THE STRUCTURE OF BOLTWOODITE
AND IMPLICATIONS OF SOLID SOLUTION TOWARD SODIUM BOLTWOODITE

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ABSTRACT

The structure of boltwoodite, monoclinic, a 7.0772(8), b 7.0597(8), c 6.6479(7) Å, β 104.982(2)°, V 320.9(1) Å^3, space group $P2_1/m$, has been refined by full-matrix least-squares techniques to an agreement factor (R) of 3.2% and a goodness-of-fit (S) of 1.13 using 760 unique observed reflections ($|F_o| \geq 4\sigma_F$) collected with MoKα X-radiation and a CCD (charge-coupled device) area detector. The structure determination provided the formula $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, $Z = 2$, which is supported by analyses done with an electron microprobe, and which differs from the previously accepted formula in the absence of a hydronium ion, the presence of an acid silicate group, and the number of H_2O. The structure contains silicate tetrahedra and uranyl pentagonal bipyramids that share edges and corners to form α-uranophane-type sheets that are parallel to (100) at $x \approx \frac{1}{4}$ and $\frac{3}{4}$. There are four distinct partially occupied sites in the interlayer that correspond to one Na, one K, and two H_2O groups. Local arrangements result in either Naϕ_6 octahedra (ϕ: unspecified anion) or Kϕ_7 polyhedra. Local arrangements of the interlayer are non-centrosymmetric, although the long-range symmetry of the structure is consistent with space group $P2_1/m$. The structure of boltwoodite permits substantial variation of interlayer composition, which is significant from the perspective of mineral stability. In addition, boltwoodite may be a key phase in determining the future mobility of certain radionuclides in a geological repository containing spent nuclear fuel.

Keywords: boltwoodite, sodium boltwoodite, uranophane, spent nuclear fuel, repository, crystal structure, uranyl mineral.

SOMMAIRE

La structure de la boltwoodite, monoclinique, a 7.0772(8), b 7.0597(8), c 6.6479(7) Å, β 104.982(2)°, V 320.9(1) Å^3, groupe spatial $P2_1/m$, a été affinée par moindres carrés sur matrice entière jusqu'à un résidu R de 3.2% et une mesure de concordance de 1.13 en utilisant 760 réflexions uniques observées ($|F_o| \geq 4\sigma_F$) prélevées avec rayonnement MoKα et un détecteur d'aire à charge couplée (CCD). L'affinement a mené à une formule révisée $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, $Z = 2$, qui concorde avec les résultats d'analyses par microsonde électronique, mais qui diffère de la formule acceptée jusqu'ici par l'absence de l'ion hydronium, la présence d'un groupe silicaté acide, et le nombre de groupes H_2O. La structure contient des tétraèdres silicatés et des bipyramides pentagonales à uranyle qui partagent des arêtes et des coins pour former des feuillets de type uranophane-α parallèles à (100) aux niveaux $x \approx \frac{1}{4}$ et $\frac{3}{4}$. Il y a quatre sites distincts partiellement occupés entre les feuillets; ils contiennent un atome de Na, un atome de K, et deux groupes de H_2O. Les agencements locaux ont comme résultat soit un octaèdre Naϕ_6 (ϕ: anion quelconque) ou un polyèdre Kϕ_7. Ces agencements inter-feuillet ne sont pas centrosymétriques, quoique la symétrie à plus grande échelle concorde avec les exigeances du groupe spatial $P2_1/m$. La structure de la boltwoodite permet des variations importantes en composition dans la position inter-feuillet, ce qui influence directement la stabilité du minéral. De plus, la boltwoodite pourrait s'avérer une phase très importante dans la question de la mobilité éventuelle de certains nucléides radioactifs dans un dépotoir de déchets nucléaires.

(Traduit par la Rédaction)

Mots-clés: boltwoodite, sodium boltwoodite, uranophane, fuel nucléaire usagé, dépotoir nucléaire, structure cristalline, minéral à uranyle.

