The crystal chemistry of the uranyl silicate minerals

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Abstract

The uranyl silicate minerals have been divided into three groups on the basis of their uranium to silicon ratios. The 1:1 group includes uranophane, beta-uranophane, boltwoodite, sodium boltwoodite, kasolite, sklodowskite, and cuprosklodowskite. A structure refinement of uranophane, a structure determination of boltwoodite, and previously reported structure determinations of most of these minerals indicate that they are composed of uranyl silicate chains made of edge-shared uranium pentagonal bipyramidal groups and silicate tetrahedra. These chains have the composition $[(UO_2)(SiO_4)]_n^{-2n}$ and are crosslinked by a bridging oxygen atom to form a uranyl silicate sheet. These sheets are crossbonded by the additional cations in the structure. The uranyl minerals with a uranium to silicon ratio of 1:3 include weeksite and haiweeite. A partial structure analysis of weeksite suggests that the structure type for this group consists of uranyl silicate chains, similar to those found in the 1:1 group, that are crosslinked by the additional silicate tetrahedra in the structure. The uranyl mineral group with a uranium to silicon ratio of 2:1 contains only the mineral soddyite. This structure is composed of uranyl silicate chains that are crossbonded by sharing a common silicon to give a three-dimensional framework structure. A new triclinic uranyl silicate mineral was discovered during this study, although there is not enough sample to describe it adequately. The locations of the uranium atoms in this structure indicate that it may not be composed of uranyl silicate chains such as those found in all the other uranyl silicate minerals.

Introduction

The known uranyl silicate minerals can be divided into several categories on the basis of their uranium to silicon ratios (Table 1). Three categories, with uranium to silicon ratios of 1:1, 1:3, and 2:1, are well defined as reported by Stohl (1974) and Stohl and Smith (1974). The minerals listed in Table 1 are the only accepted uranyl silicates as indicated by Fleischer (1980).

1:1 Uranyl silicate group

Structure determinations were carried out for six of the members of the group with a uranium to silicon ratio of 1:1. The structure of uranophane was originally determined by Smith *et al.* (1957), and is revised in this study. The structure of beta-uranophane was determined by Smith and Stohl (1972). A structure analysis of boltwoodite was carried out

during this study. The structure of kasolite was originally determined by Huynen *et al.* (1963), and was revised by Mokeeva (1965), and by Rosenzweig and Ryan (1977). The sklodowskite structure was analyzed by Mokeeva (1959), and refined by Huynen and Van Meerssche (1962), by Mokeeva (1964), and by Ryan and Rosenzweig (1977). The cuprosklodowskite structure was originally determined by Piret–Meunier and Van Meerssche (1963), and was revised by Rosenzweig and Ryan (1975). The formulas listed in Table 1 for uranophane and boltwoodite are based on this work whereas the other formulas come from the most recent structural papers for each mineral.

The description, properties, and cell constants of sodium boltwoodite were reported by Chernikov *et al.* (1975). There has not been any structure work on this mineral. Its cells constants, however, are very similar to those of the other 1:1 uranyl silicate minerals, indicating that it probably contains the same uranyl silicate sheets.

Table 1. Members of the uranyl silicate mineral group separated on the basis of their uranium to silicon ratios

Uranium:Silicon Ratios			Questionable composition
1:1	1:3	2:1	
Uranophane $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 2H_2O$	Weeksite $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$	Soddyite $(UO_2)_2(SiO_4) \cdot 2H_2O$	New mineral
Beta-uranophane $Ca(UO_2)(UOOH)(SiO_4)(SiO_3OH) \cdot 4H_2O$	Haiweeite $Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$		
Boltwoodite $K(H_3O)(UO_2)(SiO_4)$			
Na boltwoodite $(Na_{0.7}K_{0.3})(H_3O)(UO_2)(SiO_4) \cdot H_2O$			
Kasolite $Pb(UO_2)(SiO_4) \cdot H_2O$			
Sklodowskite $Mg(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 4H_2O$			
Cuprosklodowskite $Cu[(UO_2)_2(SiO_3OH)_2] \cdot 6H_2O$			

1:3 Uranyl silicate group

The formulas for the two known 1:3 uranyl silicate minerals that are listed in Table 1 were taken from Fleischer (1980). The mineral weeksite, which was originally called gastunite by Honea (1959), was described by Outerbridge *et al.* (1960) and was named for Dr. Alice Weeks. The name weeksite was retained due to the many conflicting descriptions of gastunite that have been reported. The composition of this mineral is usually written with Si_6O_{15} groups on the basis of infrared data and chemical analyses.

Haiweeite was named for its type locality near the Haiwee Reservoir in the Coso Mountains, California, and was described by McBurney and Murdock (1959). The composition was originally reported as $CaO \cdot 2UO_3 \cdot 6SiO_2 \cdot 5H_2O$, although these authors indicated that the spherulitic aggregates of crystals are probably made up of two minerals with varying water contents. The inner part of the spherulite, with higher indices of refraction, was considered to be meta-haiweeite and can be produced from the outer material by heating. However, meta-haiweeite has not been adequately described and has therefore not been accepted as a mineral (M. Fleischer, Smithsonian Institution, personal communication). Outerbridge *et al.* (1960) showed that there is a very strong similarity between the powder patterns of weeksite and haiweeite.

The mineral ranquilite, which was reported by Abeledo *et al.* (1960), is actually haiweeite and has been discredited (Fleischer, 1980). Ursilite $(Ca,Mg)_2(UO_2)_2(Si_3O_{14}) \cdot 9H_2O$ (Chernikov *et al.*, 1957) has not been adequately described and is not accepted as a mineral (M. Fleischer, Smithsonian Institution, personal communication). There are no previously reported structure determinations in the 1:3 group.

2:1 Uranyl silicate group

The only known mineral that occurs in the 2:1 uranium to silicon group is soddyite. This mineral was originally described by Schoep (1922) from Kasolo, Zaire, and was named in honor of the English radiochemist Frederick Soddy. Gorman (1952) described the physical properties, morphology, and powder pattern of soddyite. He indicated that it usually occurs as zoned transparent and opaque material, both of which have the same powder patterns. The crystal structure of soddyite was originally proposed by Stohl (1974) and Stohl and Smith (1974) on the basis of a partial structure analysis of a synthetic hydrated uranyl germanate analogue that was reported by Legros *et al.* (1972). The proposed soddyite structure is essentially identical to the completed uranyl germanate structure reported in Legros and Jeannin (1975). The proposed soddyite structure was sub-

stantiated by a structure analysis carried out on a synthetic soddyite crystal by Belokoneva *et al.* (1979). The formula for soddyite in Table 1 is based on this crystal structure.

New mineral

The new mineral that was discovered during this research has an appearance and powder pattern very similar to soddyite. A chemical analysis cannot be carried out due to the small amount of sample.

The 1:1 group of uranyl silicates

The refinement of uranophane

The composition $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 5H_2O$ occurs in two polymorphic forms as the minerals uranophane and beta-uranophane. The structure of uranophane was originally determined by Smith *et al.* (1957), although they were not successful in locating the water molecules. They suggested the possible presence of hydronium ions to balance the charge. A structure analysis of beta-uranophane by Smith and Stohl (1972) indicated that the extra hydrogen atoms in the structure that are necessary to balance the charge might be bonded to the free uranyl oxygen atoms and the free oxygen atoms of the silicate tetrahedron as indicated by the formula in Table 1. Therefore, a structure refinement of uranophane was carried out in order to locate the water molecules and thereby clarify the relationships between these two minerals.

