American Mineralogist, Volume 97, pages 750–754, 2012

Revision of the crystal structure and chemical formula of weeksite, $K_2(UO_2)_2(Si_5O_{13})\cdot 4H_2O$

KARLA FEJFAROVÁ,[1] JAKUB PLÁŠIL,[2,*] HEXIONG YANG,[3] JIŘÍ ČEJKA,[4] MICHAL DUŠEK,[1]
ROBERT T. DOWNS,[3] MADISON C. BARKLEY,[5] AND RADEK ŠKODA[2]

[1]Institute of Physics ASCR, v.v.i., Na Slovance 2, 18221, Praha, Czech Republic
[2]Institute of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37, Brno, Czech Republic
[3]Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.
[4]Department of Mineralogy and Petrology, National Museum, Václavské náměstí 68, CZ-115 79, Praha 1, Czech Republic
[5]Arizona Historical Society, 1502 W Washington Street, Phoenix, Arizona 85007, U.S.A.

ABSTRACT

The previously published structure determination of weeksite from the Anderson mine, Arizona, U.S.A., suggested that it is orthorhombic, *Cmmb*, with $a = 14.209(2)$, $b = 14.248(2)$, $c = 35.869(4)$ Å, and $V = 7262(2)$ Å^3, and an ideal chemical formula $(K,Ba)_{1-2}(UO_2)_2(Si_5O_{13})\cdot H_2O$. Using single-crystal X-ray diffraction, electron microprobe analysis, and thermal analysis, we reexamined weeksite from the same locality. Our results demonstrate that weeksite is monoclinic, with the space group *C*2/*m* and unit-cell parameters $a = 14.1957(4)$, $b = 14.2291(5)$, $c = 9.6305(3)$ Å, $\beta = 111.578(3)°$, $V = 1808.96(10)$ Å^3, and an ideal formula $K_2(UO_2)_2(Si_5O_{13})\cdot 4H_2O$. The previously reported orthorhombic unit cell is shown to result from twinning of the monoclinic cell. The structure refinement yielded $R_1 = 2.84\%$ for 1632 observed reflections [$I_{obs} > 3\sigma(I)$] and 5.42% for all 2379 reflections. The total H_2O content derived from the structure refinement agrees well with that from the thermal analysis. Although the general topology of our structure resembles that reported previously, all Si sites in our structure are fully occupied, in contrast to the previous structure determination, which includes four partially occupied SiO_4 tetrahedra. From our structure data on weeksite, it appears evident that the orthorhombic cell of the newly discovered weeksite-type mineral coutinhoite, $Th_xB_{1-2x}(UO_2)_2Si_5O_{13}\cdot 3H_2O$, needs to be reevaluated.

Keywords: Weeksite, uranyl silicate, crystal structure, X-ray diffraction, open framework

INTRODUCTION

Weeksite is one of 19 known uranyl silicates that occurs in nature as a secondary alteration product typically found in the oxidized zones of uranium deposits. Uranyl silicate minerals have been the subject of extensive investigations in the past two decades (e.g., Burns 1999, 2005), not only because of their bearing on the genesis and weathering processes of uranium deposits, but also because of their formation as a result of the alteration of spent nuclear fuel under conditions similar to those that were expected at the proposed repository at Yucca Mountains, Nevada (Finn et al. 1996; Wronkiewicz et al. 1996; Finch et al. 1999). For example, weeksite was identified as an alteration product in batch tests using modified groundwater from Yucca Mts. and actinide-bearing borosilicate waste glass (Buck and Fortner 1997), as well as an interaction product between simulated nuclear wastes and crystalline silicate rocks (Oji et al. 2006). Detailed knowledge of the crystal chemistry of uranyl silicates, therefore, is critical to understanding the long-term performance of a geological repository for nuclear waste and the incorporation of other actinide elements, present in spent nuclear fuel, into their structures (Burns et al. 1997, 2000; Burns 1999; Chen et al. 1999, 2000; Friese et al. 2004; Klingensmith et al. 2007).

