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THE CRYSTALLOGRAPHY OF META-AUTUNITE (I)[1]

MALCOLM ROSS, *U. S. Geological Survey, Washington 25, D. C.*

INTRODUCTION

The exact unit-cell size and space-group symmetry of meta-autunite (I), $Ca(UO_2PO_4)_2 \cdot nH_2O$, have been in dispute for some time, for example, see Takano (1961), Donnay and Donnay (1955), Makarov and Ivanov (1960) and Volborth (1959). In this paper data are presented in an attempt to give a more complete answer to these crystallographic questions.

There appear to be three hydration states for autunite. Autunite is the fully hydrated phase, meta-autunite (I) is in the next lower hydration state, and meta-autunite (II) (not found occurring naturally) is in the lowest hydration state. The exact number and positions of the water molecules in the autunites are not known.

The material examined here is from the Daybreak mine, Mt. Spokane, Washington and is similar to that studied by Leo (1960). The autunite and meta-autunite (I) crystals from Mt. Spokane vary in color from light to very dark green, almost black. Leo found the U^{4+} content of the darker crystals to be higher than that of the lighter crystals. The darker phase also had higher indices of refraction and a higher density than the lighter phase. Leo gives the formula

$$(Ca, Sr, U^{4+})_{0.97}(UO_2)_{1.86-1.98}(PO_4)_{2.00} \cdot 9.77H_2O$$

for the darker autunite and the formula

$$(Ca, Sr, U^{4+})_{0.99}(UO_2)_{1.96}(PO_4)_{2.00} \cdot 10.64H_2O$$

for the lighter autunite. Although an attempt was made to maintain the autunite crystals in the fully hydrated state prior chemical analysis there was probably some dehydration to meta-autunite (I). For other pertinent data on the chemical and physical properties of autunite and meta-autunite (I) from Mt. Spokane the reader is referred to Leo's paper.

EXPERIMENTAL WORK

Both light and dark green, nearly black meta-autunite (I) crystals were examined by Buerger precession techniques. Many small crystals were photographed and only those which gave unusually sharp Bragg reflections were selected for a complete study. Zirconium-filtered molybdenum radiation ($K\alpha = 0.7107$ Å) was used for most photographs. Buerger pre-

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TABLE 1. UNIT-CELL DATA FOR META-AUTUNITE (I), $Ca(UO_2PO_4)_2 \cdot nH_2O$

	Present study[1]	Donnay and Donnay (1955)
Unit cell	Tetragonal	Tetragonal
a (Å)	19.78 ± 0.02	19.82
c (Å)	16.92 ± 0.03	8.49
Laue group	$4/mmm$	$4/mmm$
Space group	$P4_222$	$P4/mmm$[2]
V (Å^3)	6620	3335
Pseudo-unit cell	Tetragonal	Tetragonal
a' (Å)	6.99	7.01
c' (Å)	8.46	8.49
Pseudo-space group	$P4/nmm$	$P4/nmm$
Density (calc.)	3.53 g/cm^3 [3]	3.50[3]
Density (obs.)	3.45–3.55 g/cm^3 [4]	3.48
Z	16	8
$\beta = \gamma$	1.579–1.586[4]	—
Forms	{110}, {001}	—
Locality	Mt. Spokane, Washington	Lauter, Saxony

[1] Size and color of crystals examined are: a) black, 0.05 by 0.20 by 0.35 mm, b) light green, 0.03 by 0.20 by 0.42 mm. Both crystals gave identical unit-cell data with $a = 19.78$ and $c = 16.92$ Å.

[2] or $P422$, $P4mm$, $P\bar{4}2m$, $P\bar{4}m2$.

[3] for $6H_2O$.

