THE CRYSTAL STRUCTURE OF META-AUTENITE, $Ca(UO_2)_2(PO_4)_2 \cdot 6H_2O$ *

Ye. S. Makarov and V. I. Ivanov

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry
of the Academy of Sciences of the USSR

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In the mineralogical literature [1, 2] the crystal structure of meta-autenite, $Ca(UO_2)_2(PO_4)_2 \cdot 6\frac{1}{2}H_2O$, is well known, based on the conjectures of Beintema [3]. On the basis of analysis of intensities of the (00l) reflections, the coordinates of the uranium atoms were fixed. Assuming a tetrahedral form for the PO_4^{3-} ions, which is well known from other phosphate structures, and also assuming a linear form for the uranic UO_2^{2+} ions, Beintema worked out the basic motif of the structure, which agrees well with the layer character of the uranium micas. However, many important details of the structure of meta-autenite remained obscure although there were attempts to refine the structure [4]. Among the unresolved problems were the precise positions of the calcium atoms and water molecules, as well as the interatomic uranium-oxygen distances, phosphorus-oxygen distances, and others.

Natural samples of meta-autenite crystals in the form of fine, scaly aggregates of yellow-green color, having a perfect (001) cleavage were received from V. I. Gerasimov. In view of the difficulty of identifying the uranium micas of the metatorbernite group by x-ray methods [5], a chemical analysis of the investigated samples was carried out by I. F. Dolmanova. The results of qualitative and quantitative chemical analysis were found to be in agreement with the generally accepted formula. It was also found that one formula unit contains 6 molecules of water.

Two of the most perfect crystals were selected for x-ray structural analysis: Crystal I had a platy habit with dimensions 0.1 × 0.2 × 0.6 mm; crystal II had an acicular habit with dimensions 0.1 × 0.1 × 0.5 mm.

From rotation photographs along the [001] and [100] directions, x-ray goniometric scanning, and measurements on the diffractometer, a primitive tetragonal cell was defined with the following dimensions: $a = 6.96 \pm 0.01$ A; $c = 8.40 \pm 0.02$ A; $c/a = 1.207$.

The choice of the larger cell suggested by G. Donnay and J. Donnay [6] seems to us to be unfounded.

Pycnometric measurements of the specific gravity of meta-autenite crystals (weighed portion ≈ 1 g) was found to equal $3.44 \approx 0.002$ g/cm^3, which gives a unit cell of one formula unit.

The indexing of the zero, first, and second level lines of rotation about the [100] direction brought out the following extinction conditions: $h + k = 2n + 1$, for $l = 0$. This indicates the space group $D_{4h}^7 = P4/nmm$.

The intensities of reflections for the zero layer plane obtained by rotating the crystal about the [100] direction were determined on the URS-50I diffractometer for both crystals. For crystal I, 72 (0kl) reflections were measured and for crystal II, 56 reflections were measured. Both photographs were taken with Cu K_α radiation.

Projections of the functions of the interatomic vectors on the (100) planes were constructed. Both crystals gave an identical projection. From these projections the coordinates of uranium atoms, occupying the position 2 (c) cz ≈ 0.108 were determined. Starting from these coordinates the signs of the structure amplitudes were defined, and projections of the electron density function were constructed on the (100) plane for every crystal for reflections within the limits of the field of $\sin \theta/\lambda \geq 0.6$.

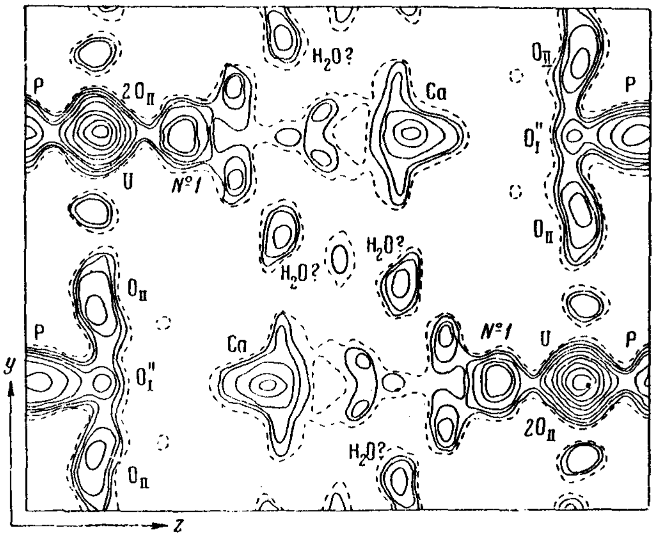

Fig. 1. Projection of the electron density function of meta-autenite on the (100) plane.