Weeksite from the Thomas Range, Juab County, Utah, was first described by Outerbridge et al. (1960) as orthorhombic, with space group *Pnnb*, unit-cell parameters $a = 14.26(2)$, $b = 35.88(10)$, and $c = 14.20(2)$ Å, and an ideal chemical formula $K_2(UO_2)_2(Si_2O_5)_3\cdot 4H_2O$ ($Z = 16$). These authors also noted the strong pseudosymmetry of this mineral. Yeremenko et al. (1977) studied two weeksite crystals from Afghanistan and obtained an average composition $(K_{1.09}Na_{0.68}Ca_{0.18}Ba_{0.07}Mg_{0.05}Al_{0.05}Sr_{0.01})_{\Sigma 2.13}(UO_2)_{1.77}(Si_5O_{13.01})\cdot 3.40H_2O$ and a monoclinc cell: $a = 9.63(1)$, $b = 7.12(1)$, $c = 7.15(1)$ Å, and $\beta = 111.9°$. Based on space group *Amm*2 and a sub-cell $a = 7.106(8)$, $b = 17.90(2)$, and $c = 7.087(7)$ Å, Stohl and Smith (1981) presented a partial structure solution ($R = 15\%$) for weeksite collected from the Anderson Mine, Yavapai County, Arizona. Using a similar sub-cell [$a = 7.092(1)$, $b = 17.888(1)$, and $c = 7.113(1)$ Å] as that given by Stohl and Smith (1981), but with a different space group (*Cmmm*), Baturin and Sidorenko (1985) obtained a slightly improved structure model ($R = 12\%$) for weeksite with the location of all Si atoms and a chemical formula $(K_{0.62}Na_{0.38})_2(UO_2)_2(Si_5O_{13})\cdot 3H_2O$ ($Z = 2$). Jackson and Burns (2001) reexamined weeksite from the Anderson Mine, Yavapai County, Arizona, and derived a full structure solution ($R = 7.0\%$) on the basis of space group *Cmmb* and unit-cell parameters $a = 14.209(2)$, $b = 14.248(2)$, $c = 35.869(4)$ Å, giving rise to a structure formula $K_{1.26}Ba_{0.25}Ca_{0.12}(UO_2)_2(Si_5O_{13})\cdot H_2O$ ($Z = 16$). Nevertheless, they also noticed obvious displacements of some cations from their corresponding special positions, indicating that their model is actually a rep-

---

* E-mail: jakub.horrak@gmail.com

0003-004X/12/0004–750$05.00/DOI: http://dx.doi.org/10.2138/am.2012.4025

resentation of an average structure. Yet, their attempts to refine the structure in space group *Cmmm*, *C*2*mm*, or *C*222 failed to produce any satisfactory solutions. An examination of the structure model of Jackson and Burns (2001) reveals some peculiar features, such as several partially occupied atomic sites (especially some Si sites). This study presents the weeksite structure determined using single-crystal X-ray diffraction data collected from an untwinned crystal, demonstrating that the real symmetry of weeksite is monoclinic (*C*2/*m*), rather than orthorhombic, as the most recent previous study reported.

EXPERIMENTAL METHODS

The weeksite sample used in this study was from the Anderson mine, Yavapai County, Arizona, U.S.A. Its chemical composition (Table 1) was analyzed using a Cameca SX100 electron microprobe at Masaryk University, Brno, with an operating voltage of 15 kV, 4 nA current, and 10 µm beam diameter. The following X-ray lines, crystals, and standards were selected to minimize line overlap: *K*α lines: Na (TAP, albite), Si (TAP, sanidine), Ca (PET, andradite), K (PET, sanidine); *L*α lines: Ba (LPET, barite); and *M*β lines: U (LPET, U metal). Peak counting times were 10–20 s for major elements and 40–60 s for minor or trace elements. Counting time on background was half of peak counting times. The measured intensities were converted to element concentrations using the "X-PHI" correction routine (Merlet 1994). Thermogravimetric analysis (TGA) of weeksite was conducted on the Stanton Redcroft Thermobalance TG 750, with a heating rate of 10 °C/min, dynamic air atmosphere, flow rate 10 mL/min, and a sample weight of 7.95 mg.

Three weeksite crystals (labeled as A, B, and C) were selected and examined using an Oxford Diffraction Gemini single-crystal diffractometer equipped with the Atlas CCD detector and monochromated Mo*K*α radiation. Interestingly, while crystals A and B displayed unit-cell parameters matching those reported by Jackson and Burns (2001), crystal C exhibited a monoclinic cell with a unit-cell volume only a quarter of that for crystals A and B (Table 2). Analysis of the X-ray diffraction data revealed that the large unit cell of crystals A and B is actually a consequence of twinning and can be obtained from the monoclinic unit cell

TABLE 1. Results of electron microprobe analyses (in wt%) of weeksite

	This work				1	2	3
Constituent	Mean	Range	St.dev.	Det. lim.			
Na_2O	0.53	0.21–0.86	0.17	0.24	0.7	2.05	2.29
K_2O	4.73	4.13–5.24	0.38	0.17	5.5	5.12	5.40
CaO	0.67	0.57–0.77	0.06	0.13	1.1	2.01	0.03
BaO	3.11	2.71–3.47	0.25	0.17	1.4	1.90	0.19
MgO						0.18	0.21
SrO						0.20	0.14
Al_2O_3					0.6	0.25	0.23
SiO_2	29.44	29.11–29.88	0.30	0.09	33.6	31.37	30.40
UO_3	55.78	55.26–56.62	0.45	0.36	51.5	49.84	53.98
H_2O*	7.02	–			6.6	6.29	6.29
Total	101.28	93.20–95.76			101.3	99.21	99.16
Na	0.176						
K	1.031						
Ca	0.123						
Ba	0.208						
ΣM site	1.537						
Si^{4+}	5.030						
UO_2	2.002						
H_2O	4.000						

