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Refinement of the crystal structure of metatorbernite

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Crystal structure

Abstract. The crystal structure of metatorbernite with composition $Cu_{0.9}(UO_2PO_4)_2 \cdot 8\,H_2O$ from Vathi, Northern Greece, has been refined, using the intensities of 365 independent reflections, measured on an automated Philips PW 1100 single-crystal diffractometer. The cell constants, refined by least squares, are $a = b = 6.972(1)$ Å, $c = 17.277(8)$ Å, $Z = 2$; space group $P4/n$; $\varrho_{\text{calc}} = 3.706$, $\varrho_{\text{obs}} = 3.52$ g cm^{-3}.

The positional and thermal parameters were refined by full-matrix least-squares calculations. Absorption correction and correction for anomalous dispersion, for all atoms, were applied. The final R value is 0.056.

The structure is essentially similar to that described by M. Ross, H. Evans and D. Appleman (1964) for metatorbernite, with a difference in the Cu atom position, which here is 1/4 1/4 0.31 instead of 1/4 1/4 0.80. The U atoms are six-coordinated by two O atoms (uranyl group) and four phosphate–oxygen atoms forming an asymmetrical tetragonal dipyramid. The Cu atoms are six-coordinated by two oxygen atoms of two different uranyl groups and four water molecules forming also an asymmetrical tetragonal dipyramid. The four water molecules form squares $Cu(H_2O)_4$, perpendicular to c, with the Cu atoms at their centers. There are two types of squares: with or without Cu atoms at their centers. The P atoms are four-coordinated by O atoms, forming the usual phosphate tetrahedra PO_4. The structure consists of infinite $(UO_2PO_4)_n$ layers isostructural with those of meta-autunite and abernathyite. The connection between two successive

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layers is effected by the Cu – uranyl – oxygen bonds and by hydrogen bonds between the water molecules. Each water molecule of a $Cu(H_2O)_4$ square is hydrogen bonded to two water molecules of a $(H_2O)_4$ square devoid of Cu, and to two oxygen atoms of a phosphate group.

Introduction

Donnay and Donnay (1955) gave unit-cell data and space group $P4_2/n$ for metatorbernite. Makarov and Tobelco (1960) reported new unit-cell parameters and space group *P4/nmm*, with 0*kl* Weissenberg data. Later, several authors have published more detailed work with powder or diffractometer data on the structures of various members of the torbernite family. A thorough investigation of metatorbernite with the ideal composition, $Cu(UO_2PO_4)_2 \cdot 8\ H_2O$, was published by Ross, Evans and Appleman (1964). Using powder and precession data they gave *P4/n* as space group and a detailed description of the crystal structure.

In the present paper a detailed study of a non-stoichiometric (deficient in Cu) metatorbernite is presented, the first from a locality in Greece. The work was carried out within the framework of a program for exact structural and geochemical investigations of various uranium minerals in Greece.

Experimental

The studied uranium-phosphate mineral (metatorbernite) was found as fissure fillings within hydrothermally altered trachytes in the Vathi area, Northern-Greece. Metatorbernite, considered as a low-temperature hydrothermal mineral, forms well crystallized platy crystals (Fig. 1) within the fissures.

The chemical formula of the studied crystal, $Cu_{0.9}(UO_2PO_4)_2 \cdot 8\ H_2O$, is in good agreement with chemical analyses of metatorbernite crystals, from the same location, performed by microprobe analysis (WDS system, Jeol 733 and Hitachi-XMA5B) in the Geological Survey of Sweden.

The selected light green platy crystal, with dimensions $0.38 \times 0.26 \times 0.012$ mm, was measured with our computer-controlled, four-circle, single-crystal diffractometer (Philips PW 1100), with Mo*Kα* (graphite monochromator) radiation (0.71069 Å). The cell constants were determined by measuring the ϑ angles of 48 strong reflections with large ϑ values directly on the diffractometer and subsequently processing them with the least-squares program LATCON, part of the X-Ray System [Stewart et al. (1976)]. The final values for the unit cells are given in the Abstract. Three-dimensional intensity data were measured with a scintillation counter in the $\vartheta - 2\vartheta$ scan mode. The intensities of 1977 reflections in the range $\vartheta = 3-24°$... ($h,k = -7$ to 7 and $l = -18$ to 4) were measured and examined.

