

THE CRYSTAL STRUCTURE OF CHLOROPHOENICITE

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ABSTRACT

Chlorophoenicite, $(\text{Mn,Mg})_3\text{Zn}_2(\text{OH})_6(\text{As}_{0.5}\text{H}_{0.5})(\text{O,OH})_3)_2$, $a=22.98$, $b=3.32$, $c=7.32$ Å, $\beta=106^\circ 0'$, $Z=2$, $C2/m$, was solved by vector sets applied to $P(uvw)$. The final $Rh0l$, $hk0=0.122$ for 330 independent reflections. The principal structural features are infinite insular slabs of the formula units parallel to a {100}. Slabs are hydrogen bonded to each other only and perfect a {100} cleavage is observed. The slabs are in turn made up of Mn-(O,OH) octahedral pyrochroite fragments or bands three octahedra wide running parallel to b [010], connected along c [001] by $\{(\text{As}_{0.5}, \text{H}_{0.5})(\text{O,OH})_3\}_\infty$ and $[\text{Zn}(\text{O,OH})_3]_\infty$ tetrahedral chains which also run parallel to b [010].

The As atoms only half populate their sites and the $\text{As}(\text{O,OH})_4$ and H_4O_4 tetrahedra apparently order over one set of equivalent positions along b [010] to form chains. As-O distances, however, are anomalous. The population sequence along a is infinitely variable and prominent streaks parallel to a^* and requiring a doubling of the b -axis are observed on photographs.

Chlorophoenicite is yet another example of a pyrochroite fragment structure in the basic manganese arsenate group.

INTRODUCTION

The unusual mineral chlorophoenicite was originally described by Foshag and Gage (1924). It is known only from the Franklin and Sterling Hill, New Jersey, zinc-manganese-iron oxide and silicate orebodies of the pyrometasomatic type in marbles, where the mineral occurs as needles and matted fibres associated with pyrochroite, gageite, willemite, etc. implanted upon open cracks and fissures. Although the mineral occurs sparingly, it has been witnessed in many collections and its identification is by no means simple due to its needle-like habit.

This paper presents the chlorophoenicite crystal structure, pursuant to a systematic study of basic manganese arsenates.

EXPERIMENTAL

The single crystal, kindly donated by Professor C. Frondel, was one of the 14 crystals morphologically examined by Palache (1935), a drawing of which can be seen on p. 123 in this classic paper. The crystal, a slender prism of 0.65 mm length elongated parallel to b [010], had 0.019 mm³ volume; 289 independent intensities of the $h0l$ level were gathered on a manual moving crystal Weissenberg geometry counter-diffractometer employing Zr-filtered Mo radiation. The crystal was then broken and 41 independent intensities of the $hk0$ level were gathered from a nearly equant fragment of 0.003 mm³ volume. These data were corrected for absorption using a polyhedral correction program written by C. W.

Burnham in 1963 for the IBM 7094 computer. Continuous diffraction streaks, explained later, prohibited collection of higher levels for refinement purposes and, consequently, the crystal structure reported herein is an *average* structure.

THE STRUCTURE CELL

No X-ray data exist in the literature for chlorophoenicite. Sets of oscillation, rotation, Weissenberg and Buerger precession photographs led to the cell parameters in Table 1. The morphological evidence favors $C2/m$ as Palache, Berman, and Frondel (1951) suggest point symmetry $2/m$. The well-developed hemipyramids rule out Cm but it is not known

TABLE 1. CHLOROPHOENICITE. STRUCTURE CELL DATA

a		$22.98 \pm 0.04 \text{ \AA}$
b		3.32 ± 0.01
c		7.32 ± 0.01
β		$106^{\circ}0' \pm 10'$
$\rho(\text{obs}^a)$		3.46 gm/cc
$\rho(\text{calc})$		3.47
Z		2
comp.	$(\text{Mn}_{2.60}, \text{Ca}_{0.30}, \text{Mg}_{1.5}) \text{Zn}_{1.95} (\text{OH})_6 [(\text{As}_{0.5} \text{H}_{0.5}) (\text{O}, \text{OH})_3]_2$	
Space group		$C2/m$
$a:b:c^b$		$6.922:1:2.054$

^a Palache (1935).

