

RIETVELD REFINEMENT OF THE CRYSTAL STRUCTURE OF OLIVENITE: A TWINNED MONOCLINIC STRUCTURE

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ABSTRACT

The crystal structure of olivenite, $\text{Cu}_2\text{AsO}_4(\text{OH})$, has been refined by the Rietveld method in the space groups $Pnmm$ and $P2_1/n$ (x axis unique). In the latter refinement, the α angle, $90.088(3)^\circ$, is significantly different from 90° , and some atomic positions are significantly different from the ideal positions in a structure with orthorhombic symmetry. Thus olivenite has $P2_1/n$ symmetry, as indicated by Toman (1977). Examination of previous structural work on libethenite suggests that this mineral may be monoclinic as well.

Keywords: olivenite, structure refinement, Rietveld method, arsenate.

SOMMAIRE

Nous avons affiné la structure cristalline de l'olivénite, $\text{Cu}_2\text{AsO}_4(\text{OH})$, par la méthode de Rietveld dans les groupes spatiaux $Pnmm$ et $P2_1/n$ (axe x considéré unique). Avec ce dernier, nous avons trouvé que l'angle α , $90.088(3)^\circ$, diffère substantiellement de 90° , et la position de certains atomes dévie de façon importante des positions idéales dans une structure strictement orthorhombique. C'est donc dire que l'olivénite possède la symétrie $P2_1/n$, comme l'avait indiqué Toman (1977). D'après les résultats d'études structurales publiées, la libéthénite pourrait bien aussi être monoclinique.

(Traduit par la Rédaction)

Mots-clés: olivénite, affinement de la structure, méthode de Rietveld, arsenate.

INTRODUCTION

Olivenite is a hydroxy-copper arsenate that is relatively common as a supergene mineral in the oxidation zone of Cu-bearing orebodies. The approximate structure was solved by Heritsch (1938) in the space group $Pnmm$. Various other space groups were reported in subsequent studies: $P2_12_12_1$ (Richmond 1940), $Pnmm$ (Berry 1951), $Pn2_1m$ (Walitzi 1963). Toman (1977) proposed that olivenite is actually monoclinic, with $P2_1/n$ symmetry (x axis unique), and that crystals are twinned. One of us (F.C.H.) had studied the structure of olivenite in the middle 1970s (unpubl. data) and had come to the same conclusion as Toman (1977). The problem of refining a twinned monoclinic structure with the unique angle approximately equal to 90° is ideally suited to the Rietveld method, as twinning is invisible to powder diffraction and does not affect the diffracted intensities. Of course, if the unique angle is exactly equal to 90° , then we have no resolution of the information on deviation from orthorhombic

symmetry. However, a small deviation from 90° allows this information to be recovered from the powder-diffraction pattern. Consequently, we decided to re-examine the structure of olivenite and compare our powder-diffraction results with the previous single-crystal results.

EXPERIMENTAL

The olivenite sample studied here is from Cornwall, England, and is deposited at the R.B. Ferguson Museum, University of Manitoba (M4429). Braithwaite (1983) listed compositional data for five samples of olivenite from Cornwall; all have no detectable Zn, but P ranges from 0 to 15 mol% (PO_4). The $\langle\text{As}-\text{O}\rangle$ distance observed from the present refinement suggests that approximately 10% of the As is replaced by P in the tetrahedral group. Powdered olivenite was spread onto 4- μm -thick XRF Prolene film using hairspray as a mounting medium. Data were collected using a Siemens D5000 automated X-ray powder-diffractometer operating in transmission geometry. A Huber incident-beam monochromator was used to obtain $\text{CuK}\alpha_1$ X-radiation generated using 40 kV and 35 mA with a fine-focus X-ray tube. The

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sample, positioned perpendicular to the incident beam at $\theta = 0$, was rotated at 120 rpm during the $\theta/2\theta$ scan. A 2-mm antiscatter slit, a 0.1-mm receiving slit, and a Kevex solid-state detector were used. Data were collected over the angular range $12 \leq 2\theta \leq 120^\circ$ using a 0.02° step-width, with 15 s counting time per step.

