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A NEW URANYL SILICATE SHEET IN THE STRUCTURE OF HAIWEEITE AND COMPARISON TO OTHER URANYL SILICATES

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ABSTRACT

The structure of haiweeite, $\text{Ca}[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2](\text{H}_2\text{O})_3$, $Z = 4$, orthorhombic, a 7.125(1), b 17.937(2), c 18.342(2) Å, V 2344.3(7) Å³, space group *Cmcm*, has been solved by direct methods and refined by full-matrix least-squares techniques to an agreement index ($R1$) of 4.2% for 1181 unique observed reflections ($|F_o| \leq 4\sigma_F$) collected using MoK α X-radiation and a CCD-based area detector. The structure contains two symmetrically distinct U^{6+} positions, each of which is occupied by nearly linear $(\text{UO}_2)^{2+}$ uranyl ions (Ur) that are coordinated by five additional O atoms arranged at the equatorial corners of pentagonal bipyramids capped by the O_{Ur} anions. There are four Si cations in tetrahedral coordination, three by O atoms only, and one by three O atoms and one $(\text{OH})^-$ group. Uranyl polyhedra share edges, forming chains parallel to [100] that are one polyhedron wide. Silicate tetrahedra share edges with the uranyl polyhedra, and are staggered along the chain length. Adjacent chains are linked through additional silicate tetrahedra, forming a sheet parallel to (001). The silicate tetrahedra form a positionally disordered crankshaft-like chain parallel to [100] that involves four-member rings. Edge-sharing dimers of partially occupied Ca polyhedra occur in the interlayer and, together with H bonds, provide linkage between adjacent uranyl silicate sheets. The linkages between silicate tetrahedra in hydrous uranyl silicates are related to the U:Si ratio, as is the mode of polymerization between silicate tetrahedra and uranyl polyhedra. With increasing Si relative to U, there is increasing polymerization of silicate tetrahedra, and a decreasing tendency for edge-sharing between uranyl polyhedra and silicate tetrahedra.

Keywords: haiweeite, uranyl silicate, structure determination.

SOMMAIRE

La structure de la haiweeite, $\text{Ca}[(\text{UO}_2)_2\text{Si}_5\text{O}_{12}(\text{OH})_2](\text{H}_2\text{O})_3$, $Z = 4$, orthorhombique, a 7.125(1), b 17.937(2), c 18.342(2) Å, V 2344.3(7) Å³, groupe spatial *Cmcm*, a été résolue par méthodes directes et affinée par moindres carrés sur matrice entière jusqu'à un résidu $R1$ de 4.2% en utilisant 1181 réflexions uniques observées ($|F_o| \leq 4\sigma_F$) et prélevées avec rayonnement MoK α et un détecteur de type CCD. La structure contient deux positions U^{6+} symétriquement distinctes, chacune en fait un ion uranyle $(\text{UO}_2)^{2+}$ presque linéaire (Ur) coordonné à cinq atomes d'oxygène additionnels disposés aux coins équatoriaux de dipyramides pentagonales ayant des anions O_{Ur} à leur sommet. La structure contient quatre cations Si en coordinance tétraédrique, dont un avec trois atomes d'oxygène et un groupe $(\text{OH})^-$. Les polyèdres à uranyle partagent des arêtes pour former des chaînes parallèles à [100] d'une largeur d'un polyèdre. Les tétraèdres de silicate partagent des arêtes avec les polyèdres à uranyle, et sont échelonnées le long des chaînes. Les chaînes adjacentes sont interliées par des tétraèdres additionnels, pour former un feuillet parallèle à (001). Les tétraèdres sont désordonnés le long d'une chaîne à allure de vilebrequin parallèle à [100], qui implique des anneaux à quatre membres. Des dimères de polyèdres de Ca partiellement occupés à arêtes partagées sont situés dans l'interfeuillet; avec les liaisons hydrogène, ils assurent les liaisons entre les feuillets adjacents de silicate d'uranyle. Les liaisons entre tétraèdres dans les silicates hydratés d'uranyle montrent une relation avec le rapport U:Si, tout comme le mode de polymérisation entre les tétraèdres de silicate et les polyèdres à uranyle. A mesure qu'augmente la proportion de Si par rapport à U, le degré de polymérisation des tétraèdres silicatés augmente, et la tendance qu'ont les polyèdres à uranyle de partager des arêtes avec les tétraèdres diminue.

(Traduit par la Rédaction)

Mots-clés: haiweeite, silicate d'uranyle, détermination de la structure.