Notes: Mean = mean of 8 analyses, calculated on the basis of 21 O pfu. Range = range of 8 analyses. St.dev. = standard deviation of the analyses (in wt%). Det. lim. = detection limit (in wt%). H_2O* = water content (in wt%) derived from the theoretical content of 4 H_2O in the crystal structure of weeksite. 1 = Outerbridge et al. (1960). 2 = Yeremenko et al. (1977), generation 1. 3 = Yeremenko et al. (1977), generation 2.

TABLE 2. Summary of data collection conditions and refinement parameters for weeksite (crystal C)

Crystal data	
Ideal structural formula	$K_2(UO_2)_2(Si_5O_{13})·4H_2O$
Space group	*C*2/*m*
Unit-cell parameters (no. reflections)	4675
a (Å)	14.1957(4)
b (Å)	14.2291(5)
c (Å)	9.6305(3)
β (°)	111.578(3)
V (Å³)	1808.96(10)
Z	4
Calculated density (g/cm³)	3.80
µ (mm⁻¹), correction type	18.80, analytical
T_{min}/T_{max}	0.265/0.570
Crystal size (mm)	0.12 × 0.07 × 0.03
Data collection	
Radiation, wavelength (Å)	Mo*K*α, 0.71073
θ range for data collection (°)	2.86–29.32
h, *k*, *l* ranges	$-19 < h < 19, -17 < k < 19, -13 < l < 13$
Axis, frame width (°), time per frame (s)	ω, 0.8, 55
Total reflections collected	28069
Unique reflections	2379
Unique observed reflections [$I_{obs} > 3\sigma(I)$]	1632
Data completeness to θ_{max} (%), R_{int}	99.82, 0.0593
Structure refinement by JANA2006	
Refinement method	Full-matrix least-squares on F^2
No. of refined parameters, constraints	154, 3
Weighting details	σ, $w = 1/[\sigma^2(I) + 0.0016I^2]$
R_{obs}, wR_{obs}	0.0284, 0.0742
R_{all}, wR_{all}	0.0542, 0.0888
Goodness-of-fit (S) on F^2_{obs}/on F^2_{all}	1.15/1.13
Largest diff. peak and hole (e/Å³)	−1.27, 0.84

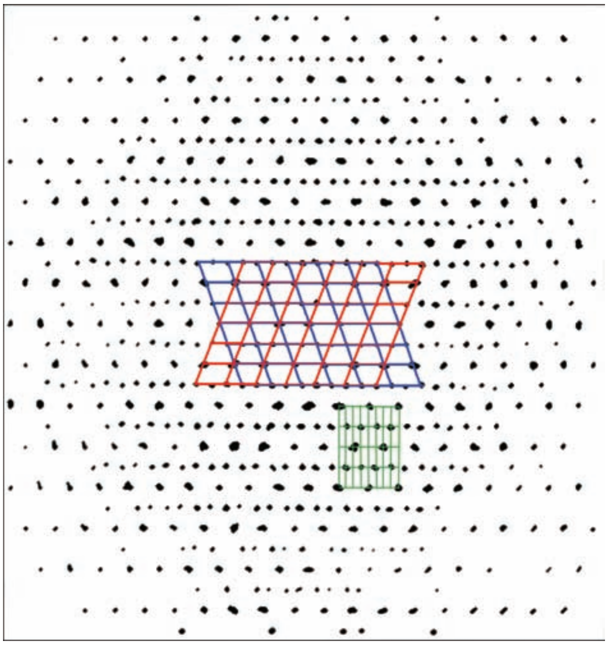

FIGURE 1. Illustration of the twinning in weeksite (red and blue net) in reciprocal space viewed along b*. Reciprocal unit-cell choice by Jackson and Burns (2001) is sketched in green. Reconstruction is based on the experimental data set. (Color online.)

of crystal C with the transformation matrix [1 0 1/0 1 0/0 0 4]. The twin law is a twofold rotation around $[4\ 0\ \bar{1}]$ of the monoclinic cell in real space or around **a*** in reciprocal space (Fig. 1). Examination of another weeksite sample in the RRUFF project collection (deposition no.: R050330, see http://rruff.info), which is also from the Anderson mine, produced a similar monoclinic unit cell as that given in Table 2. Therefore, the structure of weeksite was solved based on the X-ray diffraction intensity data collected from the untwinned crystal C using the charge-flipping algorithm of Superflip program (Palatinus and Chapuis 2007) and refined using JANA2006 (Petříček et al. 2006). Details of data collection and structure refinements are listed in Table 2.

