A STUDY OF PHOENICOCHROITE—ITS STRUCTURE AND PROPERTIES

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Abstract

The poorly described species phoenicochroite occurs at several localities in Arizona. Material from the Potter-Cramer mine provides new information on the species. Phoenicochroite is associated with crocoite, cerussite, mimetite, and vauquelinite in the oxidized zone of galena-bearing veins. Analysis gives PbO 80.88, CrO_3 18.08; total 98.96, corresponding to $Pb_2O(CrO_4)$. The mineral is dark, cochineal red with a yellowish-orange streak; $H=2\frac{1}{2}$; $\rho=7.01$ (meas.) 7.075 (calc.). It occurs in anhedral cleavable translucent masses. Good cleavage on $\{\bar{2}01\}$ is easily seen; poorer cleavages are on $\{001\}$, $\{010\}$, and $\{011\}$. Phoenicochroite is monoclinic: space group $C2/m$, $a=14.001$, $b=5.675$, $c=7.137$Å; $\beta=115°13'$; $Z=4$. Strongest lines from x-ray powder photographs are: 3.380(10), 2.979(10), 6.43(5), 6.34(5), 2.831(5), 1.862(5), 2.475(4), 2.263(4) Å. The indices of refraction are $\alpha=2.38_D$, $\beta=2.44_D$, and $\gamma=2.65_D$; $X=b$, $Y\wedge c=-2°$. Optically $(+)$ with $2V_z$ (meas.)$=58°$; $2V_z$ (calc.)$=60°$. Dispersion is moderately strong with $\rho>v$. Only one relatively poorly developed crystal suitable for goniometry was found. Forms recognized were $\{010\}$, $\{100\}$, $\{\bar{2}01\}$, and $\{\bar{2}11\}$. The axial ratio is 2.467:1:1.258.

The mineral is isostructural with lanarkite and the structure contains independent chromate tetrahedra; Pb atoms are in special position on mirror planes. The additional oxygen is associated with and tetrahedrally coordinated by the Pb atoms.

Introduction

Since first described in 1833 phoenicochroite has remained poorly defined although it is rather widely known. Specimens labeled phoenicochroite from Beresov were obtained from the following: British National Museum, Musée de Mineralogie de l'École des Mines, Harvard Museum, Queens University, and the private collection of John Jago. All of these specimens exhibit a mineral which agrees with the scanty data given in the original description. Recent work by Bariand (unpublished manuscript, private communication) and Temple (1956) tends to verify the fact that there is no confusion regarding the identity of phoenicochroite. The specimen from the British National Museum was particularly helpful in establishing the identity of phoenicochroite. It clearly shows "tabular rhombic prisms" (Haidinger, 1845) and dissolves in 1:1 HCl while precipitating $PbCl_2$.

It is our purpose to better define phoenicochroite, and we have chosen to base our study on material from the Potter-Cramer property (Williams, 1968) where it occurs in abundance.

Physical Properties and Occurrence

Phoenicochroite is invariably dark cochineal red (Munsell 2.5R 4/10 with yellowish-orange (Munsell 5YR 6/12) streak. The hardness is $2\frac{1}{2}$ and sectility may be observed on tiny cleavable flakes. The specific gravity of a 23 mg fragment was 7.01 (average of 8 trials on the Berman balance).

Cleavage plates up to 25 mm across have been observed. Large polycrystalline masses of the mineral seldom show crystal faces. Cleavable masses are translucent and thin cleavage fragments are quite transparent.