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INTRODUCTION

Uranyl silicates are common constituents of the oxidized portions of U deposits (Fron del 1958, Finch & Ewing 1992, Percy *et al.* 1994), and typically form as a result of the alteration of uraninite. Uranyl silicates are important for understanding the genesis of U deposits, as well as fluid-rock interactions during the weathering of U deposits or the mine and mill tailings that result from resource utilization. Uranyl silicates are also significant to the disposal of nuclear waste. Laboratory simulations have demonstrated that they form owing to the alteration of spent nuclear fuel under conditions similar to those expected at the proposed repository at Yucca Mountain, Nevada (Finn *et al.* 1996, Wronkiewicz *et al.* 1996). Boltwoodite, sodium boltwoodite and α -uranophane are the uranyl silicates most often encountered in such tests, although Wilson (1990) identified haiweeite among the products of corrosion of spent nuclear fuel.

Of the fourteen uranyl silicate minerals, nine have a U:Si ratio of 1:1; these are α -uranophane, β -uranophane, boltwoodite, kasolite, sklodowskite, cuprosklodowskite, oursinite, sodium boltwoodite, and swamboite. The structures are known for six of these; each contains sheets of edge- and corner-sharing uranyl pentagonal bipyramids and silicate tetrahedra. Soddyite, with a U:Si ratio of 2:1, involves a framework of edge-sharing uranyl pentagonal bipyramids and silicate tetrahedra. Haiweeite and weeksite both have a U:Si ratio of 1:3, and occur only as very small crystals, making structure determinations difficult. Structure models proposed for these minerals (Stohl & Smith 1981, Baturin & Sidorenko 1985, Rastsvetaeva *et al.* 1997) involve unique and unusual connectivities. Jackson & Burns (2001) reported a refined structure for weeksite. As part of our ongoing studies of uranyl minerals, the structure of haiweeite has been refined using data collected with a CCD-based detector, and the results are reported herein.

PREVIOUS STUDIES OF HAIWEEITE

Haiweeite was described by McBurney & Murdoch (1959) from the Haiwee reservoir, Coso Mountains, Inyo County, California, and has since been found at several localities in Austria, Japan, Iran and Brazil. McBurney & Murdoch (1959) reported a monoclinic unit-cell with dimensions a 15.4, b 7.05, c 7.10 Å, β 107.9°. Rastsvetaeva *et al.* (1997) proposed a structure using X-ray-diffraction data collected for a twinned microcrystal. It involved a new type of sheet of uranyl pentagonal bipyramids and silicate tetrahedra, but the model could not be fully refined, and resulted in an agreement index (R) of 11.8%, space group $P2_12_12_1$, and unit-cell dimensions a 14.263(3), b 17.988(3), c 18.395(3) Å.

EXPERIMENTAL

Haiweeite from Teofilo Otoni, Minas Gerais, Brazil was obtained from the collection of Dr. Mark Feinglos. Tufts of acicular crystals of haiweeite involved crystals attaining ~0.2 mm in length but only ~0.02 mm wide. A crystal that exhibited uniform optical properties and sharp extinction between crossed polarizers, with approximate dimensions 0.16 × 0.02 × 0.02 mm, was mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector and a crystal-to-detector distance of 5 cm. A discussion of the application of CCD detectors to the analysis of mineral structures was provided by Burns (1998).

A sphere of data was collected using monochromatic MoK α X-radiation and frame widths of 0.3° in ω , with 180 s used to acquire each frame. Several hundred frames of data were analyzed to locate diffraction maxima for determination of the unit cell. All peaks were found to be consistent with an orthorhombic C -centered unit-cell with dimensions a 7.125(1), b 17.937(2), c 18.432(2) Å, which were refined using least-squares techniques. The peaks are sharp, with no evidence of twinning. Data were collected for $3^\circ \leq 2\theta \leq 56.7^\circ$ in approximately 124 hours; comparison of the intensities of equivalent reflections collected at different times during the data collection showed no evidence of decay. The three-dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semiempirical absorption-correction was done on the basis of the intensities of equivalent reflections, with the crystal modeled as an ellipsoid. Systematic absences indicated that the unit cell is C -centered. A total of 12,378 intensities were measured; merging of equivalent reflections gave 1584 unique reflections ($R_{\text{INT}} = 8.5\%$) with 1181 classed as observed ($F_o \leq 4\sigma_F$).

Rastsvetaeva *et al.* (1997) reported a unit cell with double the a dimension obtained in the current study. Our data were carefully scrutinized and found to contain no reflections that required doubling of the a unit-cell dimension. However, subsequent solution and refinement of the structure (see below) revealed some split atomic sites, indicating that the structure model represents an average structure. Prior to publication, data were recollected for the same crystal using a new APEX detector and a goniometer equipped with a monocrapillary, resulting in significantly increased sensitivity to X-rays as compared to the first-generation CCD detector used in the original study. No reflections were found in the new data that required doubling of the a unit-cell dimension. As a further check, integration using SAINT was performed with the a dimension doubled, giving intensity values for 47,926 potential reflections that would require doubling of the a dimension if observed; none were found to be greater than three sigma. We conclude that the a dimension of the crystal studied is 7.125(1) Å.

