

Refined crystal structure of beta-uranophane, $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$

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ABSTRACT

The crystal structure of beta-uranophane with the lattice constants $a = 13.966(2)$, $b = 15.443(4)$, $c = 6.632(1)$ Å, $\beta = 91.38^\circ(2)$ has been refined. It shows that the space group is $P2_1/a$ and that the basic structural features determined previously are correct. However, bond-strength sums, calculated using the refined interatomic distances, reveal that the apical oxygens of all SiO_4 tetrahedra must be $(\text{OH})^-$ ions and that the H bonds play as important a role as Ca in linking sheets that have the formula $[(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2]^{2-}$. Hence the structural formula should be $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$ instead of $\text{Ca}(\text{UO}_2)(\text{UOOH})(\text{SiO}_4)(\text{SiO}_3\text{OH}) \cdot 4\text{H}_2\text{O}$ as suggested earlier. Studies of the same mineral with DTA, DTG, and infrared spectroscopy support this conclusion.

INTRODUCTION

Beta-uranophane is dimorphous with uranophane with the chemical formula $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ (analyzed by Novacek in 1935 and 1939; see Gorman and Nuffield, 1955). Gorman and Nuffield (1955) and later Smith and Stohl (1972) determined the space group of beta-uranophane as $P2_1/a$, whereas Weissenberg photographs of Mokeeva (1963) had indicated a lower symmetry, suggesting the space group $P\bar{1}$ or $P1$ for this mineral. There are also differences in the reported lattice constants (Table 1), those of Smith and Stohl (1972) being somewhat smaller in comparison to others.

There are also other discrepancies in the literature data; for example, Smith and Stohl (1972) gave the chemical formula as $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ and suggested that the water content in beta-uranophane is likely to vary. The question of whether charge balance is achieved by the presence of $(\text{OH})^-$ ions or $(\text{H}_3\text{O})^+$ ions in the structure has not been unequivocally answered, although Smith and Stohl (1972) preferred to write the structural formula as $\text{Ca}(\text{UO}_2)(\text{UOOH})(\text{SiO}_4)(\text{SiO}_3\text{OH}) \cdot 4\text{H}_2\text{O}$. Hence a refinement of the structure was undertaken to clarify the discrepancies and to contribute to the stereochemistry of U in uranyl silicate minerals (Stohl and Smith, 1981).

EXPERIMENTAL METHOD AND RESULTS

The specimen of beta-uranophane used in this investigation was from Roessing (South-West Africa) and was kindly donated by Mr. W. R. Kahn. The sample contained idiomorphic crystals, showing a well-developed cleavage on (010). Some of the crystals are found elongated parallel to the a axis.

The chemical formula was verified by determining the weight percentages of the oxides UO_3 , CaO , and SiO_2 by X-ray fluorescence. Care was taken to determine the water content as accurately as possible using the colorimetric method. The average of two determinations yielded a water content of 5.5 molecules, thereby suggesting the chemical formula $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot$

$5.5\text{H}_2\text{O}$, which agrees with those of Novacek (1935 and 1939, cited in Gorman and Nuffield, 1955). In order to determine if $(\text{OH})^-$ or $(\text{H}_3\text{O})^+$ ions were present, two infrared spectra of beta-uranophane were made with a Beckmann spectrophotometer using the KBr disc method and covering the range $4000\text{--}200\text{ cm}^{-1}$. Three distinct absorption bands were observed (3500 , 3400 , 3270 cm^{-1}) in the range $3600\text{--}2800\text{ cm}^{-1}$; additional bands were seen at about 1650 and 1180 cm^{-1} . One spectrum of the same specimen made using an emulsion with Nujol also confirmed these observations.

In order to study the nature and role of H bonds, differential thermal analyses and X-ray powder patterns at temperatures up to 400°C were made.

