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WATER AND INTERLAYER OXONIUM IN HYDRATED URANATES

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ABSTRACT

The results of the chemical analyses of forty-four synthetic hydrated uranates obtained by various authors show that bivalent or univalent cations replace water continuously. The general formulas

$$mXO\cdot 2UO_3\cdot (4-2m)\cdot H_2O$$

and

$$mXOH\cdot 2UO_3\cdot (4-2m)H_2O$$

fit all the known uranate minerals. The replacement of water is interpreted by postulating presence of oxonium and

$$X^{2+}_{\mathrm{m}}(H_3O)^{+}_{2-\mathrm{m}}[(UO_2)_2O_{2+\mathrm{m}}(OH)_{2-\mathrm{m}}]$$

$$X^{+}_{\mathrm{m}}(H_3O)^{+}_{2-\mathrm{m}}[(UO_2)O(OH)]_2$$

A structure model is proposed in which X^{++}, X^{+}, H_3O^{+} are interlayer connections. An interpretation of dehydration phenomena accounts for the chemical formulae of compounds such as curite and $2XO\cdot 5UO_3\cdot 3H_2O$.

INTRODUCTION

A study of the uranium compounds traditionally called "hydrated uranates" reveals a confusion, further aggravated by the use of different, often mutually contradictory designations.

As long ago as 1950, Brasseur observed the striking similarities shown by all compounds of general formula

$$mXO\cdot nUO_3\cdot pH_2O \qquad (1)$$

where m, n and p are integers and where X stands for Ca, Ba or Pb. The similarity of the X-rays patterns and the existence of a common pseudohexagonal sublattice with approximate subcell dimensions:

$$a' = 7.06\ \text{Å}$$
$$b' = 4.08\ \text{Å}$$
$$c' = 7.32\ \text{Å}$$

reveal an analogous substructure for all the hydrated uranates. Moreover, the negative optical character of the crystals, the small angle $2V$ between the optic axes and the cleavage perpendicular to the acute bisectrix must be due to a layer structure. On this basis, Toussaint and Brasseur (1959) have proposed a structure similar to that of calcium and strontium orthoüranates (Zachariasen, 1948; Loopstra and Rietveld, 1969), in which the uranyl ions are sixfold coordinated.

CONTINUOUS REPLACEMENT OF WATER BY XO

Systematic attempts at synthesis of compounds identical to the natural minerals pointed out the existence of uranates in which strontium and ammonium play the same role as lead, barium and calcium. The works of Gillard and Potdevin (1959), Protas (1959) and Stuart and Whateley (1969) show that the hydrated uranates of an X^{2+} cation do not exist only for distinct stoichiometric proportions but in fact constitute an unbroken series the composition of which is a continuous function of the ratio of the concentrations $[U]/[X]$ of the solutions used for the synthesis. Table 1 illustrates this fact for synthetic compounds prepared by different authors. The first column gives the chemical formula proposed by the authors. The second and third columns give the molar proportions of XO and water respectively for uranium concentration of two moles per chemical formula. The data are calculated from the results of the chemical analyse. The fourth column represents the value of the sum of two molar concentrations: $(2XO+H_2O)$ for uranates of bivalent cations and (NH_3+H_2O) for ammonium uranates. The reason for these choices will become apparent further on. For $UO_3 \cdot 2H_2O$, the notations are those of Christ and Clark (1960) combined with those of Wheeler, Dell and Watt (1964). It is remarkable that the X^{2+} concentration decreases when the degree of hydration increases whereas the sum of molar concentrations $(2XO+H_2O)$ remains practically constant, close to the errors of analysis, even for large changes in the ratio X/U. A balanced least-squares calculation gives the following regression line:

$$x = 1.892 - 0.455\, y \qquad (2)$$

with a correlation coefficient $r=0.979$. x and y are respectively the molar concentrations in XO and H_2O. The calculation of the confidence limits shows that the regression line (2) may also be written

$$x = 2 - 0.5\, y \qquad (3)$$

with a confidence probability of about 0.90. Figure 1 represents the results of the least-squares calculation. The values proposed in the regression line (3) are amply ratified by the formulae of well known minerals:

$UO_3 \cdot 2H_2O$ (schoepite)

and

$PbO \cdot 2UO_3 \cdot 2H_2O$ (wolsendorfite).