Phoenicochroite and the new mineral hemihedrite[1] are the earliest

TABLE 1. Morphological Data for Phoenicochroite

Monoclinic—$2/m$

$a:b:c = 2.467:1:1.258$ $\quad \beta = 115°13'$ $\quad \mu = 64°47'$

$p_0:q_0:r_0 = .510:1.138:1;$ $\quad p_2:q_2:r_2 = .448:1:.879$

$p_0' = .563$ $\quad q_0' = 1.258$ $\quad x_0' = .471$ $\quad \rho_0 = 25°13'$

		ϕ	ρ	ϕ_2	$\rho_2 = B$	C	A
b	010	0°00'	90°00'	—	0°00'	90°00'	90°00'
a	100	90 00	90 00	0 00	90 00	67 47	0 00
d	$\overline{2}01$	−90 00	33 16	123 16	90 00	58 29	123 16
p	$\overline{2}11$	−27 33	54 49	123 16	43 34	68 53	112 12

chromates to form in the oxide assemblage. The phoenicochroite is surficially altered to crocoite and the chromates are then replaced by cerussite, mimetite, and vauquelinite. The chromates often occur in veinlets up to several feet away from the nearest altered galena, although it tends to form only in proximity to partly fresh galena.

Morphology

Although crudely formed crystals are not uncommon (at Beresov as well as the Arizona locality), only one measurable crystal has been found among the Arizona material. Morphological data presented in Table 1 are based on the X-ray cell parameters and all forms found on the measurable crystal are presented.

The habit is characterized by elongation on [010] with marked flattening on $\{\overline{2}01\}$ which is also a plane of easy cleavage. The elongated blades

[1] Name approved by the Commission on New Mineral Names, International Mineralogical Association. Description to be published.
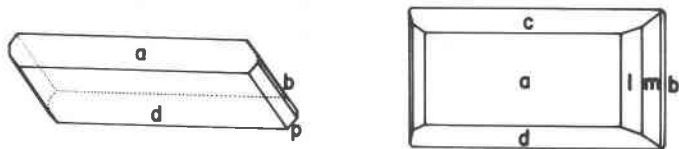
Fig. 1. Left—crystal from the Potter-Cramer mine. Right—crystal from Beresov, B.M. 94718, purposely shortened on [c] to emphasize "tabular rhombic" symmetry. This crystal shows, in addition, c {001}, l {310}, and m {110}

are commonly terminated by $\{\bar{2}11\}$. The one crystal found is presented in Figure 1.

A fine specimen from the British National Museum (M.—94718) has crystals showing, in addition, {001}, {110}, and {310}. These crystals are elongate on [001] and flattened on {100}.

CHEMICAL COMPOSITION

An emission spectrographic analysis of material from the Potter-Cramer mine showed the following: Pb, 72 weight precent; Cr, 10; Si; 0.063; Mg, 0.0014; Al, 0.016; Sr, 0.027; Ca, 0.079; Cu, trace. A 16 mg sample of the same material was analyzed for Pb and Cr by atomic absorption. The results are shown in Table 2. The formula obtained is Pb_2O (CrO_4).

OPTICS

In thin section phoenicochroite is orange to yellow orange with feeble peochroism and absorption of $X < Y < Z$. Cleavage on $\{\bar{2}01\}$ is easily seen and grinding enhances the poorer cleavages on {001}, {010}, and {011}. Dispersion is moderately strong with $\rho > v$.

The optic orientation is somewhat unusual with $X = b$, $Y \wedge c = -2°$

TABLE 2. CHEMICAL ANALYSIS OF PHOENICOCHROITE

	1	2	3	4
PbO	80.88	81.73	.3662	81.70
CrO₃	18.08	18.27	.1827	18.30
Total	98.96	100.00		

G. Roseveare, Arizona Bureau of Mines, Analyst.

1. Weight percent.
2. Analysis recalculated to 100 percent.
3. Oxide proportions.
4. $Pb_2O(CrO_4)$

TABLE 3. X-RAY CRYSTAL DATA FOR PHOENICOCHROITE

$a = 14.001(7)$ Å.	$V = 512.909$ Å³.
$b = 5.675(3)$ Å.	$\rho_o = 7.01$
$c = 7.137(5)$ Å.	$\rho_c = 7.075$
$\beta = 115.22°$	$Z = 4$
Space group: $C2/m$	

and $Z \wedge c = {}^+88°$. The measured $2V_Z$ is $58°$ and calculated $2V_Z$ is $60°$ for the NaD line.