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* Translation of: Kristallicheskaya Struktura Metaotenita $Ca(UO_2)_2(PO_4)_2 \cdot 6H_2O$, Doklady Akademii Nauk, SSSR, vol. 132, no. 3, 1960, pp. 673-676.

The projection of electron densities on the (100) plane for crystal I is shown in Fig. 1.

The peaks which correspond to the U atoms with a weight of 380, to the P atoms with a weight of 90, to the phosphorus oxygens O_{II} with a weight of 36, to the Ca atoms with a weight of 42, and to one of the atoms of uranium oxygen O''_{I} with a weight of 39, were clearly shown. The low value of the intensity of the peak of calcium corresponds to the statistical distribution of one atom of calcium in the twofold position 2 (c). In order to determine and to refine the coordinates of other atoms, projections were constructed for differential Patterson functions and electron density functions, with the deletion of the uranium atoms (for crystal I). The fitting of the experimental structure amplitudes to an absolute scale was carried out by the Wilson-Harker method [7, 8]. For crystal I the following parameters of reduction were determined: $K_0^{I} = 1/220$, $B^{I} = 1.6$; for crystal II: $K_0^{II} = 1/160$, $B^{II} = 0.8$. The determination of the absolute values of F_{exp} was carried out using the formula

$$F_{\text{exp.}} = \sqrt{\frac{I_{\text{exp.}}}{K_0}} \cdot e^{B\frac{\sin\theta}{\lambda}}.$$

On the differential projection of the electron density function (Fig. 2), the peaks corresponding to the H_2O molecules and the second uranic oxygen O'_{I} became clearly apparent. The presence of the split peak at the uranium position, corresponding to atoms of oxygen from the tetrahedron encircling phosphorus (they must be projected to one point), can to all appearances be explained as a result of the inaccuracy of the determination of the signs of the differential structure factors ($F_{exp}-F_U$) in constructing the projection.

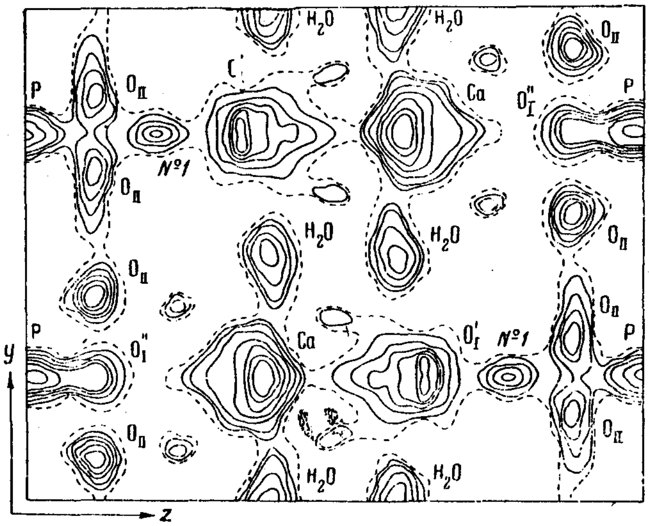

Fig. 2. Projection of the differential electron density function on the (100) plane, constructed from values of ($F_{exp}-F_U$).

We cannot explain the appearance of peak No. 1, which was also present in the standard projections for both crystals.

Analyses of the differential projections of the Patterson functions and of the electron density functions enabled us to refine precisely the positions of the atoms in the structure of meta-autenite. On the basis of the space group D_{4h}^{7} = P4/nmm, the following positions were found for the atoms:

2 U atoms at 2 (c): z = 0.106;
2 O'_{I} atoms at 2 (c): z = 0.343;
2 O''_{I} atoms at 2 (c): z = 0.893;
2 P atoms at 2 (a);
8 O_{II} atoms at 8 (i): x = 0.584, z = 0.106;
1 Ca atom statistically distributed over 2(c): z = 0.612;
6 H_2O molecules statistically distributed over 8 (j): x = 0.486; z = 0.392.