Upper-level precession photographs (hkl with $l = -1, -2$) showed that many reflections of the type $h\bar{k}l$ and hkl with large h and k ($h, k > 4$) possessed slight differences in intensities, thus confirming the observations of Mokeeva (1963). The internal consistency index (Sheldrick, 1976) calculated for the equivalent reflections assuming a monoclinic symmetry is found to be equal to 0.067 and reflects the observed discrepancies in the intensities.

Precession photographs ($h0l$), exposed for about a week, showed only three weak reflections with odd values for h . No $0k0$ reflections with k odd could be observed in any photograph.

Though the precession photographs showed the crystals to be triclinic with an a axis of 13.966 Å, the lattice constants refined with the first fifty-three lines ($\theta = 0\text{--}32^\circ$) of a Guinier powder pattern showed the crystals to be metrically monoclinic with an a axis of 6.983 Å. In Table 1, the a axis has been multiplied by two to conform with the observations made on single-crystal photographs. The refined Guinier powder data showing observed and calculated d values are given in Table 2.¹

The crystal chosen for the structure refinement has an approximate size of $0.076 \times 0.14 \times 0.24$ mm. The axis of elongation was made parallel to the ϕ axis of the diffractometer. The calculated linear absorption coefficient, μ , is 220 cm^{-1} . The

¹ To receive a copy of Tables 2 and 3, order Document AM-86-322 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

Table 1. Lattice constants of beta-uranophanes hitherto studied

No.	a	b	c	α	β	γ	V	Space group
1*	14.01	15.55	6.64		91.0		1446.3	$P2_1/a$
2*	13.98	15.49	6.64	90.0	91.67	90.0	1437.3	$P\bar{1}$ or $P1$
3	13.898(11)	15.394(14)	6.609(5)		91.42(2)		1413.5	$P2_1/a$
4	13.966(2)	15.443(4)	6.632(1)		91.38(2)		1430.2(4)	$P2_1/a$

Note: References are (1) Gorman and Nuffield (1955), (2) Mokeeva (1963), (3) Smith and Stohl (1972), and (4) this study. Numbers in parentheses represent one estimated standard deviation (esd) and refer to the last decimal place.

* a and c have been exchanged.

intensity data were collected on a Phillips 4-circle automatic diffractometer with $\text{MoK}\alpha_1$ radiation and a graphite monochromator. Altogether, 5006 reflections were measured in one hemisphere of reciprocal space with a radius ($= \sin \theta/\lambda$) of 0.595. The data were corrected for Lorentz, polarization, and absorption effects.

Before carrying out the refinement, an attempt was made to determine the presence of an inversion center using the piezoelectric method of Salje (1972). As the crystals were too small, a powder sample was used. No measurable piezoelectric effect could be observed. Statistical tests on the observed structure factors indicated centrosymmetry. Hence $P2_1/a$ or $P\bar{1}$ appeared to be the likely space group for beta-uranophane, though the metric monoclinicity of the unit cell and the systematic extinctions favored the former. In that case, it must be assumed that the three very weak violations of the glide are due to Renninger effects, and the differences in the intensities of the symmetry-equivalent reflections must be attributed to absorption effects, though care was taken to correct them as accurately as possible. In order to determine how the observed differences in the intensities affect the atomic parameters, the refinement was carried out in both space groups. For calculations in $P\bar{1}$, 2866 reflections with

$|F|_{\text{obs}} > 6\sigma_{|F|_{\text{obs}}}$ were used, whereas for those in $P2_1/a$, they were reduced to 1635 unique reflections (Table 3). The refinement was carried out with the SHELX-76 program (Sheldrick, 1976) using atomic scattering factors for neutral atoms (*International Tables*, 1974) and anomalous scattering factors given by Cromer and Libermann (1970). The U coordinates given by Smith and Stohl (1972) were used as starting parameters, and the positions of all the remaining non-H atoms were determined after a few cycles of refinement and successive difference Fourier calculations. At the beginning, isotropic temperature factors were used for all atoms, and subsequently, anisotropic temperature factors were used for U and Ca. In the case of $P\bar{1}$, the refinement converged with weights $w = 1/[\sigma^2(|F|_{\text{obs}}) + 0.0003|F_{\text{obs}}|^2]$ to $R = 0.050$ ($R_w = 0.054$), where