Indices were determined in S-Se melts which were checked for refringence before crystallization by the Brewster method. The indices are as follows: $\alpha = 2.38_D$, $\beta = 2.44_D$, and $\gamma = 2.65_D$.

X-RAY UNIT CELL PARAMETERS, SPACE GROUP, AND POWER PATTERN

A cleavage fragment of phoenicochroite was ground to an approximately spherical shape having a radius of about 0.06 mm. Diffractometer measurements of 17 axial reflections were used to refine the unit cell dimensions by the method of least squares. The space group was determined as $C2$, Cm, or $C2/m$ from observations of systematic omissions on Weissenberg photographs, and the centric refinement of the structure

TABLE 4. STRONG X-RAY DIFFRACTION LINES OF
PHOENICOCHROITE FROM SELECTED LOCALITIES

Potter-Cramer Property		Pack Rat Claims		Wickenburg		Beresov (Jago)		Beresov (Harvard)	
I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)
5	6.43			3	6.46	4	6.40	4B	6.40
5	6.34	4	6.37	3	6.33				
3	5.96	2	5.99	2	5.97	2	5.99	3	5.96
3	4.40			3	4.44	3	4.42	3	4.42
3	3.58	5	3.59			7	3.60	4	3.59
10	3.380	7	3.387	10	3.389	10	3.39	10	3.386
3	3.221	5	3.234	2	3.232	4	3.26	3	3.278
10	2.979	10	2.983	9	2.985	10	2.989	10	2.981
5	2.831	4	2.836	5	2.837	3	2.840	4	2.834
3	2.510	4	2.520	2	2.514	3	2.523		
4	2.475	4	2.483	2	2.482	3	2.484		
3	2.361					1	2.372		
4	2.263	4	2.267	3	2.267	3	2.267		
5	1.862			5B	1.871	3	1.872		

TABLE 5. X-RAY POWDER DATA FOR PHOENICOCHROITE
(CuKα=1.5418 Å; Ni Filter) Camera diameter 114.59 mm

Phoenicochroite Potter-Cramer Locality				Phoenicochroite Potter-Cramer Locality			
I	d (meas.)	d (calc.)	hkl	I	d (meas.)	d (calc.)	hkl
5	6.43	6.46	001	4	1.771	1.769	$\bar{6}22$
5	6.34	6.33	200	3	1.745	1.746	802
3	5.96	5.97	$\bar{2}01$			1.745	$\bar{3}31$
1	5.18	5.18	110	4	1.720	1.724	710
3	4.40	4.44	$\bar{1}11$			1.716	$\bar{8}01$
2	3.77	3.79	201	2	1.688	1.694	620
3	3.58	3.55	$\bar{2}02$	4	1.658	1.662	$\bar{5}14$
1	3.477	3.492	$\bar{4}01$			1.656	$\bar{8}03$
10	3.380	3.387	310	3	1.622	1.623	$\bar{1}14$
3	3.221	3.228	002	2	1.604	1.607	512
1	3.022	2.984	$\bar{4}02$	1	1.562	1.567	$\bar{5}31$
10	2.979	2.983	$\bar{1}12$	4	1.522	1.519	711
2	2.876	2.880	$\bar{3}12$	4	1.499	1.500	$\bar{9}12$
5	2.831	2.838	020			1.498	602
1	2.647	2.650	311	3	1.465	1.468	$\bar{8}21$
1	2.577	2.598	021	2	1.418	1.419	040
		2.589	220	2	1.368	1.370	133
3	2.510	2.510	$\bar{5}11$			1.367	$\bar{7}32$
4	2.475	2.480	202	2	1.326	1.325	622
3	2.361	2.368	$\bar{2}03$	2	1.292	1.291	005
		2.366	$\bar{5}12$	1	1.280	1.280	$\bar{5}34$
3	2.312	2.313	510	2B	1.256	1.255	$\overline{10}.2.2$
4	2.263	2.263	$\bar{6}02$	1	1.230	1.231	242
1	2.191	2.186	$\bar{3}13$			1.229	802
3	2.105	2.113	420	2	1.205	1.206	$\bar{4}42$
		2.111	600			1.205	115
2	2.051	2.056	$\bar{4}22$	2B	1.188	1.190	$\bar{8}25$
3	1.978	1.989	$\bar{6}03$			1.186	$\overline{11}.1.4$
2	1.943	1.950	$\bar{5}11$	1	1.177	1.178	640
1	1.926	1.893	402	1	1.160	1.160	$\overline{12}.0.2$
5	1.862	1.868	712	1	1.140	1.139	713
		1.867	222				
		1.865	$\bar{7}11$				
		1.858	421				