In constructing standard projections of the measured intensities, corrections for the Lorentz and polarization factors were introduced. In constructing differential projections, the temperature factor was also taken into account. Absorption was not calculated this is the fundamental shortcoming in studies of uranium micas, since it does not prove possible to prepare spherical crystals of these minerals. The reliability index R = $\Sigma (F_{exp}-F_{theor})/\Sigma (F_{exp})$, calculated for 75 values of F (0k*l*) for both crystals, was found to be 0.148.

A section of the structure of meta-autenite on the (110) plane is shown in Fig. 3.

From the atomic positions determined above, the following interatomic distances were computed:

$U - O'_{I} = 1.99A$, $O'_{I} - 4H_2O = 2.36A$,
$U - O''_{I} = 1.79A$, $O'_{I} - O_{II} = 3.06A$,
$U - 4O_{II} = 2.32A$, $O''_{I} - 4H_2O = 3.53A$,
$P - 4O_{II} = 1.47A$, $O''_{I} - O_{II} = 4.35A$,
$O_{II} - O_{II} = 2.31A$, $Ca - O'_{I} = 2.27A$,
$H_2O - H_2O = 1.83A$, $Ca - O''_{I} = 2.35A$.

The asymmetry of the uranic group should be noted: $U\text{-}O'_{I}$ = 1.99 A, and $U\text{-}O''_{I}$ = 1.79 A. This can be explained by the fact that O'_{I} is more strongly bound to the surrounding water molecules and to the oxygen atoms of the phosphate group than is O''_{I} (this can be seen from the table of interatomic distances). It is also interesting to note the anomalously short distance $H_2O\text{-}H_2O$ = 1.84 A. This feature is also found in the structure of metatorbernite [9].

We examined the values obtained for the interatomic distances in the structure of meta-autenite from the point of view of their agreement of the empirical law of Zachariasen concerning the correlation between the "bond length" and the "bond strength" for structures containing uraninite [10, 11].

There are two possible interpretations of the valence states of uranium in the structure of meta-autenite.

1. Starting with the pentavalent state of phosphorus P^{5+} and the divalent state of O_{II}^{2-} oxygen, we obtain a bond strength for $U\text{-}O_{II} = 0.75$. The total of four such bonds will be: $0.75 \times 4 = 3$. For a distance $U\text{-}O'_I = 1.99$A, 1.12 is the corresponding bond strength, according to Zachariasen. For a $U\text{-}O''_I$ distance of 1.79 A, the bond strength is 1.60. Thus, the sum of all the bond strengths of the uranium atoms with the oxygen atoms is $3 + 1.12 + 1.60 = 5.72$, which corresponds roughly to the hexavalent state of uranium. The bond strength of the calcium atoms with the atoms of the uranic oxygens – $0.88 + 0.40 = 1.28$ – for example, corresponds to the statistical distribution of one Ca^{2+} atom in the twofold position 2 (c). In that case the crystallochemical formula of meta-autenite will be $Ca^{2+}(UO_2^{2+})_2(PO_4^{3-})_2 \cdot 6H_2O$.

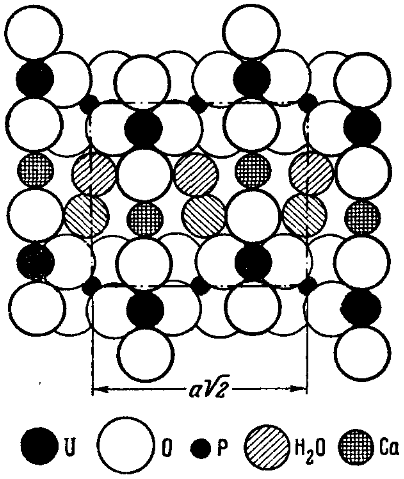

Fig. 3. Section of the structure of meta-autenite on the (110) plane.

2. Starting with the experimentally determined value of the $U\text{-}O_{II}$ bond length = 2.32 A, we discover (according to Zachariasen) that the strength of that bond is 0.60. Then the sum of all the bond strengths of the uranium atoms with the oxygen atoms will be $0.60 \times 4 + 1.12 + 1.60 = 5.12$, which corresponds to the pentavalent state of uranium. The lack of positive charges in the structure can be compensated by H_3O^+ hydroxonium ions. In that case, the crystallochemical formula of meta-autenite will be

$Ca^{2+}(H_3O^+)_2(UO_2^+)_2 \cdot (PO_4^{3-})_2 \cdot 4H_2O$.

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