TABLE 1. DATA FROM CHEMICAL ANALYSES

Formulas	Reference	XO	H_2O	$2XO+H_2O$ or NH_3+H_2O
$UO_3\cdot 2H_2O$ schoepite I	(a)	0.00	3.76	3.76
$UO_3\cdot 2H_2O$	(b)	0.00	4.07	4.07
$UO_3\cdot 2H_2O$ schoepite IIβ	(c)	0.00	3.97	3.97
$PbO\cdot 7UO_3\cdot 12H_2O$	(b)	0.29	3.53	4.11
$PbO\cdot 7UO_3\cdot 12H_2O$	(b)	0.30	3.64	4.24
$PbO\cdot 7UO_3\cdot 12H_2O$	(b)	0.30	3.75	4.35
$PbO\cdot 6UO_3\cdot 10H_2O$	(a)	0.31	3.38	4.00
$CaU_6O_{16}(OH)_6\cdot 8H_2O$	(b)	0.32	3.79	4.43
$CaU_6O_{16}(OH)_6\cdot 8H_2O$	(b)	0.33	3.66	4.32
$CaU_6O_{16}(OH)_6\cdot 8H_2O$	(b)	0.33	3.73	4.39
$BaO\cdot 6UO_3\cdot 10H_2O$	(a)	0.33	3.11	3.77
$BaO\cdot 6UO_3\cdot 10H_2O$	(a)	0.33	3.38	4.04
$CaO\cdot 6UO_3\cdot 10H_2O$	(a)	0.33	3.69	4.35
$BaU_6O_{16}(OH)_6\cdot 8H_2O$	(b)	0.33	3.66	4.32
$BaU_6O_{16}(OH)_6\cdot 8H_2O$	(b)	0.34	3.80	4.44
$CaO\cdot 6UO_3\cdot 10H_2O$	(d)	0.35	3.32	4.02
$SrO\cdot 6UO_3\cdot 10H_2O$	(a)	0.35	3.27	3.97
$SrU_6O_{16}(OH)_6\cdot 7H_2O$	(b)	0.36	3.41	4.13
—	(e)	0.46	2.87	3.79
$PbO\cdot 4UO_3\cdot 5H_2O$	(b)	0.48	3.13	4.09
$PbO\cdot 4UO_3\cdot 5H_2O$	(b)	0.49	3.04	4.02
$PbO\cdot 4UO_3\cdot 5H_2O$	(b)	0.52	3.00	4.04
$2SrO\cdot 7UO_3\cdot 10H_2O$	(b)	0.54	2.96	4.04
$0.9\ SrO\cdot 3UO_3\cdot 4.2H_2O$	(a)	0.56	2.79	3.91
$2\ SrO\cdot 7UO_3\cdot 10H_2O$	(b)	0.59	2.96	4.44
$3PbO\cdot 8UO_3\cdot 10H_2O$	(b)	0.60	2.86	4.06
$BaO\cdot 3UO_3\cdot 5H_2O$	(b)	0.62	3.13	4.37
$BaO\cdot 3UO_3\cdot 5H_2O$	(b)	0.63	2.94	4.20
$BaO\cdot 3UO_3\cdot 5H_2O$	(d)	0.64	3.21	4.49
$NH_3\cdot 3UO_3\cdot 5H_2O$	(c)	0.66	3.34	4.00
$NH_3\cdot 3UO_3\cdot 5H_2O$	(e)	0.67	2.57	3.91
$BaO\cdot 3UO_3\cdot 4H_2O$	(a)	0.68	2.68	4.04
$3PbO\cdot 8UO_3\cdot 10H_2O$	(b)	0.69	2.50	3.88
$PbU_2O_7\cdot 2H_2O$	(b)	0.86	2.09	3.81
$PbU_2O_7\cdot 2H_2O$	(b)	0.95	1.92	3.82
—	(e)	0.93	1.85	3.71
$PbU_2O_7\cdot 2H_2O$	(b)	0.98	1.94	3.90
$PbO\cdot 2UO_32H_2O$	(d)	0.99	2.03	4.01
	(e)	1.00	1.90	3.90
$NH_3\cdot 2UO_3\cdot 3H_2O$	(c)	1.00	2.90	3.90
$PbU_2O7\cdot 2H_2O$	(b)	1.06	2.07	4.19
$BaO\cdot 2UO_3\cdot 2H_2O$	(a)	1.13	1.88	4.14
$PbO\cdot 2UO_3\cdot 2H_2O$	(a)	1.15	1.75	4.05
$2NH_3\cdot 3UO_3\cdot 4H_2O$	(c)	1.28	2.80	4.08

(a) Peters (1967)
(b) Protas (1959)
(c) Cordfunke (1962)
(d) Potdevin and Brasseur (1958)
(e) Gillard and Potdevin (1959).