TABLE 3. Atomic coordinates, site occupancies and atomic displacement parameters (in angstroms) for weeksite (crystal C)

Atom	Wyck., site	Occ.	x	y	z	U_{eq}
U	8*j*, 1	1	0.09933(2)	0.24679(2)	0.89678(3)	0.0119(1)
K1*	4*i*, *m*	0.95(1)	–0.0707(2)	0	0.8602(4)	0.037(1)
K2*	4*i*, *m*	0.93(1)	0.2460(3)	0	0.8433(5)	0.054(2)
Si1	4*h*, 2	1	0	0.3068(2)	0.5	0.017(1)
Si2	8*j*, 1	1	0.1875(1)	0.2498(1)	0.2495(2)	0.0116(7)
Si3	8*j*, 1	1	0.2986(2)	0.1100(1)	0.5004(2)	0.0184(8)
O1	8*j*, 1	1	0.4105(4)	0.1224(4)	0.4996(7)	0.033(2)
O2	8*j*, 1	1	0.0712(4)	0.2440(4)	0.1370(6)	0.023(2)
O3	8*j*, 1	1	0.2472(4)	0.2551(4)	0.1367(6)	0.024(2)
O4	8*j*, 1	1	0.0366(4)	0.2437(3)	0.6473(6)	0.024(2)
O5	8*j*, 1	1	0.2162(4)	0.1560(4)	0.3546(6)	0.027(2)
O6	4*i*, *m*	1	0.2705(6)	0	0.4998(8)	0.022(3)
O7	8*j*, 1	1	0.2892(4)	0.1573(4)	0.6467(6)	0.026(2)
O8	8*j*, 1	1	0.1020(4)	0.1201(4)	0.9055(6)	0.029(3)
O9	8*j*, 1	1	0.0990(4)	0.3727(4)	0.8972(7)	0.032(3)
O10	4*i*, *m*	1	0.4310(7)	0	0.841(1)	0.053(4)
O11	4*i*, *m*	1	–0.2624(8)	0	0.845(2)	0.058(6)
O12	2*c*, 2/*m*	0.72(3)	0	0	0.5	0.036(4)†
O13	4*h*, 2	0.26(2)	0	–0.079(2)	0.5	0.036(4)†
O14	8*j*, 1	0.28(1)	–0.046(2)	–0.0614(4)	0.602(3)	0.036(4)†
O15	8*j*, 1	0.264(2)	–0.092(2)	–0.064(2)	0.398(3)	0.036(4)†
O16	4*i*, *m*	0.24(2)	–0.445(2)	0	0.702(4)	0.02(1)†

Notes: Wyck., site = Wyckoff notation, site symmetry. Occ. = site occupancy. U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor.
* Refined solely with K atoms; however, other elements are present at the sites as indicated WDS analysis.
† Refined isotropically.

TABLE 4. Selected interatomic distances for weeksite

U		K1		K2	
U–O8	1.804(6)	K1–O8	2.888(6)	K2–O8	2.891(7)
U–O9	1.792(6)	K1–O8$^{\text{iv}}$	2.991(7)	K2–O8$^{\text{vii}}$	2.891(7)
U–O2$^{\text{i}}$	2.489(6)	K1–O8$^{\text{vi}}$	2.991(7)	K2–O9$^{\text{vii}}$	3.213(6)
U–O2$^{\text{ii}}$	2.322(6)	K1–O8$^{\text{vii}}$	2.888(6)	K2–O9$^{\text{viii}}$	3.213(6)
U–O3$^{\text{i}}$	2.488(5)	K1–O11	2.67(1)	K2–O10	2.63(1)
U–O3$^{\text{iii}}$	2.317(6)	K1–O14	2.77(3)	K2–O11$^{\text{iv}}$	2.93(2)
U–O4	2.235(5)	K1–O14$^{\text{vii}}$	2.77(3)	K2–O15$^{\text{ii}}$	2.70(2)
<U–O$_{Ur}$>	1.798	K1–O5$^{\text{ii}}$	3.214(5)	K2–O15$^{\text{v}}$	2.70(2)
<U–O$_{Eq}$>	2.370	K1–O5$^{\text{vii}}$	3.214(5)	K2–O7	3.134(7)
		K1–O2$^{\text{ii}}$	3.472(6)	K2–O7$^{\text{vi}}$	3.134(7)
		K1–O2$^{\text{vii}}$	3.472(6)	K2–O3$^{\text{iii}}$	3.489(6)
		<K1–O>	3.031	K2–O3$^{\text{xviii}}$	3.489(6)
				K2–O6	3.45(1)
				<K2–O>	3.067
Si1		Si2		Si3	
Si1–O1$^{\text{iii}}$	1.62(6)	Si2–O2	1.609(5)	Si3–O1	1.602(7)
Si1–O1$^{\text{x}}$	1.62(6)	Si2–O3	1.607(7)	Si3–O5	1.600(5)
Si1–O4	1.596(5)	Si2–O5	1.634(6)	Si3–O6	1.614(3)
Si1–O4$^{\text{ii}}$	1.596(5)	Si2–O7	1.616(6)	Si3–O7	1.611(7)
<Si1–O>	1.608	<Si2–O>	1.617	<Si2–O>	1.607