STRUCTURE REFINEMENT

The Rietveld structure-refinement was done using the program DBWS-9006PC (Sakthivel & Young 1990) installed on an IBM RS-6000 computer. Atomic scattering factors were taken from Ibers & Hamilton (1974). R indices are of the form given in Table 1 and are expressed as percentages.

Refinements were done in the space groups $Pnmm$ and $P2_1/n$ using the atomic parameters reported by Toman (1977) as the starting models (*i.e.*, $\alpha = 90.0^\circ$) and constraining the displacement factors of the anions to be the same. Diffraction peaks were modeled using the Thompson - Cox - Hastings modified pseudo-Voigt profile-function corrected for asymmetry up to $29^\circ 2\theta$. The backgrounds were refined using fifth-order polynomials. In the space group $Pnmm$, 39 parameters were refined, and converged to a final $R_{\text{BRAGG}} = 6.02\%$, $R_p = 12.55\%$, $R_{\text{wp}} = 17.48\%$, and a goodness-of-fit of 2.36. In the space group $P2_1/n$, 50 parameters were refined, converging to a final $R_{\text{BRAGG}} = 5.88\%$, $R_p = 12.03\%$, $R_{\text{wp}} = 16.72\%$, and a goodness-of-fit of 2.26. The possibility of convergence to a local minimum was examined by repeating the refinement with the O(1) atom displaced to the other side of the mirror plane; this resulted in convergence at the same arrangement as before, indicating that there is only one minimum close to this approximate arrangement. Final

TABLE 1. DETAILS OF THE REFINEMENT

	$Pnmm$	$P2_1/n$
a (Å)	8.5894(2)	8.5894(2)
b	8.2076(2)	8.2073(2)
c	5.9286(1)	5.9285(1)
α ($^\circ$)	90	90.088(3)
R_{BRAGG}	6.02	5.88
R_p	12.55	12.03
R_{wp}	17.48	16.72
R_{exp}	7.40	7.39
GOF*	2.36	2.26
$R_{\text{BRAGG}} = 100 \Sigma I_o - I_c / \Sigma I_o$		
$R_p = 100 \Sigma y_i - y_a / \Sigma y_i $, y_i = intensity at step i		
$R_{\text{wp}} = 100 \{ \Sigma w_i (y_i - y_{ci})^2 / \Sigma w_i y_i^2 \}^{1/2}$		

* GOF = Goodness-of-fit = $[R_{\text{wp}}/R_{\text{exp}}]$

TABLE 2. FINAL ATOMIC PARAMETERS* FOR ORTHORHOMBIC AND MONOCLINIC REFINEMENTS OF OLIVENITE

	$Pnmm$			B (Å ²)
	x	y	z	
As	0.2507(3)	0.2624(3)	0	0.51(6)
Cu(1)	0.8805(3)	0.3624(3)	0	1.30(7)
Cu(2)	0	0	0.2510(5)	0.93(7)
O(1)	0.1060(13)	0.4012(14)	0	1.1(2)
O(2)	0.4163(12)	0.3654(14)	0	1.1(2)
O(3)	0.8992(12)	0.1198(13)	0	1.1(2)
O(4)	0.2347(8)	0.1511(9)	0.7733(13)	1.1(2)
	$P2_1/n$			B (Å ²)
	x	y	z	
As	0.2503(3)	0.2627(3)	0.0052(11)	0.70(6)
Cu(1)	0.8807(3)	0.3624(3)	-0.0023(12)	1.38(7)
Cu(2)	-0.0016(10)	-0.0007(9)	0.2501(5)	0.96(7)
O(1)	0.1069(13)	0.4022(13)	0.0551(21)	0.37(18)
O(2)	0.4171(11)	0.3667(13)	-0.0076(46)	0.37(18)
O(3)	0.8998(11)	0.1213(12)	0.0029(42)	0.37(18)
O(4)	0.2135(16)	0.1499(24)	0.2269(30)	0.37(18)
O(5)	0.2577(16)	0.1528(24)	0.7710(30)	0.37(18)

* A single B value was refined for all O positions in each structure model.

