TEI-507

Subject Category: GEOLOGY AND MINERALOGY

DEPARTMENT OF THE INTERIOR

CONTRIBUTION TO THE CRYSTALLOGRAPHY OF URANIUM MINERALS

By
Gabrielle Donnay
J. D. H. Donnay

This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey standards and nomenclature.

April 1955

United States Geological Survey
Washington, D. C.

Prepared by the Geological Survey for the
UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service, Oak Ridge, Tennessee

33376

Printed in USA, Price 30 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

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GEOLOGICAL SURVEY

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Trace Elements Investigations Report 507

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*This report concerns work done partly on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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ABSTRACT

Applying their recently described integrating precession technique, the authors show that most of the existing crystal data on uranyl vanadates, phosphates, and arsenates must be revised. This report gives new cell dimensions (in A, all ± 0.3 percent) and space groups, obtained from rotation, Weissenberg, and precession X-ray photographs; specific gravity (S.G.) determinations made with the Berman balance; and number (Z) of formula units per cell.

Metatyuyamunite has diffraction aspect Pna* and Pnan is a pseudo-space-group. S.G. = 3.92 ± 0.05 (May Day), 3.61 ± 0.05 (Small Spot). Sundberg and Sillén's monoclinic cell dimensions and space group of synthetic anhydrous carnotite are checked on synthetic (S.G. = 4.80 ± 0.05) and on Cane Springs material (S.G. = 4.70 ± 0.05). Twinning is detected by X-rays in carnotite, twin plane (001), index 3, obliquity _ca_. 1°. Sengierite, reported as orthorhombic by Vaes and Kerr, is monoclinic: a = 10.62, b = 8.10, c = 10.11, beta 103°36' ± 10', $P2_1/a$ (C2h-5), S.G. = 4.41, Z = 2. Its powder pattern is indexed.

The following minerals of the metatorbernite I group are treated as tetragonal, the symmetry found by X-rays. Metatorbernite (Cornwall, S.G. 3.70): a = 6.98, c = 17.41, $c' = c/2 = 8.70_5$, c/a = 2.495, c'/a = 1.248, $P4_2/n$ (C4h-4), pseudo - P4/nmm, Z = 2. Meta-autunite I (Lauter, S.G. = 3.48): a = 19.82, a' = (a cos 45°)/2 = 7.01, c = 8.49,

$c/a = 0.428_2$, $c/a' = 1.211$, P***, pseudo-P4/nmm, Z = 8. Uranocircite (Madagascar): $a = 9.87$, $a' = a \cos 45^{\circ} = 6.98$, $c = 16.85$, $c' = c/2 = 8.42_5$, $c/a = 1.708$, $c'/a' = 1.208$, P***, pseudo-P4/nmm, Z = 4. Metazeunerite (Saxony): $a = 7.11$, $c = 17.38$, $c' = c/2 = 8.69$, $c/a = 2.444$, $c'/a = 1.222$, P4/nmm (D4h-7), pseudo-P4/nmm, Z = 2. ("Uranospinite", U. S. National Museum C4394, $a = 7.04$, $c = 17.31$, $c' = 8.65$, P4/nmm, is identified as metazeunerite.) The following data were obtained without the help of the integrating precession technique. Abernathyite (Temple Mt.): $a = 7.17$, $c = 9.07$, $c/a = 1.266$, P4/nmm, Z = 2. Novacekite (sample labelled "troegerite", Schneeberg, S.G. = 3.23): $a = 7.11$, $c = 20.06$, $c/a = 2.823$, $P4_2/n$ (C4h-4), pseudo-P4/nmm, Z = 2. Metanovacekite, $Mg(UO_2)_2(AsO_4)_2 \cdot 4H_2O$ (Schneeberg, S.G. = 3.49): $a = 7.12$, $c = 8.60$, $c/a = 1.209$, P4/n (C4h-3), pseudo-P4/nmm, Z = 1, a hydrate not previously known.

A new chemical formula, $3PbO \cdot 8UO_3 \cdot 4H_2O$, is proposed for curite, orthorhombic, $a = 12.50$, $b = 13.01$, $c = 8.40$, Pna*, Z = 2, S.G. = 7.4 (H. T. Evans), 7.37 (calc.).

INTRODUCTION

Recent work on uranium minerals includes the publications of a group at Harvard and those of the Toronto workers which fall into two series entitled "Studies of uranium minerals" and "Studies of radioactive compounds", respectively. They are primarily concerned with crystal geometry and mineralogy. Studies dealing more especially with crystal structures have been published by a group of chemists in Stockholm. The crystal structure of autunite, accepted as the type for a large number of other species, was proposed by Beintema (1938). For each mineral species studied in this report, we shall make a brief analysis of previous work in the literature.

The crystal structures that have been published to date on uranium minerals of the layer type are not refined structures. They are based on qualitative estimation of intensities only; they give crude agreement at best between observed and calculated intensities and therefore must be considered reasonable hypotheses, resting mainly on packing considerations, rather than definitely established structures. The purpose of this work is to make accurate structure determinations of uranium minerals. The first prerequisite then is to obtain absorption-corrected intensity data, because the errors due to absorption cannot be neglected in crystals containing such heavy atoms as uranium. This task proved to be the chief stumbling block at the outset of this investigation. It led to the adoption of a new technique, one advantage of which is to increase the diffracted intensities several hundredfold as compared with the precession method that uses optimum crystal size. Preliminary photographs showed that most of the existing crystal data on uranyl vanadates, phosphates, and arsenates had to be revised. The present report deals with these new data: cell dimensions and space groups.

Each of the minerals under investigation forms one or several hydrates. Furthermore the water content may vary with temperature and humidity. The changes in the d(001) spacing (parallel to the micaceous cleavage) with changes in humidity and temperature indicate that the water of hydration is situated between structural layers (001) and that the rate at which equilibrium is attained varies with the species and in particular with the metal ion. Equilibrium is most rapidly established with calcium compounds and most slowly with copper compounds. Unless otherwise stated, the crystals were studied at temperatures ranging from 68° to 75° F and humidities of 50 to 60 percent.

The data reported have been obtained from rotation, equi-inclination Weissenberg, and precession photographs. Powder patterns were taken with a view to ascertaining their reliability for identification purposes. All lengths will be given in A units, to ± 0.3 percent, except those obtained from powder patterns which are given to ± 0.1 percent. The numerical values of the X-ray wavelengths used in this work are: Mo$K\alpha$ 0.7107, Cu$K\alpha$ 1.5417 A (Bragg, 1948). The radiation was monochromatized by means of zirconium and nickel filters.

This work was supported in part by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

AN INTEGRATING PRECESSION TECHNIQUE

The minerals with uranyl layer structures present unusual experimental difficulties to the X-ray diffraction worker who wants to obtain reliable intensities. The high uranium content renders an absorption correction imperative, but all attempts to abrade crystals into spheres by means of the Bond grinder were unsuccessful because of the prominent micaceous cleavage. Dr. William Barnes of Ottawa who has had considerable experience with the Bond instrument kindly agreed to try to grind sengierite crystals into spheres for us, but even he had to concede defeat. Professor Ray Pepinsky placed his S. S. White industrial airbrasive unit at our disposal and kindly ground cylindrical specimens for us, but such hard-to-get cylinders were not wholly satisfactory, as they are meant to be used with the Weissenberg camera and a different cylinder would have to be prepared for each layer.

It occurred to us that instead of bathing a small crystal in the X-ray beam we might try to "bathe the beam in the crystal" by taking advantage of the cleavage. We were thus led to use large crystal slices of uniform thickness parallel to the reciprocal-lattice net to be photographed with the precession camera.

The new technique is based on the following property of Buerger's precession method: the incident beam makes a constant angle μ and all diffracted beams make equal angles ν with the normal to the reciprocal-lattice net that is being photographed. The angle μ is the precession angle, that is, the half angle of the precession cone. The angle ν is the half angle of the diffraction cone.