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INTRODUCTION

Boltwoodite, a uranyl silicate of the uranophane group, was first described from Pick's Delta mine, Emery County, Utah by Frondel & Ito (1956), and has since been identified from several localities. The currently accepted formula for boltwoodite is $(H_3O)K[(UO_2)(SiO_4)](H_2O)$ (Stohl & Smith 1981). Several investigators have suggested that Na can partially replace K in the structure (Honea 1961, Chernikov *et al.* 1975, Strunz & Tennyson 1983, Pu 1990). Chernikov *et al.* (1975) described sodium boltwoodite from an unspecified occurrence of uranium mineralization within the Kyzylsai ore field, Chu-Ili Mountains, southwest Balkhash region, Kazakhstan (Pekov 1998). Boltwoodite and sodium boltwoodite are apparently not isostructural, although the structures are probably closely related. The structure of boltwoodite has monoclinic symmetry (Stohl & Smith 1981), but the original description of sodium boltwoodite indicates that its structure is orthorhombic (Chernikov *et al.* 1975). However, Vochten *et al.* (1997) recently synthesized sodium boltwoodite and demonstrated that the structure is probably monoclinic, with a unit cell that is similar to that of boltwoodite, except that the *a* dimension is doubled.

The structure of boltwoodite was reported for a twinned crystal by Stohl & Smith (1981). The data were of low resolution, with the refinement of the structure based upon 201 independent reflections with a maximum 2θ of 35°, and resulted in an agreement index (*R*) of 10.9%. The study showed that the structure of boltwoodite contains the α-uranophane-type sheet of silicate tetrahedra and uranyl pentagonal bipyramids. Stohl & Smith (1981) did not locate the H atoms in the structure, but assumed that an $(H_3O)^+$ hydronium ion is present, as suggested by electroneutrality requirements. Vochten *et al.* (1997) used sums of bond valences calculated for the atomic sites in the structure reported by Stohl & Smith (1981) to argue that SiO_3OH groups are present in the structure, rather than a hydronium anion. Infrared spectra obtained for synthetic boltwoodite are consistent with the presence of SiO_3OH in the structure (Vochten *et al.* 1997).

Wronkiewicz *et al.* (1996) identified both boltwoodite and sodium boltwoodite on samples of UO_2 treated in unsaturated drip tests under oxidizing conditions that were designed to model the behavior of spent nuclear fuel in a geological repository. In addition, boltwoodite and uranophane form when spent nuclear fuel is altered under oxidizing conditions in contact with water derived from the proposed nuclear waste repository at Yucca Mountain, Nevada (Finn *et al.* 1995, 1996). Ongoing experiments indicate that a variety of radionuclides, including the fission products ^{90}Sr and ^{137}Cs, are being retained to a large extent with the products of alteration (Finn *et al.* 1996), suggesting that uranophane-group minerals may be incorporating radionuclides into their crystal structures. Thus, these minerals may be key phases in determining the future mobilities of some of the radionuclides under repository conditions.

EXPERIMENTAL

X-ray diffraction

The specimen of boltwoodite selected for study is from near Rössing, Namibia. The specimen contains several clusters of acicular crystals up to ~1 cm in length. A crystal fragment with approximate dimensions $0.11 \times 0.04 \times 0.02$ mm was selected for study. The crystal was mounted on a Siemens PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Burns (1998) discussed the application of CCD detectors to the analysis of mineral structures.

The data were collected using monochromatic MoKα X-radiation and frame widths of 0.3° in ω, with 40 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions. These were refined (Table 1) with 1662 reflections using least-squares techniques. Data were collected for $3° \le 2\theta \le 56.6°$ in approximately 16 hours; comparison of the intensities of equivalent reflections collected at different times during the data collection showed no significant decay. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Siemens program SAINT. An empirical absorption-correction was done by minimizing the intensity variation of symmetrically equivalent reflections with the crystal shape modeled as an ellipse using the program SADABS (G. Sheldrick, unpublished). A total of 1952 reflections were collected, of which there were 812 unique reflections ($R_{INT} = 3.1\%$), with 760 classed as observed ($|F_o| \ge 4\sigma_F$).

