OBSERVATIONS ON CONICHALCITE, CORNWALLITE, EUCHROITE LIROCONITE AND OLIVENITE

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Abstract

Conichalcite, is orthorhombic, Pnam; the unit cell with a=7.40, b=9.21, c=5.84A contains 4[CuCaAsO₄(OH)], calculated specific gravity, 4.33. Higginsite and some specimens of erinite give the same x-ray powder pattern as conichalcite.

Cornwallite is monoclinic, $P2_1/a$; the unit cell with a=17.61, b=5.81, c=4.60A, $\beta=92^\circ15'$ contains $2[\text{Cu}_6(\text{AsO}_4)_2\cdot(\text{OH})_4]$. Specific gravity 4.68 (calc.) 4.17 (Church, 1868). Several specimens of erinite give the same x-ray powder pattern. The powder patterns indicate the existence of an isostructural series with pseudomalachite.

Euchroite is orthorhombic, $P2_12_12_1$. The unit cell with a=10.07, b=10.52, c=6.12A contains $4[Cu_2AsO_4(OH) \cdot 3H_2O]$, calculated specific gravity 3.45, measured 3.41. Optical orientation Z=b, optic plane (001).

Liroconite is monoclinic, I2/a. The unit cell with a=12.70, b=7.57, c=9.88A, $\beta=91^{\circ}23'$ contains $4[Cu_2Al(As,P)O_4(OH)_4 \cdot 4H_2O]$ calculated specific gravity 2.95, measured 3.01.

Olivenite is orthorhombic, Pmnm. The unit cell with a=8.22, b=8.64, c=5.95A, contains $4[Cu_2AsO_4(OH)]$ with calculated specific gravity 4.45, measured 4.378. Leucochalcite from Wilhelmine mine Spessart Germany (type locality) and from Majuba Hill, Nevada give the same x-ray powder pattern.

In the course of a study of natural hydrous and basic copper phosphates and arsenates a large number of museum specimens of these interesting minerals have been examined. X-ray powder diffraction patterns of all specimens have revealed numerous misidentifications and has indicated that a number of the older mineral names apply to the same mineral. This was particularly true of the green copper minerals occurring in finely crystalline and botryoidal crusts. The results of this study of pseudomalachite, cornetite and clinoclasite have already appeared (Berry, 1950; Palache & Berry 1946). In the present paper the results are given for several of the arsenates.

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& Davies, 1947). The data on conichalcite have also appeared in abstract (Berry 1948).

CONICHALCITE AND "HIGGINSITE"

Conichalcite was first described by Breithaupt (1849) with analyses by Fritsche on reniform and massive material from Spain. The mineral was later recognized and analysed by Hillebrand (1884) from Tintic, Utah. Higginsite was described by Palache & Shannon (1920) as well crystallized material from the Higgins mine, Bisbee, Arizona. Strunz (1939) gives unit cell dimensions for higginsite and finds that conichalcite and higginsite give almost identical x-ray powder patterns. Independently, Richmond (1940) determined the unit cell dimensions and space group for higginsite.

In the present study numerous museum specimens labelled conichalcite and erinite were examined. All the conichalcite specimens and some of the erinite specimens gave an x-ray powder pattern identical with that from a crystal of higginsite, kindly provided from the type material by Professor C. Frondel of Harvard University. This pattern was obtained from the following specimens:

Conichalcite: Simon Mine, Mineral Co., Nevada (HM, 86387); Tintic, Utah (QM, M8282, A561-2); Copperopolis, Tintic (ROM, M20135); Tintic (ROM, M20128); Calavada mine, Yerrington, Nevada (HM, Goudey); Napa Valley, California (USNM, 13584).

"Higginsite": Higgins mine, Bisbee, Arizona (HM, 92923, type material).

"Erinite": Tintic, Utah (ROM, E3001), (ROM, M6761); Redruth Cornwall (USNM, R5377); Utah (AMNH, 15311)

"Mixite"; Utah (ROM, M18910)

One of these specimens labelled "erinite" (ROM, E3001) yielded a small crystal from a radiating group suitable for study on the Weissenberg goniometer. The films yielded the following lattice dimensions:

$$a=7.40$$
 $b=9.26$ $c=5.87$ A (A. R. Graham)
 $a=7.42$ $b=9.21$ $c=5.84$ A (Strunz, 1939)¹
 $a=7.43$ $b=9.22$ $c=5.86$ A (Richmond, 1940)¹

in close agreement with the values given by Strunz and Richmond. In order to obtain satisfactory agreement between measured and calculated spacings in the x-ray powder pattern (Table 1) the following lattice dimensions were chosen:

$$a = 7.40$$
, $b = 9.21$, $c = 5.84$ A

Three of the specimens examined here (ROM, E3001, M20135; HM, 86387), including that used for single crystal study, gave an x-ray powder

¹ Converted to new Angstrom wave lengths.

pattern slightly contracted compared to the others, indicating a slightly larger unit cell. The pattern given in table 1 represents that given by "higginsite" and most of the conichalcite specimens. The variation may be due to substitution of phosphorus for arsenic but a further x-ray study of carefully analysed materials would be necessary to establish this.

Composition and cell content. Strunz (1939) and Richmond (1940) show clearly that the unit cell content of higginsite is 4[CuCaAsO₄(OH)] with

Table 1. Conichalcite—CuCaAsO₄(OH): X-Ray Powder Pattern Orthorhombic, Pnam, a=7.40, b=9.21, c=5.84A; Z=4