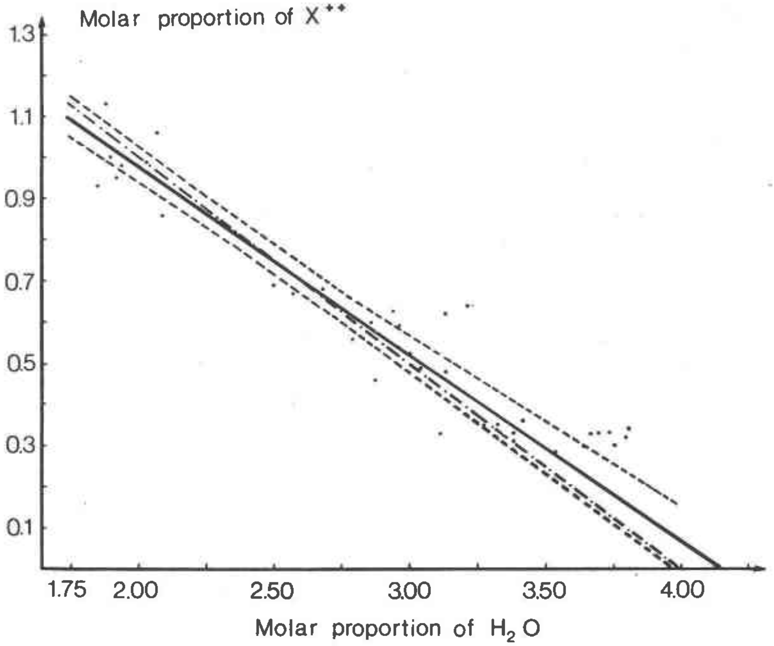

FIG. 1. Least squares calculation. The solid line represents Eq. (2); the dot-and-dash line corresponds to Eq. (3); and the dashed lines give the confidence bands.

Consequently, formula (1) must be written

$$mXO \cdot 2UO_3 \cdot (4 - 2m)H_2O \tag{4}$$

For the ammonium uranates, the formula

$$mNH_3 \cdot 2UO_3 \cdot (4 - m)H_2O \tag{5}$$

agrees with the results of Stuart and Whateley (1969). Therefore, formulae as dissimilar as those of the hydrated uranates are more closely related that would seem at first sight. Formula (4), however, cannot represent hydrated uranates as it fails to account some important experimental results.

First, the infrared study of some hydrated uranates (Deane, 1962: Stuart and Whateley, 1969) shows the presence of uranyl (UO^{2+}) and hydroxyl (OH^-) ions in the structure. Secondly, the D.T.A. curves reveal two peaks; one around 130°C and the other near 240°C (Potdevin and Brasseur, 1958; Peters, 1966; Stuart and Whateley, 1969) except for α- and β-$UO_3 \cdot 2H_2O$ II where these peaks are significantly displaced (Wheeler, Dell, and Wait, 1964; Stuart and Whateley, 1969). Thirdly the thermogravimetric analysis, in many cases, reveals a sudden change in the curvature of the curves (Potdevin and Brasseur, 1958; Protas, 1969; Peters, 1968). The last two observations require two species of water in these compounds and thus confirm the presence of OH^- ions in the structure. Finally, formula (2) does not explain the continuous substitution of X^{2+} for water.

FIVEFOLD COORDINATION

In 1963, Evans suggested that uranyl ion are fivefold coordinated to oxygen and hydroxyl ions. His theory is based on the knowledge of the position of uranium atoms in becquerelite $CaO \cdot 6UO_3 \cdot 10H_2O$ and billietite $BaO \cdot 6UO_3 \cdot 10H_2O$ where the U–U distances fall into two groups: between 3.75 and 4.05 Å; between 4.54 and 4.69 Å.