Chemical analysis

Chemical analysis was done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data

TABLE 1. MISCELLANEOUS INFORMATION CONCERNING BOLTWOODITE

a (Å)	7.0772(8)	Crystal size (mm)	0.11 x 0.04
b (Å)	7.0597(8)		x 0.02
c (Å)	6.6479(7)		
β (°)	104.982(2)	Total ref.	1952
V (Å^3)	320.9(1)	Unique ref.	812
Space group	*P*2$_1$/*m*	R_{int}	3.1%
F(000)	370	Unique $|F_o| \ge 4\sigma_F$	760
μ (mm^{-1})	24.5	Final *R*	3.2%
D_{calc} (g/cm^3)	4.144	*S*	1.13

Unit cell contents: $2\{(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}\}$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for *m* observations and *n* parameters

reduction was done with a conventional PAP routine. The operating voltage was 15 kV, and the beam current was 0.20 μA. To prevent sample burn-up and to limit Na volatilization and migration, a beam 30 μm in diameter was employed, the broadest the sample size would allow. There was no apparent chemical zoning using the back-scatter electron detector. Data for all elements in the sample were collected for 25 s or 0.50 % precision, whichever was attained first. A 100-s energy-dispersion scan indicated no elements with Z greater than 8, other than those reported here. The following standards were used for the electron-microprobe analysis: albite (Na$K\alpha$), sanidine (K$K\alpha$), diopside (Ca$K\alpha$), sanbornite (Si$K\alpha$) and synthetic UO_2 (U$M\alpha$). Data for standards were collected for 50 s or 0.25 % precision, whichever was attained first. K counts were corrected for an overlap with U. The results of two analyses, performed on two crystals of boltwoodite in parallel growth, are given in Table 2. H_2O was calculated by stoichiometry from the results of the crystal-structure analysis.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Siemens SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Systematic absences of reflections indicated that the space group is either $P2_1/m$ or $P2_1$. Stohl & Smith (1981) concluded that the sheets of silicate tetrahedra and uranyl pentagonal bipyramids are consistent with

TABLE 2. ELECTRON MICROPROBE DATA (wt. %) ON BOLTWOODITE

	1	2		1	2	Struct.
Na$_2$O	2.59	2.74	Na**	0.37	0.39	0.42(3)
K$_2$O	5.69	5.14	K	0.53	0.48	0.56(2)
CaO	0.06	0.18	Ca	0.01	0.01	–
SiO$_2$	14.48	14.46	Si	1.05	1.06	1
UO$_3$	68.85	68.22	U	1.05	1.05	1
H$_2$O*	8.25	8.17	H$_2$O	2	2	2.0(1)
Total	99.92	98.91				

* calculated based on stoichiometry
** formula calculated assuming total cations = 3

$P2_1/m$, whereas the K atoms and H_2O groups located in the interlayer require a reduction of the symmetry to $P2_1$. The structure was solved in $P2_1/m$ using Patterson methods. The initial structure-model contained all of the atomic sites that correspond to the sheets of silicate and uranyl polyhedra, but no interlayer sites. Refinement of the atomic positional and isotropic-displacement parameters resulted in an R of 10.3% for the observed reflections. Refinement after conversion of the displacement parameters to an anisotropic form gave an R of 6.0%.