I	d(meas.)	hkl	d(calc.)	I	$d(\text{meas}_*)$	hkl	d(calc.)	I	d(meas.)	hkl	d(calc.)
3	5.73A	110	5.769A			(310	2.383A	5	1.822A	331	1.826A
2	4.91	011	4.932	3	2.36A	230	2,363	4	1.720	∫203	1.723
5	4.10	111	4.104			122	2.340	6	1.720	420	1.716
1	3.93	120	3.910	2	2.29	202	2.292			223	1.614
2	3.70	200	3.700	4	0.01	∫212	2,224	7	1.609	332	1.606
2	3.42	210	3.433	1	2.21	231	2.190			133	1.605
1	3.25	121	3.249		0.05	222	2.052	2	1.560	402	1.562
9	3.14	201	3.125	4	2.05	132	2.034	3	1 507	∫060	1.535
40	2.84	∫220	2.884	$\frac{1}{2}$	1.963	240	1.955	3	1.527	152	1,524
10	2.84	130	2.836			241	1.854			•	
10	0.50	∫112	2,605			400	1.850				
10	2.59	221	2.586	4	1.843	312	1.846				
5	2.56	131	2.551			113	1.845				
1	2.46	022	2.466			232	1.837				
I	d(meas.)	I	d(me	as.)	I	d(mea	s.) I	d(n	neas.)	I	d(meas.)
i	1.479A	. 4	1,3	301A	1	1,115	A 3	1.	.002A	1 2	0.814
1	1.462	1	1.2	274	3	1.099		0.	.989	1	0.803
+	1.442	1/2		246	1 2	1.079	1 4	0.	926	1	0.794
1	1.415	3	1.2	211	à à	1.064	l ∮b	0	.906		
± 2 ≟	1.381			189	1	1,039	177	0	. 836		
Į.	1.371	1/2 1/2	1.1	145	4	1,018	150		.826		

b-broad line.

calculated specific gravity, 4.33, in good agreement with the measured value 4.33. The available analyses of conichalcite by Fritsche (Breithaupt, 1849, Cordoba, Spain), Hillebrand (1884, Tintic, Utah) and Michel (1909, Maya-Tass, Akmolinsk, Siberia) differ notably in the water content of 5.61, 5.52, and 5.15 per cent respectively compared with 3.41 per cent given by Shannon (Palache & Shannon, 1920) for higginsite. Very finely crystalline materials of this type do show a higher water content than well formed crystals, this has been already noted in a survey of pseudomalachite analyses (Berry, 1950).

The name conichalcite is preferred to higginsite for this mineral since it has priority and the analyses lead to a cell content which is essentially the same as that found for higginsite, the well crystallized material.

CORNWALLITE AND "ERINITE"

Cornwallite, erinite and conichalcite are names which have been associated with green botryoidal crusts which are generally hydrous copper arsenates in composition. Conichalcite, discussed briefly in the first section of this paper, contains calcium in addition to copper. Eleven specimens labelled erinite were available for study; four gave the x-ray powder pattern of conichalcite and seven gave an x-ray powder pattern similar to the pattern given by most of the cornwallite specimens. The following specimens are referred to in this section:

1. "Erinite" (YM, Brush Coll., 3064) Mammoth mine, Tintic District, Utah. Dark green, fine crystalline crust on olivenite crystals and massive enargite.

2. "Erinite" (YM, 7310) Mammoth mine, Tintic District, Utah. Dark green, fine

crystalline crust coating and replacing azurite crystals.

3. Cornwallite (BM, AG, 2) Cornwall. Green, thin botryoidal coating.

4. "Erinite" (BM, 39508) Ireland, "near type" material given to the British Museum by Haidinger in 1858. Light green, fine crystalline radiating crust.

5. Cornwallite (USNM, 105188) Tintic, Utah. X-ray powder pattern by United States

Geological Survey.1

6. Cornwallite (Hatfield Goudey) Majuba Hill, Nevada. Light green crust.

7. "Erinite" (USNM, C4200) Eureka, Nevada. X-ray powder pattern by United States Geological Survey.

8. "Erinite" (USNM, 48112) Tintic, Utah, Green crust with clinoclasite.

9. "Erinite" (HM, Holden Collection) Centennial Eureka mine, Tintic, Utah. Thin dark green fine crystalline coating over enargite in vugs, some later nodules of malachite.

10. Cornwallite (BM, 35618) St. Day United mines, Gwennap, Cornwall, Green

cryptocrystalline material.

- 11. Cornwallite (BM, 55559) St. Day United Mines, Gwennap, Cornwall. Fine crystalline green material.
- 12. Cornwallite (USNM, R5568) Cornwall, England. Green cryptocrystalline nodules with olivenite.

13. "Erinite" (BM, 61333) Gunnislake mine, Calstock, Cornwall, Light green globular aggregate with limonite.

14. Cornwallite (BM, 36469) Wheal Unity, Gwennap, Cornwall. Green globular coating.

The x-ray powder patterns given by these materials will be discussed later.

Crystallography. The specimens all showed radiating botryoidal crusts up to 1 mm. thick. On material 1 the crust was distinctly crystalline under the binocular microscope $(20\times)$, after several trials a fragment was detached from the surface which showed two poor reflections on the optical goniometer. The crystal fragment was adjusted about the edge between these two faces. Rotation, zero and first layer Weissenberg films showed the crystal to be monoclinic with b as the rotation axis. Precession

¹ Compared through courtesy of Dr. Charles Milton, personal communication February 11, 1948.

films about an axis parallel to each face and perpendicular to the b axis showed the two faces to be c(001) and a(100). The films yielded the following measured lattice spacings

$$d(100) = 17.6$$
 $d(010) = 5.81$, $d(001) = 4.60$ A, $\beta^* = 87^{\circ}45'$

giving monoclinic lattice dimensions

$$a=17.61$$
, $b=5.81$, $c=4.60$ A, $\beta=92^{\circ}15'$

These dimensions are similar, but all slightly larger, than those found for pseudomalachite:

$$a = 17.06$$
, $b = 5.76$, $c = 4.49$ A, $\beta = 91^{\circ}02'$ (Berry, 1950)

The observed diffractions conform to the conditions: (hkl) present in all orders, (h0l) present only with h=2n, (0k0) present with k=2n; these criteria are characteristic of the space group $C_{2h}^5 - P2_1/a$. This same space group was derived for pseudomalachite.

Composition and cell content. The unit cell dimensions for cornwallite combined with the measured specific gravity 4.17 (Church, 1868) give the molecular weight of the unit cell M=1182.4. Table 2 shows the analysis of cornwallite by Church (1868) and the atomic contents of the unit cell using the above value for M.

	1	2		3	4	5
CuO	59.95	8.80	Cu	8.80	10	59.94
As_2O_5	30.47	1.55	As	3.10	4	34.63
P_2O_5	2.71	0.23	P	0.46	4	-
$\mathrm{H}_2\mathrm{O}$	8.23	5.40	H	10.80	8	5.43
	101.36		O	23.10	24	100.00

TABLE 2. CORNWALLITE: ANALYSIS AND CELL CONTENT

Cornwall; anal. Church (1868).
 Unit Cell content.
 Number of atoms in the unit cell.
 Ideal cell content 2[Cu₆(AsO₄)₂(OH)₄].
 Composition for ideal cell content.