A crystal slice, larger than the cross section of the X-ray beam, is cleaved or ground to uniform thickness parallel to the net of the reciprocal lattice. It is mounted on the precession instrument by means of a narrow glass lath (cut from a cover glass) rather than a capillary tube. If μ is kept constant, the diffracting volume of the crystal has the shape of a right circular cylinder with oblique bases, whose altitude is equal to the thickness of the slice. This volume is rigorously constant for all layers if the beam is strictly collimated. It remains approximately constant in case of a divergent beam, if the thickness is small with respect to the diameter of the direct beam. The diameter of the beam being 1 mm, a crystal slice a few hundredths of a millimeter thick is usually adequate. Edge effects are also minimized if the thickness is kept small. For a given layer the diffracted beams strike the photographic film at a constant angle, so that, if the thickness of the slice were vanishingly small, all the diffracted spots would be elliptical and would have constant area and shape. As the thickness is finite, the spot results from the superposition and the overlap of a series of ellipses, limited at one end by the ellipse produced by the lower side of the slice and at the other end by the ellipse coming from the upper side of the slice. The extent of the overlap depends on the azimuth of the reflection around the normal to the slice. In all cases the center portion of the spot gives the integrated intensity of the reflection, provided the ratio of the slice thickness to the diameter of the direct beam is kept small, because under this condition all the ellipses making up one spot contribute to its central portion. (An ellipse is construed as being due to an infinitesimal thickness dt in the slice of thickness t.) Divergence of the beam has been used in the past to insure that diffracted spots would yield integrated intensities. In the present method too, a divergent beam is all to the good. It follows that the precession films obtained by this method can be measured on a recording microphotodensitometer.

To give absolute intensities, the film must be calibrated with a standard slice cut from a crystal with parameterless crystal structure, say fluorite.

The length of the path of the diffracted beam through the crystal is a constant, equal to $t \sec \nu$, for any one layer. It follows that absorption corrections are not required for the intensities yielded by any one precession photograph.

The intensities from the various layers can be related to one another as follows. Let I_0 and I_n be the intensities from the zero and n^{th} layers respectively, t the slice thickness in mm, μ_c and μ_a the linear absorption coefficients in the crystal and in air, d^* (in A^{-1}) the interplanar distance of the reciprocal-lattice nets under investigation, λ (in A) the wavelength. On the precession camera built by Charles Supper, the crystal-to-film distance (in cm) is $6(1 - nd^*\lambda)$. We find

$$\ln \frac{I_0}{I_n} = t\mu_c \frac{\cos\nu_0 - \cos\nu_n}{\cos\nu_0 \cos\nu_n} - 6\mu_a\, nd^*\lambda.$$

One of the advantages of this method is that the exposure times are short, especially when the crystal slice has optimum thickness,

$$t = 1/\mu_c.$$

As a result, spots too weak to be seen on photographs obtained by conventional methods become visible on the patterns, and the data thus obtained led to a redetermination of space groups and cells.

This method has been published in abstract form (Donnay and Donnay, 1954).

VANADATES

Three minerals have been studied: metatyuyamunite, carnotite, and sengierite. Their crystal structures are closely related, as shown by comparison of the intensities of the diffracted beams. Unconventional settings have been found desirable in order to bring out structural similarities.

Metatyuyamunite, $Ca(UO_2)_2(VO_4)_2 \cdot 3\text{-}5H_2O$

Material.--(1) from May Day mine, Mesa County, Colo. Sample no. LRS/6BX/49. Chemical analysis: K_2O 2.89, CaO 5.42, BaO 0.28, SrO 0.08, UO_3 57.68, V_2O_4 1.27, V_2O_5 18.39, H_2O 13.53, Rem. 0.10, total 99.64 (Analyst, A. M. Sherwood, U. S. Geol. Survey). Water redetermined under controlled atmosphere and recalculated: K_2O 3.10, CaO 5.83, BaO 0.30, SrO 0.09, UO_3 62.12, V_2O_4 1.33, V_2O_5 19.79, H_2O 7.33, Rem. 0.11, total 100.00 (Analyst, A. M. Sherwood, U. S. Geol. Survey).

(2) From Small Spot mine, Calamity, Mesa County, Colo. Sample no. JJK/1/52 (hydrated). Chemical analysis: UO_3 57.08, V_2O_5 20.31, V_2O_4 0.55, CaO 6.03, H_2O 16.03, recalculated to total 100.00 (Analyst, A. M. Sherwood, U. S. Geol. Survey). Later analysis (on same vial of material): CaO 6.22, UO_3 66.80, V_2O_4 2.25, V_2O_5 18.27, H_2O 6.57, total 100.11 (Analyst, A. M. Sherwood, U. S. Geol. Survey). Received from T. W. Stern.

(3) Synthetic. Sample prepared by K. J. Murata.

Morphology.--Thin cleavage flakes, mostly irregular in shape, with an occasional straight edge. No faces other than the cleavage plane (001). The latter gives optical reflection that is sufficient for adjusting the crystal on the two-circle goniometer. No angles could be measured, however.

Method.--The flake is mounted in prism position for precession work. The X-ray beam is normal to the flake. The zero-level pattern a*b* is found normal to the c axis.

Precession and Weissenberg patterns, for material (1) and (2). A powder pattern, for material (3).

X-ray patterns.--Single-crystal patterns are characterized by streaky reflections, which are evidence of disorder or crystal distortion.

Crystal data on metatyuyamunite.--Orthorhombic.

a 10.63, b 8.36, c 16.96, a:b:c = 1.272:1:2.029 (May Day);

a 10.54, b 8.49, c 17.34, a:b:c = 1.241:1:2.042 (Small Spot);

a 10.38, b 8.46, c 17.02, a:b:c = 1.227:1:2.012 (synthetic).

Cell content: 4 formula units. Diffraction aspect Pna*; space group Pnam (D2h-16) or Pna2 (C2v-9). The cell also shows a pseudo-space-group Pnan (D2h-6). As Pna2 is a subgroup of Pnan. it may be more probable than Pnam. Tests for pyroelectricity and piezoelectricity have not been made as yet to check the absence of a center.

Chemical composition.--The variations in all three cell dimensions are an expression of the variations in composition. The chemical analyses can be rewritten as chemical formulas:

$K_{0.61}Ca_{0.96}Ba_{0.02}Sr_{0.01}(UO_2)_2(VO_4)^{-3}_{2.00}(VO_4)^{-4}_{0.15} \cdot 3.75H_2O$ (May Day; $Ca_{0.95}(UO_2)_2(VO_4)^{-3}_{1.70}(VO_4)^{-4}_{0.23} \cdot 3.12H_2O$ (Small Spot). In the May Day analysis, the sum of the positive charges balances that of the negative ones: 6.59+ against 6.60-. In the Small Spot formula: 5.90+ against 6.02-. Using the balance of charges as a reliability criterion, we shall limit the discussion of isomorphous substitutions to the May Day formula.

Inasmuch as cation exchange experiments have shown that potassium, barium, and strontium can substitute for calcium (Hillebrand, 1924;

Murata et al., 1950), the admixture hypothesis seems to be ruled out. Further support for this conclusion is found in the easy replaceability of calcium by copper resulting in synthetic sengierite. (See this report, under Sengierite.)

The replacement of calcium by potassium, however, cannot be invoked in the case of the May Day formula, where the calcium closely approximates the ideal value of 1 and potassium is clearly additional. The excess positive charge due to the potassium is balanced by additional $(VO_4)^{-4}$. The general formula should thus be written

$$CaK_{4x}(UO_2)_2(VO_4)_2^{-3}(VO_4)_x^{-4} \cdot 3\text{-}5H_2O,$$

which cannot be explained on any structural grounds. In the analyses reported in the literature (Palache et al., 1951), the amount of potassium is surprisingly low, as compared to what it is in the May Day analysis. In these analyses calcium could indeed be conceived as being replaced by potassium, but, inasmuch as neither uranium nor vanadium could be oxidized to provide compensation of charge, the latter could only be achieved by substituting two potassium ions for one calcium ion, which would entail disorder in the crystal structure.