Within the symmetry constraints of the space group $P2_1/m$, there are four symmetrically distinct sites in the interlayer, as shown by the difference-Fourier map (Fig. 1). Local site-geometries and electron densities indicate that these sites correspond to K and Na cations and two H_2O groups, as labeled in Figure 1. The interlayer sites were added to the structure model. Refinement of the occupancy factors for the interlayer sites indicated that each is partially occupied, and the constraint that the occupancy of the Na and $H_2O(7)$ sites is identical was imposed on the model (see below).
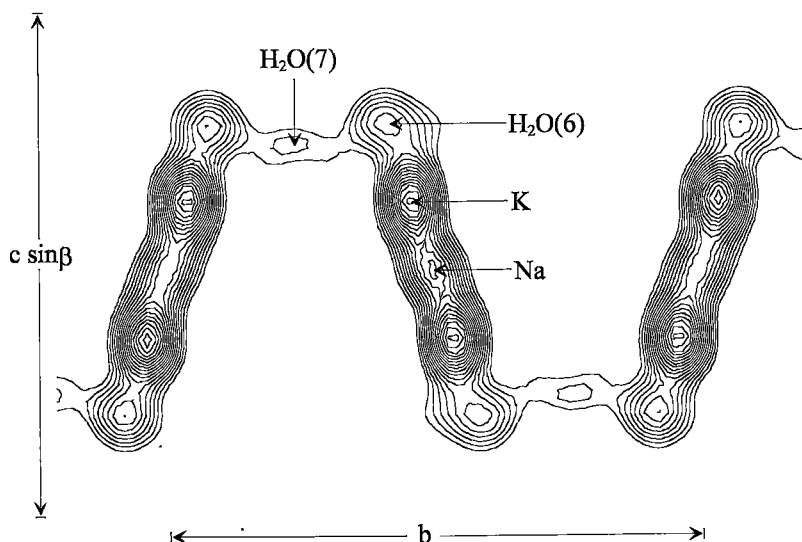

FIG. 1. Difference-Fourier map at $x = 0$ projected along [100]. The calculation was done without the interlayer constituents included in the model. The contour interval is 0.5 e/Å^3, with the lowest contour line corresponding to 2 e/Å^3.

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TABLE 3. FINAL ATOMIC PARAMETERS FOR BOLTWOODITE

	x	y	z	$*U_{eq}$	$**U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.52463(5)	¾	0.63810(5)	141(2)	247(3)	71(2)	110(2)	0	58(2)	0
Si	0.4320(5)	¾	0.1481(5)	178(6)	296(16)	122(13)	122(13)	0	64(12)	0
K[a]	0.046(1)	0.037(2)	0.641(2)	431(37)						
Na[a]	0	0	½	626(79)						
O(1)	0.786(1)	¾	0.668(2)	279(20)	244(43)	327(51)	275(48)	0	86(36)	0
O(2)	0.263(1)	¾	0.597(1)	275(19)	195(40)	377(52)	255(46)	0	62(34)	0
O(3)	0.566(1)	¾	0.988(1)	214(16)	324(43)	155(36)	183(39)	0	102(33)	0
O(4)	0.5246(9)	0.0740(8)	0.6888(2)	281(14)	630(43)	64(24)	153(25)	18(25)	108(26)	-6(21)
OH(5)	0.203(2)	¾	0.030(2)	407(25)	366(55)	536(67)	364(58)	0	177(46)	0
H$_2$O(6)[a]	0.921(3)	0.925(3)	0.201(3)	639(74)						
H$_2$O(7)[a]	0.938(5)	¾	0.245(9)	1110(197)						

$*U_{eq} = U_{eq}$ Å^2 x 10^4
$**Uij = U_{ij}$ Å^2 x 10^4
[a] occupancy factors: K = 0.28(1), Na = 0.21(2), H$_2$O(6) = 0.53(3), H$_2$O(7) = 0.21(2)

Refinement of the entire model, including anisotropic-displacement parameters for the atoms contained within the sheets of silicate and uranyl polyhedra, isotropic-displacement parameters for the interlayer sites, the occupancy factors for the interlayer constituents, and a weighting scheme for the structure factors, resulted in a final R of 3.2% for the 760 observed unique reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (S) of 1.13. In the final cycle of refinement, the mean parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 2.09 and -2.04 e/Å^3. The positions of the interlayer constituents represent a long-range average configuration with several possible local arrangements (see below). Some of the local arrangements violate the center of symmetry in space group