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 Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

The systematic absences and reflection statistics are consistent with space groups *Cmcm*, *Cmc2₁*, and *Ama2*. The structure was solved by direct methods in all three space groups, and models that initially included only the positions of the U cations were extended by inspection of difference-Fourier maps calculated after refinement of the models. In each space group, displacement of some atoms from special positions and partial occupancies of some sites were required to obtain a crystal-chemically realistic structure. The space group *Cmcm* provided the best model, on the basis of more realistic polyhedron geometries and the agreement factor (*R*1), which was ~1.0% lower than those for any of the other models. We therefore conclude that the space group of the long-range structure is *Cmcm*, but displacement of some atoms from special positions indicates that a lower symmetry occurs locally in the structure. An *R*1 value of 8.9% was obtained for a model that included all atomic positional parameters and that accounted for isotropic displacement of the atoms. The displacement parameters for all atoms except O(8) were converted to anisotropic forms, and were refined, together with the positional parameters for all atoms and a weighting scheme (Table 1) of the structure factors, resulting in a final *R* index of 4.2%, calculated for the 1181 unique observed reflections ($F_o \geq 4\sigma_F$), and a goodness-of-fit (*S*) of 0.96. Attempts to refine the anisotropic displace-

TABLE 1. MISCELLANEOUS INFORMATION CONCERNING HAIWEEITE

<i>a</i> (Å)	7.125(1)	Crystal size (mm)	0.16 x 0.02
<i>b</i> (Å)	17.937(2)		x 0.02
<i>c</i> (Å)	18.342(2)	Total ref.	12,378
<i>V</i> (Å ³)	2344.3(7)	Unique ref.	1584
Space group	<i>Cmcm</i>	<i>R_m</i> (%)	8.5
<i>F</i> (000)	1800	Unique $ F_o \geq 4\sigma_F$	1181
μ (mm ⁻¹)	14.4	Final <i>R</i> 1 (%)	4.2
<i>D_{calc}</i> (g/cm ³)	2.835	<i>S</i>	0.96
Unit-cell contents: 4[Ca[(UO ₂) ₂ Si ₂ O ₁₂ (OH) ₂](H ₂ O) ₃]			
<i>R</i> 1 = $\Sigma(F_o - F_c) / \Sigma F_o $			
<i>S</i> = $[\Sigma w(F_o - F_c)^2 / (m - n)]^{1/2}$, for <i>m</i> = 1181 obs. and <i>n</i> = 129 param.			
$w = 1 / [\sigma^2(F_o^2) + (0.0754 \times P)^2 + 50.93P]$, $P = (\max(F_o^2, 0) + 2 \times F_c^2) / 3$			

ment parameters for O(8) resulted in physically unrealistic values. In the final cycle of refinement, the average parameter shift/esd was 0.000. The final atom-position parameters and anisotropic-displacement parameters are given in Table 2, and selected interatomic distances and angles are given in Table 3. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Projection of the structure along [100] reveals uranyl silicate sheets parallel to (001), with Ca and H₂O groups in the interlayer (Fig. 1).

Cation polyhedra

The structure of haiweeite contains two symmetrically distinct U⁶⁺ cations, each of which is strongly

TABLE 2. FINAL ATOMIC PARAMETERS FOR HAIWEEITE

	<i>x</i>	<i>y</i>	<i>z</i>	* <i>U_{eq}</i>	** <i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₁₂</i>	<i>U₁₃</i>	<i>U₂₃</i>
U(1)	0	0.39036(4)	¼	126(2)	77(3)	85(3)	215(4)	0	0	0
U(2)	½	0.28612(3)	¼	149(2)	89(3)	91(3)	266(5)	0	0	0
Si(1)	0	0.2148(2)	¼	169(12)	95(23)	11(22)	399(36)	0	0	0
Si(2)	½	0.4608(3)	¼	230(13)	69(22)	93(24)	527(41)	0	0	0
Si(3) [#]	0.1079(7)	0.0871(3)	0.3524(3)	161(10)	88(22)	170(23)	224(26)	17(19)	16(18)	1(19)
Si(4) [#]	0	0.5858(4)	0.2744(4)	125(14)	90(27)	63(27)	222(36)	0	0	-7(24)
Ca(1) [#]	0	0.3887(4)	0.4850(4)	404(18)	726(57)	270(33)	219(33)	0	0	-33(24)
O(1)	0	0.1606(6)	0.3212(6)	285(24)	274(56)	217(52)	365(66)	0	0	143(46)
O(2)	½	0.5154(6)	0.3199(8)	360(29)	203(53)	188(53)	690(91)	0	0	-72(56)
O(3)	0.324(1)	0.4049(5)	¼	272(24)	90(43)	136(45)	591(75)	-37(37)	0	0
O(4)	0.177(1)	0.2703(5)	¼	258(22)	79(41)	123(42)	573(70)	-26(37)	0	0
O(5)	0	0.3899(9)	0.3470(7)	477(38)	371(74)	840(112)	220(67)	0	0	-177(64)
O(6) [#]	0	0.509(1)	0.274(1)	295(51)	312(110)	421(129)	153(104)	0	0	122(80)
O(7)	½	0.2873(8)	0.3485(7)	409(34)	286(64)	715(101)	226(64)	0	0	139(55)
O(8) [#]	½	0.1623(9)	0.2727(8)	126(37)						
O(9) [#]	-0.176(2)	0.5845(8)	0.3316(9)	285(34)	98(61)	339(84)	417(91)	-45(58)	87(60)	5(67)
OH(10) [#]	0.083(2)	0.088(1)	0.4390(9)	428(45)	241(75)	746(133)	297(89)	64(83)	127(70)	-62(82)
H ₂ O(11) ^{&}	0.172(6)	0.092(2)	0.551(2)	633(153)	686(271)	1108(367)	105(151)	-791(266)	-110(159)	164(172)
H ₂ O(12) ^{&}	0.102(8)	0.271(2)	0.453(2)	929(233)	2047(675)	427(209)	314(194)	760(309)	17(257)	-155(161)
H ₂ O(13) ^{&}	-0.107(5)	0.520(2)	0.422(2)	474(169)	510(220)	353(183)	557(227)	-54(169)	255(189)	-166(167)