In order to explain the longer U–U distances, Evans (1963) imagines that, in a layer $(UO_2(OH)_2)$ analogous to the layers in calcium and strontium orthoüranates (Zachariasen, 1948; Loopstra and Rietveld, 1969), one pair of OH^- ions is replaced by one oxygen atom. The latter is situated near the center of the line that joins two uranium atoms separated by the larger distances (Fig. 2). Evans thus finds a pentagonal co-

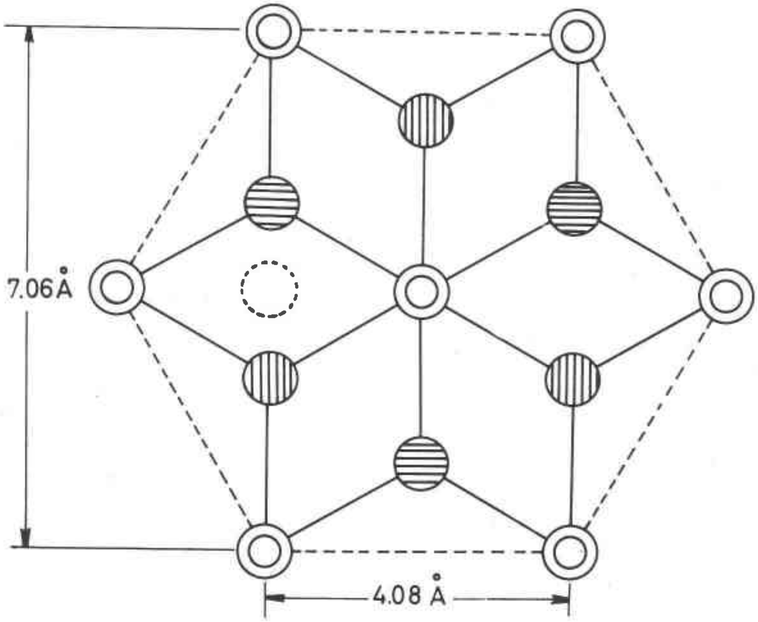

FIG. 2. Coordination 5 (after Evans). Double circles are uranyl ions, dark circles are hydroxyl ion. Two hydroxyl ions are replaced by one oxygen (dotted circle).

TABLE 2. EVANS' CHEMICAL FORMULAE

Name of mineral	Formula (4)	N	Formula with fivefold coordinated uranyl
Schoepite	$UO_3 \cdot 2H_2O$	32 [c, d, e]	$(UO_2)_3O(OH)_4 \cdot 4H_2O$
Vandendriesscheite	$PbO \cdot 8UO_3 \cdot 14H_2O$ [b]	32 or 80 [f]	$Pb_3(UO_2)_{24}O_{14}(OH)_{26} \cdot 29H_2O$
Billietite	$BaO \cdot 6UO_3 \cdot 10H_2O$	12 or 24 [d, g]	$Ba(UO_2)_6O_4(OH)_6 \cdot 7H_2O$
Fourmarierite	$PbO \cdot 4UO_3 \cdot 6H_2O$	32 [c, d]	$Pb_3(UO_2)_{12}O_{10}(OH)_{10} \cdot 13H_2O$
"Triuranates"	$BaO \cdot 3UO_3 \cdot 4H_2O$	24 [c, e]	$Ba(UO_2)_3O_3(OH)_2 \cdot 3H_2O$
Masuyite(?)[a]	$3PbO \cdot 8UO_3 \cdot 10H_2O$	?	$Pb_9(UO_2)_{24}O_{26}(OH)_{14} \cdot 23H_2O$
Wolsendorfite	$PbO \cdot 2UO_3 \cdot 2H_2O$	12	$Pb_3(UO_2)_6O_8(OH)_2 \cdot 5H_2O$
	$NH_3 \cdot 3UO_3 \cdot 5H_2O$ (h)	36	$(NH_4)(UO_2)_3O_2(OH)_3 \cdot 3H_2O$
	$NH_3 \cdot 2UO_3 \cdot 3H_2O$ (h)	48	$(NH_4)_3(UO_2)_6O_5(OH)_5 \cdot 5H_2O$
	$2NH_3 \cdot 3UO_3 \cdot 4H_2O$ (h)	6	$(NH_4)_2(UO_2)_3O(OH)_{28} \cdot 2H_2O$

(a) The name of the compound $3PbO \cdot 8UO_3 \cdot 10H_2O$ is uncertain. We do not know the values of the cell constants and consequently the value of N.