$P2_1/m$. A refinement conducted in space group $P2_1$ gave an R factor of 3.3%. However, the refinement was unsatisfactory because of high correlation among parameters, and several of the anisotropic-displacement parameters became non-positive-definite. Therefore, results for the space group $P2_1/m$ are reported, although this space group is consistent only with the long-range structure. The final atomic-positional parameters and anisotropic-displacement parameters are given in Table 3, selected interatomic-distances and angles are given in Table 4, and a bond-valence analysis is provided in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR BOLTWOODITE

U-O(2)	1.802(9)		K-O(2)f	2.60(1)
U-O(1)	1.812(9)		K-O(1)g	2.77(1)
U-O(3)	2.270(8)		K-O(2)h	2.78(1)
U-O(4)a,b	2.312(5) x2		K-H$_2$O(6)I	2.92(2)
U-O(4)c,d	2.449(6) x2		K-H$_2$O(6)g	2.94(2)
<U-O$_{Ur}$>	1.807		K-O(1)c	3.02(1)
<U-O$_{eq}$>	2.358		K-OH(5)j	3.25(1)
			<K-φ>	2.897
Si-O(3)e	1.596(9)			
Si-OH(5)	1.61(1)		Na-H$_2$O(7)c,g	2.41(4) x2
Si-O(4)c, d	1.625(6) x2		Na-O(2)f,h	2.524(6) x2
<Si-O>	1.614		Na-O(1)c,g	2.743(7) x2
			<Na-φ>	2.559
O(2)-U-O(1)	177.8(4)			
O(2)-U-O(3)	90.5(4)		O(3)e-Si-OH(5)	111.7(5)
O(2)-U-O(4)a,b	89.0(2) x2		O(3)e-Si-O(4)c,d	113.7(3) x2
O(2)-U-O(4)c,d	87.8(3) x2		OH(5)-Si-O(4)c,d	108.6(3) x2
O(1)-U-O(3)	91.7(4)		O(4)c-Si-O(4)d	99.7(4)
O(1)-U-O(4)a,b	91.3(2) x2		<O-Si-O>	109.3
O(1)-U-O(4)c,d	90.3(3) x2			
O(3)-U-O(4)a,b	81.7(1) x2		H$_2$O(7)c-Na-H$_2$O(7)g	180
O(3)-U-O(4)c,d	149.5(1) x2		O(2)f-Na-O(2)h	180
O(4)a-U-O(4)b	163.2(3)		O(1)c-Na-O(1)g	180
O(4)a,b-U-O(4)c,d	67.8(2) x2		H$_2$O(7)c,g-Na-O(2)f,h	110(1) x2
O(4)a,b-U-O(4)c,d	128.7(1) x2		H$_2$O(7)c,g-Na-O(2)f,h	70(1) x2
O(4)c-U-O(4)d	61.0(3)		H$_2$O(7)c,g-Na-O(1)c,g	102(1) x2
			H$_2$O(7)c,g-Na-O(1)c,g	78(1) x2
			O(2)f,h-Na-O(1)c,g	83.8(2) x2
			O(2)f,h-Na-O(1)c,g	96.2(2) x2

a = x, ½-y, z; b = x, y+1, z; c = 1-x, 1-y, 1-z; d = 1-x, ½+y, 1-z; e = x, y, z-1; f = x, y-1, z; g = x-1, y-1, z; h = -x, 1-y, 1-z; i = 1-x, y-½, 1-z; j = x, y-1, z+1

