Recently, Evans (1963) presented an excellent review of the known crystal structures containing the uranyl ion, and drew certain general conclusions regarding the stability of the several types of uranyl ion coordination from a study of these structures. As an important feature of his paper, Evans (1963) discusses the possible structures of the natural uranium oxide hydrates and their salts, and presents compelling arguments for considering that the uranyl groups in these compounds have pentagonal coordination. These minerals include becquerelite, $\text{CaO} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$; billietite, $\text{BaO} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$; fourmarierite, $\text{PbO} \cdot 4\text{UO}_3 \cdot 4\text{H}_2\text{O}$; masuyite, formula uncertain; schoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (phases I, II, and III); and vandendriesscheite, formula uncertain (phases I and II); the detailed crystallography of these has been given by Christ and Clark (1960). Evans considers that the very large crystal unit cells of these pseudohexagonal minerals, containing from 12 to 432 uranium atoms, result essentially from the problem of packing pentagonal units into a layer arrangement that is consistent with crystal symmetry. A proposed structure is illustrated for billietite and becquerelite (Evans' Fig. 4); the structure leads to the corresponding chemical formulas $\text{Ba}_6[(\text{UO}_2\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$ and $\text{Ca}_2[(\text{UO}_2\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$. This structure, with a planar layer of charge $-2$, is most attractive in explaining the stability, as well as the complexity, of this kind of salt; it seems much more likely than the one resulting from a puckered-hexagon OH$^-$ coordination, with a neutral $\text{UO}_2(\text{OH})_2$ layer, that was originally proposed by Christ and Clark (1960).

In the study reported by Christ and Clark (1960), a number of crystals of the several uranium oxide hydrates were examined optically and by x-ray precession camera techniques from time to time over a period of months. It was found that becquerelite, billietite, fourmarierite, and masuyite were completely stable, but that schoepite and vandendriesscheite altered spontaneously and continuously to form crystallographically distinct phases in parallel intergrowth. These alterations in schoep-
ite,\(^1\) which were not readily explained on a structural basis at the time of the original study, can now be reexamined in light of Evans' discussion.

Unit-cell data for the three phases of schoepite are given in Table 1. Observations on the alteration of schoepite taken from the paper of Christ and Clark (1960) are as follows. Crystals of schoepite commonly occur with an amber-brown core completely or partially surrounded by a derivative golden-yellow rim which retains the morphology of the original crystal, and which itself yields distinctive single-crystal patterns. The brown part consists chiefly of schoepite I, and the yellow part mostly of schoepite II or schoepite III. Examination under the binocular microscope reveals that the rim is usually threaded by numerous small tubes, lying approximately parallel to (001), radiating from the brown core to the external surface of the crystal. The crystals alter continuously, at varying rates, with the formation of schoepite II or III and concomitant decrease of schoepite I. The rate is not affected by x-ray dosage. When the crystals are kept for several months in an atmosphere saturated with water vapor at room temperature, the same spontaneous unidirectional process continues.

With the structure originally proposed (Christ and Clark, 1960), these observations were explained by assuming that some of the interlayer water was ejected to form a more stable variation of the same type of layer structure, \(i.e.,\)

\[
\text{UO}_2(OH)_2\cdot 2\text{H}_2\text{O} \rightarrow \text{UO}_2(OH)_2\cdot (1 - x)\text{H}_2\text{O} + x\text{H}_2\text{O}
\]

Phase I | Phase II or III
---|---

On the basis of Evans' discussion (Evans, 1963) a completely alternative

\(^1\) Vandendriesscheite also alters spontaneously in a manner similar to schoepite, but its chemical formula is uncertain.
explanation of these observations that seems much more reasonable, can be provided, as follows.