<u>Hydration</u>.--It is known that the water content varies, with a corresponding range in density of 3.64 to 4.35 (Hillebrand, 1924, in Palache et al., 1951). Inasmuch as hydration studies indicated two distinct hydrates, 3-5 and 5-8.5H_2O, (Stern et al., 1954), single-crystal work was undertaken to confirm them.

A single crystal (Small Spot) was mounted for X-ray study, placed in a calcium chloride desiccator for several days, X-rayed, then placed back in the desiccator for several more days, X-rayed again, and so on for several weeks. Only the c length was found to change. It decreased by about 3 percent, from 17.34 to 16.84 A. The opposite experiment was also performed. The crystal was kept in 100 percent humidity and repeatedly X-rayed. The c length stayed at 17.34. The high c value reported in Dana (Palache et al., 1951, p. 1045) could not be reproduced. H. T. Evans (personal communication) suggests that, inasmuch as "the recent work on powdered samples of metatyuyamunite by Stern, Stieff, Girhard, and Meyrowitz (in press) definitely establishes the existence of a high hydrate, properly designated tyuyamunite, with composition approximately

$$Ca(UO_2)_2(VO_4)_2 \cdot 8.5H_2O,$$

apparently, the hydration of metatyuyamunite is sufficiently sluggish, especially for single crystals, that not enough was transformed in the experiments to become apparent on the X-ray patterns."

Hydration has an effect on the streakiness of the X-ray reflections. The streaks become longer with increased water content.

Density.--With the cell dimensions of the May Day metatyuyamunite and the corresponding chemical formula (mol. wt 920.82) the calculated density is 4.04 g. cm^{-3}. The observed density, obtained by means of the Berman balance, for the May Day material, is 3.92 ± 0.05 g. cm^{-3}. For the Small Spot material, the density is 3.61 ± 0.05 g. cm^{-3}.

Previous work on metatyuyamunite.--The only X-ray data in the literature are the cell dimensions (in A):

$$a\ 10.40,\ b\ 8.26,\ c\ 19.41,\ a:b:c = 1.26:1:2.35,$$

which were obtained by Weiss-Frondel (1949, in Palache et al., 1951, p. 1045). The data given in the present report have appeared in abstract form (Donnay and Donnay, 1953), where they were given as pertaining to tyuyamunite.

Carnotite, $K_2(UO_2)_2(VO_4)_2\cdot 0\text{-}3H_2O$

Material.--(1) From Cane Springs Pass, near Moab, Utah. Specimen U. S. National Museum 95332, kindly lent by Dr. W. Foshag. Chemical analysis available (Hess and Foshag, 1927). (2) Synthetic (anhydrous?) carnotite, prepared by K. J. Murata (Prep. no. 7A). Sample obtained from H. T. Evans.

Morphology.--Thin cleavage flakes parallel to (001), occasionally bounded by narrow (010) faces. Reflections on the goniometer are very poor.

Method.--Adjustment of the crystal for Weissenberg and precession patterns was made on the microscope between crossed nicols by making use of the extinction direction that is normal to an edge. This direction is $\underline{b} = \underline{b}^*$. It was placed along the axis of the goniometer head. A powder pattern was also taken; grinding of the sample resulted in its partial dehydration, as inferred from the change in $\underline{c}$ (see below).

X-ray patterns.--Streaky reflections, as in tyuyamunite.

Crystal data on carnotite.--Monoclinic.
a 10.47, b 8.41, c 6.91, beta 103°40' ± 10'; a:b:c = 1.245:1:0.822 (Cane Springs); from powder pattern, c = 6.69 ± 0.05 (partially dehydrated).
a 10.46, b 8.40, c 6.59, beta 103°40' ± 20'; a:b:c = 1.245:1:0.784 (synthetic). Cell content: 2 formula units. Space group $P2_1/a$ (C2h-5).

Twinning.--Carnotite shows twinning by reticular merohedry. Twin law: reflection in twin plane (001) or 180° rotation about twin axis

[100] (the two statements are equivalent in view of the point-group symmetry 2/m). Twin index 3; twin obliquity *ca.* 1°. Composition surface, planar and reticular, (001).

The multiple cell whose pseudo-symmetry governs twinning is a sextuple cell, defined either by the net (001) and the row [106], or by the net $(\bar{6}01)$ and the row [100]. The axial elements of carnotite lead to the prediction of two correspondent twins: the one just described and another, which is defined either by reflection in $(\bar{6}01)$ or by 180° rotation about [106], two equivalent statements in view of the point-group symmetry. The correspondent twins can be told apart on inspection of the *c*a** precession photograph: the observed twin law requires that the *a** axes of the two twinned crystals make an angle of about 27°, which has indeed been ascertained on the photograph, while the other twin law would demand that the *c** axes meet at an angle of about 2°, which was ruled out as the two *c** axes were found in exact coincidence. Twinning was detected by X-ray methods, for no crystal was suitable for optical goniometry.

Chemical composition.--The chemical analysis (Hess and Foshag, 1927) can be rewritten as the following formula

$$K_{1.78}Ca_{0.10}Na_{0.10}Mg_{0.04}Al_{0.02}(UO_2)_2(VO_4)_{2.24} \cdot 0.66H_2O.$$

(The sample had been dried over concentrated sulfuric acid before being analyzed.)

Hydration.--The synthetic material gave the same cell dimensions as the anhydrous carnotite of Sundberg and Sillén (1949) within our limits of error. It was then placed in an atmosphere at 100 percent humidity for one day. The *c* length increased from 6.59 to 6.63 Å.

Placing the sample in the humid atmosphere again for several more days did not result in any further increase of c. It must be concluded that hydration of this material is a slow process, much slower than that of tyuyamunite. Yet, in the high state of hydration, water molecules must not be held very tightly, for they can be lost on grinding (as shown by the powder pattern).

Density.--With the cell dimensions of the Cane Spring carnotite and the corresponding chemical formula (mol. wt 874.20), the calculated density is 4.91 g. cm^{-3}. The observed density, measured by means of the Berman balance on a crystal from the same locality, is 4.70 ± 0.05 g. cm^{-3}.

For the synthetic material and the anhydrous formula (mol. wt 848.24), the calculated density is 5.00 g. cm^{-3}; the observed, 4.80 ± 0.05 g. cm^{-3}.

Previous work on carnotite.--The only X-ray work is that of Sundberg and Sillén (1949) on synthetic anhydrous material.[1] Cell dimensions obtained from powder patterns are (in Å) a 10.43_0, b 8.40_3, c 6.59_0, all ± 0.01, beta 104.2°, a:b:c = 1.242:1:0.784. Space group $P2_1/a$ (C2h-5). Cell content: $4KUO_2VO_4$. Calculated density 5.03 g. cm^{-3}. (Crystal setting re-oriented by interchanging Sundberg and Sillén's a and c axes.)

Sundberg and Sillén proposed a crystal structure. It consists of uranyl vanadate layers, parallel to (001), separated by potassium ions, which are embedded between layers to such an extent that the thickness of a layer is close to the interplanar distance d(001). Although the main features of this structure are very reasonable, its details cannot be considered as established. The qualitative agreement between calculated

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[1] Note following misprint in Sundberg and Sillén, p. 350, lines 6 and 7 from bottom: instead of (011), read (100).

and observed intensities, given for the hk0 and h0ℓ reflections, is not sufficiently satisfactory.

The presentation given in Dana (Palache et al., 1951, p. 1043) should be corrected by transforming Sundberg and Sillen's setting, used under Structure cell, to the setting used in this report (see above) as the latter is used throughout the text, first in the discussion of the layer structure, then in the description of the morphology and cleavage. The optical properties in Dana are referred to an orthorhombic setting, which has the same c axis as the setting used in this report.