indicates the space group to be $C2/m$. Crystal data are presented in Table 3.

Powder diffraction patterns made of phoenicochroite from several localities are given in Table 4. The indexed pattern shown in Table 5 was produced in a Norelco, Straumanis-type camera having a diameter of

114.59 mm, using Ni-filtered CuKα radiation. The line intensities of all patterns were estimated visually. Indexing was achieved by comparing measured values of $\sin^2\theta$ with values calculated on a CDC 6400 computer.

Structure Data Collection

A four-circle automatic diffractometer was used to collect intensity data on the 0.06 mm sphere previously described. Of the 675 reflections obtainable with CuKα radiation, 496 were collected and of these 408 were considered to be observed on the basis of having intensities greater than 1.8σ. The intensities were corrected for Lp effects and for absorption by linear interpolation of the spherical corrections taken from the *International Tables for X-ray Crystallography, Vol. III*, 304, 305 (1959) with μR equal to 8.9. The intensities were then reduced to structure factors.

Structure Determination

The Pb-Pb vectors were identified in a 3-dimensional Patterson synthesis and were attributable to two Pb atoms in special positions (i) on the mirrors in space group $C2/m$. The Pb coordinates were determined by graphical analysis of the Patterson and the Pb-Cr vectors were used to determine the Cr coordinates. The Cr atom also occupies the special position (i). The two Pb and one Cr atoms produced an initial R factor ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.250. Two cycles of full matrix least squares refinement with isotropic temperature factors reduced R to 0.168. A difference synthesis revealed four oxygen atoms. Two chromate oxygens were in special positions (i) on the mirror, one chromate oxygen was in general position and, together with its mirror relation, completed the chromate tetrahedron. The fourth oxygen was in special position (h) on the 2-fold rotor with a y coordinate of about $\frac{1}{4}$. Other peaks on the difference map were less than half as high as those of the oxygens.

Least squares refinement reduced R to 0.148 and it was apparent that uncorrected absorption due to non-sphericity of the crystal was causing difficulty. Plots of $|F_c|/|F_o|$ versus the data collection angles χ, ϕ, and 2θ revealed a strong, nearly linear trend with χ. The positive slope indicated that the crystal was slightly elongated parallel to the ϕ axis (b). Removal of this trend and least squares refinement reduced R to 0.075. Elongation along the ϕ axis implies absorption error relative to θ as well as to χ and as no trend was observed relative to θ it was apparent that the θ-related portion of the error had been absorbed by the temperature factor refinement and anisotropic refinement appeared unjustified. A second set of plots versus χ, ϕ, and 2θ showed that the χ error had been corrected and revealed a fluctuation versus ϕ which seemed to indicate

that the crystal was slightly triaxial in the section normal to the rotation axis. An approximate removal of the ϕ-related error followed by least squares refinement reduced R to 0.063 and the refinement was terminated.

The atomic scattering factors used were those for atoms of Cr and O which are given in the *International Tables for X-ray Crystallography*, Vol. III, 202–204 (1962) and for the Pb atom those given on page 212 of

TABLE 7. ATOMIC PARAMETERS FOR PHOENICOCHROITE[a]

	x	y	z	B
Pb_1	.4794 (1)	.0000	.2328 (2)	.82 (5)
Pb_2	.3569 (1)	.5000	.3870 (2)	.94 (5)
Cr	.1693 (6)	.0000	.1593 (11)	.97 (12)
O_1	.0930 (31)	.0000	.8984 (58)	2.8 (7)
O_2	.2989 (27)	.0000	.2005 (48)	1.4 (5)
O_3	.1448 (23)	.2345 (53)	.2662 (40)	2.6 (5)
O_4	.5000	.2413 (63)	.5000	2.0 (6)

[a] Standard deviations in parentheses refer to the last digits. Atomic numbering is shown in Figure 2.

the same volume. The observed and calculated structure factors are listed in Table 6[1] and the atomic parameters are given in Table 7.