On the basis of the present evidence, it seems likely that schoepite I crystallizes with a pseudohexagonal structure in which the uranyl ions are located at small but significant distances from the nodes of a regular hexagonal net and are coordinated by irregular puckered hexagons of OH− groups. This unstable structure transforms spontaneously by ejection of water from the UO₂(OH)₂ sheet, with the formation of a new sheet structure in which the requirements of pentagonal coordination are more nearly fulfilled. Alternative schemes for accomplishing this are

\[
\begin{align*}
16\text{UO}_2\text{(OH)}_2 & \rightarrow (\text{UO}_2)_{16}\text{O}_4\text{(OH)}_{24} + 4\text{H}_2\text{O} & (1) \\
16\text{UO}_2\text{(OH)}_2 & \rightarrow (\text{UO}_2)_{16}\text{O}_8\text{(OH)}_{20} + 4\text{H}_2\text{O} & (2) \\
16\text{UO}_2\text{(OH)}_2 & \rightarrow (\text{UO}_2)_{16}\text{O}_8\text{(OH)}_{14} + 8\text{H}_2\text{O} & (3)
\end{align*}
\]

The compositions of the resulting layers are consistent with the space groups Pbnm and Pbca (Table 1), which contain only fourfold and eightfold positions. For the pentagonal coordination postulated by Evans (1963), each oxygen bridges 3 uranyls and each uranyl has 5 oxygens as nearest neighbors, hence the ratio of oxygen to uranyl is 5:3 = 1.67. In (1) and (2) above, the postulated layers have the ratio O:UO₂ = 1.75, and in (3) O:UO₂ = 1.5. The first of these ratios implies a structure in which the uranyls have, on the average, slightly greater than pentagonal coordination, corresponding to a total of 28 oxygens instead of 26.7 for each 16 uranyls. The ratio 1.5 would correspond to a defect pentagonal structure reflecting a deficiency of 2.7 oxygens for each 16 uranyls. The production of a pentagonal sheet from a puckered hexagonal one, by the ejection of water in the way suggested, requires relatively minor readjustments of the oxygens or hydroxyls remaining; this can be seen readily from Fig. 4 of Evans’ paper (Evans, 1963).

Our postulates lead to possible structures for schoepite II containing the original amount of interlayer water, with formulas (1) (UO₂)₁₆O₄(OH)₂₄·1₆H₂O, (2) (H₂O)₄[(UO₂)₁₆O₈(OH)₂₀]·1₂H₂O, or (3) (UO₂)₁₆O₈(OH)₁₆·1₆H₂O. The first and third have neutral layers, and the second a layer of charge −4, with interlayer hydronium ions. The oxide formula corresponding to (1) and (2) is UO₃·1₂H₂O, and that corresponding to (3) is UO₃·1₄H₂O. The existence of the UO₃·1₂H₂O phase is clearly predicted by the isobaric thermal decomposition of UO₃·xH₂O diagram of Hütting and von Schroder (in Katz and Rabinowitch, 1951, p. 284), while the UO₃·1₄H₂O phase is not precluded; this diagram has had no previous structural explanation. To account for the increase in cell volume of 171 Å³ in schoepite III over schoepite II (Table 1), it is postulated that schoepite III has one of the possible layer structures given by reactions
(1), (2), or (3), but retains eight additional water molecules per unit cell as interlayer water. The volume per \( \text{H}_2\text{O} \) thus retained, \( 171/8 \approx 21 \, \text{Å}^3 \), is a reasonable one. Thus, possible formulas for schoepite III would be (1a) \( (\text{UO}_2)_6\text{O}_8(\text{OH})_{24} \cdot 20\text{H}_2\text{O} \), (2a) \( (\text{H}_3\text{O})_4[(\text{UO}_2)_6\text{O}_8(\text{OH})_{20}] \cdot 16\text{H}_2\text{O} \), or (3a) \( (\text{UO}_2)_8\text{O}_8(\text{OH})_{16} \cdot 20\text{H}_2\text{O} \). The corresponding oxide formula for (1a) and (2a) is \( \text{UO}_3 \cdot 2\text{H}_2\text{O} \), that for (3a) is \( \text{UO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O} \). Thus, on this basis, schoepite I and schoepite III may be polymorphs. Whether schoepite I transforms directly to schoepite III, or whether schoepite II takes up water to form schoepite III, is not known. In any event, it seems likely that schoepite II is chemically distinct from schoepite I, and that schoepite II and schoepite III have different water contents. We also note, that the compound \( (\text{UO}_2)_6\text{O}_8(\text{OH})_{16} \cdot 16\text{H}_2\text{O} \), would, upon loss of all interlayer water, become \( (\text{UO}_2)_8\text{O}_8(\text{OH})_{16} \), i.e., \( \text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \), which is a well-established uranyl hydrate. \( \text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \) is the first hydrate to appear on the diagram of Hütting and von Schroder (in Katz and Rabinowitch, 1951, p. 284). Dawson et al. (1956) have given directions for preparation of what they believe to be the pure phase \( \text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \), and list x-ray diffraction powder data for it; unfortunately, unit-cell data are not available.