[4] Leo (1960).

cession photographs of the hk0, hk1, hk2, hk4, hk6, hhl, h(h+4)l, and h(h+8)l reciprocal lattice nets were made. Exposure times were approximately 80 hours. The unit-cell data found in the present study are compared in Table 1 to those given by Donnay and Donnay (1955) for meta-autunite (I) from Lauter, Saxony (U. S. National Museum Nos. 1342, 5675). Prior to the study by Donnay and Donnay most workers recognized only the pseudo-cell with $a = 7.0$ Å and $c = 8.5$ Å. The pseudo-cell is rotated 45° about the c-axis with respect to the true cell. All x-ray photographs show $4/mmm$ Laue symmetry. The following condition limiting the possible reflections was observed:

$$001: l = 2n.$$

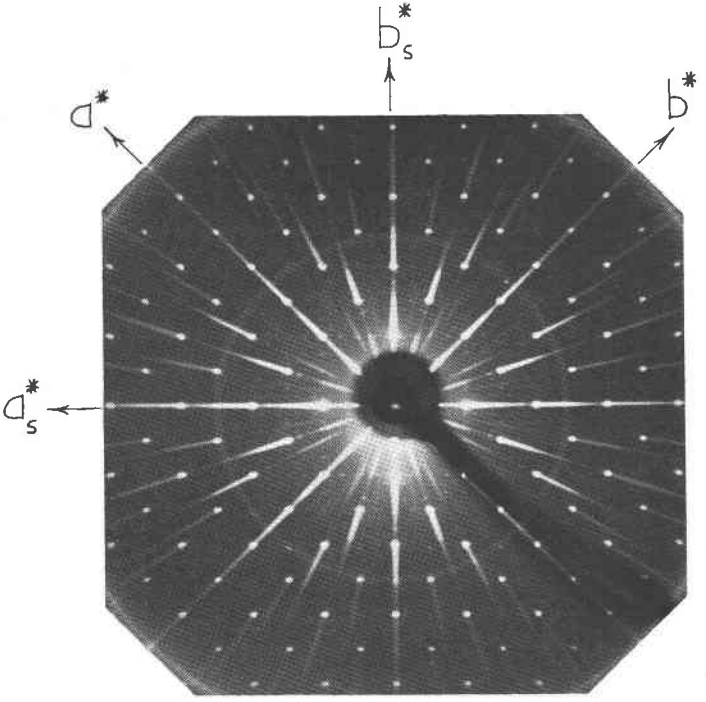

FIG. 1. *hk*0 Buerger precession photograph taken with zirconium-filtered molybdenum radiation of meta-autunite (I) from Mt. Spokane, Washington, showing weak super-lattice reflections. The subscript (s) refers to the axes of the pseudo-cell with $a=b=6.99$ Å.

The space group is thus $P4_22$. The pseudo-cell with $a=6.99$ Å and $c=8.46$ Å shows the following condition limiting the possible reflections:

$$hk0: h + k = 2n.$$

The space group for the pseudo-cell is $P4/nmm$. Figure 1 shows a Buerger precession photograph of the hk0 reciprocal lattice net of meta-autunite (I). The weak super-lattice reflections are apparent. The fact that Donnay and Donnay also observed these weak reflections on a sample from a different locality indicates that the large a-dimension of 19.8 Å is typical of this mineral. The only disagreement with the data of Donnay and Donnay is that the present study indicates a doubling of the c-dimension. This doubling is indicated by extremely weak spots appearing in the hk1 photographs. Films made with copper radiation show the presence of the 221, 441, 881, 041, 081, 0.12.1, 261, 481, and 4.12.1 reflections. Films made with molybdenum radiation show the presence of the 441, 481, 4.20.1, 4.28.1, 8.16.1, 8.24.1, 12.20.1, 12.24.1, and 16.20.1 reflections.

The Autunite Structure Problem

The identity of the unit-cell parameters of the light- and dark-green crystals indicates that U^{4+} does not enter the meta-autunite (I) structure. The strongest line of uraninite was observed in x-ray powder patterns of the black autunite crystals (Leo, 1960, p. 115). It is probable, as Leo suggests in his paper, that the UO_2 in the chemical analyses is due to finely disseminated particles of uraninite. These particles probably cause the darkening of the autunite crystals.