^b Morphological $a:b:c=2.323:1:2.168$ (Palache, *et al.*, 1951). Note that $3 \times a=6.969$.

if doubly terminated crystals were observed. In any event, $C2/m$ rather than $C2$ was assumed and the structure analysis is consistent with this conclusion.

There are several unusual features about the structure cell of chlorophoenicite. Using the only known chemical analysis of Foshag in Foshag, Berman, and Gage (1927), the cell contents are nearly $(\text{Mn}_{5.20}, \text{Zn}_{3.90}, \text{Ca}_{0.60}, \text{Mg}_{0.30}) (\text{OH})_{14} (\text{AsO}_4)_2$. It is clear that a fully ordered structure with no vacancies could not have space group $C2/m$ since the tetrahedral arsenate groups would have to be situated on a set of inversion centers which is geometrically impossible. However, b -axis rotation photographs show continuous streaks requiring a doubling of that translation. These streaks are readily noticeable, as seen in Figure 1 and are parallel to a^* on c -axis Weissenberg photographs. The streaks, indicative of semirandom disorder, are explicable on the basis of the crystal structure which was revealed from analysis of the b -axis projection. This projection is most favorable since the $h0l$ diffraction spectra are devoid of streaks. $C2$ and

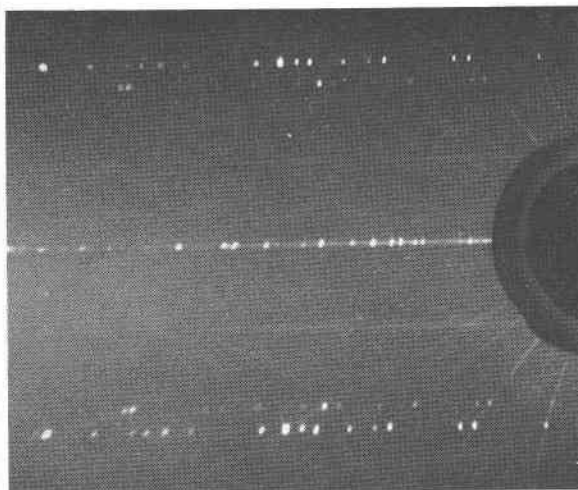


FIG. 1. The b -axis rotation photograph of chlorophoenicite. Unfiltered Cu radiation.

$C2/m$ are indistinguishable in this projection, except for the vector densities. The vector densities, incidentally, assist in determining the proper choice of space groups. It may also be remarked that the short b -translation prohibits atom overlap, thus allowing for unambiguous interpretation of $P(uw)$.

SOLUTION OF THE STRUCTURE

The structure was solved by vector sets applied to $P(uw)$. Each atom species over the set of equivalent general positions $(xz; \bar{x}\bar{z})$ in plane group $p2$ with $a' = a/2$, $c' = c$, has arbitrarily scaled vector density proportional to Z^2 at $(2x, 2z)$, where Z is the atomic number. Two atomic species R and S in independent general positions create two vectors $(x, z)_R - (x, z)_S$ and $(x, z)_R - (\bar{x}, \bar{z})_S$ each of weight $2Z_R Z_S$.

The Patterson projection, $P(uw)$, in Figure 2 is relatively simple in appearance, though the solution of the structure was not obvious at first. Initially, the strongest vectors, such as A , B , and C were assumed to be interatomic distances of metal pairs in two sets of independent positions. This pursuit was unsuccessful. It was later noted that vectors like D , E , and F must be metal-oxygen vectors by reason of stereochemistry and vector density. Since $b = 3.32 \text{ \AA}$ for the average structure, and since octahedral coordination is expected for the transition metals, the octahedra (if regular) must be oriented with edges parallel to b [010]. It requires only a little imagination to see the octahedral images welling forth out of $P(uw)$! The arrangement of octahedra sketched in Figure 2 re-