A second observation that is now explicable in terms of the structural relations of schoepite I, II, and III, proposed above, is the following. When schoepite I is subjected to pressure from a dissecting needle, or from grinding, it disintegrates into a yellow powder (Christ and Clark, 1960). Schoepite II and III do not change even on prolonged grinding. This yellow powder consists solely of the monohydrate \( \alpha-\text{UO}_3 \cdot \text{H}_2\text{O} \) (Christ and Clark, 1960), described by Zachariasen (in Katz and Rabinowitch, 1951, p. 285). Thus, the unstable schoepite I readily transforms to \( \alpha-\text{UO}_3 \cdot \text{H}_2\text{O} \), whereas the more stable schoepite II and schoepite III do not. For the process involving the decomposition of schoepite I, i.e.,

\[
\text{UO}_3 \cdot 2\text{H}_2\text{O} \rightarrow \alpha = \text{UO}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}
\]

then, \( \Delta G^\circ > 0 \). Whether the stabilities of schoepite II and III are due to rate processes, or are truly thermodynamic stabilities, cannot be assessed without further work. There is another monohydrate, \( \beta-\text{UO}_3 \cdot \text{H}_2\text{O} \), (see below). In principle, at least, the delineation of the stability fields of all of these various hydrates can be established by measurement of the vapor pressure of water, at various temperatures, over the several equilibrium systems indicated by the foregoing discussion. However, no definitive phase equilibria work appears to have been done on the \( \text{UO}_3 \cdot \text{H}_2\text{O} \) system to date.

The fact that when schoepite I decomposes spontaneously under pressure, it changes to \( \alpha-\text{UO}_3 \cdot \text{H}_2\text{O} \) rather than to \( \beta-\text{UO}_3 \cdot \text{H}_2\text{O} \), suggests that the \( \alpha \)-form is more stable than the \( \beta \)-form. \( \alpha-\text{UO}_3 \cdot \text{H}_2\text{O} \), i.e., \( \alpha-\text{UO}_2(\text{OH})_2 \),
on the basis of its symmetry and unit-cell dimensions (Zachariasen, in Katz and Rabinowitch, 1951, p. 285), undoubtedly has the puckered hexagon coordination around the uranyl ion. β-UO₂(OH)₂ has been described by Bergström and Lundgren (1956) as face-centered orthorhombic, Fmmm, and by Roof, Cromer, and Larson (1964) as primitive orthorhombic, Pbca. However, in either case the coordination of the uranyl ion is found to be fourfold; in the face-centered cell it would be square. The pressure transformation indicates that fourfold coordination is a less stable coordination than sixfold, for the monohydrate. However, again, kinetic factors may be involved. Actually, if each of the two monohydrates can be brought to equilibrium with the same lower hydrate (e.g., UO₃·½H₂O) at a given temperature, and the vapor pressure of water measured over each equilibrium system, then the monohydrate contained in the system with the lowest vapor pressure, would, by definition, be the stable form. Thus, a rather unique opportunity would be afforded to correlate the crystallographer's "stability" with the more usual thermodynamic one.

These considerations have provided a fresh starting point for new experimental work on the schoepite structures and their transformations, and such work has been undertaken in this laboratory.

REFERENCES