(b) Formula $PbO_8 \cdot UO_3 \cdot 14H_2O$ seems more accurate than $PbO \cdot 7UO_3 \cdot 12H_2O$, because there are two uranium atoms per subcell,[c] and the cell must contain a integral number of chemical formulas.

(c) Protas (1959).

(d) Christ and Clark (1960).

(e) Peters (1966, 1967).

(f) The value of N depends on the values adopted for cell constants b and c; it has been calculated from the data of Christ and Clark (1960).

(g) Brasseur (1949), and Frondel and Cuttita (1953) have shown that billietite exists in two distinct crystallographic forms.

(h) Debets and Loopstra (1963).

ordination (also encountered in some uranium compounds that are very different from the hydrated uranates studied here). The chemical formulae must therefore be revised. One oxygen or hydroxyl ion is common to such a way that 5/3 O(OH) are attributed to each uranyl ion. Electrical neutrality unambiguously determines the composition of the layers. Table 2 gives Evans' chemical formulae for some compounds and the number N of uranium atoms in the cell.

This formulation of the chemical composition of the hydrated uranates stands in contradiction to some time-honored conceptions.

1) The cell does not contain an integral number of chemical formulae. In fact, this happens only if the cell contains six or twelve times the pseudohexagonal subcell.

2) It seems strange to find a uranyl ion coordinated to five oxygen ions in a pseudohexagonal compound and even in an hexagonal one (Debets and Loopstra, 1963).

3) Although Evans' theory takes into account the presence of uranyl and hydroxyl ions and the existence of two species of water, it cannot possibly explain the dehydration process of these compounds. For example, the thermogravimetric analysis of $UO_3 \cdot 2H_2O$, independently of the phase under consideration, shows two stages of dehydration (Protas, 1969; Stuart and Whateley, 1969). The first step gives a compound of

stoichiometric composition $UO_3 \cdot 0.8H_2O$, traditionally called α-$UO_2(OH)_2$. The formula in Table 2 gives a compound of stoichiometric composition $UO_3 \cdot 0.66H_2O$. Only a very hypothetic transmutation of O^{2-} into $2(OH)^-$ could give the traditional α-$UO_2(OH)_2$. Another example is given by the compound $3\,PbO \cdot 8UO_3 \cdot 10H_2O$ which transforms into curite ($3\,PbO \cdot 8UO_3 \cdot 5H_2O$) at 110°C (Protas, 1959). The formula in Table 2 leads to $9PbO \cdot 24UO_3 \cdot 7H_2O$.

4) The hypothesis of pentacoordinated uranyl ions does not explain the continuous substitution of metal ion for water.

The Oxonium Hypothesis

The substitution

$$X^{2+} \leftrightarrow H_2O$$

is only possible with a positive ion of the water molecules. Indeed, it is necessary to preserve the electrical neutrality of the compound. The too large difference between the ionic radii of the X^{++} or X^+ and H^+ cations does not allow the exchanges

$$X^{2+} \leftrightarrow 2H^+, \text{ and } O^{2-} \leftrightarrow OH^-$$

or

$$X^+ \leftrightarrow H^+$$

imagined by Gillard and Potdevin (1959), Debets and Loopstra (1963) and Stuart and Whateley (1969). Thus, the only possible exchange is:

$$X^{2+} \leftrightarrow H_3O^+ \quad \text{and} \quad O^{2-} \leftrightarrow OH^- \tag{6}$$

or

$$X^+ \leftrightarrow H_3O^+ \tag{7}$$

Assuming that $2p$ moles in $2UO_3 \cdot 4H_2O$ may be replaced by X^{2+} or X^+, that is to say the quantity of water to be written as $p(H_3O)^+(OH)^-$ and using (4) and (5), we obtain two new expressions for each formula previously proposed. Formulae (8) and (10) give the result when the balance of water is assumed to be molecular water and formulae (9) and (11) correspond to water as hydroxyl ions.

$$X^{2+}_{m}(H_3O)^{+}_{p-m}[(UO_2)_2O_{2+m}(OH)_{p-m}] \cdot (4-2p)H_2O \tag{8}$$

$$X^{2+}_{m}(H_3O)^{+}_{p-m}[(UO_2)_2O_{m+2p-2}(OH)_{8-3p--m}] \tag{9}$$

$$X^{+}_{m}(H_3O)^{+}_{p-m}[(UO_2)_2O_2(OH)_p \cdot (4-2p)H_2O] \tag{10}$$

$$X^{+}_{m}(H_3O)^{+}_{p-m}[(UO_2)_2O_{2p-2}(OH)_{8-3p}] \tag{11}$$

Note that p takes a fixed value for all of the hydrated uranates. As shown by Table 1 and formulae (4) and (5), we have:

$$1.25 \leq 0 \leq 2.00. \tag{12}$$

Moreover, it is evident that the number of ions of each species in the cell must be an integer.