TABLE 5. BOND-VALENCE* (vu) ANALYSIS FOR BOLTWOODITE

	U	Si	K**	Na**	Σ
O(1)	1.579		0.177 (0.049 $^{x2}\rightarrow$) 0.090 (0.025 $^{x2}\rightarrow$)	0.078 $^{x2}\downarrow$ (0.016 $^{x2}\rightarrow$)	1.759
O(2)	1.610		0.281 (0.078 $^{x2}\rightarrow$) 0.173 (0.096 $^{x2}\rightarrow$)	0.141 $^{x3}\downarrow$ (0.030 $^{x2}\rightarrow$)	1.922
O(3)	0.643	1.079			1.722
O(4)	0.592 $^{x2}\downarrow$ 0.453 $^{x2}\downarrow$	0.997 $^{x2}\downarrow$			
OH(5)		1.039	0.048 (0.014 $^{x2}\rightarrow$)		1.066
H$_2$O(6)			0.118 (0.033 $^{x2}\rightarrow$) 0.112 (0.031 $^{x2}\rightarrow$)		0.128
H$_2$O(7)				0.192 $^{2}\downarrow$ (0.041 $^{x2}\rightarrow$)	0.082
Σ	5.923	4.112	1.000	0.824	

*Bond-valence parameters for U^{6+} from Burns et al. (1997) and for K from Brese & O'Keeffe (1991)
**Bond-valence contributions into anion sums scaled to cation site occupancy

RESULTS

Sheet of silicate and uranyl polyhedra

The sheet of silicate tetrahedra and uranyl pentagonal bipyramids that occurs in the structure, together with its sheet anion-topology derived using the method of Burns et al. (1996), is shown in Figure 2. Burns et al. (1996) identified sixteen structures, eight of which correspond to minerals, that have sheets based upon the uranophane sheet anion-topology shown in Figure 2b. Five structures have sheets that are topologically
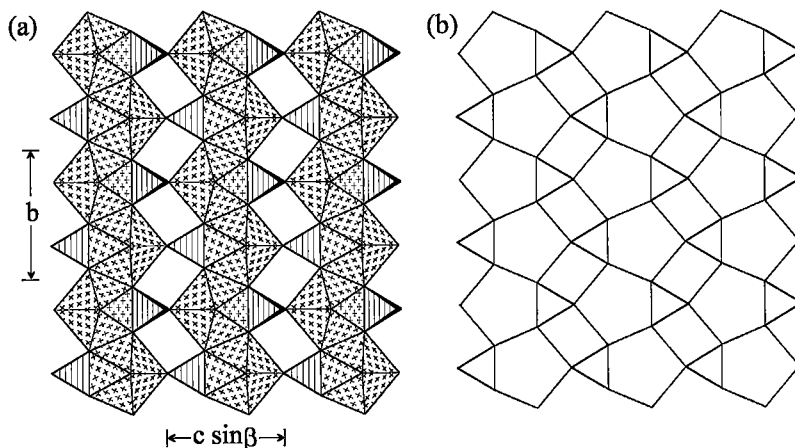
FIG. 2. (a) Sheet of silicate tetrahedra and uranyl polyhedra that occurs in the structure of boltwoodite at $x \approx \frac{1}{4}$ and $\frac{3}{4}$ projected along [100]. The uranyl polyhedra are shaded with crosses, and the silicate tetrahedra are shaded with parallel lines. (b) The sheet anion-topology corresponding to the sheet shown in (a) derived using the method of Burns *et al.* (1996).

identical to the sheet in the boltwoodite structure; these correspond to α-uranophane (Ginderow 1988), cuprosklodowskite (Rosenzweig & Ryan 1975), sklodowskite (Ryan & Rosenzweig 1977), and kasolite (Rosenzweig & Ryan 1977), and to $Mg[(UO_2)(AsO_4)]_2(H_2O)_4$ in which arsenate rather than silicate tetrahedra are present (Bachet *et al.* 1991).