The unit cell content agrees rather poorly with the ideal cell content suggested by the similarity of this mineral with pseudomalachite, $2[Cu_5(PO_4)_2(OH)_4]$. The number for H is high and the numbers of atoms of Cu and As are low. The divergence from the ideal is similar to that found for many analyses of pseudomalachite. It was pointed out in the discussion of the analyses of pseudomalachite (Berry, 1950) that good agreement with the ideal cell content was found for analyses of coarsely crystalline materials; while colloform or botryoidal finely crystalline materials possess a higher water content. Cornwallite or erinite has never been reported as occurring in coarsely crystalline form.

The ideal cell content 2[Cu₅(AsO₄)₂(OH)₄] gives a calculated specific gravity 4.68 which is considerably higher than the measured values 4.17 (cornwallite, Church, 1868) 4.043 (erinite, Turner, 1828). The analysis shows substitution of phosphorus for arsenic to the extent of one-half atom which would account for part of the discrepancy. The measured value is probably low since the material is a botryoidal crust on olivenite. In the study of pseudomalachite colloform and cryptocrystalline materials were found to give distinctly lower values for the specific gravity. Our specimens all consisted of colloform crusts over olivenite, enargite or altered rock, consequently visibly pure fragments large enough for a Berman balance determination were not obtainable.

The calculated specific gravity, 4.68, for $2[Cu (AsO_4)_2(OH)_4]$, is not inconsistent when compared with the calculated values, 4.34 for pseudomalachite $2[Cu_5(PO_4)_2(OH)_4]$; 4.45 for olivenite $4[Cu_2AsO_4(OH)]$; and 3.94 for libethenite $4[Cu_2PO_4(OH)]$.

In table 3 the available analyses of cornwallite are reduced to atomic proportions on the basis of 24 atoms of oxygen. The numbers of atoms show a similar variation to that shown by pseudomalachite analyses and the average numbers of atoms show reasonable agreement with the ideal numbers for $2[Cu_5(AsO_4)_2(OH)_4]$ except in the number for hydrogen. Analysis 1 by Turner (1828) is the only one which shows good agreement with the ideal composition.

	1	2	3	4	5	6	A	В
Cu	10.20	9.53	9.36	9.37	9.15	9.04	9.44	10
As P	4.00	3.75	3.76	3.66	3.22	$\frac{3.46}{-}$	3.73	4
Н	7.60 24.00	$10.20 \\ 24.00$	10.36 24.00	10.96 24.00	11.20 24.00	12.60 24.00	10.49 24.00	8 24

Table 3. Cornwallite and "Erinite"; Analyses Reduced to 24 Atoms of Oxygen

Hillebrand (1888) states, with reference to analyses 3 and 6 table 3, that if the material is dried over H₂SO₄ instead of in air the water content would be 6.08 per cent and 5.93 per cent instead of 7.22 and 9.15 respectively and if the lower water content is used the ratio CuO:As₂O₅:H₂O is much closer to that indicated by Turner's analysis (5:1:2 as also re-

^{1. &}quot;Erinite," Cornwall, anal. Turner (1828) "approximate analysis" includes Al_2O_3 —1.77. 2 and 4. "Erinite" Mammoth mine, Tintic, Utah. anal. Pearce (1886) analysis 2 includes Fe_2O_3 —0.85, CaO—0.43, SO_3 trace. 3 and 6. "Erinite," American Eagle mine, Tintic, Utah, anal. Hillebrand (1888) analysis 3 includes ZnO—1.06, CaO—0.32, Fe_2O_3 —0.14 and analysis 6 includes ZnO—0.59, CaO—0.51, Fe_2O_3 —0.20. 5. Cornwallite Cornwall, anal. Church (1868).

quired by the structural formula proposed here). These percentages of water are not far from the value 5.43 required by the structural formula. These observations by Hillebrand lend support to the conclusion, indicated by the present studies on cornwallite and pseudomalachite, that the colloform and botryoidal materials contain non-crystalline inclusions which result in higher water content, lower arsenic or phosphorus and copper content and lower specific gravity.

X-ray powder pattern. Materials 1-9 give exactly identical x-ray powder diffraction patterns (Figure 2). The pattern for material 10 (Figure 3) is diffuse but otherwise identical with material 1. The pattern for material 1 (used for single crystal study) is reproduced in Figure 2. The estimated intensities and measured spacings from this pattern are listed in table 4 together with the indices and calculated spacings as far as d=2.22 A. Materials 11 (Figure 4) and 12 give patterns which differ slightly in the relative intensities and spacings of the lines from the pattern of material 1. Materials 13 (Figure 5) and 14 give patterns closely similar to the pattern of pseudomalachite (Figure 6). The pattern for material 14 is very diffuse. The observed intensities and measured spacings for materials 1, 11, 13, 14 and pseudomalachite (Berry, 1950)

Table 4. Cornwallite— $Cu_5(AsO_4)_2OH_4$: X-Ray Powder Pattern* Monoclinic, $P2_1/a$; a=17.61, b=5.81, c=4.60A, $\beta=92^{\circ}15'$; Z=2

hkl d(calc.)

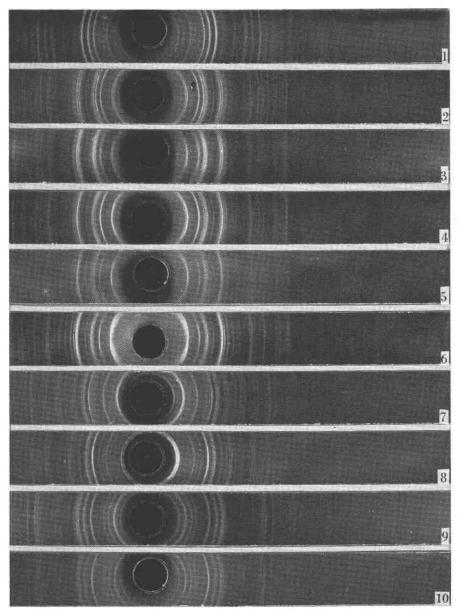
I d(meas.) hkl d(calc.)

d(meas.)

d(calc.)