Weeks and Thompson (1953) presumably used our setting. Their monoclinic b axis is the old orthorhombic a axis, of Larsen's optical data (Palache et al., 1951).

To our knowledge, twinning of carnotite had not been previously reported. The information contained in this report has been published in abstract form (Donnay and Donnay, 1953).

Sengierite, $Cu(UO_2)_2(VO_4)_2 \cdot 10H_2O$ (?)

Material.--From Haut-Katanga, Belgian Congo. Specimen U. S. National Museum 106025 obligingly lent by Dr. W. Foshag. At the request of Dr. H. Buttgenbach, Professor Emeritus of the University of Liège, Belgium, Dr. Schuiling, Director of the Department of Geology, Union Minière du Haut-Katanga, Belgian Congo, kindly sent us all the sengierite available to him, so that the chemical analysis could be repeated.

Morphology.--Of the three vanadates under consideration, sengierite is the only one that occurs in crystals suitable for optical goniometry.

Habit: monoclinic rhombic plates (001), thin or very thin tabular (001) to prismatic [110]. Several crystals were measured on the goniometer. The best angular values obtained are: *c*(001): *a*(100) = 76°40' ± 5', *c*(001): *s*(201) = 51°40' ± 5', and $\varphi(1\bar{1}0) - \varphi(110)$ = 105°30' ± 10' with (001) in polar position. They yield the following axial elements:

a:b:c = 1.316:1:1.236 beta = 103°40'.

Forms observed: *c* {001} , *m* {110} , *a* {100} , *s* {201} , and *p* {111}. Morphological space group $P2_1/a$ (C2h-5).

Methods.--The crystals used for X-ray work were adjusted optically on the two-circle goniometer. Weissenberg, precession, and powder patterns were taken.

X-ray patterns.--The diffraction spots given by sengierite are all sharp. The lack of streaky reflections indicates a completely ordered crystal structure. Sengierite, therefore, is to be chosen for structure analysis. In order to secure intensity data, a complete set of Weissenberg equi-inclination patterns was obtained, consisting of six layers taken about the *c* axis, with Cu$K\alpha$ radiation. The crystal used for this set of pictures was a small, roughly circular disk, 0.03 mm in diameter, obtained (instead of the desired sphere) with the Bond sphere grinder. The optimum crystal size, $2/\mu$, is 0.026 mm. The higher the layer the more intense the spots turn out to be, indicating that absorption greatly affects the intensities. It will be necessary, therefore, to re-take the data by means of the new method (see section on Technique). In this particular mineral, because of the monoclinic symmetry, the face (001) is not a reciprocal-lattice net, and the crystal will have to be ground into a plate at an angle to the cleavage.

Precession patterns a*b*, b*c*, and c*a*, and upper levels were taken; also rotation patterns about c, b, and [110]. A powder pattern has been indexed.

Crystal data on sengierite.--Monoclinic. a 10.62, b 8.10, c 10.11, beta $103^{\circ}36' \pm 10'$; a:b:c = 1.311:1:1.284 (Haut-Katanga). Cell content: 2 formula units. Space group $P2_1/a$ (C2h-5).

Powder data on sengierite.--An indexed powder pattern, taken in CuKα radiation, is given in table 1.

Twinning.--Some indication of twinning led us to investigate the possibility of twinning from the reticular viewpoint. Several twin laws could be predicted, among which twinning by reflection in twin plane (100) or by 180° rotation about [401] would seem most likely, with twin index 2 and twin obliquity ca. 5'. The experimental evidence, however, is inconclusive.

Chemical composition of sengierite.--The chemical analysis in the literature (Vaes and Kerr, 1949) cannot claim any accuracy, in view of the scarcity of the material that was available to the chemist. It led to the formula $Cu(UO_2)(VO_4)OH \cdot 5H_2O$, in which the ratio of cupric ion to uranyl vanadate would thus be twice the ratio of calcium ion to uranyl vanadate in tyuyamunite.

The similarity of the X-ray patterns, including intensities, and the near-equality of the a, b, and β axial elements for sengierite and carnotite point to a similarity in chemical formulas. The fact that sengierite can be obtained from tyuyamunite (see under Hydration) further supports this view. The formula given after the name sengierite as section heading, and followed by a question mark, is the one to be expected. The material sent by Dr. Schuiling was submitted for analysis to the U. S. Geological Survey. According to H. T. Evans (private communication), no useable analysis was obtained.

Hydration.--A sengierite crystal was kept in a desiccator for several days, then re-examined by X-ray methods. The cell dimensions showed no change. The crystal was then placed in a 100 percent humidity atmosphere for several days, and again X-rayed. The cell dimensions remained constant. On the basis of these results, sengierite should be a definite hydrate.

Comparing the observations on hydration for the three vanadates under consideration leads to the following conclusion. The relative change in inter-layer distance with change in water content varies inversely with the value of the distance--the closer the uranyl-vanadate layers the higher the percentage expansion when the water content increases. In the case of carnotite, the interlayer distance of the anhydrous material is d(001) = 6.40 A; it increases 8 percent on hydration. Metatyuyamunite, with an interlayer distance equal to $c/2$ = 8.5 A, shows an increase of about 2 percent. Sengierite, whose interlayer distance is d(001) = 9.82 A, shows no change at all.

The species in which the water molecules are the most loosely held, namely tyuyamunite, is also the only one that was found to exchange its metal ion. A single crystal of metatyuyamunite, mounted for X-ray study, was dipped into a potassium nitrate solution for several days, then X-rayed again. It was found to have partly altered to carnotite. When dipped into a solution of cupric nitrate (0.5 f), metatyuyamunite was found to change completely to sengierite in 9 days. The sengierite crystal was pseudomorphous after metatyuyamunite.

It would appear that sengierite should be found wherever tyuyamunite and copper minerals occur together. On this basis it should occur on the Colorado Plateaus.

Density.--A redetermination of the density on the Berman balance gave the value 4.41 g. cm^{-3}, as compared with ca. 4 in the literature. Our value was obtained on a small fragment (0.75 mg). The calculated density, obtained with the given cell dimensions and 4 formula units of Vaes and Kerr, is 4.37 g. cm^{-3}. With the hypothetical formula given in the section heading, the calculated density becomes 3.99 g. cm^{-3}.

Previous work on sengierite.--The only publication on sengierite is a preliminary description by Vaes and Kerr (1949). The mineral was misinterpreted as orthorhombic, with the following indexing of the forms: c $\{001\}$, p $\{111\}$, a $\{010\}$, m $\{110\}$, s $\{011\}$. It can be seen that s is not in a zone with two p faces and that the zone mam is not at 90° from the c face. This is the explanation of the reported steep dipyramids "$\{331\}$ or $\{441\}$". Inasmuch as cp was measured as 50°40', the calculated angles (001) : (331) and (001) : (441), in the orthorhombic hypothesis, are 74°43' and 78°25', respectively. The measured angle cm being 82°, however, the announced dipyramid should have been indexed $\{661\}$, for 6 tan cp = tan 82°13'. The excellent photograph (Vaes and Kerr, 1949, p. 111) shows a plate lying on c. It can be seen to be monoclinic because the faces a and m are visible (they would appear as lines if the orthorhombic hypothesis were correct) and the intersection of s with p is not parallel to the long diagonal of the plate, as it would be if s were tautozonal with p faces. The interfacial angles given by Vaes and Kerr are in our notation, c (001) : p (111) = 50°40' and m (110) : m ($1\bar{1}0$) = 105°23'.

The data given in the present report have appeared in abstract form (Donnay and Donnay, 1953).