A very high quality, clear crystal from Shinkolobwe, Katanga was selected for the structure refinement. This very small crystal, measuring $10 \times 12 \times 215$ μm, was chosen to minimize absorption effects. The refined cell constants, which were obtained during the alignment segment of data collection on a Picker FACS–1 four-circle diffractometer, are shown in Table 2. This structure refinement substantiated the $P2_1$ space group that was reported by Smith *et al.* (1957). The $P2_1/a$ pseudosymmetry was also substantiated because the $(h0l)$ reflections with h odd are much weaker than the $(h0l)$ reflections with h even. A data set consisting of 525 independent reflections with a maximum 2θ value of $35°$ was measured using $MoK\alpha$ radiation. Measurable intensities could not be obtained above $35°$ 2θ because of the small crystal size. Thirty-two of the reflections were unobserved, and their observed structure factors were set at zero. The intensities were corrected for absorption effects and Lorentz-polarizaton effects using the program ACAC by Wuensch and Prewitt (1965). The atom locations reported by Smith *et al.* (1957) were refined

using the full matrix least squares program ORFLS by Busing *et al.* (1962). These refined atom positions were used to calculate a three-dimensional Fourier map and a three-dimensional difference Fourier map which showed the locations of four possible oxygens, from water molecules, in the general positions of $P2_1$ around the calcium atoms at distances of approximately 2.4 to 2.6Å. Throughout this analysis, all the atoms in the sheet were refined using the restrictions of the pseudosymmetry, whereas the calcium atoms and oxygens from the water molecules were refined using the $P2_1$ space group. A refinement of this entire structure with isotropic temperature factors gave $R = 0.081$. The observed and calculated structure factors are given in Table 3.[2] The hydrogen atoms could not be located. The largest electron differences in the final difference Fourier were less than 1/2 electron/Å[3]. Table 4 lists the atomic coordinates and isotropic temperature factors for the atoms of uranophane, and Table 5 shows the bond distances and angles in the structure. The high temperature factors shown in Table 4 are normal for uranyl silicate structure determinations. Figure 1 shows a stereo view of the sheet structure.

Structure determination of boltwoodite

The sample used in this analysis is from the New Method Mine in Amboy, California, and was lent to the authors by Paul Moore of the University of Chicago. The identification of this sample was verified by comparing its Guinier powder pattern to a pattern of the type material from the Delta Mine on the southern edge of the San Rafael Swell, Emery County, Utah (U.S. Museum sample number 112710). This comparison proved that the sample used in this analysis was boltwoodite, and also substantiated the fact that the powder pattern of boltwoodite reported by Honea (1961) (PDF 13–218 and 29–1026) contained several extra lines (7.53Å, 3.91Å, 3.75Å, and 2.08Å). The 7.53Å line is probably a gypsum peak and the 3.91Å line is probably a brochantite peak. These two minerals are found in association with the type material. Table 6 shows the *d*-spacings measured from Guinier powder patterns of the New Method Mine sample and the type material, and a pattern that was calculated from the present

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[2]To receive a copy of Table 3, order Document AM-81-156 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue NW, Washington, DC 20009. Please remit $1.00 in advance for the microfiche.

Table 2. The crystallographic data for the 1:1 minerals. The listings of the cell constants for beta-uranophane and cuprosklodowskite have been shifted so that they can be easily compared to the structurally equivalent values in the other minerals

Uranophane[1]	Beta-uranophane[2]	Boltwoodite[3]	Na: boltwoodite[4]
a = 15.858±0.015Å	b = 15.394±0.014Å	a = 7.073±0.002Å	a = 27.40±0.05Å
b = 6.985±0.007	a = 13.898±0.011	b = 7.064±0.001	b = 7.02±0.02
c = 6.641±0.005	c = 6.609±0.005	c = 6.638±0.001	c = 6.65±0.02
β = 97°33'±2'	β = 91°25'±1'	β = 105°45'±1'	
$P2_1$	$P2_1/a$	$P2_1$	$P2_12_12_1$
Fiber parallel b	Fiber parallel a	Fiber parallel b	
Sheet parallel (100)	Sheet parallel (010)	Sheet parallel (100)	

Kasolite[5]	Sklodowskite[6]	Cuprosklodowskite[7]	
a = 6.704±0.002Å	a = 17.382±0.006Å	b = 9.267±0.008Å	
b = 6.932±0.002	b = 7.047±0.001	a = 7.052±0.005	
c = 13.252±0.007	c = 6.610±0.002	c = 6.655±0.005	
β = 104°13'±2'	β = 105°54'±12'	α = 109°14'±3'	
		β = 89°50'±3'	
		γ = 110°1' ±4'	
$P2_1/c$	$C2/m$	$P\bar{1}$	
Fiber parallel b	Fiber parallel b	Fiber parallel a	
Sheet parallel (100)	Sheet parallel (100)	Sheet parallel (010)	

References: 1. This work; 2. Smith and Stohl (1972); 3. This work; 4. Chernikov *et al*. (1975); 5. Rosenzweig and Ryan (1977); 6. Ryan and Rosenzweig (1977); 7. Rosenzweig and Ryan (1975).

structure determination using a program from Smith (1963). The cell constants for boltwoodite (Table 2) that were used to calculate the *d*-spacings for this powder pattern were obtained from a least squares refinement of the underlined Guinier powder data for the type material. This refinement was carried out with a program by Appleman and Evans (1973). The cell constants determined during the alignment segment of single crystal data collection are not reported because the intensities for most reflections were very weak.

All of the boltwoodite crystals analyzed by precession and Weissenberg techniques were twinned. The two overlapping lattices, which had reflections of the type $(hk\bar{h})$ in common, were related by reflection across $(10\bar{1})$. The only systematic extinctions were $(0k0)$ with $k = 2n+1$, so that the possible space groups were $P2_1$ or $P2_1/m$. The twinned crystal used in this structure determination measured $20\times15\times115$ μm and had no sphenoidal terminations. A data set consisting of all possible reflections up to a 2θ value of 35° was collected from the twin lattice with the greater intensity. A total of 223 independent reflections, including 22 multiple reflections with a component from each twin, was measured with MoKα radiation. A comparison of intensities of the two lattices indicated that the reflections of one lattice had an average intensity of approximately 25 percent

of the intensity of the equivalent reflections of the predominant lattice. In the initial stages of structure analysis, 20 percent of the intensity of overlapping twin reflections was subtracted, whereas in the final stages of analysis, these reflections were omitted. Only an approximate absorption correction was carried out using the program ACAC because the twinning was not visible optically, and therefore the volume distribution of the twins was unknown.

The structure was solved from a three-dimensional Patterson map. The uranium, silicon, and oxygen atoms were located in positions which indicated a sheet structure very similar to that in uranophane. The two potassium atoms in the unit cell were located in general positions binding the sheets together and proving that the space group had to be $P2_1$. However, it was not possible to refine the y coordinates for the uranium and silicon atoms because the y coordinates kept switching back and forth across the mirror plane which would be present if the symmetry were $P2_1/m$. In addition, oxygens 3 and 3B showed very high correlation coefficients between their x and z coordinates, indicating that the uranyl silicate sheet has $P2_1/m$ pseudosymmetry. The presence of the potassium atoms and hydronium ions therefore causes the symmetry to degenerate from $P2_1/m$ to $P2_1$. The final R-factor which was calculated with isotropic temperature factors is 0.109. The

Table 4. Atomic coordinates for uranophane. The space group is $P2_1$. (Standard errors in parentheses.)

Atom	x	y	z	B
U(1)	0.2557(2)	0.7822(6)	0.1344(5)	0.8(1)
U(2)	-0.2557(2)	-0.7822(6)	-0.1344(5)	0.8(1)
Si(1)	0.284(1)	0.281(4)	0.339(3)	0.8(5)
Si(2)	-0.284(1)	-0.281(4)	-0.339(3)	0.8(5)
O(1)	0.371(3)	0.795(9)	0.138(8)	2.7(13)
O(2)	-0.371(3)	-0.795(9)	-0.138(8)	2.7(13)
O(3)	0.143(3)	0.757(9)	0.123(8)	1.3(12)
O(4)	-0.143(3)	-0.757(9)	-0.123(8)	1.3(12)
O(5)	0.271(4)	0.453(9)	0.187(9)	2.1(13)
O(6)	-0.271(4)	-0.453(9)	-0.187(9)	2.1(13)
O(7)	0.258(4)	0.095(9)	0.181(8)	2.1(13)
O(8)	-0.258(4)	-0.095(9)	-0.181(8)	2.1(13)
O(9)	0.229(3)	0.292(9)	0.523(8)	1.0(12)
O(10)	-0.229(3)	-0.292(9)	-0.523(8)	1.0(12)
O(11)	0.381(3)	0.272(9)	0.432(8)	2.2(13)
O(12)	-0.381(3)	-0.272(9)	-0.432(8)	2.2(13)
$H_2O(1)$	0.069(3)	0.345(10)	0.359(8)	3.6(15)
$H_2O(2)$	0.991(3)	0.010(9)	0.196(8)	1.1(12)
$H_2O(3)$	0.936(3)	0.610(9)	0.558(8)	2.9(14)
$H_2O(4)$	0.993(4)	0.507(10)	0.945(7)	2.6(14)
Ca	0.019(1)	0.672(3)	0.280(3)	2.9(5)

observed and calculated structure factors for this structure determination of boltwoodite are given in Table 7.[3] The final atomic coordinates and isotropic temperature factors are listed in Table 8, and the important distances and angles are shown in Table 9.