$$R = \frac{\sum(|F_{\text{obs}} - F_{\text{calc}}|)}{\sum|F|_{\text{obs}}} \quad \text{and}$$

$$R_w = \frac{\sum(\sqrt{w}|F_{\text{obs}} - F_{\text{calc}}|)}{\sum(\sqrt{w}|F|_{\text{obs}})},$$

whereas in the case of $P2_1/a$, the values obtained for R and R_w are 0.047 and 0.050, respectively. Note that the R value is not significantly improved by lowering the symmetry.

Table 4. Atomic coordinates and isotropic temperature factors of beta-uranophane

Atom	x	y	z	U_{iso}
U1	0.0194(1)	0.2600(0)	0.2631(1)	0.008*
U2	0.2313(1)	0.7397(0)	0.4707(1)	0.007*
Ca	0.1899(3)	0.4848(3)	0.2821(8)	0.019*
Si1	0.0181(4)	0.2224(4)	0.7293(10)	0.014(1)
Si2	0.2667(4)	0.1944(3)	0.0638(10)	0.015(1)
O1	0.258(1)	0.354(1)	0.479(3)	0.025(4)
O2	0.989(1)	0.146(1)	0.231(3)	0.020(3)
O3	0.727(1)	0.877(1)	0.429(2)	0.019(3)
O4	0.051(1)	0.373(1)	0.300(2)	0.016(3)
O5	0.182(1)	0.220(1)	0.208(3)	0.016(3)
O6	0.889(1)	0.765(1)	0.409(2)	0.025(4)
O7	0.358(1)	0.200(1)	0.223(3)	0.011(3)
O8	0.567(1)	0.747(1)	0.420(3)	0.030(4)
O9	0.977(1)	0.716(1)	0.075(3)	0.018(3)
O10	0.725(1)	0.744(1)	0.138(3)	0.020(3)
OH1	0.982(1)	0.880(1)	0.211(3)	0.027(4)
OH2	0.745(1)	0.907(1)	0.004(3)	0.021(4)
OW1	0.544(1)	0.949(1)	0.167(3)	0.027(4)
OW2	0.360(1)	0.491(1)	0.325(3)	0.034(4)
OW3	0.804(1)	0.591(1)	0.032(3)	0.043(5)
OW4	0.875(1)	0.502(1)	0.370(3)	0.029(4)
OW5	0.131(2)	0.005(1)	0.231(4)	0.053(5)

Note: Numbers in parentheses represent 1 esd and refer to the last decimal place. Designations of atoms are similar to those of Smith and Stohl (1972). The O1 to O4 are uranyl oxygens, O5 to O8 link two uraniums with Si, O9 to O10 link one U with Si, OH1 to OH2 are $(\text{OH})^-$ ions. OW1 to OW5 are water molecules.

* For U1, U2, and Ca, U_{iso} was calculated from anisotropic temperature factors.

DISCUSSION

The refinement of the structure of beta-uranophane in the triclinic space group, $P\bar{1}$, yielded atomic coordinates which confirmed the $P2_1/a$ symmetry within the accuracy of the determination. This observation and the fact that there is no improvement in the R value by lowering the symmetry show unequivocally that the space group of beta-uranophane should be $P2_1/a$ as determined by Gorman and Nuffield (1955) and Smith and Stohl (1972). The atomic parameters arrived at after refinement in $P2_1/a$ are given in Table 4. The interatomic distances are given in Table 5. The basic structure determined by Smith and Stohl (1972) is found to be correct. It consists of sheets of composition $[(\text{UO}_2)_2(\text{SiO}_4)_2]^{4-}$ with the SiO_4 tetrahedra along each edge of a $(\text{UO}_2)_2\text{O}_5$ chain pointing alternately up and down with respect to the plane of the sheet (Fig. 1). The Ca ions and water molecules are located between the sheets (Fig. 2).