Using the values of N (Table 2), we get:

$$\text{for } UO_3 \cdot 2H_2O: \qquad p = \frac{n}{16} \tag{13}$$

$$\text{for } 2NH_3 \cdot 3UO_3 \cdot 4H_2O: \qquad p = \frac{n'}{3} \tag{14}$$

where n and n' are integers. Equations (12), (13) and (14) are compatible only for p equals 2. One can verify that p equals 2 is also valid for all the compounds of Table 2. For this value of p, (8) is identical to (9) and (10) identical to (11) and we have:

$$X^{2+}_{m}(H_3O)^{+}_{2-m}[(UO_2)_2O_{2+m}(OH)_{2-m}] \tag{15}$$

and

$$X^{+}_{m}(H_3O)^{+}_{2-m}[(UO_2)_2O_2(OH)_2] \tag{16}$$

Formula (15) is the general formula proposed by Brasseur in 1962 and (16) is its modification for uranates of univalent ions. It is remarkable that formulae (15) and (16) reveal a sixfold coordinated uranyl ion in contradiction with Evans' theory. We also see that in the uranates of univalent cations, the constitution of the layers does not change with the ratio $[X]/[U]$. This can explain the replacement of H_2O by NH_3 and the high values of m, obtained by Stuart and Whateley (1969), as compared with the values of m encountered in the hydrated uranates of bivalent cations. For examples, the formulae of compounds synthethised by Cordfunke (1962) can be written:

$UO_3 \cdot 2H_2O$	$(H_3O)[(UO_2)O(OH)]$
$NH_3 \cdot 3UO_3 \cdot 5H_2O$	$(NH_4)(H_3O)_2[(UO_2)O(OH)]_3$
$NH_3 \cdot 2KO_3 \cdot 3H_2O$	$(NH_4)(H_3O)[(UO_2)O(OH)]_2$
$2NH_3 \cdot 3UO_3 \cdot 4H_2O$	$(NH_4)_2(H_3O)[(UO_2)O(OH)]_3$

Some experiments confirm the presence of oxonium ions in these compounds. A simple experiment consists in replacing the postulated oxonium ions by univalent ions, which should be possible since the ionic radii are approximatively equal. Peters (1965) performed these experiments on uranates of bivalent cations for the following ions: NH_4^+, K^+, Rb^+ and Cs^+. Chemical analysis shows that the fixation of a univalent ion is compensated by the disappearance of an equivalent quantity of water (thermogravimetric analysis). The constancy of the ratio similarity of the Debye-Scherrer powder patterns taken $[XO]/[UO_3]$, before and after the exchange, and the changes in cell dimensions do not leave any doubt as to the replacement of water by the univalent ion. The cell dimensions vary linearly with the ionic radius of the univalent ion; this is characteristic of the exchange. Similar exchanges have been realized with halogen ions and show the existence of hydroxyl ions. Two additional conclusions can be stated:

1) In exchanges with positive ions, the *c* axis varies much more than the *a* and *b* axes, so that the distance between the uranium planes is appreciably modified. This is the reason why H_3O^+ is considered to be linking these planes together. The same may be said for X^{2+} and X^+ ions, which continuously replace the oxonium ions.
2) Whereas exchanges are important in XOH compounds and confirm the value $p=2$, there are much weaker in halogenides. This observation confirms the existence of structural OH^- in the layers. We expect shortly to publish results of infra-red and N.M.R. experiments which irrefutably show the presence of oxonium ion in hydrated uranates.