Table 1.--X-ray powder data on sengierite.

hkl	d(calc.)A	d(obs.)A	I 1/	hkl	d(calc.)	d(obs.)A	I 1/
001	9.824	9.82±.08	V.V.St.	$11\bar{3}$	3.102	3.094±.008	St.
110	6.370			013	3.036		
011	6.249			212	2.976		
$11\bar{1}$	5.741	5.75±.03	M	$31\bar{2}$	2.972	2.970±.007	M
200	5.159			$21\bar{3}$	2.910		
$20\bar{1}$	5.090			221	2.908	2.901±.007	V.W.
111	5.021	5.02±.02	W	$22\bar{2}$	2.871		
002	4.912	4.91±.02	V.St.	122	2.873		
210	4.352			311	2.839	2.832±.007	M
$21\bar{1}$	4.309			113	2.754	2.744±.006	W
012	4.200			$32\bar{1}$	2.655		
$11\bar{2}$	4.197			$40\bar{1}$	2.654		
201	4.180	4.179±.015	M	320	2.621		
$20\bar{2}$	4.070			130	2.611		
020	4.048	4.037±.015	M	031	2.603		
120	3.770			$12\bar{3}$	2.585		
021	3.743	3.735±.012	St.	400	2.580		
112	3.642			$31\bar{3}$	2.573		
$21\bar{2}$	3.637			$13\bar{1}$	2.562	2.550±.006	M
$12\bar{1}$	3.625			023	2.546		
211	3.614			$40\bar{2}$	2.545		
121	3.422			$41\bar{1}$	2.522		
003	3.276	3.262±.009	W	222	2.511		
$31\bar{1}$	3.225			203	2.510		
202	3.200	3.197±.009	St.	$32\bar{2}$	2.508	2.495±.006	V.W.
220	3.185	3.179±.009	St.	131	2.487		
$22\bar{1}$	3.169			$22\bar{3}$	2.471		
310	3.165	3.144±.009	St.	410	2.458		
022	3.124			004	2.456		
$12\bar{2}$	3.123			$20\bar{4}$	2.454		
$20\bar{3}$	3.118			312	2.431		

Table 1.--X-ray powder data on sengierite--Continued.

hkl	d(calc.)A	d(obs.)A	I 1/
$41\bar{2}$	2.428		
321	2.427		
$11\bar{4}$	2.413		
213	2.397	2.398±.005	W
230	2.392		
$23\bar{1}$	2.385		
123	2.373		
032	2.366		
$13\bar{2}$	2.365		
401	2.362		
014	2.351		
$21\bar{4}$	2.349	2.345±.005	V.W.
$40\bar{3}$	2.309		
231	2.268	2.267±.005	V.W.
411	2.268		
$32\bar{3}$	2.254		
132	2.251		
$23\bar{2}$	2.249		
$41\bar{3}$	2.221		
$42\bar{1}$	2.220		
114	2.187		
$31\bar{4}$	2.184		
420	2.176	2.163±.004	W
322	2.157		
$42\bar{2}$	2.155		
$12\bar{4}$	2.144		
$33\bar{1}$	2.141		
223	2.133		
330	2.123	2.124±.004	M
$13\bar{3}$	2.104		
024	2.100		
$22\bar{4}$	2.099		
402	2.090	2.087±.004	M+
033	2.083		
232	2.063		
313	2.063		
$33\bar{2}$	2.062		
$51\bar{1}$	2.054	2.051±.004	W
$23\bar{3}$	2.041		
421	2.040		
204	2.039		
$40\bar{4}$	2.035		
040	2.024		
412	2.024		
$51\bar{2}$	2.021		
331	2.016		
$42\bar{3}$	2.006	2.009±.003	M
$20\bar{5}$	2.000		
510	2.000		
140	1.986		
133	1.985		
041	1.982		
124	1.981		
$32\bar{4}$	1.979		
214	1.977		
$41\bar{4}$	1.974	1.971±.003	V.W.
$14\bar{1}$	1.965		
005	1.965		
$11\bar{5}$	1.960	1.951±.003	V.W.
$21\bar{5}$	1.942		
141	1.930		
$33\bar{3}$	1.914		
$51\bar{3}$	1.913		
015	1.909	1.898±.003	V.W.
$43\bar{1}$	1.893		
323	1.888		
240	1.885		
$24\bar{1}$	1.881	1.881±.003	W
$52\bar{1}$	1.880		
511	1.877		
042	1.872		
$14\bar{2}$	1.872		
430	1.865		
$31\bar{5}$	1.861		
422	1.857		
$52\bar{2}$	1.855		
332	1.853		
$43\bar{2}$	1.852	1.850±.003	W
$13\bar{4}$	1.845		
520	1.839		
233	1.838		
241	1.822		
403	1.828		
224	1.821		
034	1.817		
$23\bar{4}$	1.816		
142	1.813		

Table 1.--X-ray powder data on sengierite--Continued.

hkl	d(calc.)A	d(obs.)A	I 1/	hkl	d(calc.)A	d(obs.)A	I 1/
$24\bar{2}$	1.813			$52\bar{4}$	1.648		
$12\bar{5}$	1.807	1.808±.003	V.W.	$11\bar{6}$	1.645		
115	1.805			$21\bar{6}$	1.644		
$22\bar{5}$	1.793			530	1.640		
413	1.783			006	1.637	1.637±.002	V.W.
$40\bar{5}$	1.779			601	1.630		
431	1.778			$42\bar{5}$	1.628		
$52\bar{3}$	1.770			234	1.627		
025	1.768			$34\bar{3}$	1.623		
$60\bar{1}$	1.767			$62\bar{1}$	1.619		
314	1.764			$13\bar{5}$	1.617		
$51\bar{4}$	1.761			522	1.614		
$60\bar{2}$	1.758}	1.756±.003	M	$62\bar{2}$	1.612		
$43\bar{3}$	1.755}			$44\bar{1}$	1.610		
$34\bar{1}$	1.754			$23\bar{5}$	1.607		
340	1.745			016	1.605		
521	1.742			$31\bar{6}$	1.604		
134	1.738			150	1.600		
$41\bar{5}$	1.738			404	1.600		
$33\bar{4}$	1.737			051	1.598		
$14\bar{3}$	1.734			611	1.598		
$32\bar{5}$	1.729			440	1.593		
$61\bar{1}$	1.726}	1.724±.002	V.W.	$53\bar{3}$	1.590		
043	1.722}			035	1.589		
512	1.720			$15\bar{1}$	1.588		
600	1.720			342	1.585	1.586±.002	V.W.
$61\bar{2}$	1.718			$44\bar{2}$	1.584		
242	1.711			620	1.583		
342	1.710			$14\bar{4}$	1.580		
205	1.707			243	1.576		
$24\bar{3}$	1.698			225	1.573		
125	1.684			151	1.570		
341	1.683			414	1.570		
610	1.683			531	1.570		
$20\bar{6}$	1.679			044	1.562		
333	1.674			$24\bar{4}$	1.562		
215	1.670			$33\bar{5}$	1.560		
$53\bar{1}$	1.669			513	1.556		
423	1.666	1.666±.002	V.W.	$12\bar{6}$	1.551	1.553±.002	V.W.
143	1.665			$22\bar{6}$	1.551		
$42\bar{4}$	1.659			250	1.545		
432	1.653			$25\bar{1}$	1.543		
$53\bar{2}$	1.651			052	1.538		
324	1.650						

Table 1.--X-ray powder data on sengierite--Continued.

hkl	d(calc.)A	d(obs.)A	I 1/
15$\bar{2}$	1.538		
441	1.537		
116	1.533		
135	1.527		
315	1.527		
44$\bar{3}$	1.522		
026	1.518		
32$\bar{6}$	1.517		
602	1.516		
433	1.513		
621	1.512		
144	1.511	1.509±.002	V.W.
251	1.510		
34$\bar{4}$	1.510		
152	1.505		
25$\bar{2}$	1.505		
334	1.502		
53$\bar{4}$	1.500	1.495±.002	V.W.
43$\bar{4}$	1.458		
007	1.404		
060	1.349		

1/ St., strong
M, medium
W, weak
V.W., very weak
V.St., very strong
V.V.St., very, very strong

PHOSPHATES AND ARSENATES

This section covers six compounds with formula $A(UO_2)_2(XO_4)_2 \cdot nH_2O$, where A stands for Cu, Ca, Ba, Mg, K_2 and X for P or As. In the literature they are referred to the metatorbernite-I group which is characterized by a primitive lattice and the next-to-highest state of hydration (for compounds forming more than one hydrate). This state of hydration is the stable one in the laboratory.