Figure 2 shows a stereo view of this structure, and Figure 3 shows a view of the potassium coordination sphere from Figure 2. The uranyl silicate sheets are parallel to (100) and are crossbonded by potassium atoms and hydronium ions. The sheets are composed of uranyl silicate chains that are parallel to the b direction of the unit cell. The potassium–oxygen bond distances can be divided into two groups: an inner group of seven bonds with distances ranging up to approximately 3.2Å and an outer group of three bonds with distances between 3.3Å and 3.5Å. This arrangement is quite similar to the potassium coordination sphere in the micas, in which there is an inner coordination sphere of six bonds with distances less than 3.1Å and an outer coordination sphere of six bonds with distances between 3.3Å and 3.5Å. However, the geometry of the potassium coordination sphere in the micas is much more regular than in boltwoodite. The locations of the extra hydrogen atoms in this structure could not be determined, although they are probably bound to the water molecules to give hydronium ions.

[3]To receive a copy of Table 7, order Document AM-81-157 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue NW, Washington, DC 20009. Please remit $1.00 in advance for the microfiche.

Structural comparison of the 1:1 minerals

The cell constants, symmetry, fiber direction and sheet orientation of the various 1:1 uranyl silicate minerals are given in Table 2. All of the structures are composed of uranyl silicate chains that are crossbonded by bridging oxygen atoms to form a uranyl silicate sheet (Figure 1). The fibrous habit of these minerals is due to the presence of the chains, and their perfect cleavage is due to the presence of the sheets. The sheets are linked by the additional cations in the structure.

The refinement of uranophane has clarified some of the relationships between this mineral and its dimorph beta-uranophane. The two-fold screw axis in uranophane lies along b within the uranyl silicate chain. The adjacent uranyl silicate sheets are parallel to (100) and are related by the a glide plane of the pseudosymmetry, which occurs at y values of 0.25 and 0.75. The equivalent uranium atoms and silicon atoms of adjacent sheets are separated by a y value of 0.06 so that adjacent sheets have almost identical orientations.

Table 5. Distances and angles in uranophane

U – O(3)	1.78+0.05 Å	}	uranyl oxygens
– O(1)	1.82∓0.05	}	
– O(7)	2.21∓0.06		
– O(9)	2.26∓0.05		bridging oxygen
– O(5)	2.34∓0.06		
– O(5)	2.43∓0.06	}	edge-shared to silicon
– O(7)	2.46∓0.06	}	
Si – O(5)	1.56∓0.07		
– O(9)	1.59∓0.06		
– O(11)	1.59∓0.06		
– O(7)	1.69∓0.07		
U – Si	3.12+0.02		across edge-shared polyhedra
– Si	3.64+0.02		across bridging oxygen
U – U	3.916+0.004		across edge-shared polyhedra

	Angles	O – O dist.
Uranyl Ion		
O(1) – U – O(3)	177+3°	
Pentagonal Ring Around Uranium		
O(9) – U – O(7)	80+2°	2.88+0.08 Å
O(7) – U – O(5)	69∓2°	2.62∓0.08
O(5) – U – O(7)	62∓2°	2.51∓0.09
O(7) – U – O(5)	66∓2°	2.62∓0.08
O(5) – U – O(9)	83∓2°	3.06∓0.09
Silica Tetrahedra		
O(5) – Si – O(7)	101+3°	2.51+0.09
O(7) – Si – O(9)	113∓3°	2.74∓0.08
O(7) – Si – O(11)	111∓3°	2.70∓0.08
O(5) – Si – O(9)	115∓3°	2.66∓0.08
O(5) – Si – O(11)	109∓3°	2.57∓0.08
O(9) – Si – O(11)	108∓3°	2.57∓0.07
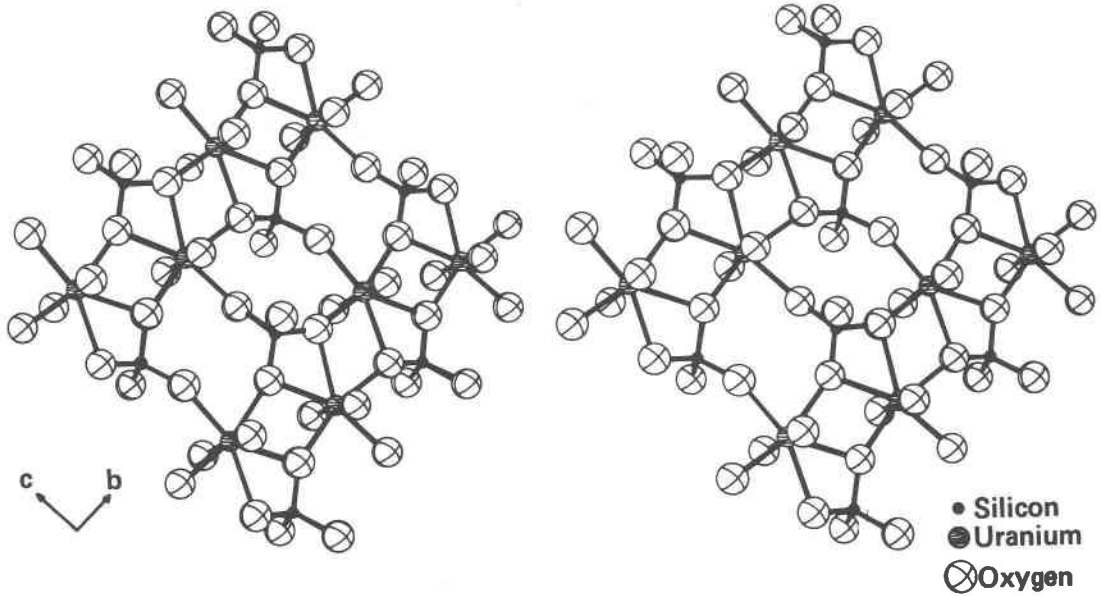
Fig. 1. Stereo view of the uranyl silicate sheet in uranophane.

Table 6. Powder patterns for boltwoodite

Honea (1961)		New Method Mine	Type material	Calculated pattern		
d meas	I/Io	d meas	d meas	d calc	I/Io	(hkl)
7.53Å	2					
6.81	10	6.809Å	6.809Å	6.808Å	100	100
6.40	5	6.398	6.393	6.390	31	001
5.45	5	5.463	5.460	5.455	17	$\bar{1}01$
4.74	4	4.741	4.739	4.739	30	011
4.32	4	4.320	4.320	4.317	14	$\bar{1}11$
4.11	2	4.131	4.133	4.134	3	101
3.91	1					
3.75	1					
		3.566	3.567	3.568	28	111
3.54	7	3.534	3.534	3.532	28	020
3.40	9	3.411	3.409	3.413	19	$\bar{2}01$
				3.404	26	200
3.13	5	3.136	3.137	3.135	44	120
3.07	1	3.092	3.091	3.091	4	021
		2.960	2.959	2.965	14	$\bar{1}21$
2.95	8			2.953	32	$\bar{1}12$
2.91	7	2.912	2.911	2.911	34	012
2.69	1B*	2.685	2.684	2.685	2	121
		2.546	2.545	2.544	7	$\bar{2}12$
2.53	3		2.533	2.534	5	211
		2.459	2.466	2.466	13	112
2.45	5		2.453	2.454	4	$\bar{2}21$
				2.451	6	220
2.34	4		2.348	2.349	4	$\bar{3}01$
2.26	5	2.269	2.268	2.269	6	300
2.21	4	2.210	2.209	2.209	12	031
					2	$\bar{1}03$
2.16	2	2.162	2.161	2.162	2	$\bar{1}31$
					2	310
2.13	3	2.131	2.129	2.130	7	003
2.11	2	2.111	2.109	2.110	4	$\bar{1}13$
					1	122
2.08	1					
2.05	3	2.043	2.044	2.052	6	$\bar{3}12$
				2.046	5	131
1.994	2	1.994	1.993	1.9919	5	$\bar{2}13$
1.983	2	1.980	1.982	1.9837	6	212
1.950	3	1.956	1.955	1.9558	7	$\bar{3}21$

* (B = broad reflection)

The structure of beta-uranophane (Smith and Stohl, 1972) is composed of sheets that are parallel to (010). In this case, however, the true symmetry is $P2_1/a$ and the a glide planes lie within the sheet at y equal 0.25 and 0.75, and the two-fold screw axes are perpendicular to these sheets at $x = 0.25$, $z = 0.0$, etc. Therefore, adjacent sheets are related by a two-fold rotation and are not in similar orientations.