Notes: Symmetry codes: (i) x, y, z+1; (ii) –x, y, –z+1; (iii) –x+1/2, –y+1/2, –z+1; (iv) –x, y, –z+2; (v) –x, –y, –z+2; (vi) x, –y, z; (vii) –x, –y, –z+1; (viii) x–1/2, –y+1/2, z; (ix) –x+1, y, –z+1; (x) x+1/2, –y+1/2, z; (xi) x+1, y, z; (xii) –x, y, –z; (xiii) x, y, z–1; (xiv) –x+1/2, –y+1/2, –z; (xv) x–1/2, y+1/2, z; (xvi) x+1/2, y+1/2, z; (xvii) –x+1, y, –z+2; (xviii) –x+1/2, y–1/2, –z+1.

During the structure refinements, all U and Si sites were assumed to be fully occupied, as indicated by the chemical analysis. However, for simplicity, we treated minor amounts of Ba, Ca, and Na as K in the refinements and allowed the populations of the two K sites to vary. In addition, the occupancies of five partially occupied H_2O sites (due to disordering) were also refined, but their isotropic displacement parameters were fixed to be the same. Final atomic coordinates and displacement parameters are presented in Table 3 and selected bond distances in Table 4. Anisotropic displacement parameters, as well as CIF, are listed as supplementary material[1].

RESULTS AND DISCUSSIONS

Chemical composition

The chemical formula of weeksite in the current IMA accepted mineral list is $(K,Ba)_{1-2}(UO_2)_2(Si_5O_{13})\cdot H_2O$, which is an idealized version of that given by Jackson and Burns (2001): $(K_{1.05}Ba_{0.25}Na_{0.02}Ca_{0.12})_{1.44}(UO_2)_{2.08}(Si_{5.07}O_{12.38})\cdot 1.46H_2O$. However, if we normalize our electron microprobe data on the basis of 21 O apfu (see below), the chemical composition of our weeksite can be expressed by the empirical formula $(K_{1.03}Ba_{0.21}Na_{0.18}Ca_{0.12})_{1.54}(UO_2)_2(Si_{5.03}O_{13})\cdot 4H_2O$, or simplified as $K_2(UO_2)_2(Si_5O_{13})\cdot 4H_2O$. The major difference between the two simplified formulas lies in the H_2O content.

From the thermogravimetric/differential thermogravimetric (TG/DTG) measurements, weeksite appears to dehydrate in several overlapping steps up to ~640–660 °C (Fig. 2). The observed loss in mass corresponds to ~6.7 wt%, which is close to that for 4 H_2O molecules in a chemical formula, lending further support to our proposed formula derived from the structure refinement (see below). The loss of ~0.5 wt% in mass between ~660 and 800 °C might result from the release of oxygen atoms or small amount of hydroxyl groups distributed over the oxygen sites.

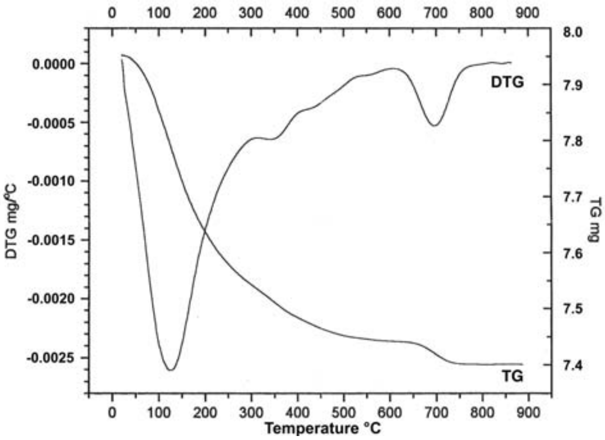

FIGURE 2. Thermal decomposition of weeksite reflected in weight-loss loss (TG) and it is difference curve (DTG).