U_{eq}* = *U_{eq}* Å² × 10⁴, *U_{ij}* = *U_{ij}* Å² × 10⁴, #positions 50% occupied, &positions 25% occupied

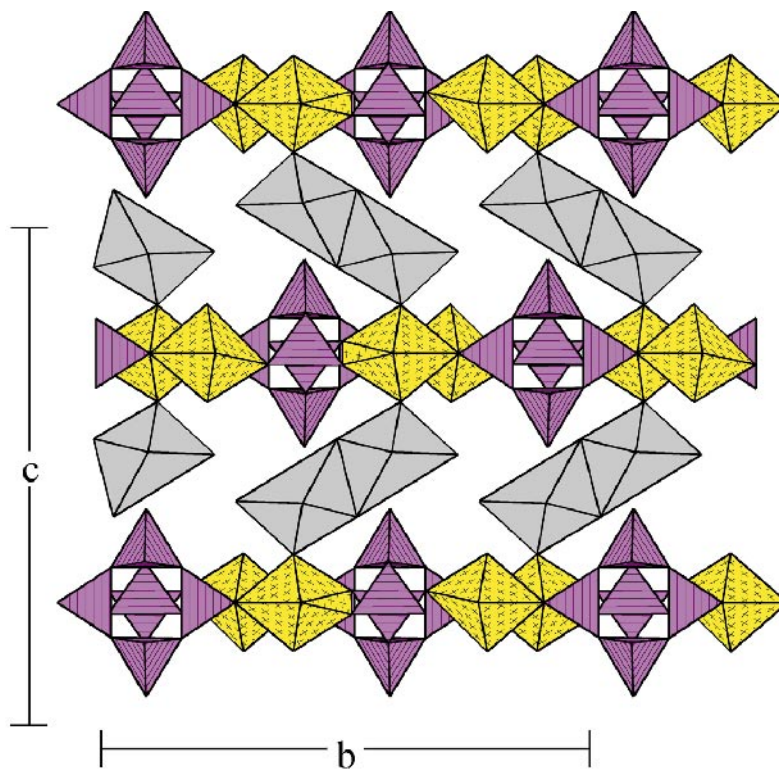


FIG. 1. Polyhedral representation of the structure of haiweeite projected along [100]. The Si tetrahedra are red, uranyl polyhedra are yellow, and Ca polyhedra are gray.

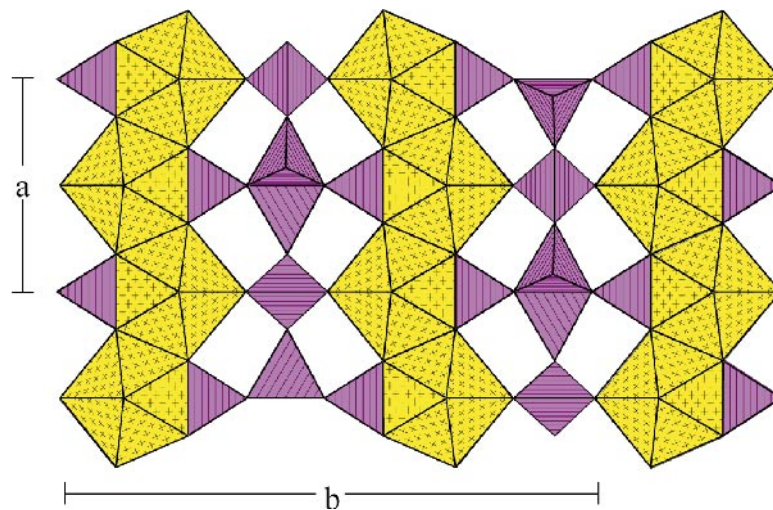


FIG. 2. Polyhedral representation of the uranyl silicate sheet that occurs in haiweeite. Legend as in Figure 1.