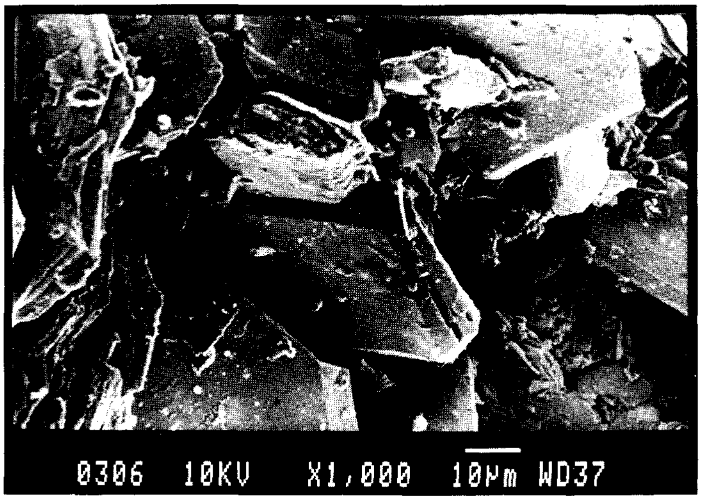

Fig. 1. Photographe of platy crystals of metatorbernite.

Of the resulting 430 unique reflections, 365 with intensities 2.5 $\sigma(I)$ were included in all subsequent calculations.

For further calculations the SHELX76 (Sheldrick, 1976) and the CORABS (Stergiou, 1984) programs were used.

Determination of the structure and refinement

The systematic absences were consistent with the space group $P4/n$. The non-hydrogen atomic positions for the metatorbernite structure reported by Ross et al. (1964), except for the Cu atom position, were used as a starting point for the refinement of the structure, carried out by full-matrix least-squares calculations with the SHELX76 program. The Cu atom position, found from a difference-Fourier synthesis, was at 1/4, 1/4, 0.31 quite different from the position 1/4, 1/4, 0.80 given by Ross et al. (1964). Non-ionized state was assumed for all atoms, and probable individual isotropic temperature factors were assigned to them. Atomic scattering factors and anomalous dispersion corrections for all atoms were obtained from Cromer and Mann (1967). A single scale-factor was used for the whole set of the reflection data.

Refinement for all non-hydrogen atoms with individual isotropic factors and unit weights reduced R to only 0.14. Since the absorption coefficient was large (μ = 197.90 cm^{-1}), an empirical absorption correction of F_{obs} was applied, with the special program CORABS, written for this purpose.

Table 1. Atomic coordinates and equivalent isotropic temperature coefficients for metatorbernite from Vathi, Greece.

Atom	Position	x	y	z	B_{eq} [Å^2]
U(1)	2*c*	1/4	1/4	0.0526(2)	2.23
U(2)	2*c*	1/4	1/4	0.5507(3)	2.85
CU	2*c*	1/4	1/4	0.3113(7)	3.24
P(1)	2*a*	1/4	3/4	0	3.18
P(2)	2*b*	1/4	3/4	1/2	3.15
O(1)	2*c*	1/4	1/4	−0.0492(6)	1.81
O(2)	2*c*	1/4	1/4	0.1537(6)	3.65
O(3)	2*c*	1/4	1/4	0.4476(6)	4.19
O(4)	2*c*	1/4	1/4	0.6524(6)	4.39
O(5)	8*g*	0.2469(46)	0.5755(22)	0.0507(12)	4.31
O(6)	8*g*	0.2636(45)	0.5807(20)	0.5533(10)	4.24
O(7)	8*g*	0.2563(46)	0.5289(39)	0.3124(22)	5.08
O(8)	8*g*	0.2402(98)	0.5115(39)	0.8056(27)	4.49

[a] This site occupied by water molecule.