This difference in the stacking of sheets affects the calcium coordination in these minerals, as shown in Figure 4. The uranyl silicate sheets for this orientation are perpendicular to the drawing above and below the calcium coordination spheres. The calcium atoms in uranophane are in seven-fold coordination, whereas those in beta-uranophane are in eight-fold coordination. The equivalent of the Ca–O4 bond in beta-uranophane is missing in uranophane, so that the other bonds move away from the Ca–O3 reference bond to compensate for the missing bond and give a more regular coordination polyhedron for the calcium atoms. The O3–Ca–O1 angle in beta-uranophane straightens by 14° to give the analogous O3–Ca–O2 angle of uranophane. This causes an increase in the distance between the sheets in uranophane, which results in the larger a dimension in uranophane relative to the b dimension of beta-uranophane.

The reason for the doubling of the fiber a dimen-

Table 8. Atomic coordinates for boltwoodite. The space group is $P2_1$. Oxygens 3 and 3B are related by the mirror plane of the pseudosymmetry. (Standard errors in parentheses).

Atom	x	y	z	B
U	0.0252(7)	0.25	0.1385(8)	0.9(2)
K	0.541(5)	0.548(6)	0.153(6)	4.4(11)
Si	0.933(5)	0.25	0.637(5)	0.9(7)
O(1)	0.290(11)	0.25	0.147(12)	0.6(14)
O(2)	0.227(11)	0.75	0.885(12)	3.9(22)
O(3)	0.022(14)	-0.079(17)	0.194(15)	4.7(21)
O(3B)	-0.022(14)	0.079(17)	-0.194(15)	4.7(21)
O(5)	0.060(11)	0.25	0.484(12)	0.9(16)
O(6)	0.294(11)	0.75	0.490(12)	3.7(21)
H_2O	0.400(14)	0.413(17)	0.689(16)	2.3(23)

sion in beta-uranophane relative to the fiber b dimension of uranophane was discussed by Smith and Stohl (1972). In these structures, a single oxygen atom of the silicate tetrahedra points either above or below the plane of the sheet. In uranophane, these oxygen atoms from adjacent tetrahedra along the same side of the chain all point in the same direction (Figure 1), whereas in beta-uranophane they alternately point up and down causing a doubling of the fiber dimension.

The c dimensions in these two minerals are very similar and represent the crossbonding of uranyl silicate chains through a bridging oxygen atom. The β angle in uranophane occurs between the a axis, which is approximately perpendicular to the sheets, and the c axis, which parallels the crossbonding between the chains. The offset of the chains along c is caused by the fact that all the bridging oxygen atoms are on the same side of the silicate tetrahedra. In beta-uranophane, the α angle, which corresponds to the β angle of uranophane, equals 90° because the oxygen atoms bonding the chains together are from alternate sides of the silicate tetrahedra and thus do not cause a resultant offset. However, this alternation does add a substantial amount of distortion to the chains so that the β angle, which occurs within the uranyl silicate sheet, is 91°25'.

The structure of uranophane also shows many similarities to the structure of boltwoodite. Both minerals have space group symmetry $P2_1$, with the twofold screw axes along the uranyl silicate chains and the uranyl silicate sheets parallel to (100). The uranyl silicate sheets in uranophane have the pseudosymmetry $P2_1/a$ so that adjacent sheets are related by the a glide plane, whereas the sheets in boltwoodite have the pseudosymmetry $P2_1/m$ and adjacent sheets are identical with an offset of 1.92Å along c. Due to this offset, the potassium atoms attain a fairly regular ten-fold coordination.

Honea (1961) indicated that there should be a close structural relationship between boltwoodite and kasolite because of their similarities in formulas, cation ionic radii, X-ray powder patterns, and infrared patterns. Two independent structure determinations carried out on kasolite by Huynen *et al.* (1963) and Mokeeva (1965) are basically identical except for the positions of the lead atoms. Huynen *et al.* (1963) reported the lead atoms in three-fold coordination, whereas Mokeeva (1965) reported that the y value for the lead atoms determined by Huynen *et al.* (1963) was off by 0.5 so that the lead atoms really occurred in eight-fold coordination. A refinement of the kasolite structure carried out by Rosenzweig and Ryan (1977) showed that Mokeeva's structure is correct. The kasolite structure is very closely related to the structure of boltwoodite. The geometric configuration of the nine bonds around the lead atoms of kasolite is basically identical to the configuration of nine of the ten bonds around the potassium atoms of boltwoodite. The difference in coordination is explained by the fact that in boltwoodite each of the water molecules is bonded to two adjacent potassium atoms along b, whereas in kasolite the water molecules are only bonded to a single lead atom. The potassium atoms in boltwoodite are crossbonded along b by sharing two uranyl oxygen atoms and a water mole-

Table 9. Distances and angles in boltwoodite

U	– O(2)	1.74+0.08 Å	uranyl oxygens
	– O(1)	1.85∓0.09	
	– O(5)	2.23∓0.08	bridging oxygen
	– O(3B)	2.35∓0.12	
	– O(3)		
	– O(3B)	2.45+0.10	edge-shared to silicon
	– O(3)		
Si	– O(5)	1.53+0.08	
	– O(6)	1.59∓0.08	
	– O(3)	1.61∓0.11	
	– O(3B)		
U	– Si	3.20+0.03	across edge-shared polyhedra
	– Si	3.54+0.03	across bridging oxygen
U	– U	3.944+0.005	across edge-shared polyhedra

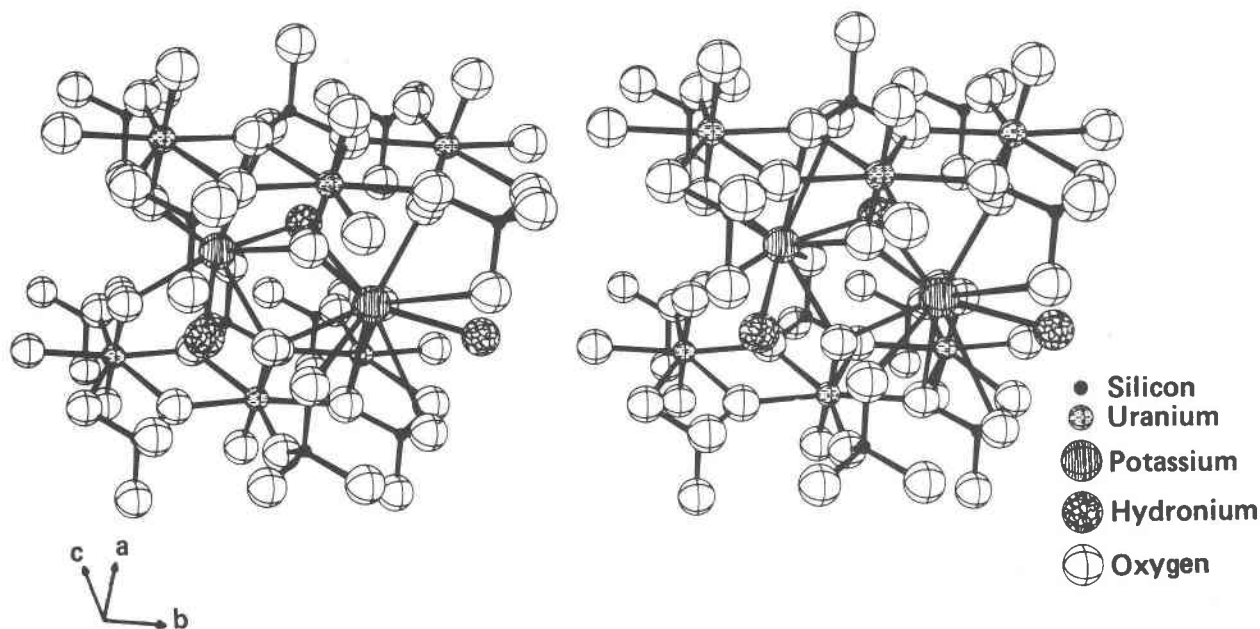| Uranyl Ion	Angles	O – O dist.
O(1) – U – O(2)	177+3°	
Pentagonal Ring Around Uranium		
O(5) – U – O(3B)	81+2°	2.98+0.12 Å
O(3B) – U – O(3)	70∓4°	2.74∓0.14
O(3) – U – O(3B)	59∓4°	2.41∓0.17
Silica Tetrahedra		
O(3) – Si – O(3B)	97+6°	2.41+0.17
O(3) – Si – O(5)	115∓4°	2.65∓0.12
O(3) – Si – O(6)	110∓4°	2.63∓0.12
O(5) – Si – O(6)	109∓4°	2.54∓0.11