2 5	5.40A 4.82	110 210	5.518A 4.849	2	2.88A	∫020	2.904A	9 2.40A	121	2.426A
6	4.60	001				120	2.866	9 2.40A		
U	4.00	111	4.600	4	2.73	220	2.759	4 0.24	$(\bar{2}21$	2.379
9	3.52	1111	3.555			411	2.748	4 2.34	221 (611	2.353
9	3.34	410	3.512	3	2.59	610	2.619			2.311
		211	3.508			320	2.603	6 2.29	710	2.307
1/2	3.34	(3.374	1	2.54	511	2.559		002	2.300
	7 00	211	3.302			601	2.518		321	2.283
10	3.20	401	3.244			511	2.481		321	2.249
8	3.10	{401	3.119	8	2.47	021	2.456	1 2.22	611	2,242
		311	3.115			121	2.440		520	2.241
6	3.00	311	3.031			601	2.430		(800	2.200
I	d(meas.		I d(m	eas.)	I	d(meas.		d(meas.)	I	d(meas.)
2	2.17A		2 1	608A	5	1.341	4 4	1,089A	1	0.884A
1	2.11			580	1	1.306	1 1	1,065	å.	0.850
1/2	2.06		1 1	547	1	1.279	1	1.038	à	0.835
3	1.873			521	1	1.247	1	1.022	. 1	0.820
2	1.828		ă 1	501	1	1,234	j.	0.999	1	0.815
1	1.791		8 1	486	1	1.218	1	0.991	2	0.805
4	1.765			457	1	1.208	2	0.938	à	0.803
			3 1	425	1	1.151	1/2	0.929	à.	0.791
	1.731			100	1.0				-	01171
3	1.731		3 1.	399	1	1.137	1/2	0.910		

^{*} Material 1.



Figs. 1–10.—X-ray powder photographs with Cu/Ni radiation; Camera radius $90/\pi$ mm. (1° θ =1 mm. on film); full size reproduction of contact prints. Fig. 1. Conichalcite. Fig. 2. "Erinite"=cornwallite, Mammoth mine, Tintic District, Utah (material 1). Fig. 3. Cornwallite, St. Day United mines, Gwennap, Cornwall (material 10). Fig. 4. Cornwallite, St. Day United mines, Gwennap, Cornwall (material 11). Fig. 5. "Erinite," Gunnislake mine, Calstock, Cornwall (material 13). Fig. 6. Pseudomalachite, Nassau, Germany (material 9 in Berry, 1950). Fig. 7. Euchroite, Libethen, Hungary. Fig. 8. Liroconite, Cornwall. Fig. 9. Olivenite. Fig. 10. "Leucochalcite"=olivenite, Majuba Hill, Nevada.

Table 5. Cornwallite—Pseudomalachite: X-Ray Powder Data

I	aterial 1 d (meas.)	Ma I	terial 11 d (meas.)	Ma I	terial 13 d (meas.)	Mat I	erial 14 d(meas.)	Pseud	d(meas.)
2 5 6	5.40A 4.82 4.60	1 2 8	5.47A 4.77 4.53	10	 4.52A	10	4.53A	10 10	4.75A 4.48A
$\frac{9}{\frac{1}{2}}$ 10	3.52 3.34 3.20	7 ½ 5	3.51 3.31 3.18	6 7	3.50	3	3.46	5 1 2 2	3.46 3.27 3.12
8	3.10	6	3,08	5	3.03	7b	3.06	${4 \choose 2}$	3.09 3.04
6	3.00	6	3.00	5	2.99			4 3	2.97 2.93
4 1 1	2.88 2.73 2.59 2.54	3 1 1 1 2	2.88 2.72 2.57 2.51	3 1	2.86 2.74 2.56			3 1	2.85 2.72 2.56
8 9 4	2.47 2.40 2.34	4 10 4	2.45 2.40 2.33	9 8 4	2.44 2.39 2.33	10b	2.40	6 8 5	2.42 2.39 2.32
6 1 2	2.29 2.22 2.17	5 1 2 1 2	2.28 2.22 2.17	5 1 2 1 2	2.25 2.21 2.15	2	2.24	5 1 1	2.23 2.19 2.12
$\frac{1}{2}$	2.11 2.06	3 1/2 1/2	2.10 2.04 1.993	3 2 1 2	2.10 2.01 1.955	1 2	2.10 2.01	3 1 2	2.09 2.01 1.963
3 2	1.873 1.828	3 1/2	1.870 1.817	$\frac{1}{\frac{1}{2}}$	1.864 1.815			1 2	1.939 1.854
1 4 3	1.791 1.765 1.731	1 5 1	1.781 1.755 1.722	14	1.770 1.738	3	1.752	4 5	1.763 1.728
1 6 2	1.678 1.645 1.608	2 4 1	1.678 1.629 1.598	$\frac{1}{2}$	1.674 1.635	2	1.580	2 1 2	1.670 1.624 1.597
2 1 3	1.580 1.547 1.521	3 1 2	1.570 1.542 1.517	3 1 3	1.569 1.536 1.504			4 2 2	1.559 1.527 1.498
1 1 2 1 2 3	1.501 1.486 1.457	3	_ 1.449	$\frac{1}{2}$	1.470 1.438	1 2	1.492 1.431	2 1 3	1.491 1.462 1.431
3	1.425	$\begin{cases} 2\\ 3\\ \frac{1}{2}\\ 1 \end{cases}$	1.435 1.414		· 			3	1.419
3	1.399	$\overset{\frac{1}{2}}{1}$	1.399	2 1	1.399 1.370	1	1.404	4 1	1.392 1.365
3 5	1.368 1.341	6	1.358 1.337	2 3	1.353 1.333	3b	1.337	2 3 2	1.350 1.335 1.319
$\frac{1}{2}$	1.306		-		-			3	1.310

b-broad line.

are given in table 5. The spacings and intensities show a gradual change from material 1, cornwallite, to pseudomalachite; the spacings decrease, some intensities increase and some decrease. The pattern given in the ASTM card files for material from Gunnislake, Cornwall appears to be very close to the pattern of material 14 and pseudomalachite.