bonded to two atoms of O, forming nearly linear $(\text{UO}_2)^{2+}$ uranyl ions (U_r) with $\text{U}-\text{O}_{U_r}$ bond lengths ≈ 1.8 Å, as is normally the case in structures that contain U^{6+} . Each U^{6+} cation is coordinated by five additional atoms of O that are arranged at the equatorial corners of pentagonal bipyramids capped by the O_{U_r} atoms. The O(6) and O(8) atoms, which occur at equatorial positions of the U(1) and U(2) polyhedra, respectively, are displaced off the mirrors owing to disorder of the silicate tetrahedra (see below). The uranyl pentagonal bipyramid is the most common coordination polyhedron observed about U^{6+} in minerals, and is the only one known in uranyl silicate minerals (Burns *et al.* 1997). The $\langle \text{U}-\text{O}_{eq} \rangle$ bond lengths, 2.36 and 2.37 Å for the U(1) and U(2) sites, respectively, compare favorably with the average of 2.37(9) Å obtained from numerous well-refined structures that contain uranyl pentagonal bipyramids (Burns *et al.* 1997).

There are four symmetrically distinct Si positions, each of which is tetrahedrally coordinated by anions. The Si(1) and Si(2) sites are coordinated only by atoms of O, with $\langle \text{Si}-\text{O} \rangle$ bond lengths of 1.62 and 1.61 Å,

respectively. The Si(3) and Si(4) cations are both displaced from their corresponding special positions. The Si(3) cation is displaced from the $8f$ position, resulting in a Si(3)–Si(3) separation of 1.54(1) Å. The Si(4) cation is displaced from the $4c$ position, with a corresponding Si(4)–Si(4) separation of 0.89(1) Å. In each case, only one of the symmetry-related pairs of sites is occupied locally. Splitting of the O(6), O(8), O(9) and OH(10) positions is associated with the disorder of the Si(3) and Si(4) cations.

Connectivity of the sheets of polyhedra

The uranyl pentagonal bipyramids share edges to form chains parallel to $[100]$ that are one polyhedron wide (Fig. 2). Each uranyl polyhedron shares an edge with a silicate tetrahedron, and the tetrahedra are staggered along the chain length (Fig. 2). Similar chains occur in α -uranophane, β -uranophane, sklodowskite, cuprosklodowskite, kasolite, and boltwoodite. However, in those structures the chains are linked to form sheets that are much different from the haiweeite sheet.