Fig. 2. Stereo view of the structure of boltwoodite.

cule to give chainlike structures. Each potassium atom in the chain is crosslinked along *c* to each of two potassium atoms in an adjacent chain by sharing a free oxygen of a silicate tetrahedron. The free oxygen atoms of the silicate tetrahedra are those that extend above or below the uranyl silicate sheet (Figure 1). In kasolite, the lead atoms are crossbonded along *b* by sharing two uranyl oxygen atoms, which is very

similar to the configuration found in boltwoodite if the water molecules are not considered. However, the crossbonding of the lead atoms along *c* in kasolite is very different from the crosslinking of the potassium atoms along *c* in boltwoodite. In kasolite, each lead atom is crosslinked along *c* to another lead atom by sharing two free oxygen atoms of the silicate tetrahedra. This causes edge-sharing of these polyhdera along *c*, which does not occur in boltwoodite. The crossbonding of the potassium coordination spheres in boltwoodite therefore gives rise to a chainlike structure, whereas the crosslinking of the lead coordination spheres in kasolite gives rise to a more planar configuration. This results in a symmetry of $P2_1$ for boltwoodite and $P2_1/c$ symmetry for kasolite. The *c* dimension in kasolite is double that of boltwoodite due to the *c* glide plane, and the *a* dimension in boltwoodite is longer than the *a* dimension in kasolite because of the larger ionic radius and lower charge on the potassium atoms as compared to the lead atoms.
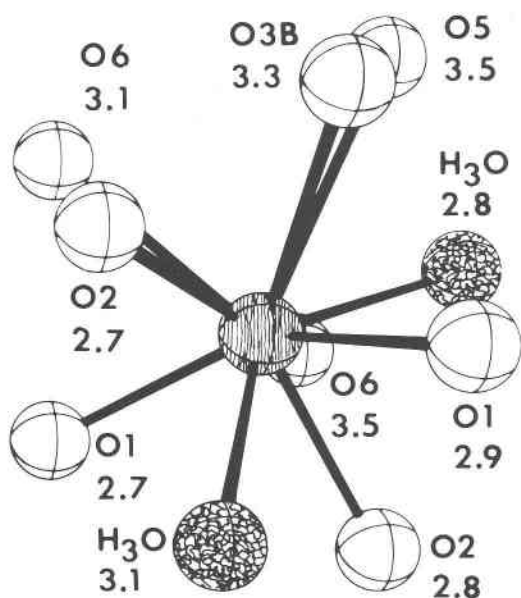
The structure of sklodowskite, as determined by Mokeeva (1959), Huynen and Van Meerssche (1962), Mokeeva (1964), and Ryan and Rosenzweig (1977), is also very similar to the other 1:1 minerals. The uranyl silicate sheets are parallel to (100), with adjacent sheets related by the *C*-centering of the $C2/m$ symmetry. This alternation of sheets results in a doubling of the *a* dimension. The *a*/2 value of 8.72Å, which is longer than the distance between the sheets in the other structures of this group, is caused by the

Fig. 3. Potassium coordination sphere in boltwoodite showing bond distances in angstroms.

O3
2.4

O11
2.4

H₂O(1)
2.5

H₂O(4)
2.5

H₂O(2)
2.4

O2
2.4

H₂O(3)
2.5

URANOPHANE

O3
2.4

O12
2.6

H₂O(1)
2.4

H₂O(2)
2.4

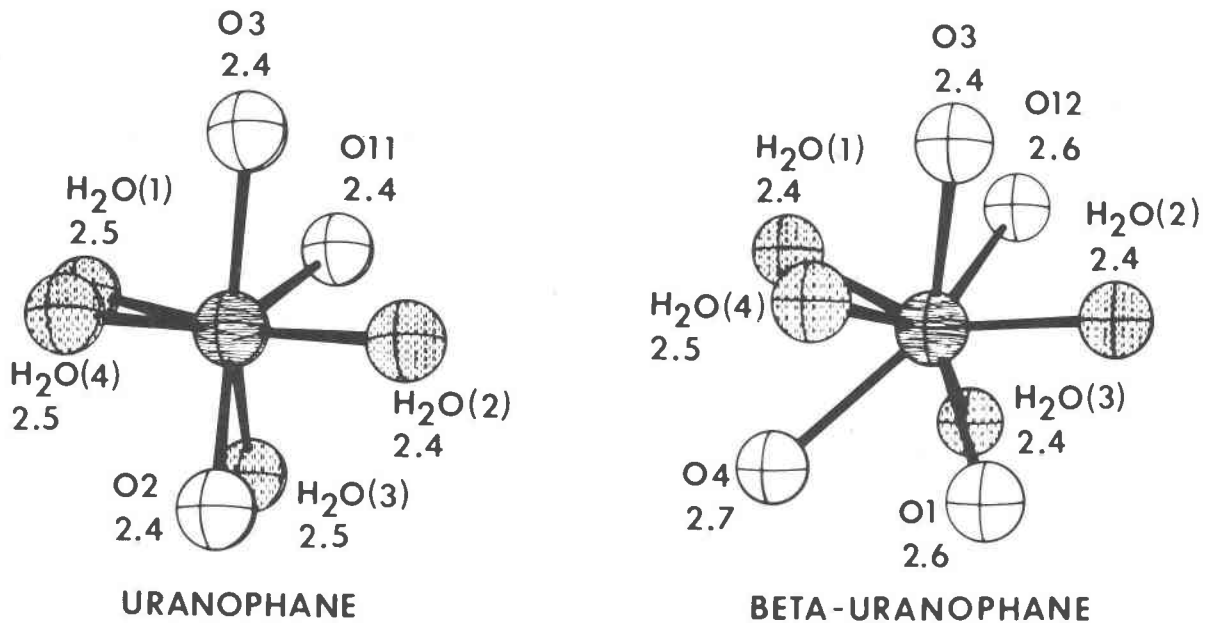H₂O(4)
2.5

H₂O(3)
2.4

O4
2.7

O1
2.6

BETA-URANOPHANE

Fig. 4. Calcium coordination spheres in uranophane and beta-uranophane showing bond distances in angstroms.

linear arrangement, parallel to a, of the magnesium atoms between the free oxygen atoms of the silicate tetrahedra of adjacent sheets. The magnesium atoms are in six-fold coordination. Ryan and Rosenzweig (1977) found a water molecule in this structure that was not bonded to the silicon, uranium, or magnesium atoms.

The structure of cuprosklodowskite was determined by Piret–Meunier and Van Meerssche (1963) and refined by Rosenzweig and Ryan (1975). This structure is very similar to the structure of sklodows-