unit-cell dimensions and miscellaneous information are given in Table 1, refined atomic parameters in Table 2, bond lengths, angles and polyhedral edge-lengths in Table 3. The observed and calculated powder-patterns are shown in Figure 1. Step-scan intensity data may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR ORTHORHOMBIC AND MONOCLINIC REFINEMENTS OF OLIVENITE

	$Pnmm$	$P2_1/n$
As-O(1)	1.686(11)	1.707(11)
As-O(2)	1.655(11)	1.669(10)
As-O(4)	1.631(8) x2	1.640(18)
As-O(5)		1.656(18)
Cu(1)-O(1)	1.963(11)	1.999(11)
Cu(1)-O(1)	1.944(11)	1.961(11)
Cu(1)-O(3)	1.998(11)	1.986(10)
Cu(1)-O(4)	2.050(7) x2	2.177(16)
Cu(1)-O(5)		1.915(17)
Cu(2)-O(4)	2.371(7) x2	2.227(17)
Cu(2)-O(2)	1.979(7)	2.006(21)
Cu(2)-O(2)	1.979(7)	1.944(21)
Cu(2)-O(3)	1.983(7)	1.968(20)
Cu(2)-O(3)	1.983(7)	1.997(20)
Cu(2)-O(5)		2.532(17)

DISCUSSION

Our results are in complete accord with those of Toman (1977). There is a small improvement in all of the R indices in going from orthorhombic to monoclinic symmetry in the refinement. In itself, this improvement is not totally convincing, but the distinctly non-orthogonal α angle of $90.088(3)^\circ$ and the similarity of our results to those of Toman (1977) indicate that olivenite is monoclinic and not orthorhombic. Comparison of the atomic coordinates for the $Pnmm$ and $P2_1/n$ refinements (Table 2) shows that the principal difference involves the z coordinate of the O(1) oxygen atom. In the monoclinic structure, it is displaced $0.0551(21)$ from the mirror plane perpendicular to $[001]$; this is a shift of 21 standard deviations from its ideal position for $Pnmm$ symmetry. A linear hypothesis test (Hamilton 1964) shows that this difference in the two results is significant at the 99% confidence limit. This value of $0.055(2)$ is statistically identical to the corresponding value of $0.058(3)$ obtained by Toman (1977) in his $P2_1/n$ refinement, with correction for twinning on (010). The next largest differences involve the x coordinates of O(4)

and O(5) in the monoclinic structure relative to the x coordinate of O(4) in the orthorhombic structure. The differences are 13 standard deviations, again significant at the 99% confidence limit. All other differences are small.

Minerals structurally related to olivenite are adamite, $Zn_2(AsO_4)OH$ (Hawthorne 1976, Hill 1976) and libethenite, $Cu_2(PO_4)OH$ (Cordsen 1978). Adamite is the Zn analogue of olivenite and has the space group $Pnmm$; because of this, it is tempting to ascribe the monoclinic symmetry of olivenite to a cooperative Jahn–Teller effect involving Cu^{2+} in an octahedral ligand-field, whereby electron–phonon coupling lowers the symmetry of the structure. However, libethenite, the P analogue of olivenite, is reported to have $Pnmm$ orthorhombic symmetry (Cordsen 1978). Why is olivenite monoclinic, whereas libethenite is orthorhombic? Inspection of the refinement results of Cordsen (1978) suggests that libethenite may be monoclinic rather than orthorhombic. The libethenite structure was refined to an R index of 3.1%. However, inspection of the refined parameters shows two large anisotropic displacements that are analogous to the largest displacements from orthorhombic symmetry