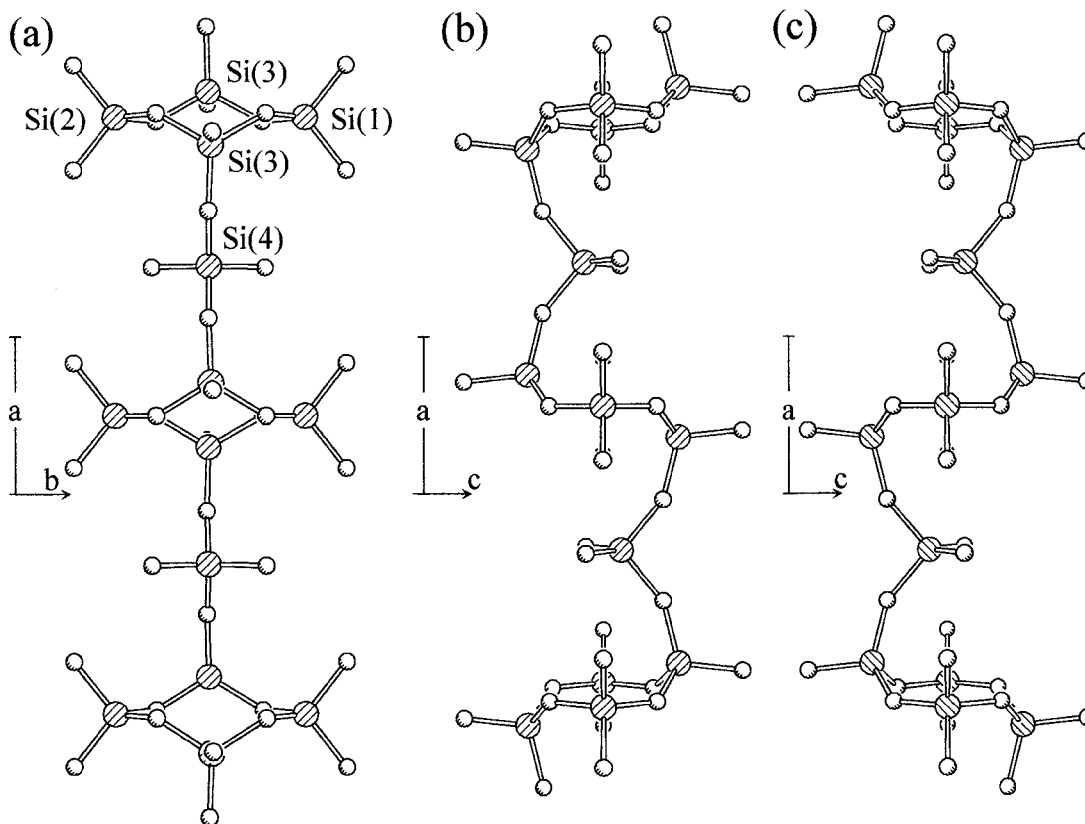


FIG. 3. Chains of silicate tetrahedra that occur in haiweeite. Si cations are shaded with parallel lines, O atoms are shaded in the lower-left or lower-right corners. See text for discussion.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR HAIWEEITE

U(1)-O(5) _a	1.78(1) x2	Si(1)-O(4) _b	1.605(9) x2
U(1)-O(6)	2.18(2)	Si(1)-O(1) _a	<u>1.63(1)</u> x2
U(1)-O(3) _b	2.324(9) x2	<Si(1)-O>	1.62
U(1)-O(4) _b	<u>2.49(1)</u> x2		
<U(1)-O ₆ >	1.78	Si(2)-O(3) _c	1.61(1) x2
<U(1)-O ₆ >	2.36	Si(2)-O(2) _a	<u>1.63(1)</u> x2
O(5)-U(1)-O(5) _a	179(1)	<Si(2)-O>	1.61
U(2)-O(7) _a	1.81(1) x2	Si(3)-O(9) _d	1.59(1)
U(2)-O(8)	2.26(2)	Si(3)-OH(10)	1.60(2)
U(2)-O(4) _c	2.320(9) x2	Si(3)-O(2) _e	1.61(1)
U(2)-O(3) _c	<u>2.472(9)</u> x2	Si(3)-O(1)	<u>1.63(1)</u>
<U(2)-O ₇ >	1.81	<Si(3)-φ>	1.61
<U(2)-O ₇ >	2.37		
O(7)-U(2)-O(7) _a	178.7(9)	Si(4)-O(8) _f	1.62(2)
		Si(4)-O(6) _a	1.63(2)
Ca-H ₂ O(12) _b	2.30(3) x2	Si(4)-O(9) _b	<u>1.63(1)</u> x2
Ca-H ₂ O(11) _{g,h}	2.45(4) x2	<Si(4)-O>	1.63
Ca-H ₂ O(13) _{i,j}	2.48(4) x2		
Ca-O(5)	2.53(1)	O(9) _d -Si(3)-OH(10)	110.2(9)
Ca-H ₂ O(13) _b	2.74(4) x2	O(9) _d -Si(3)-O(2) _e	110.5(7)
		O(9) _d -Si(3)-O(1)	113.4(7)
O(4)-Si(1)-O(4) _b	103.4(7)	OH(10)-Si(3)-O(2) _e	108.6(9)
O(4) _b -Si(1)-O(1) _a	111.7(3) x4	OH(10)-Si(3)-O(1)	107.0(8)
O(1)-Si(1)-O(1) _a	<u>106.7(9)</u>	O(2) _e -Si(3)-O(1)	<u>106.9(6)</u>
<O-Si(1)-O>	109.5	<φ-Si(3)-φ>	109.4
O(3)-Si(2)-O(3) _c	102.7(7)	O(8) _f -Si(4)-O(6) _a	115(1)
O(3) _c -Si(2)-O(2) _a	112.3(3) x4	O(8) _f -Si(4)-O(9) _b	110.7(7) x2
O(2)-Si(2)-O(2) _a	<u>105.3(9)</u>	O(6) _a -Si(4)-O(9) _b	109.7(7) x2
<O-Si(2)-O>	109.5	O(9)-Si(4)-O(9) _b	<u>100(1)</u>
		<O-Si(4)-O>	109.3

a = x, y, 1/2-z; b = -x, y, z; c = 1-x, y, z; d = x+1/2, y-1/2, z; e = x-1/2, y-1/2, z; f = x-1/2, y+1/2, 1/2-z; g = x-1/2, 1/2-y, 1-z; h = 1/2-x, 1/2-y, 1-z; i = -x, 1-y, 1-z; j = x, 1-y, 1-z