Optical data. New determinations of optical data have not been made largely because the indices lie above the range of oils readily available. Data on material 8 (USNM 48112) are given by Larsen (1921) who also gives data for "cornwallite (USNM, Roebling Coll.) Cornwall, England" which probably applies to material 12.

	nX	nY	nL
"erinite" (material 8)	1.820	1.86	1.88
cornwallite (material 12?)	1.81	1.815	1.85
pseudomalachite (Barth & Berman, 1930)	1.785	1.850	1.862

The available optical data show roughly a gradation from cornwallite to pseudomalachite. The indices for cornwallite are probably inaccurate since the mineral decomposes in oils containing As₂S₃ and S, with evolution of gas and development of crystals (Larsen, 1921).

The x-ray data clearly indicate that cornwallite and erinite are the same mineral but show a gradation to pseudomalachite, due probably to phosphorus substituting for arsenic. This is supported by the meagre optical data. The name erinite has priority and the composition ascribed to erinite from Turner's analysis is the same as the structural formula deduced here. Material labelled erinite (material 4) by Haidinger is identical with cornwallite. However the name erinite has been misused for chalcophyllite by some early authors and the mineral has been shown to be a Cornish mineral rather than from Ireland as stated by Haidinger, (Dana, 1892). It is proposed here that the name cornwallite be retained for this mineral.

EUCHROITE

Euchroite was first named by Breithaupt (1823) and described by Haidinger (1825) from Libethen, Hungary. The mineral has not been reported from any other locality. Two specimens, ROM M15178 and USNM 47056 from Libethen, Hungary were used in this study. Well formed green crystals, one to five millimeters in length are implanted in rusty sericite schist. Three specific gravity determinations were made on a clean crystal weighing 28 mg., using the Berman balance. The average compares closely with other determinations.

3.41 (Steacy, 1946)3.389 (Haidinger, 1825)3.42 (Church, 1895)3.44 (Frondel, priv. comm.)

Structural crystallography. A crystal about one millimeter in length, was easily detached from the first specimen referred to above. Using unfiltered copper radiation, rotation and Weissenberg films were made about the c (axis of elongation) and b axes, yielding the following orthorhombic lattice dimensions:

$$a = 10.07$$
, $b = 10.52$, $c = 6.12$ A

The observed diffractions conform to the conditions (hkl), (0kl), (h0l) and (hk0) all present, (h00) present with h=2n, (0k0) present with k=2n, (00l) present with l=2n. These criteria are characteristic of the space group.

$$D_2^4 = P2_12_12_1$$

Geometrical crystallography. On crystals of euchroite from Libethen, Haidinger (1825) obtained orthorhombic elements:

$$a:b:c=0.6088:1:1.0379$$

Haidinger's elements agree closely with the structural elements in a different setting

b:c:a=0.9635:1:0.5866 (Haidinger, 1825)

a:b:c=0.057 :1:0.582 (structural elements)

TABLE 6. EUCHROITE: OBSERVED FORMS

Haidinger (1825)	Steacy (1946)	Structure
c(001)	b(010)	b(010)
b(010)		a(100)
n(011)	m(110)	m(110)
e(101)		n(011)
d(102)		d(021)
m(110)	e(101)	e(101)
s(230)		s(302)
l(120)		l(201)

Measurement of three crystals (Figure 11) from our specimens revealed only the forms b(010), m(110) and e(101) with measured angles in fair agreement with angles calculated from the structural elements (Table 7). The faces of e(101) on our crystals gave poor reflections therefore the observed angles $(101) \wedge (\overline{101})$ are rough measurements.

Composition and cell content. The volume of the unit cell of euchroite together with the measured specific gravity 3.41 gives the molecular weight of the unit cell M=1331.7. Using this value for M, the five available analyses of euchroite give the unit cell contents shown in Table 8.

TABLE 7. EUCHROITE: OBSERVED	AND CALCULATED ANGLES
------------------------------	-----------------------

A lo	Observed	Calculated	Calculated	
Angle	Range	Average	(Structure)	(Haidinger
(101) ∧ (101)	63°26′-64°26′ (4)	63°56′	62°36′	62°40′
$(010) \land (110)$	46 08 -46 35' (6)	46 19	46 15	46 04

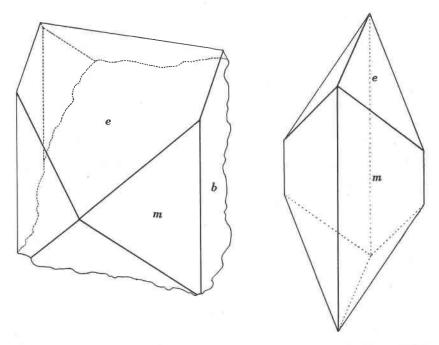


Fig. 11.—Euchroite, Libethen, Hungary. Crystal drawing showing the forms b(010), m(110), e(101).

Fig. 12. Liroconite, Cornwall. Crystal drawing showing the forms m(110), e(011).

The numbers of atoms agree closely with the average numbers (A) and the ideal number (B) for the cell content represented by the formula.

$$8CuO \cdot 2As_2O_5 \cdot 14H_2O = 4[Cu_2AsO_4(OH) \cdot 3H_2O]$$

This formula yields the calculated specific gravity 3.45, in close agreement with the measured values.

X-ray powder pattern. One of the crystals of euchroite from the same specimen as the crystal used for Weissenberg study was crushed, and the x-ray film obtained from this powder with filtered CuK radiation is re-

TABLE 8. EUCHROITE: ANALYSIS AND CEL

	1	2	3	4	5	A	\mathbf{B}
CuO	47.85	46.97	46.99	48.09	47.26	47.45	47.10
As_2O_5	33.02	34.42	32.42	33.22	30.90	22.00	
P_2O_b	_				1.48	33.09	34.20
$\mathrm{H_{2}O}$	18.80	19.31	19.31	18.39	19.28	19.02	18.70
	99.67	100.70	98.72	99.70	98.92	100.56	100.00
Cu	8.02	7.88	7.89	8.07	7.93	7.96	8
As	3.82	4.00	3.76	3.86	3.90*	3.87	4
H	27.86	28.62	28.62	27.26	28.28	28.19	28
O	31.50	32.19	31.60	31.35	31.57	31.64	32

Libethen, Turner, (1825). 2–3 Libethen, Kühn, (1844) (3 includes CaO 1.12).
 Libethen, Wöhler, (1844).
 Libethen Church, (1895). A. Average composition and cell content. B. Ideal composition and cell content for 4[Cu₂AsO₄(OH) · 3H₂O].

