

THE CRYSTAL STRUCTURE OF CLINOCHALCOMENITE

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Received March 16, 1982.

Clinochalcomenite was found in 1979^[1] in an oxidized zone of an uranium occurrence located in Gansu Province, China. The crystal structure described in this paper gives further evidence that clinochalcomenite is the isomer of chalcocite, its formula being $\text{Cu}[\text{SeO}_3] \cdot 2\text{H}_2\text{O}$. Its cell is monoclinic, with $a_0 = 8.177 \text{ \AA}$, $b_0 = 8.611 \text{ \AA}$, $c_0 = 6.290 \text{ \AA}$, $\beta = 97^\circ 16'$ and $Z = 4$. The space group is $P2_1/n$. The diffraction intensities were collected on the four-circle diffractometer, and the structure was solved by use of the Patterson projection and Fourier method. Based on refinement by least-squares (full matrix), a final residual R of $0.08 (I > 2.5\sigma)$ was given. In the structure of clinochalcomenite, Cu^{2+} has sixfold coordination, surrounded by four O atoms and two H_2O molecules to form a distorted octahedron; Cu-O atomic distances range from 1.97 to 2.53 \AA . Two octahedrons are connected to form a pair by sharing an edge in common. The octahedron pairs are connected by the trigonal pyramid SeO_3 . The average atomic distance for Se-O is equal to 1.68 \AA .

I. COLLECTION OF EXPERIMENTAL DATA

After space group and cell dimensions of clinochalcomenite were determined from Weissenberg photographs, the diffraction intensities were measured with the Philips PW 1100 four-circle diffractometer with experimental conditions given below: Radiation $\text{MoK}\alpha$ $2\theta = 5^\circ$ to 46° ; total number of independent reflexions 673; total observed $I > 2.5\sigma = 368$; crystal dimensions $0.03 \times 0.05 \times 0.07 \text{ mm}$. Intensities were corrected by Lorentz-Polarization factors, but no correction for absorption was made.

II. MEASUREMENT AND REFINEMENT OF ATOMIC COORDINATES

For convenience of calculation, we make use of space group $P2_1/a$ and transform the hkl index and the cell dimensions as follows:

$$a_0 = 9.660 \text{ \AA}, b_0 = 8.615 \text{ \AA}, c_0 = 6.285 \text{ \AA}, \beta = 122.89^\circ.$$

According to $|F_{h0l}|^2$ and $|F_{0kl}|^2$, the Patterson projection $P(U, W)$ and $P(V, W)$ were calculated along the b - and a -axis respectively. Considering the height and direction of the peaks, the distribution map of the fourth order minimum function was drawn and transformed to the symmetry map of $P2_1/n$. This map is similar to the

projection for the synthetic $Zn[SeO_3] \cdot 2H_2O$ given by В. Ф. Гладкова^[2]. The difference between the two projections is that the position of Zn is substituted by Cu. This similarity is not occasional, because the space groups of clinochalcomenite and the synthetic $Zn[SeO_3] \cdot 2H_2O$ are both $P2_1/n$, their cell dimensions are also similar. So these two compounds should be taken as isostructure.

The Fourier synthesis was made by using the preliminary measured values of atomic coordinates for Cu and Se, the values of oxygen atoms for $Zn[SeO_3] \cdot 2H_2O$, the

Table 1
Atomic Coordinates for Clinochalcomenite

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.4775	0.3621	0.3565	0.0079	0.0014	0.0072	-0.0013	0.0004	-0.0136
Se	0.1518	0.8542	0.6012	0.0048	0.0030	0.0094	0.0011	-0.0041	-0.0092
O _I	0.2145	0.6815	0.6740	0.0106	0.0148	0.0092	0.0081	-0.0150	-0.0085
O _{II}	0.4682	0.4153	0.6695	0.0100	0.0036	0.0054	0.0061	-0.0132	-0.0317
O _{III}	0.0024	0.8154	0.4533	0.0129	0.0033	0.0233	0.0114	-0.0046	-0.0394
O _{IV(H₂O)}	0.1897	0.4415	0.3749	0.0052	0.0111	-0.0043	-0.0113	-0.0178	0.0183
O _{V(H₂O)}	0.4304	0.1403	0.4217	0.0124	0.0059	0.0288	0.0064	0.0240	0.0294

Table 2
Atomic Distances (Å) and Bond Angles (°) in Clinochalcomenite SeO_3 Trigonal Pyramid

Se—O _I	1.657	O _I —Se—O' _{II}	102.0
Se—O' _{II}	1.720	O' _{II} —Se—O _{III}	98.5
Se—O _{III}	1.661	O _{III} —Se—O _I	104.4
O _I —O' _{II}	2.624	O _I —O' _{II} —O _{III}	60.7
O' _{II} —O _{III}	2.562	O' _{III} —O _{III} —O _I	60.8
O _{III} —O _I	2.622	O _{III} —O _I —O' _{II}	58.5