The refinement, however, shows that five water molecules are present instead of four (Smith and Stohl, 1972), and their peak heights in difference maps are about the same as those of the other oxygens in the structure. Hence there is no evidence for partial occupancy. The short Si-O distances and O-O distances reported by Smith and

Table 5. Interatomic distances (Å) and angles (°) in beta-uranophane

U1-O4	1.808(12)	U2-O1	1.798(14)
U1-O2	1.818(14)	U2-O3	1.829(14)
U1-O9	2.277(17)	U2-O10	2.216(17)
U1-O7	2.337(14)	U2-O6	2.250(16)
U1-O5	2.390(14)	U2-O8	2.316(18)
U1-O8	2.460(19)	U2-O5	2.445(15)
U1-O6	2.528(17)	U2-O7	2.485(14)
Mean	2.231	Mean	2.191
Ca-OW1	2.386(16)	Si1-O8	1.577(19)
Ca-OW3	2.394(21)	Si1-O9	1.610(17)
Ca-O3	2.395(15)	Si1-O6	1.619(18)
Ca-OW2	2.395(18)	Si1-OH1	1.628(16)
Ca-OW4	2.505(18)	Mean	1.609
Ca-O1	2.579(16)	Si2-O5	1.588(16)
Ca-O4	2.607(15)	Si2-OH2	1.639(15)
Ca-OH2	2.615(17)	Si2-O7	1.646(15)
Mean	2.485	Si2-O10	1.647(17)
		Mean	1.630
O4-O9	2.86(2)	O4-U1-O9	88.0(6)
O4-O7	2.95(2)	O4-U1-O7	89.8(6)
O4-O5	3.05(2)	O4-U1-O5	92.3(6)
O4-O8	3.18(2)	O4-U1-O8	94.9(6)
O4-O6	2.98(2)	O4-U1-O6	85.0(6)
O2-O9	2.99(2)	O2-U1-O9	93.1(6)
O2-O7	2.99(2)	O2-U1-O7	91.4(6)
O2-O5	2.92(2)	O2-U1-O5	86.7(6)
O2-O8	2.92(2)	O2-U1-O8	84.6(6)
O2-O6	3.21(2)	O2-U1-O6	93.6(6)
O9-O7	3.08(2)	O9-U1-O7	83.7(5)
O9-O5	3.04(2)	O9-U1-O5	81.2(5)
O7-O8	2.69(2)	O7-U1-O8	68.0(6)
O5-O6	2.76(2)	O5-U1-O6	68.2(5)
O8-O6	2.50(2)	O8-U1-O6	60.1(6)
Mean	2.94		
O1-O10	2.96(2)	O1-U2-O10	94.3(6)
O1-O6	2.87(2)	O1-U2-O6	89.4(6)
O1-O8	2.96(2)	O1-U2-O8	90.9(6)
O1-O5	2.93(2)	O1-U2-O5	85.7(6)
O1-O7	3.25(3)	O1-U2-O7	97.4(6)
O3-O10	2.82(2)	O3-U2-O10	87.8(6)
O3-O6	2.85(2)	O3-U2-O6	88.1(6)
O3-O8	3.01(2)	O3-U2-O8	92.3(6)
O3-O5	3.08(2)	O3-U2-O5	91.1(6)
O3-O7	2.88(2)	O3-U2-O7	82.3(6)
O6-O10	2.88(2)	O6-U2-O10	80.4(6)
O8-O10	2.93(3)	O8-U2-O10	80.4(6)
O6-O5	2.76(2)	O6-U2-O5	71.9(6)
O8-O7	2.69(2)	O8-U2-O7	67.9(6)
O5-O7	2.48(2)	O5-U2-O7	60.5(5)
Mean	2.89		
OW1-OW3	3.35(3)	OW1-Ca-OW3	89.0(6)
OW1-O3	3.25(3)	OW1-Ca-O3	85.8(5)
OW1-OW4	3.35(3)	OW1-Ca-OW4	86.3(6)
OW1-O4	2.90(2)	OW1-Ca-O4	70.8(5)
OW1-OH2	3.09(2)	OW1-Ca-OH2	76.3(5)
OW3-OW2	3.50(3)	OW3-Ca-OW2	93.8(7)
OW3-O4	3.08(3)	OW3-Ca-O4	75.9(6)
OW3-OH2	2.93(2)	OW3-Ca-OH2	71.5(6)
OW2-O3	2.85(2)	OW2-Ca-O3	73.1(5)
OW4-O3	2.76(2)	OW4-Ca-O3	68.5(5)
OH2-O3	2.88(2)	OH2-Ca-O3	69.9(5)
OW2-O1	2.77(2)	OW2-Ca-O1	67.5(5)
OW2-OH2	3.07(2)	OW2-Ca-OH2	75.5(6)
OW4-O1	3.08(2)	OW4-Ca-O1	74.5(5)
OW4-O4	3.08(2)	OW4-Ca-O4	74.0(5)
O1-O4	3.12(2)	O1-Ca-O4	73.8(5)
O8-O9	2.65(3)	O8-Si1-O9	112.3(9)
O8-O6	2.50(2)	O8-Si1-O6	102.8(9)
O8-OH1	2.66(2)	O8-Si1-OH1	112.3(9)
O9-O6	2.67(2)	O9-Si1-O6	111.4(8)
O9-OH1	2.69(2)	O9-Si1-OH1	112.3(9)
O6-OH1	2.58(2)	O6-Si1-OH1	105.2(8)
Mean	2.63	Mean	109.4