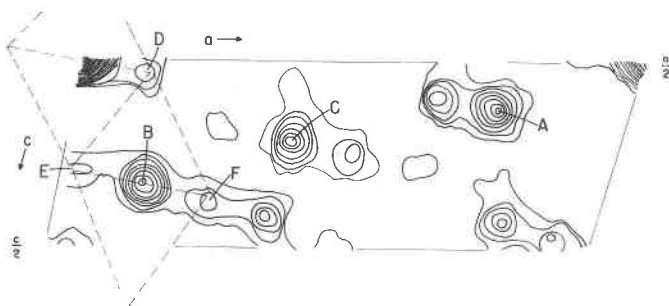


FIG. 2. $P(uvw)$ of chlorophoenicite with a portion of the octahedral band superimposed.

quires a metal at the cell origin and from this model all vectors could be labelled. The first trial model with metals only (one at the origin, three in independent general positions) using the scattering curves for Mn only gave $R_{h0l}=0.48$ after two cycles of coordinate refinement. Allowing the multipliers to vary (thus, approximating electron density for the sites) and adding oxygen at *D*, *E*, and *F* gave $R_{h0l}=0.34$ after two more cycles. A Fourier electron density map was prepared and the remaining three oxygen atoms appeared. As is seen on this map, the background is remarkably free from strong false peaks and comparison with $P(uvw)$ shows striking similarities. Accidental coincidence of vectors of the type $R_{x,z}$ - $S_{x,z}$ with molecular image vectors contributes to this similarity. Crude coordinates were obtained from this Fourier map for all ten atoms in the asymmetric unit.

REFINEMENT

Scattering curves were prepared for Mn^{2+} , Zn^{2+} , As^{3+} and O^- from the International Tables, Vol. 3 (1962). Three cycles of least-squares coordinate refinement gave $R_{h0l}=0.155$. The structure was now apparent and it permitted calculation of the *y*-coordinates, which must be either 0 or 1/2 for the space group $C2/m$. Including the $hk0$ data, $R_{h0l,hk0}=0.152$ for 330 independent reflections. Full matrix least-squares coordinate and isotropic temperature factor refinement gave after three cycles, $R_{hk0,h0l}=0.122$, all shifts being within their limits of error. All experimentally gathered reflections were included in the refinement and they were each weighted at unity. Final atom coordinates appear in Table 2, and the $F_{obs}-F_{calc}$ tables are in Table 3.¹

¹ Table 3 has been deposited as Document No. 9899 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C., 20540. Copies may be secured by citing the document number, and remitting in advance \$1.25 for photoprints or \$1.25 for 35 mm. microfilm.

TABLE 2. CHLOROPHOENICITE. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

	x	y	z	B
Mn (1)	0	0	0	0.89 (11)
Mn (2)	0.0888 (2)	$\frac{1}{2}$	0.3656 (7)	1.25 (9)
Zn	.2076 (1)	0	.2207 (5)	0.96 (7)
$\frac{1}{2}$ As	.3823 (3)	0	.1047 (8)	0.51 (10)
O (1)	.0222 (9)	0	.3002 (28)	1.18 (36)
O (2)	.0657 (9)	$\frac{1}{2}$.0430 (29)	1.33 (37)
O (3)	.1561 (8)	0	.3914 (26)	0.93 (34)
O (4)	.2548 (9)	$\frac{1}{2}$.2587 (29)	1.31 (37)
O (5)	.4059 (13)	0	.3246 (43)	3.58 (70)
O (6)	.3394 (9)	$\frac{1}{2}$.0471 (29)	1.41 (39)

DISCUSSION OF THE STRUCTURE

The crystal structure of chlorophoenicite has some surprising features (Fig. 3). Zinc occurs in special positions ($x0z$) with two degrees of freedom. It is tetrahedrally coordinated, requiring a new interpretation of the