Takano (1961) has suggested that the large cell found by Donnay and Donay (1955) is incorrect and that a pseudo-cell with $a=6.972$ Å, and $c=8.47$ Å is actually the correct one. Takano obtained his data with a diffractometer (and Weissenberg camera?) using copper radiation. Such techniques cannot be expected to pick up the very weak reflections that indicate a larger unit cell. Makarov and Ivanov (1960) have attempted to solve the structure of meta-autunite (I) on the basis of the sub-cell. These workers collected 0kl and hk0 intensity data with rotation techniques using copper radiation. The choice of an incorrect space group by Makarov and Ivanov forced them to propose a structural model in which one calcium atom must be distributed over two positions (2*c*) and six water molecules over eight positions (8*j*) of space group $P4/nmm$. Their structure, based on an electron density map projected on (100) confirms Beintema's (1938) proposed structure for the $(UO_2PO_4)_n^{n-}$ layers, but their proposal for the positions of the interlayer calcium and water molecules cannot be considered correct. By calculating Fourier projections in the incorrect space group, they have forced a false statistical distribution of these atoms.

The difficulty encountered by various workers in the study of the minerals of the autunite group is due to the fact that the large contribution of the heavy uranium atoms to the observed intensities tends to obscure the contributions of the light oxygen atoms and cations. Also, for compounds which contain heavy elements such as uranium, x-ray absorption errors will generally be large, particularly if copper radiation is used. The absorption of x-rays will tend to further obscure the contributions of the light atoms to the reflections.

The uranium atoms in the autunite type structures usually occupy special positions, and consequently, will contribute scattering intensity only to certain special classes of reflections corresponding to a pseudo-cell. In such cases the true cell and symmetry can be deduced only by taking into account the other classes of very weak reflections. Because it is the light oxygen atoms that determine the principles of coordination, bonding, and packing in these structures, these weak reflections may

play a crucial role in the crystal structure analysis. An attempt to propose a structure based on the pseudo-cell on the assumption that the true structure is a minor distortion of it will probably lead to anomalous results. The need for careful attention to the weak classes of reflections has been demonstrated by Ross and Evans (1962), and Ross (1962) in their study of the crystal structures of the autunite-like compounds $K(UO_2AsO_4)\cdot 3H_2O$ (abernathyite), $NH_4(UO_2AsO_4)\cdot 3H_2O$, $K(H_3O)(UO_2AsO_4)_2\cdot 6H_2O$, and $Cu(UO_2PO_4)_2\cdot 8H_2O$ (meta-torbernite).

In order to ensure the determination of the correct crystallography by recording the very weak x-ray reflections, the following procedures have been found to be most essential:

(1) very small, well crystallized single crystals are studied,

(2) photographs are taken with molyebdnum radiation using long exposure times (50 to 200 hours),

(3) the Buerger precession camera is used for it gives the clearest and most easily interpretable photographs, and

(4) precession photographs are taken especially of the reciprocal lattice net planes parallel to the flattened {001} form of the thin crystal plates (for example, hk0, hk1, etc.) so as to minimize the absorption errors (Donnay and Donnay, 1955).

References

Beintema, J. (1938) On the composition and the crystallography of autunite and the meta-autunites. *Rec. travaux chim. Pays-Bas* **57,** 155–175.

Donnay, Gabrielle and J. D. H. Donnay (1955) Contribution to the crystallography of uranium minerals. *U. S. Geol. Survey Rept.* **TEI-507.**

Leo, G. W. (1960) Autunite from Mt. Spokane, Washington. *Am. Mineral.* **45,** 99–128.

Makarov, E. S. and V. I. Ivanov (1960) Crystal structure of meta-autunite, $Ca(UO_2)_2(PO_4)_2\cdot 6H_2O$. *Doklady Akad. Nauk SSSR,* **132,** 673–676 (in Russian).

Ross, Malcolm (1962) The crystallography, crystal structure, and crystal chemistry of various minerals and compounds belonging to the torbernite mineral group. Ph.D. Thesis, Harvard University, Cambridge, Mass.

——— and H. T. Evans, Jr. (1962) The crystal structures and crystal chemistry of various members of the metatorbernite group (abs.). *Am. Mineral.* **47,** p. 202.

Takano, Yukio (1961) X-ray study of autunite. *Am. Mineral.* **46,** 812–822.

Volborth, A. (1959) Strontian meta-autunite from the Daybreak mine, Mt. Spokane, Washington. *Am. Mineral.* **44,** 702–711.