DESCRIPTION OF THE STRUCTURE

After completion of the structure it was discovered that the resulting structure is isostructural with that of lanarkite, $Pb_2O(SO_4)$, which was studied by Binnie (1951). The present work verifies that the tetrahedral anion is positioned and oriented approximately as Binnie had placed it on the basis of an analogy to the structure of PbO. The structure is shown in projection viewed parallel to the b axis in Figure 2. Bond distances and angles are given in Table 8. The Cr-O distances average 1.674 Å. and the angles within the CrO_4 tetrahedron range from 108.4° to 110.3°. The additional oxygen is associated with and tetrahedrally coordinated by the Pb atoms. The Pb-O distances in this tetrahedron are relatively short (2.26 and 2.35 Å.) and the angles range from 102.0° to 117.0°.

[1] To obtain a copy of Table 6, order NAPS Document No. 00946 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022, remitting $2.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.
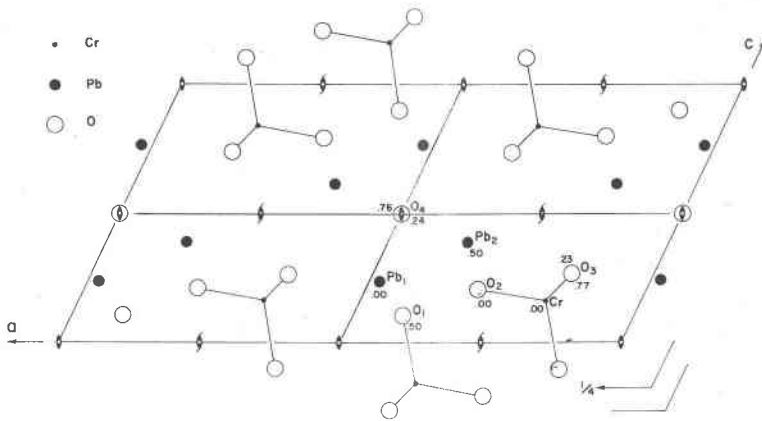
FIG. 2. The crystal structure of phoenicochroite shown in projection from the $+b$ direction.

TABLE 8. DISTANCES AND ANGLES IN PHOENICOCHROITE[a]

i	j	d_{ij}	i	j	k	$Angle_{ijk}$
Cr	O_1	1.70 Å	O_1	Cr	O_2	108.5°
Cr	O_2	1.71	O_1	Cr	O_3	110.3
Cr	O_3	1.64	O_2	Cr	O_3	109.7
			O_3	Cr	O_3	108.4
Pb_1	O_1	3.02				
Pb_1	O_2	2.44	Pb_1	O_4	Pb_1	105.6
Pb_1	O_3	2.69	Pb_1	O_4	Pb_2	107.9
Pb_1	O_4	2.26	Pb_1	O_4	Pb_2	117.0
			Pb_2	O_4	Pb_2	102.0
Pb_2	O_1	2.43				
Pb_2	O_2	3.09	Minimum Non-bonded Distances			
Pb_2	O_3	3.11	i	j	d_{ij}	
Pb_2	O_3	2.82	Pb_1	Pb_1	3.61 Å	
Pb_2	O_4	2.33	Pb_2	Cr	3.41	
			Cr	Cr	4.30	

[a] Atomic numbering is shown in Figure 2.

and recognizing the one measurable phoenicochroite crystal from the Potter-Cramer material used in this study. Computer time was provided by the Computer Center, University of Arizona.

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