All the specimens studied were kindly lent by Dr. W. Foshag of the U. S. National Museum. No chemical analysis was available for any of them. Authentication of the material was made by single-crystal X-ray patterns, the cell dimensions being compared with those in the literature. Confirmation by study of synthetic material would, therefore, be desirable. We have requested Professor C. Frondel, of Harvard University, to lend us the crystals that were synthesized in his laboratory.

There is ample morphological and optical evidence in the literature, some of it confirmed by the present study, that the true symmetry of minerals in this group is lower than tetragonal, either orthorhombic or monoclinic, whereas the space group obtained by X-rays is a tetragonal one. Now, by definition, the symmetry of a crystal is the symmetry common to all its properties. In the present case strain could account for the biaxial character of a tetragonal crystal; pseudomorphism of a tetragonal species after an orthorhombic or monoclinic one could account for the morphology; but neither one nor the other explanation could account for both optics and morphology. Malformation has been invoked (Palache et al., 1951, p. 985) to explain angular deviations, but malformation does not interfere with the law of constancy of angles. The optical properties, according to Beintema (1938, p. 163), "must be attributed to water having been taken up in the crystal lattice". However, weak reflections (not seen by Beintema, but now observable, see below) to which the water molecules do contribute do not show any departure from tetragonal symmetry. The possibility remains that all X-ray intensity data have been obtained from twins composed of two orthorhombic, pseudo-tetragonal crystals of equal volumes, in which the twin operation would be a 90° rotation about the c axis. The noted "sectoral crystals" could be such twins. The crystal-structure analysis, now in progress, should run into difficulties if intensities obtained from a twin are used as though they were single-crystal data.

The minerals under consideration were considered to be isostructural by previous authors. In fact the cells and space groups that have been reported are pseudo-cells and pseudo-space groups. Larger tetragonal cells and different space groups have now been found, by taking weak reflections into account. The structural interpretation is that all structures consist of the same kind of uranyl phosphate and uranyl arsenate layers, that the orientations of the phosphate (or arsenate) tetrahedra within the layers may differ and that the sites of metal atoms and water molecules between the layers may also differ. In the pseudo-cell there was no position of low enough multiplicity to accommodate the metal atoms, so that disorder had to be postulated, with half the sites of a position left vacant. In the new cell such a disorder need not be postulated. All positions can have all their sites filled, except those positions on which the variable number of water molecules must be placed. For such a group of minerals that have certain structural features in common, leading to similarity of X-ray patterns but that cannot be called "isostructural" because their crystal structures are not identical, the term "homeostructural" may be found useful.

The crystal data are summarized in table 2.

Metatorbernite, $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$

Material.--(1) From Cornwall, England. U. S. National Museum 13111. (2) From Katanga district, Belgian Congo. U. S. National Museum 94782.

Morphology.--The morphology approximates tetragonal symmetry. Thin square tablets (001), with edges bevelled off by (101) and (100). The

Table 2.--Crystal data on the phosphates and arsenates.

	Metatorbernite $Cu(UO_2)_2(PO_4)_2\cdot 8H_2O$ Cornwall, England	Meta-autunite I $Ca(UO_2)_2(PO_4)_2\cdot 2\text{-}6H_2O$ Lauter, Saxony	Uranocircite $Ba(UO_2)_2(PO_4)_2\cdot 8H_2O$ Madagascar	Metazeunerite $Cu(UO_2)_2(AsO_4)_2\cdot 8H_2O$ Saxony
a	6.98 A	19.82 A	9.87 A	7.11
a	--	$a/2\sqrt{2} = 7.01$	$a/\sqrt{2} = 6.98$	--
c	17.41	8.49	16.85	17.38
c'	$c/2 = 8.70_5$	--	$c/2 = 8.42_5$	$c/2 = 8.69$
c/a	2.495	0.4282	1.708	2.444
c'/a'	1.248	1.211	1.208	1.222
Space group	$P4_2/n$	P***	P***	P4/nmm
Pseudo-space-group	P4/nmm	P4/nmm	P4/nmm	P4/nmm
Z	2	8	4	2
ρ calc.	3.67	3.50 ($6H_2O$)	4.10	3.87
ρ obs.	3.70	3.48	4.08 (Falkenstein, Saxony)	3.64 (Schneeberg)

Table 2.--Crystal data on the phosphates and arsenates--Continued.

	Abernathyite* $KUO_2AsO_4 \cdot 4\ H_2O$ Temple Mountain	Novacekite* $Mg(UO_2)_2(AsO_4)_2 \cdot 9\ H_2O$ Schneeberg, Saxony	Metanovacekite* $Mg(UO_2)_2(AsO_4) \cdot 4\ H_2O$ Schneeberg, Saxony
a	7.17	7.11	7.12
a'	--	--	--
c	9.07	20.06	8.60
c'	--	--	--
c/a	1.266	2.823	1.209
c'/a'	--	--	--
Space group	$P4/nmm$	$P4_2/n$	$P4/n$
Pseudo-Space-group	--	$P4/nmm$	$P4/nmm$
Z	2	2	1
ρ calc.	3.71	3.23	3.49
ρ obs.	--	3.23	3.49

*Integrating precession technique was not used.

corners are truncated by (110) faces. Deviations from tetragonal symmetry could be ascertained on the goniometer, although few reflections were good enough to yield satisfactory measurements and axial elements could not be calculated from morphology.

A plate was mounted with one of the sides of the square parallel to the axis of the goniometer head. The zone was measured and turned out not to be tetragonal: signals of quality D were obtained from two faces, (101) and $(10\bar{1})$, signals of quality A from the two faces (001) and $(00\bar{1})$, giving the angles:

$$(001):(101) = 49^\circ 50' \text{ (second value } 50^\circ 6'\text{)},$$

$$(00\bar{1}):(10\bar{1}) = 48^\circ 20' \text{ (second value, } 48^\circ 17'\text{)}.$$

The crystal symmetry can at most be monoclinic. If it were to be considered tetragonal, the above measurements would give $\underline{c}/\underline{a} = 1.15 \pm 0.03$, but interfacial angles differing by almost two degrees would have to be considered equal. In an attempt to decide between monoclinic and triclinic symmetry, another crystal was measured. The two zones including (001) were measured in turn. On one of them, the preceding angle of *ca.* $49^\circ 40'$ was found again (F reflection), and another angle of *ca.* 95° (F reflection). On the second zone, an angle $(001):(0\underline{k\ell}) = 51^\circ 7'$ (D reflection) was found and another, $(001):(0\underline{\bar{k}\ell})$ = *ca.* 49° (F reflection). No angle of 90° could be found. With reflections of such poor quality, however, no conclusion can be drawn. On a third crystal, an angle $(001):(100) = 90^\circ 59'$ (D reflection on 100) was obtained. This face (100) was later set normal to the X-ray beam on the precession camera, and the reciprocal-lattice net was found to be off by about 1°. The face (001) was later found to coincide with the $(001)^*$ net. Were it not for their optical anomalies (see Palache et al., 1951, p. 991), these crystals could be interpreted as pseudomorphs.

Methods.--For precession pictures the crystal was mounted with (100) in polar position, the cleavage plate (001) being set normal to the X-ray beam. Rotation and equi-inclination Weissenberg patterns were obtained about both the a and c axes.