kite except that the copper atoms that occur between sheets are bonded in a linear arrangement to a uranyl oxygen atom from each of the adjacent sheets instead of a free oxygen atom of the silicate tetrahdedra from each sheet, as in sklodowskite. The longer b dimension of cuprosklodowskite, as compared to $a/2$ of sklodowskite, is therefore a result of the approximately linear crossbonding arrangement of cuprosklodowskite (uranium–oxygen–copper–oxygen–uranium), which produces a longer distance betwen the sheets than the approximately linear crosslinking ar-
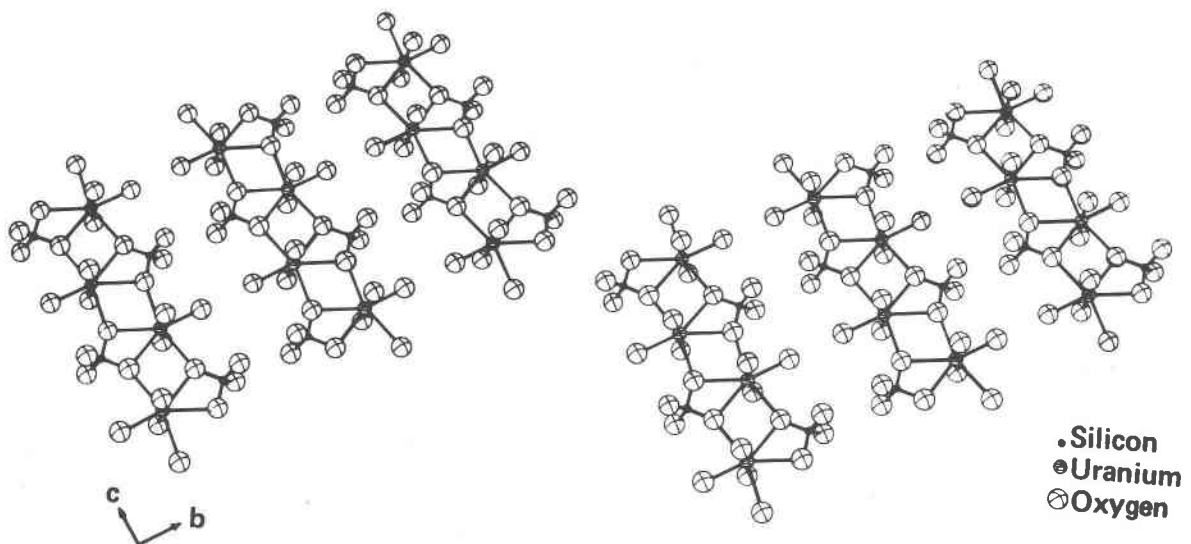

c
b

• Silicon
⊖ Uranium
⊗ Oxygen

Fig. 5. Stereo view of the uranyl silicate chains in weeksite.

rangement of sklodowskite (silicon–oxygen–magnesium–oxygen–silicon). Rosenzweig and Ryan (1975) reported a weighted R-factor of 0.0263 although they could not find the extra hydrogen atoms in the structure. They did, however, locate an additional water molecule that is not bonded to the silicon, uranium, or copper atoms.

The uranyl silicate sheet in the mineral group with a uranium to silicon ratio of 1:1 has the formula $[(UO_2)_2(SiO_4)_2]_n^{-4n}$ where n is the number of groups per unit cell. For kasolite, n = 0.5 so that the −2 charge from the sheet is completely balanced by the lead atoms. Boltwoodite and sodium boltwoodite also have a value of n = 0.5. In these cases, however, the singly charged potassium and sodium atoms are not sufficient to balance the −2 charge of the sheet. Crystal structure analyses do not show how these charges are balanced. Therefore, each of these structures must have an additional hydrogen atom present to balance the charge. Uranophane, beta-uranophane, sklodowskite, and cuprosklodowskite have n = 1 so that the charge on the sheet is −4. This charge is only half satisfied by the doubly charged cation in each structure. Therefore, each of these structures must have two hydrogen atoms present per unit cell. The locations of these hydrogen atoms could not be determined in any of the structure determinations of the 1:1 minerals. However, the structure analyses of each mineral indicated the most probable locations for the hydrogen atoms on the basis of crystal chemical considerations. These are shown by the formulas in Table 1. The formulas for uranophane and boltwoodite are based on this work whereas the other formulas are from the most recent structural paper for each mineral.

The degree of hydration and the role of the water in the structures of the 1:1 uranyl silicate minerals have been the subject of some controversy. Several different values have been reported for the hydration states of most of the 1:1 minerals on the basis of chemical analyses. Uranophane and beta-uranophane have been reported with the following composition: $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot XH_2O$ where X = 4.5 to 7 (Gorman and Nuffield, 1955; Smith and Stohl, 1972). The composition for sklodowskite has been reported as $MgO \cdot 2UO_3 \cdot 2SiO_2 \cdot YH_2O$ where Y is either 6 or 7 (Gorman, 1957). The cuprosklodowskite composition has been reported as $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$ (Rosenzweig and Ryan, 1975). The original composition of boltwoodite was determined by Frondel and Ito (1956) as $K_2O \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$, although Honea (1961) indicated that the formula should be $K_2O \cdot 2UO_3 \cdot 2SiO_2 \cdot 3H_2O$ with the possibility of some additional zeolitic water. Some of the water in these minerals is water-of-crystallization, combined as part of the first coordination sphere around the interlayer cation. A small part of the water is involved in the electronic charge balance of the uranyl silicate sheet. It either replaces terminal oxygens with hydroxyl ions (most likely as SiO_3OH or $UOOH$) or occurs as hydronium ions between the sheets. The rest of the water, which is probably the variable amount reported, is zeolitic in nature and occurs in the large open spaces between the sheets.

Five water molecules per two uranyl groups were found in the structures of beta-uranophane (Smith and Stohl, 1972) and uranophane. The structure determinations of sklodowskite (Ryan and Rosenzweig, 1977) and cuprosklodowskite (Rosenzweig and Ryan, 1975) each yielded seven water molecules per two uranyl groups. The structure determination of boltwoodite showed three water molecules per two uranyl groups. Any additional water in these minerals would be present as zeolitic water.

The crystal structure determinations on the minerals uranophane, beta-uranophane, boltwoodite, kasolite, sklodowskite, and cuprosklodowskite show that they all contain similar sheet structures. However, the sheets show varying amounts of distortion due to the different sizes and charges on the cations between the sheets. An indication of the amount of distortion that is present in these structures can be obtained by comparing the unit cell dimensions parallel to the fiber direction. According to the data in Table 2, kasolite has the smallest fiber dimension ($b = 6.932$Å) indicating a large amount of chain distortion, and boltwoodite has the largest fiber dimension ($b = 7.064$Å) indicating a low amount of chain distortion. Fitting a plane to each of two edge-shared UO_5 groups, the uranium and the five equatorial oxygens, and calculating the angle between these planes indicates the amount of distortion that occurs along the

Table 10. Atomic coordinates for weeksite. These values are based on the partial structure analysis in the pseudocell with space group $Amm2$

Atom	x	y	z
U	0.0	0.198	0.0
Si	0.0	0.130	0.523
O(1)	0.25	0.307	0.546
O(2)	0.0	0.180	0.693
O(2B)	0.0	0.180	0.307
O(3)	0.194	0.071	0.487
O(4)	0.0	0.429	0.473

uranyl silicate chains. In boltwoodite, the atoms in a UO_5 group are statistically planar and the normals to the planes through edge-shared UO_5 groups make an angle of 0.0° to each other. In kasolite, however, these UO_5 groups are not planar, and the normals to the best fit planes of edge-shared UO_5 groups make an angle of 20.6° to each other.

Structure determination of the 1:3 group mineral weeksite

Weeksite is the only member of the 1:3 uranium to silicon compositional group for which acceptable crystals could be obtained. The sample used in this analysis was from the Anderson Mine, Yavapai County, Arizona, and was lent to the authors by Mr. Bill Hunt of Sun City, Arizona. The acicular crystals measured approximately $25 \times 25 \times 200 \ \mu m$ and occurred as radiating aggregates, up to 1 mm in diameter, on a sandstone matrix. The comparison of a Guinier powder pattern of this sample with a pattern taken of the type material number 115886 from the U.S. National Museum verified its identification.

The unit cell and space group of weeksite were determined by Dr. Joan Clark and Dr. George Ashby of the U.S. Geological Survey, and were reported by Outerbridge *et al.* (1960). They reported that this mineral belongs to space group *Pnnb* and has an extremely strong pseudosymmetry, with the dimensions of the pseudocell half those of the real cell and with pseudocell extinctions which indicate the presence of an *A*-centered lattice. Therefore, there are five possible space groups for the pseudocell: *Ammm, Amm2, Am2m, A2mm,* or *A222*.

Many crystals from the Anderson Mine sample were checked on a precession camera in an effort to find a single crystal that was suitable for structure analysis. Alignment photographs of these crystals showed elongated white radiation streaks and splitting at the ends of the streaks, both of which are indicative of multiple crystals. A complete set of photographs, taken on a large crystal, showed several individuals in very close orientations. These photographs substantiated the *A*-centered pseudocell and verified the fact that all the dimensions of the real cell were double those of the pseudocell.

A complete set of precession photographs, taken on a crystal measuring $25 \times 25 \times 200 \ \mu m$, showed a very slight splitting at the ends of the white radiation streaks. The extinctions on these photographs indicated a face-centered lattice so that the possible space groups of the real cell were: *Fmmm, Fmm2, Fm2m, F2mm,* or *F222*. There were also additional

extinctions present that could not be explained on the basis of these space groups. For example, the $(hk0)$ zone had all indices even, but also had $k = 4n$. The previously reported *Pnnb* symmetry is a subset of the possible face-centered space group and could not therefore be verified or disproved.