Table 5—Continued

O5-OH2	2.64(2)	O5-Si2-OH2	109.5(8)
O5-O7	2.48(2)	O5-Si2-O7	100.3(8)
O5-O10	2.72(2)	O5-Si2-O10	114.3(8)
OH2-O7	2.65(2)	OH2-Si2-O7	107.5(8)
OH2-O10	2.68(2)	OH2-Si2-O10	109.5(9)
O7-O10	2.78(2)	O7-Si2-O10	115.2(8)
Mean	2.66	Mean	109.4
OW1-O9	2.77(2)	OW2-OH1	2.74(2)
OW1-OW4	2.85(2)	OW2-O2	2.86(2)
OW1-OW1	2.97(2)	OW2-OW5	2.96(3)
OW3-O10	2.71(2)	OW5-OH2	2.72(3)
OW3-OW4	2.79(3)	OW5-OH1	2.84(2)
OW3-O4	3.08(3)	OW5-O2	2.93(2)
OW3-O9	3.10(2)	OW5-OW2	2.96(3)
OW4-OW3	2.79(2)		
OW4-OW1	2.85(2)		

Note: Numbers in parentheses represent 1 esd and refer to the last decimal place. O-O edges of cation polyhedra up to 3.5 Å. Otherwise O-O distances up to 3.1 Å are listed.

Stohl (1972) are found to be slightly longer (Table 5). Some of the O-O distances that do not belong to the cation polyhedra are shorter than 3.1 Å, suggesting the presence of H bonding (Brown, 1976).

In order to derive a H-bonding scheme, the individual bond strengths for the metal cations were calculated at first using the formula given by Brown and Wu (1976) and Brown (1981). Bond strength sums of 6.09, 6.39, 1.98, 4.25, and 4.01 valence units were obtained for U1, U2, Ca, Si1, and Si2, respectively. Considering the standard deviations in the metal-oxygen distances, the agreement between the calculated bond strengths and the valences of the cations should be considered quite good. Hence reliable bond strength sums (without considering H⁺)