---

[1] Deposit item AM-12-021, CIF and Anisotropic Displacement Parameters. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

Similar results were also observed by Tarkhanova et al. (1975) and Čejka (1999).

Crystal structure

The main features of the weeksite structure determined from this study are quite similar to those presented by Jackson and Burns (2001). The $(UO_2)O_5$ uranyl pentagonal bipyramids share equatorial edges to form chains parallel to [100], which in turn share edges with SiO_4 tetrahedra. The uranyl silicate chains are linked to crankshaft-like chains of vertex-sharing SiO_4 tetrahedra, resulting in layers that are connected through vertex-sharing between SiO_4 tetrahedra to form an open framework. The mono- and divalent cations (K^+, Ba^{2+}, Ca^{2+}, and Na^+), as well as H_2O molecules, are situated in the channels of the uranyl silicate framework (Fig. 3). However, there are also some marked differences between the two structures. For example, the structure of Jackson and Burns (2001) contains 48 nonequivalent atomic sites, with 4 occupied by U, 10 by Si, 6 by M (=K, Ba, Ca, and Na), 26 by O, and 2 by H_2O. Moreover, 4 Si and 2 O sites are only 50% occupied and some SiO_4 tetrahedra share edges or faces with each other, which is apparently energetically unfavorable. In contrast, our structure consists of only 22 symmetrically distinct atomic sites (Table 3), with 1 occupied by U, 3 by Si, 2 by M, 9 by O, and 7 by H_2O. All Si sites are fully occupied in our structure and there is no edge sharing between SiO_4 tetrahedra.

Experimental structural formula of weeksite obtained from the refinement and bond-valence analysis (Table 5) is $K_{1.88}H^+_{0.12}[(UO_2)_2(Si_5O_{13})](H_2O)_4$, $Z = 4$. The presence of H^+ in the formula is just formal, to keep it electroneutral. The real mechanism of charge-balance is substitution of M^+ and M^{2+} elements at the K sites, as suggest results of microprobe analysis and lower values of occupational factors obtained from the structure refinement.

DISCUSSION

Another noticeable difference between the structures of Jackson and Burns (2001) and this study is manifested in the positions and quantity of H_2O molecules. Whereas Jackson and Burns (2001) observed two H_2O sites located in a plane of six-member rings of silicate tetrahedra, we found in sum 3.94 H_2O groups distributed over two fully occupied and five partially occupied sites (Table 3 and Fig. 3). The refined occupancies for H_2O sites are consistent with our thermal analysis discussed above, as well as the previously proposed H_2O content in weeksite (Outerbridge et al. 1960; Stohl and Smith 1981).

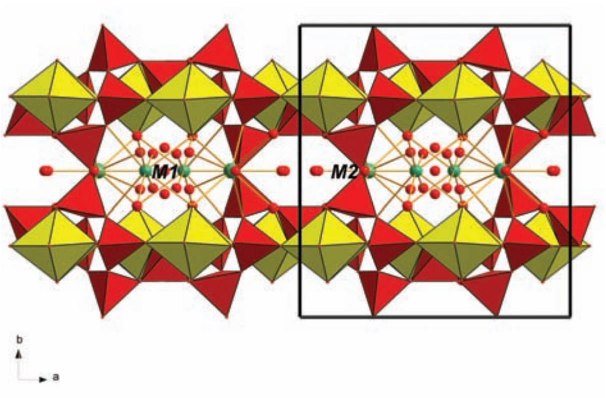

FIGURE 3. Polyhedral representation of weeksite structure viewed along [001] with labeled M-sites in the interlayer. Uranyl pentagonal bipyramids are yellow, silicate tetrahedra are red; atoms related to M-sites are green and oxygen atoms are red. The unit-cell edges are outlined. (Color online.)

TABLE 5. Bond-valence analysis for weeksite

	U	K1	K2	Si1	Si2	Si3	ΣBV	Assig.
O1				1.01×2↓		1.06	2.07	O^{2-}
O2	0.43, 0.59	0.03×2↓			1.04		2.09	O^{2-}
O3	0.43, 0.60		0.03×2↓		1.05		2.10	O^{2-}
O4	0.70			1.08×2↓			1.78	O^{2-}
O5		0.05×2↓			0.97	1.07	2.09	O^{2-}
O6			0.03			1.02×2→	2.07	O^{2-}
O7			0.07×2↓		1.02	1.04	2.12	O^{2-}
O8	1.61	0.13×2↓ 0.10×2↓	0.13×2↓				1.97	O^{2-}
O9	1.65		0.05×2↓				1.70	O^{2-}
O10			0.26				0.26	H_2O
O11		0.23	0.11				0.35	H_2O
O12							0.00	H_2O
O13							0.00	H_2O
O14		0.18×2↓					0.18	H_2O
O15			0.22×2↓				0.22	H_2O
O16							0.00	H_2O
ΣBV	6.01	1.21	1.38	4.18	4.08	4.19		

Notes: Values are expressed in valence units (v.u.). Multiplicity is indicated by ×↓→; K–O bond strengths from Brown and Altermatt (1985); Si–O bond strengths from Brese and O'Keeffe (1991); U^{6+}–O bond strengths ($r_0 = 2.051$, b = 0.519) from Burns et al. (1997b). While taking into account of K1/K2 site occupancies, ΣBV obtained are 1.15 and 1.28 v.u., respectively.