X-ray patterns.--All reflections are sharp, as in sengierite. The weak reflections (namely, all those with ℓ odd) are barely visible on a rotation pattern about c, obtained with MoKα radiation in 18 hours. They are not observed at all on a zero-layer Weissenberg pattern about a, obtained with CuKα in 24 hours. With the integrating precession technique and CuKα radiation, a 20-hour exposure yielded a layer of (otherwise) weak reflections, for instance, the layer of the hkl reflections, that could be measured on the micro-densitometer.

Crystal data on metatorbernite.--The following data refer to the symmetry of the crystal as observed by X-rays. Tetragonal: a 6.98, c 17.41, c/a = 2.495 (Cornwall). Cell content: 2 formula units. Space group $P4_2/n(C^4h\text{-}4)$. Pseudo-cell: a 6.98, c' = c/2 = 8.70_5, c'/a = 1.248, with pseudo-space-group $P4/nmm(D^4h\text{-}7)$. Density: 3.67 (calc.), 3.70 (obs., Cornwall).

Hydration.--A crystal of metatorbernite, mounted for X-ray study, was dipped in water for two days, then re-examined by X-rays. It showed the presence of both metatorbernite, with unchanged cell dimensions, and torbernite. It follows that copper uranyl phosphate, like copper uranyl vanadate, is a definite hydrate. The relatively strong bonding between copper and water observed in other hydrated copper salts, for example in $CuCl_2 \cdot 2H_2O$, can be held responsible for the absence of zeolitic water.

The transformation of the metatorbernite to torbernite was still not completed after the crystal had been dipped in water for 10 days.

Previous work.--Berry (in Palache et al., 1951, p. 991) gives cell dimensions (in kX units) and calculated density of 3.76 on material from Cornwall: a 6.95 ± 0.03, c 8.60 ± 0.04, c/a = 1.238 = 2.476/2. His cell is our pseudo-cell.

Crystal structure of metatorbernite.--The doubling of the c dimension and accompanying change in space group necessitates recasting the crystal structure, which so far had been tacitly assumed to be isostructural with that of meta-autunite, proposed by Beintema (1938). The following hypothesis is now being investigated:

Origin at center ($\bar{1}$). Conditions limiting possible $hk\ell$ reflections, in addition to space-group conditions, are stated after each special position below:

Cu at $2a$ 1/4,1/4,1/4	$h + k + \ell = 2n$
U at $4e$ 3/4,1/4,z_1	$\ell = 2n$
O of UO_2 at $4e$ 3/4,1/4,z_2(z_3)	
P at $4f$ 1/4,1/4,z_4	$h + k + \ell = 2n$
O of PO_4 at $8g$ $x_1,y_1,z_5(z_6)$	no condition
O of H_2O at $8g$ $x_2,y_2,z_7(z_8)$	no condition

The value of z_7 must be equal to 1/4 on crystallochemical grounds (because Cu is at height 1/4).

UO_2 does not contribute to the weak reflections ($hk\ell$ with ℓ odd); Cu and P contribute only to those weak reflections for which ℓ is odd and $h + k$ is odd (these reflections form an anti-centered net on an $hk\ell$-layer precession pattern, with ℓ odd); and the very weak reflections for which ℓ is odd and $h + k$ is even are due entirely to the contributions of the oxygen of the phosphate groups and that of the water molecules. These oxygen atoms in positions 8g are the only atoms in the structure that are responsible for the lowering of the symmetry from P4/nmm to $P4_2/n$.

Meta-autunite I, $Ca(UO_2)_2(PO_4)_2 \cdot 2\text{-}6H_2O$

Material.--(1) From Lauter, Saxony. U. S. National Museum 1342 and 5675. (2) From France. U. S. National Museum 79981.

Morphology.--The description of autunite plates applies to meta-autunite. The latter, however, is the stable form under laboratory conditions.

Methods.--Precession pictures of both axial planes with upper levels for (001)*; rotation about a and c; Weissenberg a-axis zero layer.

X-ray patterns.--Two effects are observed on the precession pictures: (1) reflection spots have the shapes of crosses on zero- and upper-level pictures parallel to (001)*; (2) several (as many as four) nets, slightly rotated in their own plane with respect to one another, are superposed on the same picture. These effects must be attributed to a slight disorientation of plates parallel to (001) in the crystal, so that the specimen becomes an aggregate of several crystals.

Crystal data on meta-autunite I.--The following data refer to the symmetry as obtained by X-rays.

Tetragonal: a 19.82, c 8.49, $c/a = 0.428_2$ (Lauter). Cell content: 8 formula units. Diffraction aspect P***, with Laue class 4/m 2/m 2/m. Pseudo-cell: $a' = a/2\sqrt{2} = 7.01$, c 8.49, $c/a' = 1.211$, with pseudo-space-group P4/nmm (D4h-7). Note that the pseudo-cell is rotated 45° with respect to the true cell. Density: 3.50 (calc., assuming 6 H_2O), 3.48 (obs., Lauter). The number of water molecules, calculated from the observed density and cell dimensions, is 5.73.

Hydration of meta-autunite.--From the variation observed in the c dimension of the same crystal, when X-rayed on different days at different humidities, it is concluded that the water content of meta-autunite varies rapidly. No detailed study of the variation of the c dimension was undertaken, but a low value of 8.43 A was obtained on a dry day on Lauter material, which is equal to the 8.42 kX (=8.44 A) reported by Beintema for meta-autunite obtained by dehydrating autunite in hot concentrated calcium chloride solution (Beintema, 1938, p. 168). The meta-autunite crystals thus obtained are pseudomorphous after autunite.

Dipping the crystal of meta-autunite into water changes it completely into autunite in about 24 hours. On the other hand, the same autunite crystal changes back to meta-autunite during an overnight exposure on the precession camera. The dehydration process was somewhat slowed down by coating the crystal with Cenco label varnish; in this manner autunite can be preserved in the laboratory for about three days.

Previous work.--Beintema (1938) studied natural autunite and its dehydration product (synthetic meta-autunite). It is surprising that Dana (Palache et al., 1951, p. 984) does not grant more recognition to meta-autunite as a natural species, for it should occur at least as abundantly as metatorbernite (the conversion of autunite to meta-autunite is more rapid than that of torbernite to metatorbernite).

Uranocircite, $Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$

Material.--From Madagascar. U. S. National Museum R8816.

Morphology.--Light-yellow aggregates of plates, from which crystals for X-ray study were cleaved.

Methods.--Precession patterns with CuKα radiation. Layers hk0, hk1, h0ℓ, hhℓ.

X-ray patterns.--Reflections somewhat streaked along c* as in meta-autunite.

Crystal data on uranocircite.--The following data refer to the symmetry of the crystal as observed by X-rays.

Tetragonal: a 9.87, c 16.85, c/a = 1.708

Cell content: 4 formula units.

Diffraction aspect P***, with Laue class 4/m 2/m 2/m.

Pseudo-cell: $a' = a/\sqrt{2} = 6.98$, $c' = c/2 = 8.42_5$, $c'/a' = 1.208$, with pseudo-space-group P4/nmm (D4h-7). Note that the pseudo-cell is turned 45° with respect to the true cell. Density: 4.10 (calc.), 4.08 (Falkenstein, Saxony, measured by Nuffield and Milne, 1953, p. 480).

Previous work.--Beintema (1938) synthesized uranocircite and gave the dimensions of the pseudo-cell: a' 6.95_2, c' 8.51_5kX. Nuffield and Milne (1953) discovered the doubling of c' and gave the following cell dimensions for Falkenstein material: a' 6.96, c 16.90 A, with the same space group as that of the pseudo-cell a'c', namely P4/nmm. They refer to the octahydrate as "meta-uranocircite".

Metazeunerite, $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$

Material.--(1) and (2) From Weisser Hirsch mine, near Schneeberg, Saxony. U. S. National Museum R5683 and R7927. Both specimens are labeled troegerite. (3) From Saxony, U. S. National Museum 94318.