The polyhedron geometries within the sheets of polyhedra in boltwoodite are consistent with those in other well-refined uranyl structures. The U^{6+} cation is strongly bonded to two O atoms, forming a nearly linear [177.8(4)°] $(U^{6+}O_2)^{2+}$ uranyl ion (*Ur*) with $<U^{6+}-O_{Ur}> = 1.807$ Å, which may be compared to $<^{[7]}U^{6+}-O_{Ur}> = 1.79(4)$ Å for numerous well-refined structures (Burns *et al.* 1997). The uranyl ion is coordinated by five O atoms that are arranged at equatorial positions of a pentagonal bipyramid. Evans (1963) noted that the pentagonal bipyramid is the most common U^{6+} coordination in solids. The $<U^{6+}-O_{eq}>$ (eq: equatorial) of 2.358 Å agrees well with the $<^{[7]}U^{6+}-\phi_{eq}>$ (ϕ: O^{2-}, OH$^-$ or H_2O) of 2.37(9) Å obtained for numerous well-refined structures (Burns *et al.* 1997). The geometry of the uranyl-bearing polyhedron, as well as the sum of bond valences at the U site (5.92 valence units, *vu*, Table 5), are consistent with the site containing only U^{6+}.

The Si cation is tetrahedrally coordinated, with $<Si-\phi> = 1.614$ Å. Three of the tetrahedron vertices correspond to O atoms that are bonded to one or two U^{6+} cations, whereas the other vertex [OH(5)] is weakly bonded to a K cation in the interlayer. The bond-valence sum at the anion position, 1.07 *vu* (Table 5), demonstrates that this anion corresponds to a hydroxyl group.

Thus, the silicate tetrahedron is an SiO_3OH group, as is found in the structures of α-uranophane (Ginderow 1988), β-uranophane (Viswanathan & Harneit 1986), cuprosklodowskite (Rosenzweig & Ryan 1975), and sklodowskite (Ryan & Rosenzweig 1977), in contrast to the SiO_4 tetrahedron reported by Stohl & Smith (1981). The presence of a SiO_3OH group in the structure of boltwoodite is supported by infrared spectra (Vochten *et al.* 1997).

Interlayer

The interlayer in the structure contains monovalent cations and H_2O groups, and the electroneutrality principle requires a total of one monovalent cation per formula unit. As shown in Figure 1, the interlayer of the structure contains four symmetrically distinct sites, which are interpreted to correspond to one K, one Na, and two H_2O sites.

Various possible local arrangements of the interlayer constituents are shown in Figure 3. The Na site is octahedrally coordinated by four O_{Ur} atoms and two $H_2O(7)$ groups; as the $H_2O(7)$ group is essential to the Na octahedron, the occupancy of the Na site and that of the $H_2O(7)$ site were constrained to be equal during the final stages of the refinement. The $<Na-\phi>$ bond-length of 2.559 Å and the sum of bond-valences at the Na site of 0.82 *vu* are consistent with occupancy of the site by Na rather than K, with somewhat longer bond-lengths than expected for an octahedron that is fully occupied. The refined site-occupancy for the Na and $H_2O(7)$ sites is 0.21(2), giving 0.42(4) Na and 0.42(4) $H_2O(7)$ per formula unit.
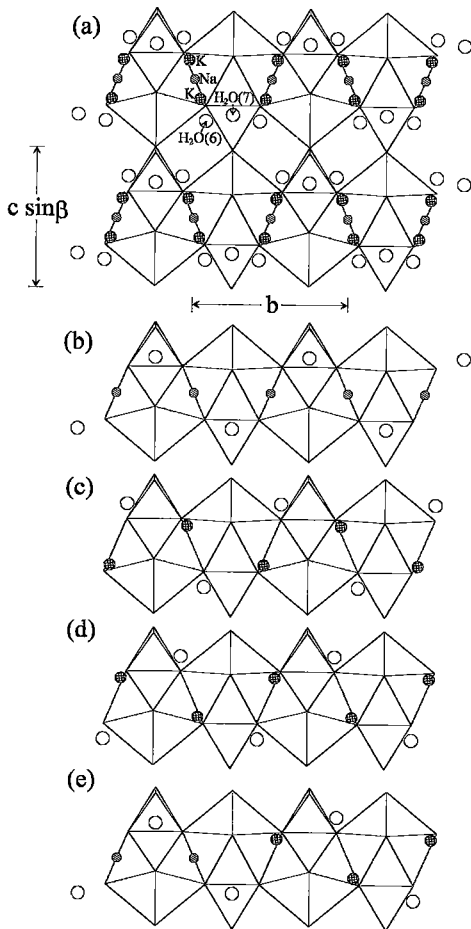
FIG. 3. Possible local arrangements of interlayer constituents in the structure of boltwoodite. The interlayer at $x \approx 0$ is shown projected along [100] onto the sheet of uranyl polyhedra at $x \approx \frac{1}{4}$. (a) Projection showing the arrangement of all interlayer sites, each of which is partially occupied. (b) Arrangement that occurs when Na sites are occupied. (c) Possible arrangement that occurs when K sites are occupied. (d) Alternate arrangement that occurs when K sites are occupied. (e) Arrangement compatible with a transition from a Na-rich to a K-rich region.