Table 2. Anisotropic temperature coefficients $U_{ij}(\times 10^4)$ for metatorbernite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	241(9)	U11	366(55)	0	0	0
U(2)	350(15)	U11	386(45)	0	0	0
CU	385(45)	U11	462(66)	0	0	0
P(1)	461(58)	U11	287(99)	0	0	0
P(2)	410(79)	U11	378(47)	0	0	0
O(1)	148(29)	U11	392(78)	0	0	0
O(2)	310(57)	U11	768(82)	0	0	0
O(3)	507(62)	U11	275(55)	0	0	0
O(4)	545(74)	U11	577(83)	0	0	0
O(5)	608(80)	545(54)	486(76)	− 90(57)	−477(51)	−163(58)
O(6)	693(79)	885(91)	33(14)	85(46)	228(59)	−176(89)
O(7)	794(87)	747(95)	391(62)	351(53)	−258(47)	51(47)
O(8)	797(88)	595(78)	315(52)	−392(66)	592(64)	−290(94)

The program (Stergiou, 1984), is based on the same principles as DIFABS (Walker and Stuart, 1983) and works in an analogous way. After the absorption correction, the R factor was reduced to 0.078. At this stage, refinement of the population parameter for the Cu atom, gave a value 0.92, which confirmed the result of the chemical analysis. The R factor was 0.076. Further refinement with anisotropic temperature coefficients for all non-hydrogen atoms gave $R = 0.056$ and $R_w = 0.055$.

The final positional parameters, with their standard errors in parentheses, and equivalent isotropic temperature coefficients for the non-hydrogen atoms are given in Table 1 and their thermal parameters in Table 2. The

Table 3. Interatomic distances [Å] in metatorbernite. The numbers next to the atom symbols refer to the corresponding atoms in Figure 2.

U(1)O6 dipyramid		**CuO6 dipyramid**	
U(1) – O(2)	1.747(10)	Cu – O(7) [4×]	1.945(27)
O(1)	1.758(10)	O(3)	2.356(17)
O(5) [×4]	2.269(15)	O(2)	2.722(17)
U(2)O6 dipyramid		**P(1)O4 tetrahedron**	
U(1) – O(4)	1.758(10)	P(1) – O(5) [×4]	1.500(5)
O(3)	1.781(10)		
O(6) [×4]	2.308(15)	**P(2)O4 tetrahedron**	
		P(2) – O(6) [×4]	1.500(5)

interatomic distances and their standard errors are given in Table 3. The arrangement of the atoms in the unit cell is shown in Figure 2. Structure factor tables and tables of interatomic distances have been deposited.[1]

Description of the structure and discussion

Detailed description of the metatorbernite structure type and of the structures of the specific crystals examined have been given by the previously mentioned investigators. The present structure is essentially similar to that described by Ross et al. (1964) for metatorbernite, except for the Cu atom position.

As can be seen from the clinographic projection of the unit cell (Fig. 2), there are four P atoms in two special positions 2a and 2b. Each of them is four-coordinated by four O atoms at a mean distance of 1.500(5) Å forming a slightly distorted tetrahedron (phosphate group) in agreement with other determinations.

The four U atoms, in special positions 2*c*, are two-coordinated by two O atoms at a mean distance 1.761(10) Å, forming the uranyl group. Furthermore each U atom is square planar coordinated by four phosphate O atoms, at a mean distance of 2.288(15) Å, forming thus asymmetrical tetragonal dipyramids. The asymmetrical coordination of the UO_2^{2+} ions found in abernathyite is retained in metatorbernite.

The two Cu atoms are also in special position 2*c* with an occupation factor 0.92. They are six-coordinated by two O atoms of two different

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[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 55523, the names of the authors and the title of the paper.