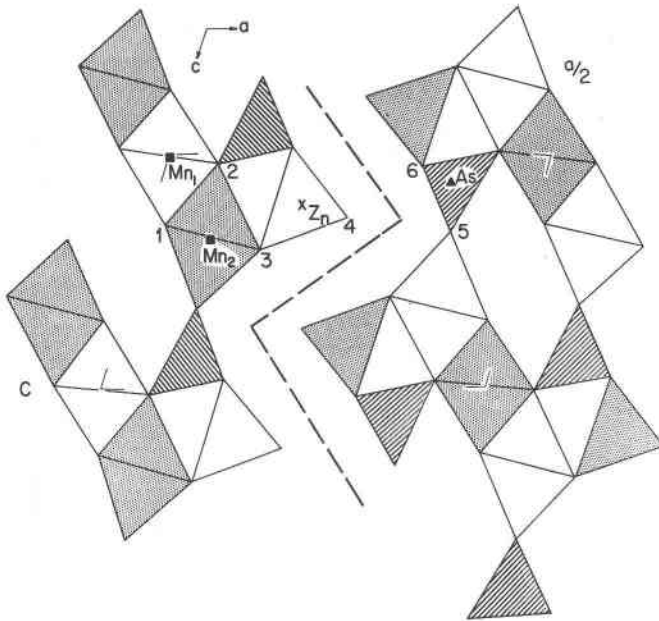
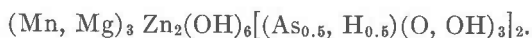


FIG. 3. Polyhedral diagram of the chlorophoenicite structure in the xz -plane. Unshaded polyhedra are centered at $y=0$, stippled at $y=1$, As-(O,OH) tetrahedra ruled NW-SE at $y=\frac{1}{2}$ and ruled NE-SW at $y=0$. The direction of cleavage is dashed in.

formula. The empirical formula is essentially $H \sim_8 Mn_3 Zn_2 AsO_{12}$ with two molecules in the cell. Some Mg and Ca proxy for Mn, but this is apparently limited.

The principal structural features are infinite insular slabs of formula units parallel to a {100}. The slabs are in turn made up of Mn-(O, OH) octahedral pyrochroite fragments or bands three octahedra wide which, by edge-sharing, run parallel to b [010]. These bands are connected along c [001] by $[Zn(O, OH)_3]_{\infty}$ tetrahedral chains and only partly occupied $[As(O, OH)_4]$ tetrahedra which also run parallel to b [010]. The structural formula is evidently



The Mn-(O, OH) octahedra and Zn-(O, OH) tetrahedra have sets of edges whose lengths define the b [010] repeat of 3.32 Å and their polyhedra are fully occupied. The As atoms, on the other hand, occupy only half their sites. Since these As-centered tetrahedra are oriented in the same fashion as the other polyhedra—with at least one edge parallel to b [010]—two unusual conditions arise. First, if As fully occupied all its sites, As-O tetrahedral chains would occur, a condition hitherto unobserved in mineral structures. Second, a required O-O edge distance of 3.32 Å associated with arsenate tetrahedra would arise, which is unreasonably long. Typical O-O distances associated with AsO_4^{3-} tetrahedra are 2.74 Å (Moore, 1968).

The peculiar behavior of As in the chlorophoenicite structure is interpreted in the following manner: $[As(O, OH)_4]$ tetrahedra alternate with $[H_4O_4]$ tetrahedra over equivalent translations along b [010] to form chains of the type $[(As_{0.5}, H_{0.5})(O, OH)_3]_{\infty}$. Thus, the As tetrahedra need not share corners with each other. This requires a doubling of b or 2×3.32 Å. The sequence along a , however, is random, even though the two kinds of tetrahedra still alternate along b [010]. Consequently, there is no unique repeat distance along a as such, so streaks are observed parallel to a^* . Alternatively, it can be stated that the repeat distance along a is so large that diffraction spots coalesce to form streaks. This one-dimensional disorder in chlorophoenicite only permits evaluation of an average structure.