Atencio et al. (2004) described a new uranyl silicate mineral, coutinhoite, with an ideal chemical formula $Th_xB_{1-2x}(UO_2)_2Si_5O_{13}\cdot 3H_2O$. From the powder X-ray diffraction data, they obtained, by analogy with weeksite, an orthorhombic unit cell: $a = 14.1676(9)$, $b = 14.1935(9)$, $c = 35.754(2)$ Å, and $V = 7189.7(2)$ Å^3. Obviously, based on our new structure data on weeksite, the crystal symmetry and unit-cell parameters of this mineral worths to be reevaluated.

Haiweeite, ideally $Ca(UO_2)_2(Si_5O_{12})(OH)_2\cdot 3H_2O$, is another uranyl silicate mineral having the U:Si ratio of 2:5, as weeksite. Haiweeite was originally described as monoclinic, with $a = 15.4$, $b = 7.05$, $c = 7.10$ Å, and $\beta = 107.9°$ (McBurney and Murdoch 1959). However, from a twinned haiweeite crystal, Rastsvetaeva et al. (1997) attained a structure model with $R = 11.8\%$ on the basis of an orthorhombic unit cell: $a = 14.263(3)$, $b = 17.988(3)$, $c = 18.395(3)$ Å, and space group $P2_12_12_1$. Burns (2001) reexamined this mineral, showed it to be orthorhombic with $a = 7.125(1)$, $b = 17.937(2)$, $c = 18.342(2)$ Å, and space group *Cmcm*. Although the structure model of Burns (2001) yielded $R = 4.2\%$ ($R_{int} = 8.5\%$), it also contains several partially (50%) occupied atomic sites, including two Si sites, representing an average structure model. The preliminary results of the new single-crystal X-ray diffraction experiments on haiweeite crystals suggest that ordered structure exists, however it needs to be investigated further.

ACKNOWLEDGMENTS

We are indebted to Jaroslav Hyršl (Kolín, Czech Republic) who kindly provided us the weeksite sample for the study. The help of Jana Ederová (Institute of Chemical Technology in Prague, Czech Republic) is highly acknowledged due to performing thermal analysis of weeksite. Comments on the topic by Thomas Armbruster (University of Bern, Switzerland) are also highly appreciated. We thank Jiří Sejkora

(National museum, Prague) for supporting the research. We also thank Peter C. Burns for his interest in this study and constructive comments. We appreciate a lot the constructive suggestions and remarks by Sergei V. Krivovichev, Stuart J. Mills, and an anonymous reviewer, as well as careful editorial handling by Ian Swainson. This research was funded by the grants P204/11/0809 of the Grant Agency of the Czech Republic to K.F. and M.D. and a long-term research plan, MSM0021622412 (INCHEMBIOL), of the Ministry of Education of the Czech Republic to R.S. and J.P. M.C.B. and R.T.D. acknowledge support by the Carnegie-DOE Alliance Center under cooperative agreement DE FC52-08 N A28554.

REFERENCES CITED

Atencio, D., Carvalho, F.M.S., and Matioli, P.A. (2004) Coutinhoite, a new thorium uranyl silicate hydrate, from Urucum Mine, Galiléia, Minas Gerais, Brazil. American Mineralogist, 89, 721–724.

Baturin, S.V. and Sidorenko, G.A. (1985) Crystal structure of weeksite $(K_{0.62}Na_{0.38})_2(UO_2)_2[Si_5O_{13}]\times 3H_2O$. Soviet Physics Doklady, 30, 435–437.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

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

Buck, E.C. and Fortner, J.A. (1997) Detecting low levels of transuranics with electron energy loss spectroscopy. Ultramicroscopy, 67, 69–75.

Burns, P.C. (1999) The crystal chemistry of uranium. In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, Geochemistry and the Environment, 38, p. 23–90. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.

——— (2005) U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. Canadian Mineralogist, 43, 1839–1894.

Burns, P.C., Ewing, R.C., and Miller, M.L. (1997a) Incorporation mechanisms of actinide elements into the structures of U^{6+} phases formed during the oxidation of spent nuclear fuel. Journal of Nuclear Materials, 245, 1–9.