* Includes P=0.28.

produced in figure 7. The estimated intensities and interplanar spacings obtained from this film are given in Table 9. The measured spacings each agree well with one or more spacings calculated from the structural lattice dimensions. The pattern agrees closely with that recorded in the A.S.T.M. card file.

Optical properties. A typical crystal of euchroite was mounted on the universal stage for redetermination of the optical orientation. 2V was also measured. The mineral is biaxial, positive with Z=b the optic plane parallel to (001) and $2V=31^{\circ}$.

LIROCONITE

Liroconite is a hydrous arsenate of copper and aluminum which occurs with other arsenates in vugs and cavities in the rusty wall rock of copper deposits in Cornwall, England. On the four specimens available for this study (UT A/2138, USNM, 103848, HM 96238, AMNH*) the crystals occur singly and as sub-parallel groups, also with a granular texture. Individual crystals range from 0.3 to 7 mm. in length, they are sky blue to verdigris-green in colour. The fourth specimen, from Wheal Unity, Gwennap, Cornwall shows both a sky blue crystalline aggregate of liroconite and well developed green crystals with azurite, malachite and clinoclasite on cuprite. These specimens including material of both

^{*} Obtained in England in 1948 from George Croker Fox collection and kindly loaned for study by Dr. Fred Pough, American Museum of Natural History.

I	d(meas.)	hkl	d(calc.)	I	d(meas.)	hkl	d(calc.)	I	$d({\rm meas}_*)$	hkl	d(calc.
8	7.37A	110	7.275A			(311	2.835			∫411	2.273
		011	5.291	9	2.83	320	2.830	- 0	2.26	420	2.271
10	5.34	020	5.260			112	2.822	2	2.20	302	2,262
		101	5.231	w	0.64	022	2.645			331	2.254
2	5.04	200	5.035	8	2.64	040	2.630	1	2.20	312	2.211
1	4.53	210	4.542			321	2.568	1/2	2.17	241	2.178
6	3.71	121	3.709	7	0.77	122	2.559	1/2	2.13	421	2.129
		(211	3.647	7	2.55	140	2.545		0.06	∫340	2.070
$\frac{1}{2}$	3.53	220	3.637			212	2.538	2	2.06	150	2.060
1	3.33	130	3.312	$\frac{1}{2}$	2.47	410	2,449		2 24	013	2.003
1 2	3.23	310	3.198	1/2	2.40	041	2.417	1/2	2.01	103	2.000
		(002	3.060			∫240	2.331			113	1.965
1	3.06	031	3.043	3	2.33	401	2,329			341	1.961
		301	2.943			(.		3	1.957	142	1.957
4	2.94	012	2.939							151	1.952
		102	2.929							· New York	
I	d(meas	.)	I d(m	eas.)	I	d(mea	s.) I	d(meas.)	I	d(meas.
1	1.903		½ 1.	537	1	1,26	9 1	1	1.090	1	0.912
1	1.859			510	1	1,23		1	1.081	1	0.900
1	1.784			455	1	1.22	1970	1	.054	1/2	0.876
1 1 2 2	1.746			412	í	1,20	7 1	1	1.037	1	0.843
2	1.710		-	389	4	1.18	1.55	1	1.026	1	0.833
2	1,664			358	1	1.16	100	(0.996	1	0.822
1	1.616			341	1	1.15		(0.974	1800	
	4 (00			044	T (5	4 40	9550		0.50		

Table 9. Euchroite: $Cu_2AsO_4(OH) \cdot 3H_2O$: X-Ray Powder Pattern Orthorhombic, $P2_12_12_1$; a=10.07, b=10.52, c=6.12A; Z=4

colours all give identical x-ray powder patterns. A fifth specimen (USNM C4207, St. Day, Cornwall) also gives the same pattern as evidenced by a film taken in the United States Geological Survey laboratories and kindly sent to us for comparison by Dr. Charles Milton (Feb. 11, 1948).

1.104

1.287

1.570

0.947

Crystallography. Crystals of suitable size from the first specimen referred to above were readily adjusted on the two-circle goniometer for single crystal x-ray measurements. Rotation, zero and first layer Weissenberg films about a, b and c axes yielded the following dimensions of the unit cell:

$$a=12.70$$
, $b=7.57$, $c=9.88$ A; $\beta=91^{\circ}23'$

The β angle was determined by direct measurement on the Weissenberg film of the (h0l) layer of the reciprocal lattice and by calculation from the measured spacings d(100), d(001), d(101), d(201) and d(503). The above value is an average of these determinations.

The observed diffractions conform to the following extinction conditions: (hkl) present only for h+k+l=2n, (h0l) present only for h=2n

and l=2n and (0kl) present only for k=2n. These extinctions are characteristic of the space group I2/a. The I lattice is retained because of the strong pseudo-orthorhombic habit of the crystals (Figure 12).

The cell dimensions give the axial ratio

a:b:c=1.678:1:1.305; $\beta=91^{\circ}23'$ (x-ray)

c:b:a=1.6808:1:1.3191; $\beta=91^{\circ}27'$ (Dana, 1892)

which compares closely to that given by Descloizeaux (Dana, 1892) when the a and c axes are interchanged. The only observed forms m(110) and e(011) are interchanged in transforming from Descloizeaux to the structural setting. The crystals (Fig. 12) are flattened and wedge-shaped with the forms m(110) and e(011) in nearly equal development; the faces of both are striated parallel to the intersection edge. Most commonly they are elongated along the new c axis with m(110) larger than e(011).

Composition and cell content. New determinations of the specific gravity of liroconite, 2.94 (Frondel, personal communication 1946) and 3.01 (Davies, 1946) agree closely with the old values 2.985 (Hermann, 1844), 2.926 (Haidinger) and 2.964 (Damour, 1845) given in Dana (1892).