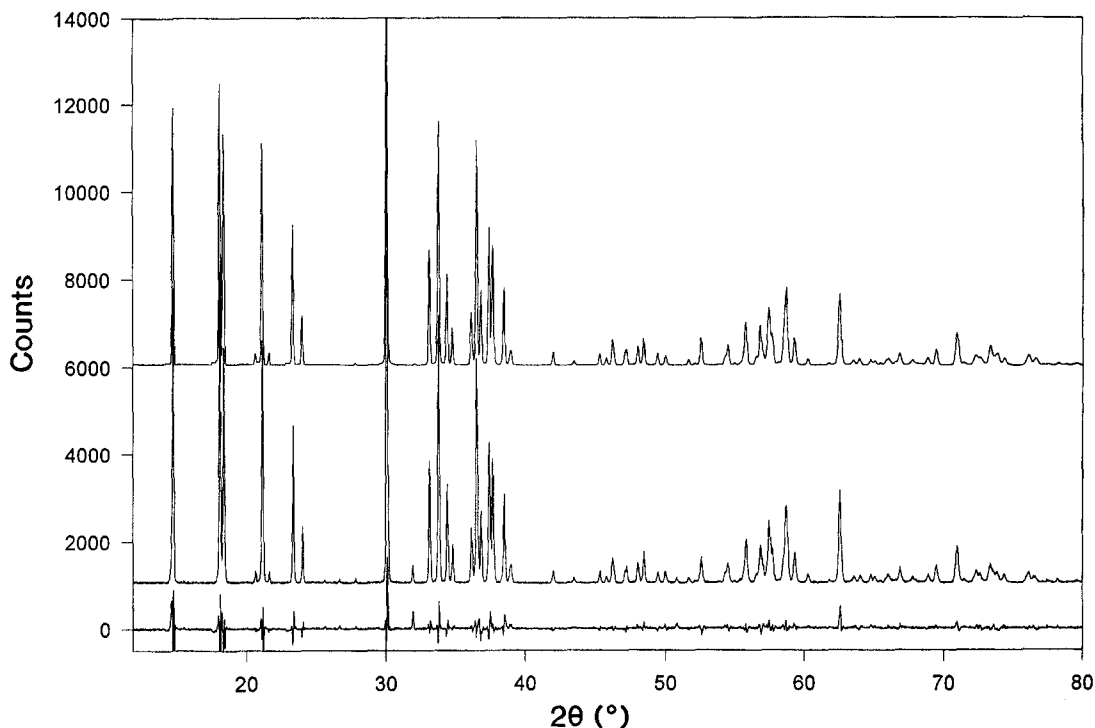


FIG. 1. The observed (middle), calculated (top) and difference (bottom) X-ray diffraction patterns for olivenite refined in the space group $P2_1/n$; the observed and calculated patterns have had 1000 and 6000 counts added to each data point for clarity.

observed in the monoclinic refinements of olivenite (Toman 1977, this work). The largest displacement occurs for the O(1) atom [labeled O(3) by Cordsen (1978)] in the z direction. The next largest displacement is for the O(4) atom [labeled O(1) by Cordsen (1978)] and occurs approximately along the Cu(2)–O(1) bond [*cf.* Cu(2)–O(4) in $Pn\bar{m}$ and $P2_1/n$ symmetries, Table 3]. Thus it is possible that libethenite also is monoclinic rather than orthorhombic, although the low R index for the orthorhombic refinement of Cordsen (1978) suggests that, if so, libethenite has a much smaller deviation from orthorhombic symmetry than olivenite.

Now let us examine the adamite structure for the same features. The maximum displacement in adamite occurs for the O(1) atom [labeled O(1) by Hawthorne (1976) and O(3) by Hill (1976)] and is in the z direction, although it is not as large as the displacement in libethenite. The next largest anisotropic displacement is for the O(4) atom [labeled O(3) by Hawthorne (1976) and O(4) by Hill (1976)], as is the case for libethenite. Also notable in the adamite structure is the Zn octahedron, which has four short equatorial anions ($<2.064>$ Å) and two long apical anions ($<2.264>$ Å). This (4 + 2) distortion is very characteristic of octahedrally coordinated Cu^{2+} . However, for Zn^{2+} , there is no electronic driving mechanism for such a distortion; the (4 + 2) distortion is an intrinsic property of the adamite arrangement, driven by local bond-valence requirements and connectivity restrictions. This indicates that this basic structural arrangement has an intrinsic tendency to distort in a direction similar to that required for local Jahn–Teller distortion if Zn^{2+} is replaced by Cu^{2+} . Is adamite actually monoclinic? The above discussion suggests this possibility, although the displacements for O(1) and O(3) are not particularly large. Possibly adamite is orthorhombic but with soft-mode behavior (Salje 1990); future work is planned to test this suggestion.

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