Two data sets were collected using a Picker FACS-1 system with Mo$K\alpha$ radiation and the slightly imperfect $25 \times 25 \times 200 \ \mu m$ crystal. The first data set consisted of 270 reflections, with 2θ less than 40°, that were permitted by the pseudocell symmetry. The cell constants obtained during the alignment segment of this data collection were as follows: $a = 7.106 \pm 0.008$Å, $b = 17.90 \pm 0.02$Å, $c = 7.087 \pm 0.007$Å. The cell constants for the real cell are double these values. The second data set consisted of 2641 reflections of the real cell with 2θ less than 35°. This set had 1175 unobserved reflections.

It is probable that the uranium atoms and most of the other atoms in weeksite do not contribute to the very weak reflections that cause the doubling of all the axes. Therefore, the pseudocell data set without an absorption correction was used in the initial stages of structure analysis. An analysis of Harker sections and Harker lines in a three-dimensional Patterson map indicated that the symmetry of the pseudocell was probably *Amm2*. The uranium atom locations were determined from the Patterson map and were used in the calculation of a three-dimensional Fourier map. The *R*-factor obtained from the refinement of only the uranium atoms in space group *Amm2* was 0.22. The analysis of this map showed several possible oxygen atom positions and a silicon atom position, which indicated a structural unit similar to the uranyl silicate chains in the 1:1 uranyl silicate minerals. Several successive sets of least squares analysis and Fourier calculations gave locations for several additional oxygen atoms and the potassium atoms, and lowered the *R*-factor to 0.15.

The remainder of the structure analysis was carried out using the real cell data set. The analysis of these data again showed the presence of uranyl silicate chains but did not reveal the locations of potassium atoms or the extra silicon atoms in the structure. Attempts were made to analyze these data using the five face-centered space groups as well as *Pnnb*. In each case, the possible extra silicon atom positions would have required edge-sharing between silicate tetrahedra, which is very unlikely.

The aspects of this structure that were determined are shown in Figure 5. This structure consists of uranyl silicate chains, similar to those found in the 1:1

Table 11. The cell constants and space groups of soddyite and the synthetic uranyl silicate and uranyl germanate

Soddyite*	$2UO_3 \cdot SiO_2 \cdot 2H_2O$**	$2UO_3 \cdot GeO_2 \cdot 2H_2O$**
$a = 8.32\text{Å}$	$a = 8.29\text{Å}$	$a = 8.179 \pm 0.001\text{Å}$
$b = 11.21$	$b = 11.27$	$b = 11.515 \pm 0.002$
$c = 18.71$	$c = 18.65$	$c = 19.397 \pm 0.002$
Fddd	*Fddd*	*Fddd*

References: *Gorman (1952); **Legros *et al.* (1972).

minerals, that are parallel to the c direction in (100) at $x = 0$. In this case, however, adjacent chains are not crosslinked to produce a sheet, but rather occur as separate units that are mirror images of each other. The adjacent chains are separated by an oxygen–oxygen distance of approximately 2.6Å, which is comparable to the oxygen–oxygen distance that occurs in a silicate tetrahedron. Therefore, it seems reasonable that some of the unlocated silicon atoms in this structure occur between the chains and link the chains together in (100). Some of these unlocated silicon atoms may also be crossbonded to give a two-dimensional arrangement of silicon tetrahedra in the (010) plane between the chains. This two-dimensional layer of silicon tetrahedra would link together some adjacent chains along the a direction. The potassium atoms probably occur between the chains along a, in positions similar to the potassium atoms in boltwoodite. The atomic coordinates for the atoms in these chains, relative to the pseudocell, are shown in Table 10.

Structure of the 2:1 mineral soddyite

The similarity between soddyite and the synthetic hydrated uranyl silicate and uranyl germanate of Legros *et al.* (1972) can be seen by comparing their cell constants, space group (Table 11), and powder patterns (Table 12). The powder pattern of soddyite was obtained on a Guinier camera using sample number R16788 from the U.S. National Museum. The research on the hydrated uranyl germanate by Legros *et al.* (1972) included a partial structure analysis in space group *Fddd*, with the origin at point symmetry 222, which located the germanium atoms in special position $8a(0,0,0)$ and the uranium atoms in special position $16g(0,0,z)$ with $z = 0.1667$. They were, however, unsuccessful in finding the oxygen atoms in this stucture. Due to the similarity between soddyite and the synthetic hydrated uranyl silicate, it is reasonable that the structure of this analogous hydrated uranyl germanate should be a model for sod-

dyite and the 2:1 mineral group. The uranium–germanium distances and uranium–uranium distances in the partial structure analysis are very similar to the uranium–silicon and uranium–uranium distances in the uranyl minerals with a uranium to silicon ratio of 1:1 and 1:3. Therefore, this structure is composed of uranyl germanate chains that are very similar to the uranyl silicate chains. The structure is made up of uranyl germanate chains that extend along the diagonals of the unit cell, and that are crossbonded by sharing a single germanium tetrahedron (Figures 6 and 7). This structure was originally proposed by Stohl and Smith (1974) and has since been sub-

Table 12. The powder patterns of soddyite and the synthetic hydrated uranyl silicate. The pattern for soddyite was measured from a Guinier pattern and the intensities were visually estimated.

Soddyite		$2UO_3 \cdot SiO_2 \cdot 2H_2O$*	
d meas	I/Io**	d meas	I/Io
6.298Å	S	6.296Å	84
4.805	M	4.831	31
4.662	VW	4.665	15
4.560	S	4.558	100
3.803	VW	3.791	15
		3.370	10
3.348	S	3.339	80
3.262	W	3.259	26
2.992	M	2.999	21
2.806	W	2.820	12
2.720	S	2.722	48
		2.657	4
		2.521	3
2.493	WB	2.487	30
2.477	VW	2.473	19
		2.463	16
		2.412	2
2.335	VW	2.331	12
2.258	VW	2.261	13
		2.214	8
		2.180	3
		2.160	2
2.099	VW	2.097	20
		2.072	6
2.046	VW	2.052	10
1.981	W	1.979	22
1.913	VW	1.912	17
		1.905	2
		1.897	6
		1.887	1
		1.878	1
1.864	W	1.865	28
		1.841	1
		1.797	1
1.772	VW	1.772	12
		1.739	4
1.706	VW	1.710	11

* Reference: Legros *et al.* (1972).
** S = strong intensity
  M = moderate intensity
  W = weak intensity
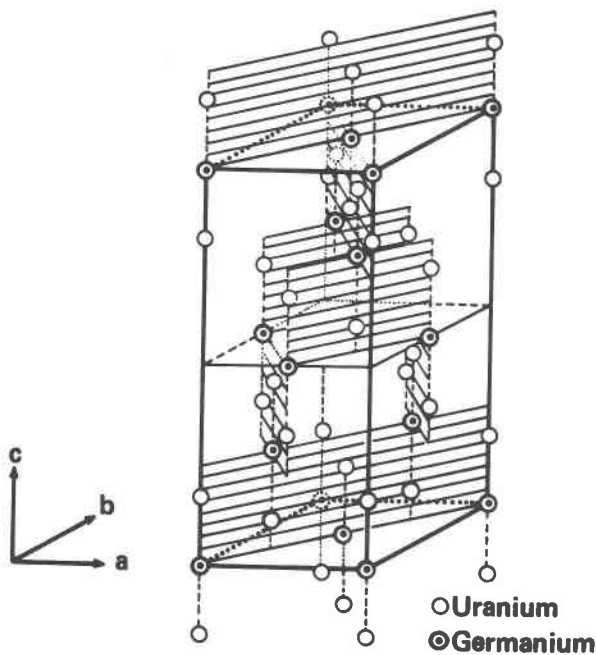 VW = very weak intensity
  B = broad reflection

Fig. 6. The three-dimensional chain structure for the hydrated uranyl germanate. The chain positions are shown by cross hatching and are superimposed on the uranium and germanium atom locations given by Legros *et al.* (1972).

stantiated by Legros and Jeannin (1975) for the uranyl germanate and by Belokoneva *et al.* (1979) for soddyite. The atom positions reported by Belokoneva *et al.* (1979) in space group *Fddd* with the origin at the center of symmetry are as follows: U(0.875, 0.875, 0.0443), Si(0.875, 0.875, 0.875), O(1) (0.695, 0.963, 0.0455), O(2) (0.026, 0.044, 0.0663) and O(3) (0.875, 0.875, 0.170).