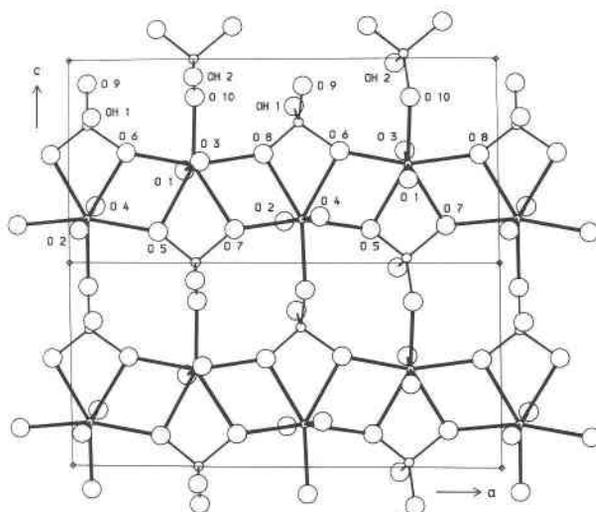


Fig. 1. A view of the $[(\text{UO}_2)_2(\text{SiO}_3\text{OH})]$ sheet in beta-uranophane parallel to the *b* axis. Two unit cells are shown. Note that the apices of the adjacent (SiO_3OH) tetrahedra in the *a* direction point alternately up and down.

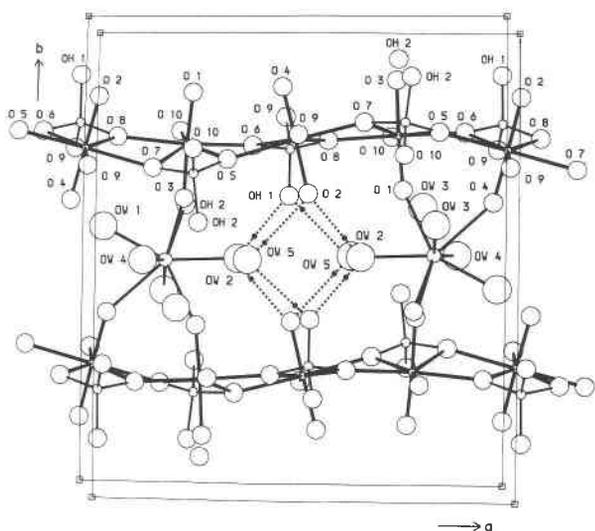


Fig. 2. A slightly tilted projection on (001) of the beta-uranophane structure illustrating the scheme of H bonding. H bonds are shown by dotted lines. Open circles with decreasing size represent water molecules, oxygens [or (OH)], Ca, Si, and U, respectively. H bonds around OW4 have been omitted for clarity.

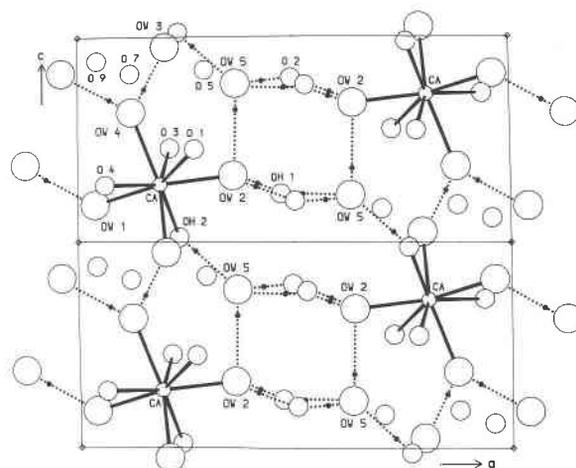


Fig. 3. A projection on (010) of a slab of the beta-uranophane structure (between $y = 0.27$ and $y = 0.73$) illustrating the scheme of H bonding. Two unit cells are shown. H bonds are shown by dotted lines. Those H atoms that play an important role in the proposed H bonds are shown as filled circles. Open circles with decreasing size represent water molecules, oxygens [or (OH)] and Ca, respectively.

around the oxygens could be calculated, and the following inferences could be made:

1. The apical oxygens (OH1 and OH2, Figs. 1, 2, and 3) of all SiO_4 tetrahedra are highly undersaturated; their bond-strength sums vary from 1.00 to 1.16 valence units, as calculated from the bond lengths in Table 5. This means that they should be receiving *large* contributions from *nearby protons*. On the basis of the H-bonding scheme proposed below, they should be defined as (OH) ions.