Table 4, a summary of pertinent interatomic distances, shows that the expected Mn-O and Zn-O distances occur in chlorophoenicite. Average distances are Mn(1)-(O, OH) 2.18, Mn(2)-(O, OH) 2.24, Zn-(O, OH) 1.96 Å. Ghose (1964) observed Zn-(O, OH) 1.95 Å for tetrahedral Zn in hydrozincite. Furthermore, the polyhedral edge distances associated with the Mn and Zn centers not only conform to averages found in other structures involving Mn^{2+} -(O, OH) octahedra and Zn-(O, OH) tetrahedra, but also are foreshortened whenever edge-sharing occurs. Shared

TABLE 4. CHLOROPHOENICITE. INTERATOMIC DISTANCES

Octahedral distances				Tetrahedral distances			
Mn(1)-O		Mn(2)-O		Zn-O		As-O	
(4) Mn(1)-O(2)	2.21 Å	2 Mn(2)-O(1)	2.22	(2) Zn-O(4)	1.96	(2) As-O(6)	1.92
(2) Mn(1)-O(1)	2.11	(2) Mn(2)-O(3)	2.24	(1) Zn-O(3)	1.94	(1) As-O(2)	1.82
Average	2.18 Å	(1) Mn(2)-O(2)	2.27	(1) Zn-O(6)	1.94	(1) As-O(5)	1.55
		(1) Mn(2)-O(5)	2.24	Average	1.95 Å		
		Average	2.24 Å				
O-O Distances for octahedra				O-O Distances for tetrahedra			
Mn(1)		Mn(2)		Zn		As	
(4) O(2'')-O(1)	3.22	^a (2) O(1)-O(2)	2.89	(2) O(3)-O(4)	3.17	(2) O(6)-O(2')	2.96
^a (4) O(2)-O(1)	2.89	^a (2) O(1)-O(3)	2.96	(2) O(6)-O(4)	3.13	(2) O(6)-O(5)	2.71
^a (2) O(2)-O(2'')	2.91	(2) O(1)-O(5)	3.24	(1) O(4)-O(4')	3.32	(1) O(6)-O(6')	3.32
(2) O(2)-O(2')	3.32	(2) O(2)-O(3)	3.26	(1) O(6)-O(3)	3.18	(1) O(5)-O(2')	2.95
Average	3.07 Å	(2) O(3)-O(5)	3.28	Average	3.18 Å		
		(1) O(1)-O(1')	3.32				
		(1) O(3)-O(3')	3.32				
		Average	3.16 Å				

Errors: X-O(≠5) 0.03, X-O(5) 0.04, O(≠5)-O(≠5) 0.04, O(5)-O(≠5) 0.05, O(5)-O(5') 0.06 Å.

^a Shared edges.

edges range from 2.89 to 2.96 Å whereas unshared edges range from 3.22 to 3.32 Å. Thus, the basis motif of chlorophoenicite—the Mn-(O, OH) octahedral bands and the Zn-(O, OH) tetrahedral chains—is well-behaved and displays no anomalous features.

The As-(O, OH) tetrahedra, on the other hand, are anomalous. As mentioned before, the tetrahedral edge distance of 3.32 Å is unreasonable. Further, the tetrahedral As-(O, OH) distances range from 1.55 to 1.92 Å. The edge distances are 2.71, 2.95, 2.96, and 3.32 Å. It is clear that the one-dimensional disorder of As atoms permits solution of an average structure only and the limitations of this crystal structure analysis do not allow for any more detailed discussion.

HYDROGEN BONDING

The corrugated slabs of chlorophoenicite formula units tuck neatly together and their boundaries define the perfect *a* {100} cleavage observed for the mineral. Across these boundaries, oxygen atoms lie in a plane such that a network of possible hydrogen bond distances can be discerned (Fig. 4). Two independent distances are found, each measuring 2.80 Å and these involve O(3), O(4), and O(6). Unfortunately, assignment of