Occupancy of the K and $H_2O(6)$ sites is locally correlated, such that one of the arrangements shown in Figure 3 occurs. The K cation is bonded to four O_{Ur} atoms, the OH(5) group, and two $H_2O(6)$ groups, giving a $K\phi_7$ polyhedron with $<K–\phi> = 2.897$ Å and a bond-valence sum of 1.00 vu at the K site (Table 5). The refined site-occupancy of the K site is 0.28(1), giving 0.56(2) K atoms per formula unit. Refinement of the site occupancy of $H_2O(6)$ gave 0.53(3), indicating that there are 1.06(6) $H_2O(6)$ per formula unit. Note that the occupancy of $H_2O(6)$ is higher than the K site, indi-

cating that not all $H_2O(6)$ bond to two K, whereas each K is probably bonded to two $H_2O(6)$.

Structural formula

The structure refinement indicates the formula $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$ for the crystal studied. This formula is different from the currently accepted formula in the absence of an hydronium ion, the presence of hydroxyl in the silicate tetrahedron, and the amount of H_2O. The results of the electron-microprobe analysis for crystals of boltwoodite from the same specimen (Table 2) confirm the K:Na ratio that resulted from the structure model.

DISCUSSION

This study demonstrates that either K or Na can be accommodated in the interlayer between the sheets of silicate and uranyl polyhedra in the structure of boltwoodite, although this is achieved by the cations assuming different positions that result in different coordination polyhedra that are consistent with cation size. It is significant that both the K cation and the considerably smaller Na cation occur in the interlayer in the same crystal, owing to the presence of appropriately sized coordination polyhedra for both cations that only require modifications of the interlayer H_2O positions, rather than the alignment of the sheets of silicate and uranyl polyhedra.

The complex paragenetic relations of uranyl minerals are further complicated by the presence of solid solution within single crystals. Mineral structures that are compatible with a range of compositions will tend to have larger stability fields than those that are compositionally inflexible. The determination or prediction of such fields of stability will require the study of crystals with a range of compositions, rather than thermodynamic measurements done for end-member compositions (*e.g.*, Nguyen *et al.* 1992).

Boltwoodite and sodium boltwoodite are phases that are likely to form in substantial quantities when spent nuclear fuel is corroded under unsaturated oxidizing conditions in contact with silica-bearing water, such as at the proposed repository at Yucca Mountain (Wronkiewicz *et al.* 1996, Finn *et al.* 1995, 1996). The flexibility of the boltwoodite structure that permits cation substitution in the interlayer has been demonstrated by the present study. Note that it may be possible for substantial amounts of Cs to substitute into the interlayer of boltwoodite or sodium boltwoodite, making these minerals key phases in determining the future mobility of the radionuclides [135]Cs and ^{137}Cs under repository conditions. A detailed understanding of the stability and crystal chemistry of minerals in the uranophane group is essential in predicting the long-term viability of a repository. Experiments are currently being undertaken to address this issue.

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