New Mineral

A new uranyl silicate mineral was collected by D. K. Smith in 1955 from the Jackpile Mine, Laguna, New Mexico. It has an appearance very similar to soddyite and occurs as opaque, yellow green, radiating crystals on a sandstone matrix. Its powder pattern is also similar to soddyite (Table 13). An emission spectrographic analysis showed the presence of uranium and silicon with trace amounts of calcium. The uranium to silicon ratio could not be determined by microprobe analysis because the mineral disintegrates in an electron beam. A series of precession photographs indicated that the mineral was triclinic. The cell constants obtained during the alignment procedure on a Picker FACS-1 system were as follows:
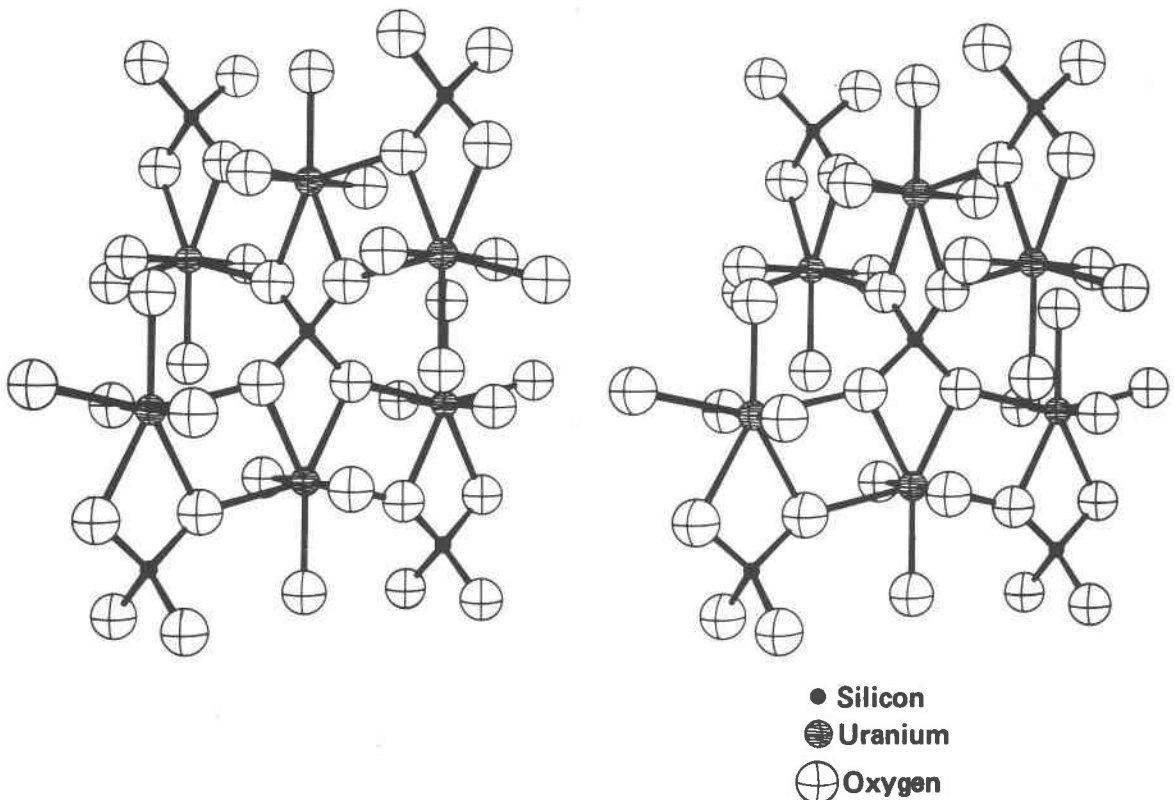

Fig. 7. Stereo view of the crossbonded chains of the uranyl germanate structure.

$a = 5.535 \pm 0.004$Å, $b = 6.117 \pm 0.004$Å, $c = 7.759 \pm 0.005$Å, $\alpha = 84°47' \pm 2'$, $\beta = 91°11' \pm 2'$, $\gamma = 96°32' \pm 2'$. A data set consisting of 336 independent reflections with 2θ values up to 35° was collected. The intensities of three standard reflections, which were measured throughout the data collection, decreased by approximately 20 percent. Because these intensities could not be brought back up to their original values by reorienting the crystal, we assumed that the crystal structure was changing in the X-ray beam.

An analysis of this data set gave an R-factor of 0.21. A uranium atom was located at $x = 0.87$, $y = 0.16$, $z = 0.79$, but the remainder of the structure could not be determined because of the poor data set and the uncertainties in the composition and properties of this new mineral. If, however, the space group is $P\bar{1}$, the uranium–uranium distance due to the center of symmetry would be 3.89Å, which is the distance between the uranium atoms in edge-shared uranium pentagonal bipyramidal groups. In this case, there would only be one such distance associated with each uranium atom rather than two as required in the uranyl silicate chain. It is, therefore, possible that this structure may be unique among the uranyl silicates.

Summary

The known uranyl silicate minerals have been divided into three groups on the basis of their uranium to silicon ratios. The dominant structural feature, which occurs in all three groups, is a uranyl silicate chain that is formed by edge-shared uranium pentagonal bipyramidal groups and silicate tetrahedra.

In the 1:1 uranyl silicate group, these chains are crosslinked by bridging oxygen atoms to give uranyl silicate sheets of composition $[(UO_2)_2 (SiO_4)_2]_n^{-4n}$. These sheets are crossbonded by the additional cations in each structure. The differences among the structures in this group, such as the dimorphs uranophane and beta-uranophane, are caused by factors such as different stacking arrangements of the sheets. A structure refinement of uranophane showed that the calcium atoms are in seven-fold coordination in contrast to beta-uranophane where the calcium atoms are in eight-fold coordination. The minerals boltwoodite and kasolite have very similar formulas, cation ionic radii, X-ray powder patterns and infrared patterns. A structure determination of boltwoodite showed that the main difference between these minerals is due to the manner in which the cation polyhedra between the sheets are crossbonded. In boltwoodite, the crossbonding of the potassium coordination polyhedra gives rise to a chainlike structure, whereas in kasolite, the crosslinking of the lead coordination spheres gives rise to a more planar configuration.

The extra hydrogen atoms, which must be present in most of these structures in order to balance the charge, were not located in any of these structural analyses. However, the structural formulas for several of these minerals show the presence of hydroxyl or hydronium ions that have been proposed on the basis of crystal chemical considerations.

A partial structure analysis of weeksite, which has a uranium to silicon ratio of 1:3, indicates that the structure is composed of uranyl silicate chains that occur as separate units. These chains are separated by an oxygen–oxygen distance of approximately 2.6Å, which is comparable to the oxygen–oxygen distance in a silicate tetrahedron. Therefore, these chains are probably linked together by the unlocated silicon atoms in this structure. The potassium atoms

Table 13. Guinier powder patterns of the new mineral and soddyite (R16788). The intensities were visually estimated

New Mineral		Soddyite	
d meas	I/I_o	d meas	I/I_o*
7.783Å	1		
6.298	7	6.298Å	S
6.041	7		
5.507	5		
4.957	9		
4.813	1	4.805	M
		4.662	VW
4.553	10	4.560	S
4.507	10		
3.902	8		
3.831	3	3.803	VW
3.714	4		
3.348	5	3.348	S
3.258	1	3.262	W
3.174	8		
2.992	1	2.992	M
		2.806	W
2.744	2		
2.720	3	2.720	S
2.595	1		
		2.493	WB
		2.477	VW
		2.335	VW
		2.258	VW
		2.099	VW
		2.046	VW
1.980	1	1.981	W
1.912	1	1.913	W
1.864	2	1.864	W

* S = strong intensity
  M = moderate intensity
  W = weak intensity
  VW = very weak intensity
  B = broad reflection

probably occur between the chains in positions similar to the potassium atoms in boltwoodite.

Soddyite is the only known uranyl mineral with a uranium to silicon ratio of 2:1. Its structure consists of uranyl silicate chains that are crosslinked by sharing a single silicate tetrahedron to give a three-dimensional framework structure.

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