Burns, P.C., Ewing, R.C., and Hawthorne, F.C. (1997a) The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. Canadian Mineralogist, 35, 1551–1570.

Burns, P.C., Olson, R.A., Finch, R.J., and Hanchar, J.M. (2000) $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$, a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass. Journal of Nuclear Materials, 278, 290–300.

Čejka, J. (1999) Infrared spectroscopy and thermal analysis of the uranyl minerals. In P.C. Burns and R. Finch, Eds., Uranium: Mineralogy, Geochemistry and the Environment, 38, p. 521–622. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.

Chen, F., Burns, P.C., and Ewing, R.C. (1999) ^{79}Se: geochemical and crystallo-chemical retardation mechanisms. Journal of Nuclear Materials, 275, 81–94.

Chen, F., Burns, P.C., and Ewing, R.C. (2000) Near-field behaviour of ^{99}Tc during the oxidative alteration of spent nuclear fuel. Journal of Nuclear Materials, 278, 225–232.

Finch, R.J., Buck, E.C., Finn, P.A., and Bates, J.K. (1999) Oxidative corrosion of spent UO_2 fuel in vapor and dripping groundwater at 90°C. In D.J. Wronkiewicz and J.H. Lee, Eds., Scientific Basis for Nuclear Waste Management XXII, 556, p. 431–438. Materials Research Society, Warrendale, Pennsylvania.

Finn, P.A., Hoh, J.C., Wolf, S.F., Slater, S.A., and Bates, J.K. (1996) The release of uranium, plutonium, cerium, strontium, technetium, and iodine from spent fuel under unsaturated conditions. Radiochimica Acta, 74, 65–71.

Friese, J.I., Douglas, M., McNamara, B.K., Clark, S.B., and Hanson, B.D. (2004) Np Behavior in Synthesized Uranyl Phases: Results of Initial Tests, p. 77. Pacific Northwest National Laboratory, Richland, Washington.

Jackson, J.M. and Burns, P.C. (2001) A re-evaluation of the structure of weeksite, a uranyl silicate framework mineral. Canadian Mineralogist, 39, 187–195.

Klingensmith, A.L., Deely, K.M., Kinman, W.S., Kelly, V., and Burns, P.C. (2007) Neptunium incorporation in sodium-substituted metaschoepite. American Mineralogist, 92, 662–669.

McBurney, T.C. and Murdoch, J. (1959) Haiweeite, a new uranium mineral from California. American Mineralogist, 44, 839–843.

Merlet, C. (1994) An accurate computer correction program for quantitative electron-probe microanalysis. Microchimica Acta, 114, 363–376.

Oji, L.N., Martin, K.B., Stallings, M.E., and Duff, M.C. (2006) Conditions conducive to forming crystalline uranyl silicates in high caustic nuclear waste evaporators. Nuclear Technology, 154, 237–246.

Outerbridge, W.F., Staatz, M.H., Meyrowitz, R., and Pommer, A.M. (1960) Weeksite, a new uranium silicate from the Thomas Range, Juab County, Utah. American Mineralogist, 45, 39–52.

Palatinus, L. and Chapuis, G. (2007) Superflip—a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. Journal of Applied Crystallography, 40, 451–456.

Petříček, V., Dušek, M., and Palatinus, L. (2006) Jana2006. The crystallographic computing system. Institute of Physics, Praha, Czech Republic.

Rastsvetaeva, R.K., Arakcheeva, A.V., Pushcharovsky, D.Yu., Atencio, D., and Menezes Filho, L.A.D. (1997) A new silicon band in the haiweete [sic] structure. Crystallography Reports, 42, 927–933.

Stohl, F.V. and Smith, D.K. (1981) The crystal chemistry of uranyl silicate minerals. American Mineralogist, 66, 610–625.

Tarkhanova, G.A., Sidorenko, G.A., and Moroz, I.Ch. (1975) First finding of a mineral of the weeksite group in the USSR. Zapiski Vserossijskogo mineralogičeskogo obščestva, 104, 598–603.

Wronkiewicz, D.J., Bates, J.K., Wolf, S.F., and Buck, E.C. (1996) Ten-year results from unsaturated drip tests with UO_2 at 90 °C: implications for the corrosion of spent nuclear fuel. Journal of Nuclear Materials, 238, 78–95.

Yeremenko, G.K., Il'menov, Ye.S., and Azimi, N.A. (1977) Find of weeksite-group minerals in Afghanistan. Doklady Akademii Nauk SSSR, 237, 226–228.

MANUSCRIPT RECEIVED OCTOBER 13, 2011
MANUSCRIPT ACCEPTED DECEMBER 9, 2011
MANUSCRIPT HANDLED BY IAN SWAINSON