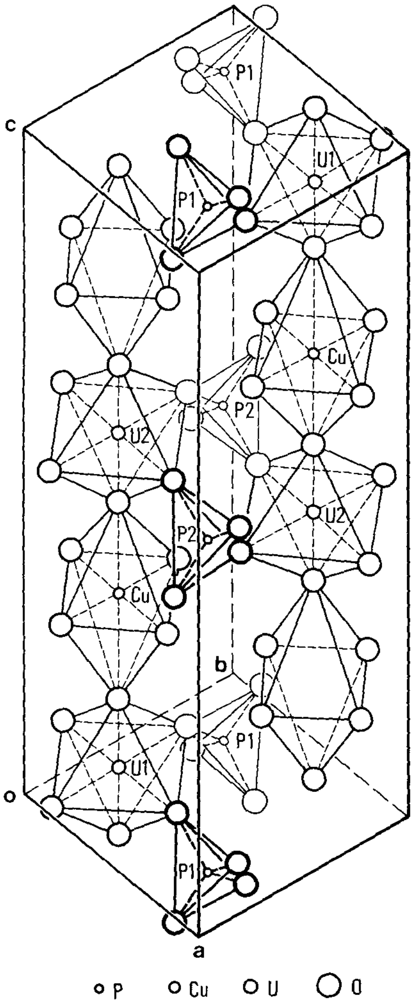

Fig. 2. Clinographic projection of the unit cell of metatorbernite parallel to [100].

uranyl groups at distances of 2.722(17) Å and 2.356(17) Å, and by four O(water) at distances of 1.945(27) Å, in a square planar coordination, forming thus asymmetrical tetragonal dipyramids. The unusually short distance Cu – O(water) indicates a rather strong covalent copper – oxygen bond. Short copper – water distances were found in many other hydrates [see references in Ross et al. (1964)].

The Cu dipyramid is connected with the U(1) and U(2) dipyramids by two common uranyl O atoms [O(2) and O(3) respectively], forming infinite columns parallel to the *c* axis at (*a*/4, *b*/4) and (3*a*/4,3*b*/4), interrupted by the empty dipyramid (1/4, 1/4 0.80). Furthermore, each uranium dipyramid is connected with four different phosphate tetrahedra by common O atoms. A simple survey of the structure shows, that the bonds in uranium dipyramids and phosphate tetrahedra are sufficiently strong. Therefore, a block of uranium dipyramids and phosphate tetrahedra of the general type $(UO_2PO_4)_n$ form an infinite layer perpendicular to the *c* axis. Thus, the structure can be described by considering successive layers of $(UO_2PO_4)_n$, connected with each other by weaker bonds, namely Cu—O(uranyl) bonds, or water—water and water—O(phosphate) hydrogen bonds. This description of the structure permits a satisfactory explanation of the connection between the layers and the plate-like growth of the crystals parallel to (001) and also their brittleness.

References

Cromer, D., Mann, J.: X-ray scattering factors computed from numerical Hartree-Fock wave functions. Univ. of California, Los Alamos USA (1967).

Donnay, G., Donnay, J. D. H.: Contribution to the crystallography of uranium minerals. US Geol. Survey Rept. TEI-507 (1955).

Makarov, E. S., Tobelko, K. I.: Crystal structure of metatorbernite. Dokl. Akad. Nauk SSSR **131** (1960) 87—89.

Ross, M., Evans, J., Appleman, D. E.: Studies of the torbernite minerals(II). The crystal structure of meta-torbernite. US Geological Survey, Washington, D.C. (1964).

Sheldrick, G. M.: "SHELX76", program for crystal structure determination. Univ. of Cambridge, England (1976).

Stergiou, A.: CORABS program, part of Thesis; Hydrothermal method for the growth of crystals and the crystal structure of As_2Te_3, As_5Te_7I, pp. 62, 63. D. Sc. Thesis, University of Thessaloniki (1984).

Stewart, J., Kruger, G., Ammon, H., Dickinson, C., Hall, S.: The X-ray system of crystallographic programs for any computer. Technical Rep. 446, Computer Science Center, University of Maryland (1976).

Walker, N., Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. **A39** (1983) 158—166.