TABLE 10. LIROCONITE: ANALYSES AND CELL CONTENT

	1	2	3	4	A	B
CuO	36.38	37.18	37.40	36.73	36.96	37.70
Al_2O_3	10.85	9.86	10.09	n.d.)	40.45	40.05
$\mathrm{Fe_2O_3}$	0.98	-		}	10.47	12.07
As_2O_5	23.05	22.22	22.40	23.85	22.56	20.42
P_2O_5	3.73	3.49	3.24	1.02	3.49	4.20
$\rm H_2O$	24.01	25.49	25.44	incomp.	25.31	25.60
	100.00	98.06	98.57	-	98.88	100.00
Cu	7.74	8.07	8.07	-	7.96	8.0
Al	3.60	3.34	3.40)	2 -	
\mathbf{Fe}	0.20		+	}	3.51	4.0
As	3.40	3.34	3.36	-	3.37	3.0
P	0.89	0.85	0.79	_	0.84	1.0
H	47.04	48.82	48.46	-	48.11	48.0
0	47.69	47.98	47.77		47.85	48.0

^{1-3.} Cornwall, England, 1. anal. Hermann (1844), G=2.985. 2-3. anal. Damour (1845), G=2.964; 4. anal. Church (1895), G=2.97. Al₂O₃ not determined, H₂O incomplete. A. Average analysis and cell content from analyses 1-3. B. Ideal composition and cell content for 4 [Cu₂Al(As, P)O₄(OH)₄·4H₂O].

The average of these measured values, 2.96, combined with the cell dimensions gives the molecular weight of the unit cell M = 1693.0.

In Table 10, this value has been used to compute the atomic content of the unit cell from the three available analyses of liroconite. The average analysis and cell content (A) agree closely with the ideal figures (B) clearly indicating the cell content.

$$8CuO \cdot 2Al_2O_3 \cdot 2(As_2O_5 \cdot P_2O_5) \cdot 24H_2O = 4[Cu_2Al(As,P)O_4(OH)_4 \cdot 4H_2O]$$

for which the calculated specific gravity is 2.95 also in close agreement with the measured values. The As = P ratio of 3:1 is clearly shown by the first three analyses, the later incomplete analysis by Church (1895) indicates a higher ratio. These authors do not state the exact colour of their analysed material, therefore further analyses would be required to explain the marked difference in colour between different specimens.

Table 11. Liroconite—Cu₂Al(As,P)O₄(OH)₄·4H₂O: X-Ray Powder Pattern Monoclinic, I2/a; a=12.70, b=7.57, c=9.88A, $\beta=91^{\circ}23'$, Z=4

I	d(meas.)	hkl	d(calc.)	I	d(meas.)	hkl	d(calc.) I	d(meas.)	hkl	d(calc.)
10	6.46A	110	6.502A	1/2	2.63A	402	2,641	A 3	2.07A	∫314	2.073
9	5.95	011	6.008	3	2.47	∫130	2.475	3	2.0711	$\sqrt{5}21$	2.070
1	4.33	211	4.332	3	2.41	004	2.469	1/2	1.994	∫033	2,003
5	3.92	∫112	3.957	4	2.44	∫123	2.446	2	1.771	$\sqrt{3}32$	1.994
3	3.92 \[112 \] 3.910 \] 4 2.44 \[\] 420 2.		2.432	2	1.914	$\sqrt{2}33$	1.918				
1	3.66	310	3.694	3	2.27	∫204	2.283	2	1.714	015	1.911
2	3.36	121	3.398	3	2.41	231	2.277	1/2	1.834	141	1.838
		013	3.013			132	2.217	1	1.787	∫523	1.792
10	3.01	{022	3.004	5	2.21	422	2.198		1.707	(530	1.790
		312	2.988			512	2.184			710	1.764
1 2	2.91	312	2.929			330	2.167	4	1.749	134	1.752
5	2.79	$\sqrt{4}11$	2.824	5	2 15	422	2.166			622	1.742
3	2.19	411	2.790	:5	2.15	323	2.159	4	1.707	∫242	1.706
		321	2.701			512	2.145		1.707	341	1.705
6	2.69	222	2.700			55					
		402	2,700								
I	d(meas	.)	I d(r	neas.)	1	d(mea	s.)	I d	d(meas.)	I	d(meas.)
1b	1.629	A	1 1	.388A	1	1.21	6A	1/2	1.058A	1/2	0.922
1b	1.588	- 1	1 1	.366	1	1.19	8	½b	1.035	1/2	0.909
3b	1.544		1 1	.342	1	1.17	4	12b	1.016	1	0.860
3b	1.512	1 2	1 1	.320	1	1.12	1	½b	0.988	1 2	0.852
2	1.457		4 1	.282	1	1.10	17	1/2	0.949	½b	0.830
1	1.410		à 1	.254	1,	1.08	0	1	0.938	$\frac{1}{2}$ b	0.811

b-broad line.

X-ray powder pattern. The x-ray powder pattern of liroconite (CuK radiation, Ni filter) is shown in Figure 8. The observed relative intensities and measured spacings of the diffraction rings are listed in Table 11

together with indices and interplanar spacings calculated from the lattice dimensions down to d=1.707A.

OLIVENITE AND "LEUCOCHALCITE"

Olivenite is the most commonly observed arsenate of copper found in nature. Lattice dimensions and space group data for olivenite are given by Heritsch (1937) and Richmond (1940). The lattice constants given by these authors are in reasonable agreement but the space groups differ markedly.

Materials. Several typical specimens of olivenite were available for study in Queen's University mineral collections and other specimens appeared during the examination of specimens labelled erinite, cornwallite and conichalcite. The principal localities for these specimens are Cornwall and Tintic, Utah.

Specimens of leucochalcite from Wilhelmine Mine (type locality) and Sommerkahl mine, Schollkrippen, Spessart, Germany were available from Harvard University mineral collections. Several specimens showing olivenite and leucochalcite from Majuba Hill, Nevada were kindly provided for study by Hatfield Goudey. Leucochalcite on the German specimens consists of small groups of radiating or matted silky fibres of greyish colour on a fracture surface in gneiss. Leucochalcite from Nevada is more abundant on our specimens. On one specimen it consists of matted silky fibres in openings in much altered rhyolite heavily stained with limonite. A second specimen shows a silky fibrous coating with a slight greenish colour with tyrolite on a fracture surface. A third specimen consists of fine silky matted and radiating fibres with a delicate greenish white colour. A fourth specimen shows solid crystals of typical olivenite grading into fine silky greenish white fibres in a rock cavity. All the above specimens of leucochalcite gave an x-ray powder pattern identical with that of olivenite (Fig. 9, 10).