Cu-O (or H₂O) Octahedron

Cu—O' _I	2.530	O' _I —Cu—O _{II}	80.8
Cu—O _{II}	2.010	O _{II} —Cu—O _{V(H₂O)}	92.0
Cu—O' _{II}	1.970	O' _{II} —Cu—O _{V(H₂O)}	89.8
Cu—O' _{III}	1.975	O' _{III} —Cu—O' _{II}	97.3
Cu—O _{IV(H₂O)}	2.441	O' _{III} —Cu—O' _I	86.4
Cu—O _{V(H₂O)}	1.982	O' _I —Cu—O _{II}	91.2
O' _{II} —O _{II}	2.581	O _{II} —Cu—O _{IV(H₂O)}	88.5
O _{II} —O _{V(H₂O)}	2.873	O' _{III} —Cu—O _{IV(H₂O)}	93.6
O' _{III} —O _{V(H₂O)}	2.794	O' _I —Cu—O _{IV(H₂O)}	86.4
O' _{III} —O' _{II}	2.961	O' _I —Cu—O' _I	85.8
O' _{II} —O' _I	3.111	O' _I —Cu—O _{V(H₂O)}	92.2
O' _I —O _{II}	3.267	O _{V(H₂O)} —Cu—O _{IV(H₂O)}	95.7
O' _{II} —O' _{II}	3.091		
O' _I —O _{V(H₂O)}	3.274		
O _{IV(H₂O)} —O _{II}	3.121		
O _{IV(H₂O)} —O' _{II}	3.235		
O _{IV(H₂O)} —O' _{II}	3.039		
O _{IV(H₂O)} —O _{V(H₂O)}	3.293		

uranium occurred in this paper enite, its formula $a = 8.611 \text{ \AA}$, $c_0 =$ reflection intensities as solved by use of least-squares the structure of O atoms and two distances range from 1.657 to 2.624 Å. The aver-

determined from with the Philips method below: Radiations used were corrected for absorption made.

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V) and $P(V, W)$ the height and diameter function was is similar to the

factor K (0.13) and the temperature factor B (1.06) calculated by the Wilson statistical method. The value thus obtained was $R = 0.33$. The structure data were refined by least-squares in turn. The final R -factor led to $R = 0.08$ ($I > 2.5$). The measured values of atomic coordinates are shown in Table 1. The main atomic distances and angles are shown in Table 2.

III. DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

1. Projection of clinochalcomenite structure on (100) is given in Fig. 1. Projection of the polyhedrons is given in Fig. 2, Cu^{2+} coordination being 6. It bonds to four oxygens and two water molecules to form a distorted octahedron. Two octahedrons in edge-sharing form a pair joined by the trigonal pyramid SeO_3 . The average atomic distance for Se-O is equal to 1.68 Å.

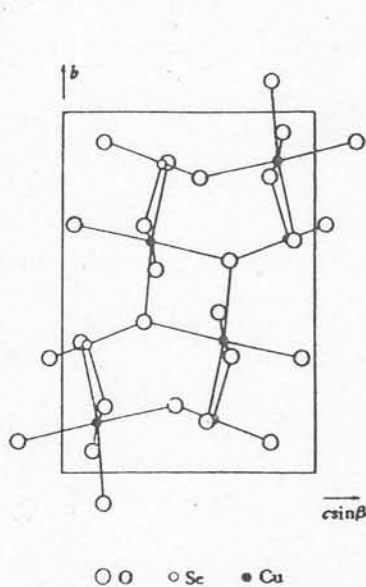


Fig. 1. Projection of the clinochalcomenite structure on (100).

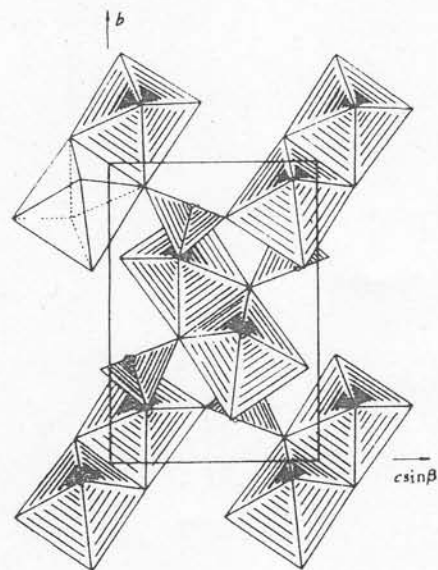


Fig. 2. Projection of the clinochalcomenite polyhedron on (100).

Because ion radius and other chemical properties of Cu^{2+} differ from those of Zn^{2+} , atomic distances and bond angles of octahedron formed by these two ions and oxygens are undoubtedly different. For example, Cu-O (or H_2O) atomic distances are from 1.97 to 2.53 Å but Zn-O (or H_2O) atomic distances are from 1.97 to 2.32 Å. Hence the cell dimensions of the two compounds have certain differences, too.

2. Although chemical compounds of clinochalcomenite and synthetic chalcomenite^[5] are the same, there are indeed distinct differences in their structure model. The structure of chalcomenite consists of chains parallel to b -axis and they are composed of Cu-O octahedrons of corner-sharing. There are trigonal pyramid SeO_3 joining the chains. This proves that clinochalcomenite and chalcomenite are two minerals of isomer.

3. The H peaks of H_2O molecule on the difference Fourier map appear incomplete. It is only based on crystallochemistry that we propose the H_2O positions, but

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We thank Wu Bomu of Institute of Biophysics, Academia Sinica, Guo Fang of Institute of Chemistry, Academia Sinica and Prof. Peng Zhizhong of Wuhan Geological College for help in the preparation of this paper.

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