Morphology.--Thin to thick square tablets beveled by faces making an angle of 68°33' (F signal) with the base, to become (011) when referred to the structural cell.

Methods.--Precession pictures. Layers hk0, hkl, h0ℓ. All in CuKα, some also in MoKα radiation.

X-ray patterns.--The same two effects are observed as on meta-autunite patterns (see above).

Crystal data.--The following data refer to the symmetry observed by X-rays. Tetragonal: a 7.11, c 17.38, c/a = 2.444 (USNM 84318). Cell content: 2 formula units. Space group P4/nmm (D4h-7). Pseudo-cell: a 7.11, c' = c/2 = 8.69, c'/a = 1.222, with same space group P4/nmm. Density: 3.87 (calc.); 3.64 (Schneeberg, measured by J. Weiss Frondel, 1951, p. 250, who considers this a low value).

Previous work.--J. Weiss Frondel (1951) found the pseudo-cell, with the dimensions a 7.13, c 8.83, c/a = 1.238 (Tintic, Utah). She states that the space group is P4/nmm "it being assumed that the point symmetry is tetragonal holohedral"; no such assumption is necessary, as the diffraction aspect and the Laue class uniquely determine the space group, in this case. She refrains from calling the octahydrate meta-zeunerite.

Remark.--"Uranospinite", U. S. National Museum C4394. Green tablets, looking like metatorbernite, were identified as metazeunerite, with cell dimensions a 7.04, c 17.31, c' = 8.65, and space group P4/nmm.

Abernathyite, $KUO_2AsO_4 \cdot 4H_2O$

Material.--From Temple Mountain. Specimen AW-150-53, obtained from Alice Weeks. Chemical analysis (Analyst, Blanche Ingram, U.S.G.S.): UO_3 57.7, P_2O_5 1.5, As_2O_5 21.6, H_2O- 4.6, H_2O+ 9.9, K_2O 1.7, total 97.0.

Morphology.--Crystals are similar in color to those of meta-autunite, but they are thicker. The cleavage (001) is less than micaceous, though still very good. The dominant prism is $\{110\}$, not $\{100\}$.

Methods.--Precession photos; layers: hk0, hkl, h0ℓ, hhℓ, MoKα radiation. Crystal mounted with (001) in polar position. The integrating technique was not used.

X-ray patterns.--The reflections are sharp.

Crystal data.--Tetragonal: a 7.17, c 9.07, c/a = 1.266. The crystals available were too small for a determination of the density. Assuming 2 formula units per cell, the calculated density is 3.71, which seems reasonable. Space group P4/mmm (D4h-7).

Previous work.--The powder diffraction pattern has been indexed by Thompson, Ingram and Gross (in press), using the lattice constants given above, as part of their type description of this species.

Novacekite, $Mg(UO_2)_2(AsO_4)_2\cdot 9H_2O$

Material.--Sample labeled "troegerite", from its type locality Schneeberg, obtained from Dr. C. Frondel by H. T. Evans, Jr.

Morphology.--Yellow plates, small, very soft, flexible, not elastic. Very poor reflections, sufficient for optical adjustment but not for goniometry.

Methods.--The available plates were too small for the integrating precession technique. It is possible that weak reflections may have escaped detection. Precession pictures; layers: hk0, hkl, h0ℓ; both CuKα and MoKα radiations.

X-ray patterns.--Extreme streakiness of spots along c*.

Crystal data.--The following data refer to the symmetry observed by X-rays. Tetragonal: a 7.11, c 20.06, c/a = 2.823 (Schneeberg).

Cell content: 2 formula units. Space group $P4_2/n$ ($C4h$-4). Pseudo-space-group $P4/nmm$. Density: 3.23 (calc.); 3.23 (meas.).

That the symmetry of the crystal must be lower than tetragonal is shown by the optical properties. The plates do not stay dark between crossed nicols on rotating the stage. They extinguish parallel to a set of striations. An immersion oil of index 1.58 roughly matches the indices of the plate. Morphologically the plates are far from square.

Previous work.--Novacekite was first described by C. Frondel (1951), as an end-member of a solid-solution series with saléeite, the corresponding phosphate. According to his cell dimensions and densities, the present sample would have an As/P at. ratio slightly greater than unity. The space group was not given.

Metanovacekite, $Mg(UO_2)_2(AsO_4)_2 \cdot 4H_2O$

Material.--(1) Same sample as under Novacekite (see above). (2) Other specimens, also labeled "troegerite", from Schneeberg. U. S. National Museum R7927 and R5683. A spectrographic analysis (at the U. S. Geological Survey) gave, in percent: U more than 10; As 5-10; Si, Mg 1-5; Ca, Y 0.1-0.5; Fe, Al, Cu 0.05-0.1. Note that no phosphate is reported in this material.

Morphology.--Yellow-green plates, not as soft as those of novacekite.

Methods.--As the integrating precession technique was not used, it is possible that weak reflections may have been overlooked and that the cell reported below is a pseudo-cell. Same precession patterns were taken as for novacekite.

X-ray patterns.--Same extreme streakiness of spots along c^* as noted for novacekite.

Crystal data.--The following data refer to the symmetry observed by X-rays. Tetragonal: a 7.12, c 8.60, c/a = 1.209 (USNM R7927). Cell content: 1 formula unit. Space group P4/n (C4h-3). Pseudo-space-group P4/nmm. Density: 3.49 ± 0.05 (meas.). The calculated molecular weight is 915.3, which corresponds to 4.0 water molecules in the formula.

Previous work.--None. To our knowledge, this hydrate has not been reported before.

APPENDIX. CURITE--A NEW CHEMICAL FORMULA, $3PbO \cdot 8UO_3 \cdot 4H_2O$

The chemical formula of curite has been in doubt. The cell dimensions of Shaub (in Dana) and his specific gravity of 7.26 could not account for the formula that had been proposed. We redetermined the cell dimensions; H. T. Evans, Jr. made a new determination of the specific gravity 7.4. A new chemical analysis (UO_3 76.49, PbO 21.08, H_2O 2.43, SiO_2 0.06, BaO 0.11, total 100.17. Analyst, R. Meyrowitz, U. S. Geological Survey) leads to the formula $(PbO)_{0.70}(UO_3)_{1.98}(H_2O)_{1.00}$ or $3PbO \cdot 8UO_3 \cdot 4H_2O$, with molecular weight 3030.25.

Curite is orthorhombic; diffraction aspect Pna*, possible space groups Pna2 or Pnam. Cell dimensions: a = 12.50 ± 0.03, b = 13.01 ± 0.03, c = 8.40 ± 0.02 A, V = 1366 A^3. With two formula units per cell, the calculated density is 7.37, in close agreement with the observed value of 7.4.

Another formula $2PbO \cdot 6UO_3 \cdot 3H_2O$ gives good agreement with chemical data, but can be ruled out because it leads to a calculated density of 8.08 and three formula units per cell. The formula given in Dana (Palache et al., 1944, v. 1, p. 629) $2PbO \cdot 5UO_3 \cdot 4H_2O$, must also be ruled out. With three formula units per cell, the calculated density is 7.10_5, which is low.

The unit cell therefore contains: 6 Pb, 16 U, 16 H, 62 O. All atomic positions in Pnam are 4- or 8-fold, in Pna2 they are 4-fold. Lead and oxygen must therefore half fill one 4-fold position each. Because the symmetry of the space group is perfectly obeyed as far as one can tell from the X-ray patterns, the distribution of the two lead atoms and the two oxygen atoms in their 4-fold positions must be perfectly random. No experimental evidence of such disorder is observed, neither diffuse reflections nor streaks.

It may be noted that the other two formulas mentioned above require uranium atoms to be in disorder too. No formula could be found which would supply all atoms in multiples of four for the cell, and which would agree with the chemical composition and the observed density.

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