X-ray studies. A typical crystal of olivenite was mounted on the two-circle optical goniometer and adjusted to rotate about the c axis. Rotation, zero, and first layer Weissenberg films were taken of this crystal about the c axis. Many of the diffractions (h0l) and (0kl) were so weak as to render the space group characteristics difficult to determine. Therefore zero layer films were taken about the a and b axes on the Precession camera. These films were taken on the same crystal without remounting.

The films yielded the lattice dimensions shown below in comparison with those of Heritsch (1937) from rotation and powder films and Richmond (1940) from rotation and Weissenberg films. A fibre of leucochalcite gave a weak rotation film with the c length of olivenite.

```
a=8.22, b=8.64, c=5.95 A (Heritsch, 1937)<sup>1</sup>

a=8.18, b=8.56, c=5.87 A (Richmond, 1940)<sup>1</sup>

a=8.24, b=8.64, c=5.95 A (olivenite, L.G.B.)

c=5.96 A ("Leucochalcite," L.G.B.)
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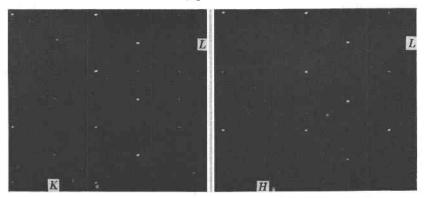
From indexing the equator layer line on rotation films Heritsch concluded that the space group should be $D_{2h}{}^1$ not $D_{2h}{}^{12}$ as in libethenite (Strunz, 1936). Richmond (1940) determined the space group as $D_2{}^4$ from Weissenberg films about a and c. The films obtained in the present study, particularly the (0kl) and (h0l) layers on precession films (Figs. 13, 14) also the (hk0) layer on a Weissenberg film clearly indicate the following extinction conditions: (hkl) all present; (0kl) all present; (h0l) present only with h+l=2n; (hk0) all present. These criteria agree with those observed by Heritsch and are characteristic of the space group $D_{2h}{}^{13}-Pmnm$ if the class is holohedral. It is probable that ${}^{l}D_{2h}{}^{1}$ is a misprint for $D_{2h}{}^{13}$ in Heritsch's paper.

Chemical composition. The analyses combined with the cell dimensions and measured specific gravity clearly show the following cell content for olivenite:

$$Cu_8As_4H_4O_{20}=4[Cu_2AsO_4(OH)]$$

The calculated specific gravity for this cell content and Heritsch's lattice dimensions is 4.45 in close agreement with the measured value 4.378.

X-ray powder pattern. The intensities and interplanar spacings for the diffractions observed on the x-ray powder films of olivenite and leucochal-



Figs. 13, 14.—Olivenite, zero layer Precession films, Cu/Ni radiation, film to specimen distance 60 mm. reproduced 2/3 actual size. Fig. 13. (0kl) showing weak diffractions (012), (023); very weak diffractions (021), (032), (041) are also present on the film. Fig. 14. (h0l) showing diffractions present with h+l=2n only.

¹ Lattice dimensions converted to new Angstrom units (1946).

cite are given in Table 12. The pattern has been indexed to d=1.488 A with close agreement between measured and calculated spacings.

Table 12. Olivente—Cu₂AsO₄(OH): X-Ray Powder Pattern Orthorhombic, Pmnm; a=8.22, b=8.64, c=5.95A, Z=4

1	d(meas.)	hkl	d(calc.)	I	d(meas.)	hkl	d(calc.)	I	d(meas.)	hkl	d(calc.)
7	5.91A	110	5.955A	7	2.39A	∫202	2.410A	1	1,740A	∫213	1.749A
9	4.82	∫011	4.900	,	2.39A	311	2,391	:4	1,740A	042	1.748
9	4.02	101	4.820	1	2 22	∫122	2.348	1	1,686	∫402	1.691
6	4.19	111	4,209	1	2.33	212	2.321	- 1	1,080	150	1.691
4	3.80	120	3,824	1/2	2.16	040	2.160	2	1 (17	332	1.651
10	2.00	∫220	2.977	,	0.00	∫140	2.089	2	1.647	223	1.651
10	2.98	002	2.975	1 2	2.08	032	2.069		1 (01	1151	1.627
4	2.70	130	2.718			330	1.985	1	1.621	510	1.615
	0.68	J221	2.663	1	1.973	141	1,971			242	1,608
6	2.65	112	2.661			312	1.963	3	1,600	303	1.607
		310	2.612		23.179(83.65)	013	1,933	200		133	1.602
1	2.59	031	2.592	1/2	1.925	1103	1.928			313	1.580
		301	2.489			411	1.895	6	1.575	422	1.574
7	2.47	131	2.472	2	1.881	331	1.883	1/2	1.556	511	1.559
20		022	2.450	-	*****	113	1,882			(440	1.489
		(į.	1.831	322	1.826	5	1.488	(004	1.487
1	d(meas	.)	I d(m	eas.)	I	d(mea	s.) I	d((meas.)	I	d(meas.)
1	1,439	A	3 1.	290A	1	1.10	6A 2		1.002A	2	0.895A

I	d(meas.)	I	d(meas.)	I	d(meas.)	I	d(meas.)	I	d(meas.)
ł	1.439A	3	1.290A	1	1.106A	2	1.002A	2	0.895A
1	1.419	1	1.281	4	1.096	2	0.984	1	0.881
1	1.404	2	1.252	1	1.090	2	0.973	3	0.872
3	1.386	å	1.192	2	1.079	1	0.964	1	0.862
1	1.364	2	1.177	1 to	1.068	1/2	0.959	1/2	0.856
2	1.354	1	1.166	4	1.052	1/2	0.949	2	0.843
4	1.327	1,2	1.126	1	1.031	ž.	0.915	2	0.816
1	1.305	1	1.114	1	1.015	1	0.904		

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