds the structural components together.

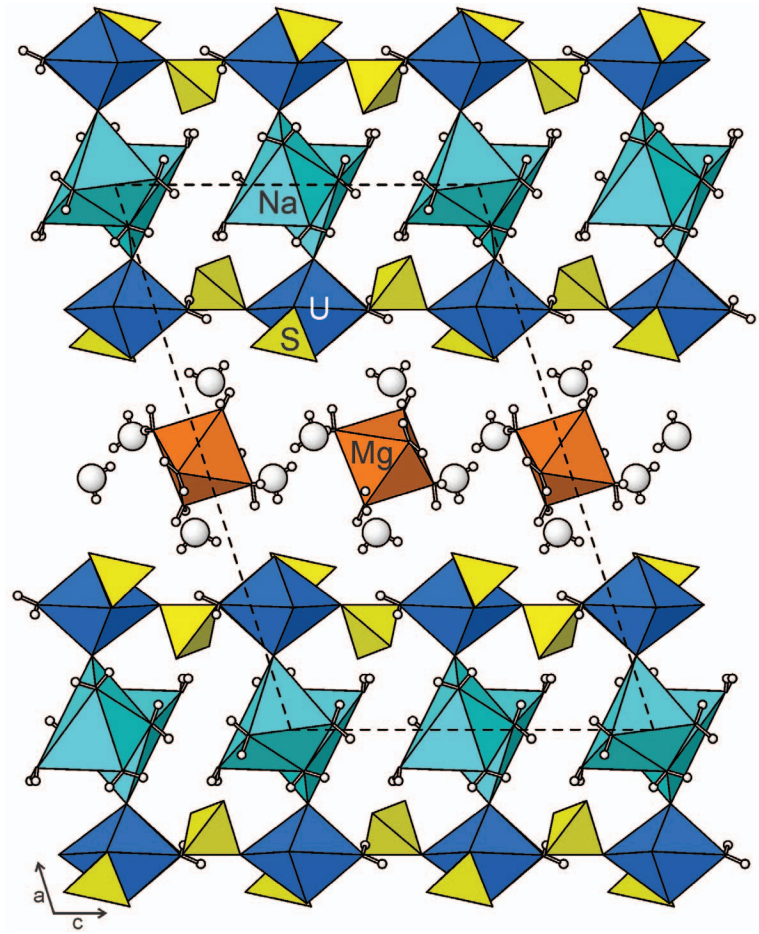

FIG. 9. The structure of wetherillite viewed down [010]. The unit cell is shown by dashed lines. O atoms of isolated H_2O groups are shown as large white spheres. H atoms are shown as small white spheres.

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