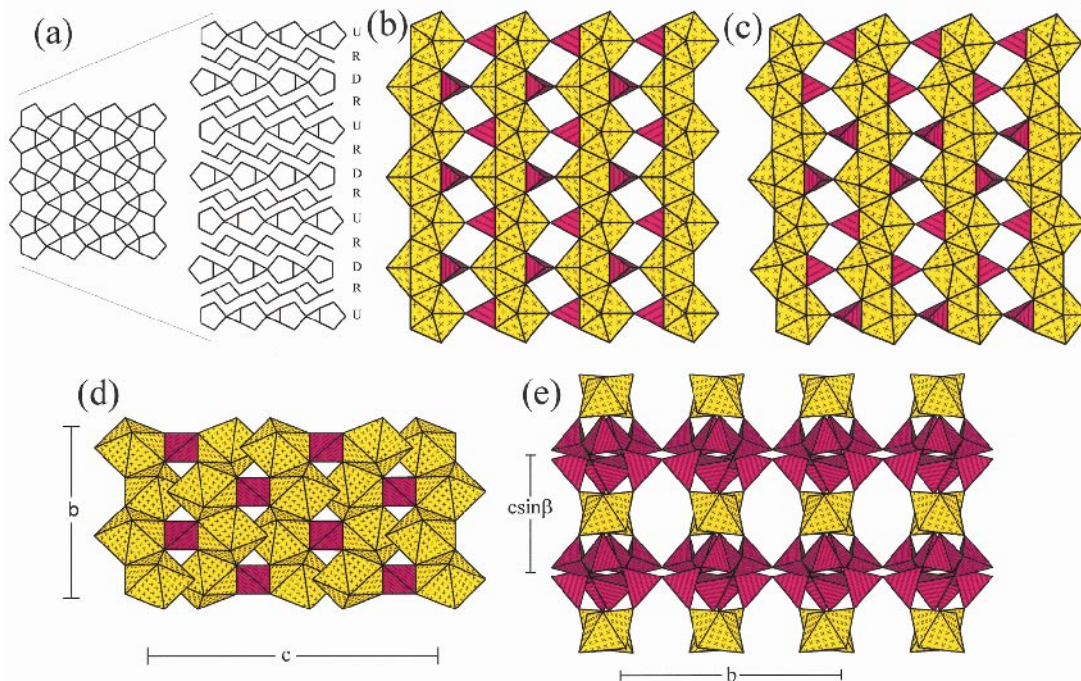


FIG. 4. Structures of uranyl silicates. (a) The uranophane anion-topology and representation of anion topology as a chain-stacking sequence. (b) The sheet that occurs in α -uranophane, boltwoodite, sklodowskite, cuprosklodowskite, and kasolite, all of which have a U:Si ratio of 1:1. (c) The sheet that occurs in β -uranophane with a U:Si ratio of 1:1. (d) The structure of soddyite with a U:Si ratio of 2:1. (e) The structure of a synthetic uranyl silicate with U:Si ratio of 1:4. Legend as in Figure 1.

Adjacent chains of uranyl polyhedra and silicate tetrahedra are cross-linked to form sheets that are parallel to (001) by sharing corners with the Si(3) and Si(4) tetrahedra, giving a chain of tetrahedra parallel to [100] (Fig. 2), as proposed by Rastsvetaeva *et al.* (1997). The Si(1), Si(2) and Si(3) tetrahedra share vertices, forming four-membered rings, with linkage between the rings provided by vertex-sharing with the Si(4) tetrahedron. The Si(4) tetrahedron also shares two vertices with uranyl polyhedra. The positional disorder of the Si(3) and Si(4) tetrahedra is associated with the occurrence of the chain in two orientations, as shown in Figures 3b and 3c. It is likely that the crystal of haiweeite studied has a domain structure associated with correlation of the orientations of the silicate chains. Information concerning the details of such domains might be attainable using transmission electron microscopy.

The interlayer

The interlayer contains one symmetrically distinct Ca cation and three H₂O groups. The site-scattering refinement indicated the Ca site is 51(1)% occupied, and the H₂O(12) and H₂O(13) groups are displaced from their corresponding special positions. The Ca is in a

highly distorted octahedral coordination comprised of five H₂O groups and an O_{Ur} anion, and Ca(O,H₂O)₆ octahedra share an edge to form a dimer. Adjacent uranyl silicate sheets are linked through the Ca dimers, as well as by H bonding.

Comparison to the structure model proposed by Rastsvetaeva et al.