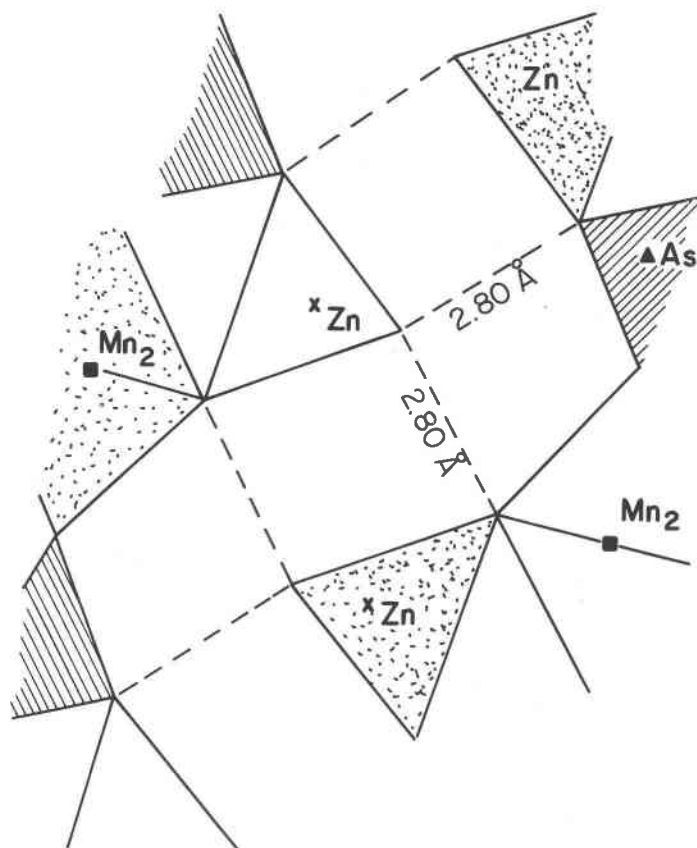


FIG. 4. Portion of the chlorophoenicite structure showing a network of hydrogen bonds (dashed).

hydrogen positions is masked by vacancies in As positions. This is evident if electrostatic bond strengths are computed (Table 5). Only O(2) and O(6) appear to be potential oxide anions. O(5) and O(6), also associated with the disordered As atoms, likely involve $O^{2-} \rightleftharpoons OH^-$ substitutions depending on whether As is present or not at a site. From Table 5, it is seen that O(2), O(5), and O(6) could be oxide anions if As fully occupied all available sites, though O(6) would be highly oversaturated.

PYROCHROITE FRAGMENTS

All basic manganese arsenates structurally analyzed so far have pyrochroite fragments as their principal units. Flinkite (Moore, 1967) is a derivative structure of pyrochroite with octahedral voids permitting

TABLE 5. ELECTROSTATIC VALENCE BOND STRENGTHS

		f
O (1)	Mn(1)+Mn(2)+Mn(2')	1.0
O (2)	Mn(1)+Mn(1')+Mn(2)+ $\frac{1}{2}$ As	1.6
O (3)	Mn(2)+Mn(2')+Zn	1.2
O (4)	Zn+Zn	1.0
O (5)	Mn(2)+ $\frac{1}{2}$ As	1.0
O (6)	Zn+As	1.7
	For fully occupied As sites:	
O (2)	Mn(1)+Mn(1')+Mn(2)+As	2.2
O (5)	Mn(2)+As	1.6
O (6)	Zn+As+As	1.7

AsO₄⁻³ tetrahedral linkages. Retzian (Moore, 1967) is similar, but includes square antiprisms. Allactite (Moore, 1968b) has double bands of pyrochroite fragments linked to each other to produce a strong sheet-like character. Gageite (Moore, 1968a), though not an arsenate, shares with chlorophoenicite the presence of octahedral triple bands, one 3.3 Å cell translation, and disorder over the tetrahedral positions.

As more of these peculiar structures come to light, two principal classes of structures appear to be prevalent. One class includes sheets of broken pyrochroite fragments (flinkite, retzian, allactite). The other class includes the fibrous minerals or the "pipe" structures, to borrow an apt term from Takéuchi (1950). Included here are chlorophoenicite, gageite, fluoborite (Takéuchi, 1950), even psilomelane (Wadsley, 1953) and hollandite (Byström and Byström, 1950), all having in common a fibrous habit with bands of edge-sharing octahedra running in that direction, linked to form bundles of tubular spaces. It is no surprise that chlorophoenicite, gageite, and fluoborite all belong to the same paragenesis at Franklin and Sterling Hill, New Jersey and often occur together. It is tempting to add that the myriads of fibrous materials encountered in the low temperature hydrothermal vein parageneses at Franklin, New Jersey or Långban, Sweden may include an abundance of novel linkages hitherto undocumented in the annals of science.

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