IDEALIZED STRUCTURE

Formulae (15) and (16) reveal layers analogous to $Ca(UO_2)O_2$ where some O^{2-} are replaced by OH^-. The hexagonal or pseudohexagonal character of the studie uranates, the dimensions of the pseudohexagonal subcell, the identity of $X^{2+}(UO_2)O_2$ with the compound given by formula (15) with $m=2$, the evidence of stratified structure and the part of connection attributed to H_3O^+, X^{2+} and X^+ are strong arguments for analogous structure of hydrated uranates and $Ca(UO_2)O_2$. The replacement of some O^{2-} by OH^- can explain the large distances U–U and the existence of two different cations H_3O^+ and X^{2+} or X^+ leads to orthorhombic symetry with large axes by juxtaposition of pseudohexagonal subcells. Formulae (15) and (16) show that to H_3O^+ or X^+ correspond one O^{2-} and one OH^- whereas to X^{2+} correspond two O^{3-}. Each H_3O^+, X^+ or X^{2+} should be coordinated to these two oxygen or hydroxyl ions (O_{II}) and to six oxygen ions (O_I^{2-}) from the uranyl groups. The idealized pseudohexagonal subcell is sketched in Figure 3.

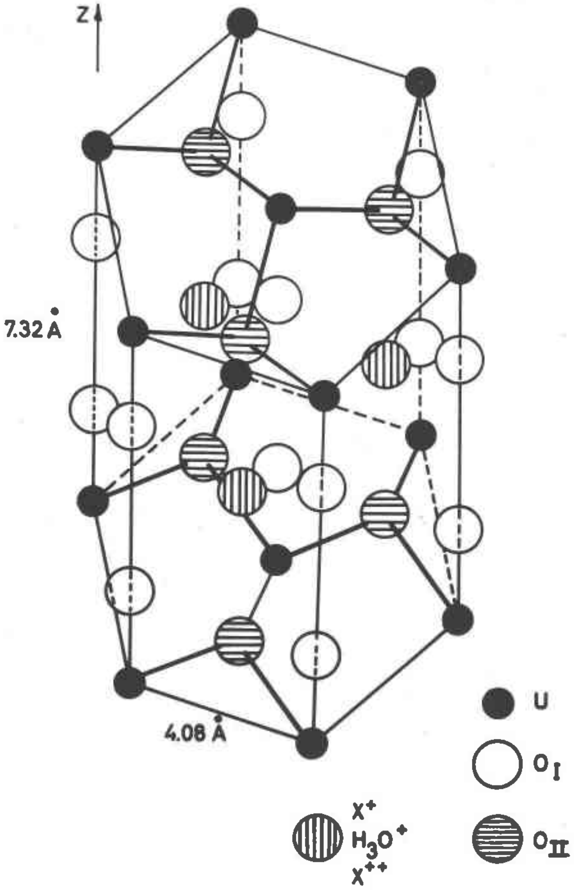

Fig. 3. Idealized structure based on pseudo-cell.

Dehydration Process

It is also possible to take into account of dehydration phenomena from formulae (15) and (16). Indeed, we can imagine the following process:

$$H_3O^+ + O^{2-} \rightarrow H_2O + OH^- \qquad (17)$$

by breaking of an hydrogen bond. Below are given some examples of application of (17):

(a) $m = 0$ $H_3O(UO_2)O(OH) \rightarrow (UO_2)(OH)_2$
(b) $m = \frac{1}{3}$ $Ca(H_3O)_5(UO_2)_6O_7(OH)_5 \rightarrow Ca[(UO_2)_3O(OH)_5]_2$
(c) $m = \frac{3}{4}$ $Pb_3(H_3O)_5(UO_2)_8O_{11}(OH)_5 \rightarrow Pb_3[(UO_2)_4O_3(OH)_5]_2$.
(d) $m = \frac{4}{5}$ $Pb_2(H_3O)(UO_2)_5O_7(OH)_3 \rightarrow Pb_2(UO_2)_5O_4)OH)_6$.

(a) explains how $UO_3 \cdot 2H_2O$ gives the traditional compound $UO_2(OH)_2$.

(b) For $m=\frac{1}{3}$ (billietite or becquerelite), the thermogravimetric curve shows a first step which correspond to a loss of about five water molecules, in agreement with (b).

(c) confirms the obtention of curite from $3PbO \cdot 8UO_3 \cdot 10H_2O$ and gives the structural formula of curite.

(d) explains the existence of the compounds $2XO \cdot 5UO_3 \cdot 3H_2O$, where X stands for Pb, Ba or Sr, obtained by Protas (1959) and Peters (1967).

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