The structure model proposed by Rastsvetaeva *et al.* (1997) involves the same connectivity of polyhedra as found in the current study, but differs in the space group and unit cell. As detailed above, no reflections could be found in the CCD-detector-collected data to support doubling of the *a* dimension, as reported by Rastsvetaeva *et al.* (1997). Our data are consistent with a *C*-centered cell, in contrast to the primitive cell used by Rastsvetaeva *et al.* (1997). Our refinement resulted in a significantly lower *R* value, and the bond lengths are about an order of magnitude more precise than those reported by Rastsvetaeva *et al.* (1997). The differences in the structure models derived from the two studies probably arise from the nature of the crystals studied. We collected data for what appears to be a single crystal; no peak splitting was observed, and all reflections could be indexed using a single orientation. In contrast, Rastsvetaeva *et al.* (1997) reported that the crystal they studied contained a “block” structure, that there were split and partially overlapping peaks in the diffraction pattern, and that it was not possible to index all reflections using a single orientation. Thus, it is possible that twinning introduced artifacts into the data of Rastsvetaeva *et al.* (1997).

COMPARISON OF URANYL SILICATE STRUCTURES

Uranyl silicates with a 1:1 U:Si ratio (α -uranophane, β -uranophane, boltwoodite, kasolite, sklodowskite, cuprosklodowskite) contain uranyl silicate sheets (Figs. 4b, c) that are based on the uranophane anion-topology (Burns *et al.* 1996). The anion topology can be obtained using a chain-stacking sequence of arrowhead (U and D) and R chains (see Burns 1999 for definitions), with adjacent arrowhead chains pointing in opposite directions (Fig. 4a). Several populations of the anion-topology are known from minerals and synthetic compounds, but only two are found in uranyl silicates. The β -uranophane-type sheet (Fig. 4c) occurs only in β -uranophane, whereas the α -uranophane-type sheet (Fig. 4b) occurs in five minerals. In both sheets the pentagons in the anion topology are populated by uranyl ions, resulting in chains of edge-sharing pentagonal bipyramids. Triangles in the anion topology become the faces of tetrahedra that are attached to the chains by edge-sharing with uranyl polyhedra, and are staggered along the chain length. The α - and β -type sheets are distinguished by the orientations of the tetrahedra (Figs. 4b, c). Tetrahedra attached to one side of the chain

of uranyl polyhedra in the α -uranophane sheet all have apices pointing in one direction, whereas the tetrahedra attached to the other side of the chain are in the opposite orientation. In contrast, the orientations of the silicate tetrahedra alternate along each side of the chain of uranyl polyhedra in the β -uranophane sheet.

Soddyite, with a U:Si ratio of 2:1, has a structure based on a framework of polymerized polyhedra (Fig. 4d). All U in the structure is in pentagonal bipyramidal coordination, with the uranyl polyhedra sharing edges to form chains, which are linked into a framework by sharing edges with silicate tetrahedra.

Burns *et al.* (2000) found a new uranyl silicate as a corrosion product of actinide-bearing borosilicate waste glass. With the formula KNa₃(UO₂)₂(Si₄O₁₀)₂(H₂O)₄, the phase has a U:Si ratio of 1:4. Uranyl square bipyramids occur in the structure, making this the only known hydrated uranyl silicate with U⁶⁺ in this coordination. Four-membered rings of silicate tetrahedra link to four additional four-membered rings by vertex-sharing, giving a sheet that contains eight-membered rings, in addition to the four-membered rings. Uranyl square bipyramids between the sheets of silicate tetrahedra link to four silicate tetrahedra each, two in each adjacent sheet (Fig. 4e). The uranyl ions are oriented subparallel to the sheets, and do not link to the silicate tetrahedra. The structure is best described as a framework of polyhedra of higher bond-valence, although it is dominated by the sheets of silicate tetrahedra.

The structure of weeksite (Stohl & Smith 1981, Baturin & Sidorenko 1985, Jackson & Burns 2001) has a connectivity similar to that found in haiweeite. The main difference is that the uranyl silicate sheets are linked by vertex-sharing involving silicate tetrahedra, resulting in an open framework structure.

There is an obvious structural trend in hydrated uranyl silicates that is related to the U:Si ratio. Uranyl silicates with U:Si ratios of 2:1 and 1:1 do not involve polymerization of the silicate tetrahedra, those with a ratio of 1:3 contain chains of vertex-sharing silicate tetrahedra, and the synthetic phase with a ratio of 1:4 contains a sheet of silicate tetrahedra. The mode of polymerization of the silicate tetrahedra with uranyl polyhedra is also related to the U:Si ratio. In soddyite, with a ratio of 2:1, each silicate tetrahedron shares two of its edges with uranyl polyhedra, but in structures with a ratio of 1:1, only one edge of each silicate tetrahedron is shared with a uranyl polyhedron, and each tetrahedron links to another uranyl polyhedron by vertex-sharing. In structures with a ratio of 1:3, some silicate tetrahedra share a single edge with a uranyl polyhedron, whereas others do not share polyhedron elements with uranyl polyhedra. Finally, in the synthetic structure with the ratio 1:4, only vertex sharing occurs between uranyl polyhedra and silicate tetrahedra, but all four equatorial vertices of the uranyl square bipyramids are shared with silicate tetrahedra of adjacent sheets.

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