2. The uranyl oxygens (O2) that are not coordinated by Ca (Figs. 1, 2, and 3) and the two oxygens (O9 and O10, Fig. 1) that link U atoms with silicons are slightly undersaturated and are likely to be acceptors of *weak* H bonds.

After having determined which oxygen anions are undersaturated, the next step was to scrutinize all OW–O approaches that fall below 3.1 Å and are not shared edges of the polyhedra coordinating Ca. This led to the following observations:

1. The oxygens OW1, OW2, OW3, OW4, and OW5 should be defined as water molecules on the basis of their bond-valence sums. All of them, excepting OW4, are located near at least one undersaturated oxygen with at least one OW–O distance being shorter than 2.80 Å. The shortest OW–O distance observed is 2.71 Å. Atom OW4 also forms weak H bonds with neighboring water molecules, OW1 and OW3 (Fig. 3).

2. None of the water molecules shows more than one OW–O bond shorter than 2.71 Å. Thus the existence of $(\text{H}_3\text{O})^+$ ions with three strong H bonds appears unlikely (Brown, 1976).

3. Two water molecules (OW2 and OW5) appear to be very important for the stability of the structure of beta-uranophane. They are located near the highly undersat-

urated apical oxygens of the SiO_4 tetrahedra and somewhat less undersaturated uranyl oxygens (O2). The distribution of the short OW–O bonds and the calculated bond strength in this part of the structure suggests that the apical oxygens must be $(\text{OH})^-$ ions, as stated earlier.

Thus a scheme of H bonding has been worked out (Figs. 2 and 3) that gives the best bond-valence sums. The valence contributions from protons were estimated, using the O–O distances (Brown, 1976). The essential feature of this scheme is that it shows neither isolated $(\text{OH})^-$ ions bonded only to Si atoms nor $(\text{H}_3\text{O})^+$ ions, but something in between, i.e., $(\text{OH})^-$ ions that interact rather strongly (bond strengths about 0.2 valence units) with the neighboring water molecules (OW2 and OW5).

The infrared spectra were initially made in the hope that they would confirm either the model of isolated $(\text{OH})^-$ or that of $(\text{H}_3\text{O})^+$, as proposed earlier (Smith et al., 1957; Smith and Stohl, 1972). However, the spectra show features supporting both the models or *at best* a scheme involving the features of both the models. Thus, the observed bands at 3500, 3400, 3270, 1650, and 1180 cm^{-1} can be attributed to the presence of (SiO_3OH) groups, which are H-bonded to the nearby water molecules.

Differential thermal analysis (DTA) showed a fairly sharp endothermic peak at 115°C, and the differential thermogravimetric analysis (DTG) a rapid loss of about 3.5–4 molecules of H_2O in the range 80–160°C. On the other hand, at about 83°C, X-ray powder patterns indicate a spontaneous transformation to an entirely new phase, which suffers slight further changes with increasing temperature. As the temperature of phase transition coincides with that at which a considerable dehydration begins, it is concluded that most of the water molecules present

stabilize the structure and that the H bond plays a vital role in the structure of beta-uranophane. The powder pattern of the high-temperature phase is similar to those of coffinite [USiO_4 , JCPDS 11-420, and $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$, JCPDS 8-304], uranothorite $[(\text{Th,U,Ce})\text{SiO}_4$, JCPDS 8-395], thorogummite $[(\text{Th,U})(\text{SiO}_4)_{1-x}(\text{OH})_{4x}]$ and thorite $[(\text{ThSiO}_4)$, JCPDS 18-1371 and 11-419].

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