

PARAMELACONITE: A TETRAGONAL OXIDE OF COPPER

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ABSTRACT

Paramelaconite is an oxide containing both cuprous and cupric copper. The ideal composition is CuO. The actual constitution is based on an oxygen-defect structure in which the loss of negative valence accompanying the omission of oxygen atoms is compensated by a change in positive valence of some cupric ions to cuprous. The observed composition may be expressed as $(\text{Cu}^{2}_{1-2x}, \text{Cu}^{1}_{2x})\text{O}_{1-x}$ where $x=0.116$.

Data derived from the morphology, etch-figures, and a Weissenberg *x*-ray study fix the crystal system as tetragonal and the crystal class as ditetragonal-dipyramidal. The mineral occurs as lustrous black crystals up to 3 cm. in size. The observed forms are {001}, {101} and {100}, with $a:c=1:1.6709$. The structure cell is body-centered tetragonal with $a_0=5.83$, $c_0=9.88$; and $a_0:c_0=1:1.695$. The observed cell contents are $\text{Cu}^{2}_{16-2x}, \text{Cu}^{1}_{2x}\text{O}_{16-x}$ where $x=1.85$. The space group is *I4/amd*. A pronounced pseudo-cell is present, having $a_0=2.915$, $c_0=4.94$, and is body-centered with the space group *I4/mmm*. The pseudo-cell probably defines the essential characters of the structure and the doubled cell may mark a superstructure based on an ordering of the cuprous ions or of the oxygen-defect positions.

The physical properties of paramelaconite are: fracture, flat conchoidal; hardness, $4\frac{1}{2}$; specific gravity, 6.04; luster, brilliant metallic-adamantine; color, black to purplish black; streak, brownish black; opaque. In polished section, it is white with a pinkish brown tint; weakly pleochroic and strongly anisotropic. The mineral is etched by $\text{FeCl}_3, \text{KCN}, \text{HCl}$ and HNO_3 but not by KOH . On heating, paramelaconite breaks down at a slow but measurable rate below 190°C. , and more rapidly with increasing temperature, to a mixture of

^{*} Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 245.

tenorite and cuprite. The crystallites of tenorite and cuprite are randomly oriented. Paramelaconite is easily soluble in cold dilute NH_4Cl or NH_4OH solution, and fragments become coated by a mixture of metallic copper and cupric oxide when placed in extremely dilute mineral acids. Spectrographic examination revealed: Fe ($>1\%$); Al, Mn, Si, Mg, Ba ($<0.1\%$); Ca, Pb, Zn, Zr, Mo, Ti ($<0.01\%$); Sn, V ($<0.001\%$).

Paramelaconite was found at the Copper Queen mine, Bisbee, Arizona, as a secondary mineral in the following association and sequence: (matrix=goethite, native copper, cuprite)→goethite→tenorite→paramelaconite (and minor cuprite)→ connellite→ malachite. The mineral alters to tenorite. Twelve specimens of black earthy or pitch-like cupric oxide, including material labelled melanochalcite, melaconite, copper-pitch and paramelaconite, proved on *x*-ray study to be either delafossite (for which a new locality, at Eureka, Nevada, is noted) or tenorite.

INTRODUCTION

Paramelaconite was originally described by Koenig in 1891 as a tetragonal modification of cupric oxide, dimorphous with tenorite. Neither the

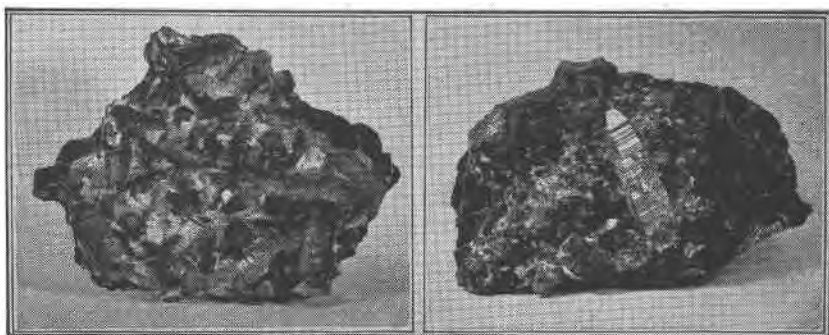


FIG. 1. The two known specimens of paramelaconite. Copper Queen mine, Bisbee, Arizona. Amer. Mus. Nat. Hist., spec. nos. 4629 and 4630. A large needle-like crystal of connellite may be seen on one specimen (left). About one-third natural size.

system of crystallization nor the composition of the mineral was established with any certainty, however, and the substance never received recognition as a valid species. Only two specimens of paramelaconite are known. These were obtained by Dr. A. E. Foote, about 1890, at the Copper Queen mine, Bisbee, Arizona, and were sold by him to the well known mineral collector Clarence S. Bement for fifty dollars apiece. Koenig examined the specimens with the permission of Bement. The Bement collection, at the time considered to be the finest private mineral collection in the United States, later passed into the possession of the American Museum of Natural History, where the two specimens are now preserved. The paramelaconite is magnificently crystallized, and is associated with a deep blue prismatic mineral which was described by Koenig as a new basic chloride of copper, under the name footeite. This mineral

was later shown to be connellite in crystals of unusual size. Photographs of the two specimens of paramelaconite are shown in Fig. 1. The writer is grateful to Dr. Fred. H. Pough, Curator, and Mr. Herbert P. Whitlock, of the American Museum for permission to remove sufficient material from the specimens for a crystallographic and chemical study of this quite unusual mineral.

CRYSTALLOGRAPHY

Morphology. The paramelaconite occurs as stout prismatic crystals up to 3 cm. in length. The crystals are tetragonal in development, with the forms $c\{001\}$, $d\{101\}$, and $a\{100\}$, as referred to the simplest structural

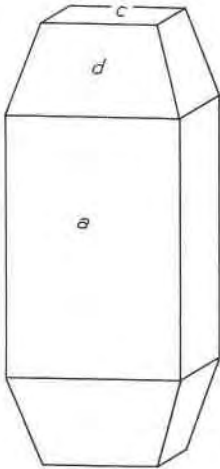


FIG. 2. Idealized crystal.

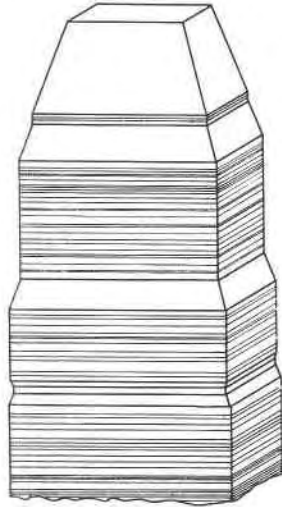


FIG. 3. Striated singly terminated crystal.

cell. An idealized crystal is shown in Fig. 2. The prism surfaces are closely striated and in part deeply grooved due to oscillatory combination with $\{101\}$, as represented in Fig. 3. The several faces of $\{101\}$ and $\{001\}$ usually are unequally developed. The crystals are attached to the matrix by one end of the vertical axis. Only one doubly terminated individual was observed. This crystal was similarly developed at both ends, with $\{001\}$ and $\{101\}$. The lower half of $\{101\}$ also occurs on singly terminated crystals as line faces in the grooves and striae on $\{100\}$. No difference in general physical appearance was detected between the several upper faces of $\{101\}$, or between the upper and lower faces of $\{101\}$ and $\{001\}$.

Koenig obtained $\{001\} \wedge \{101\} = 58^\circ 50'$, for which the $a:c$ ratio was erroneously calculated as 1:1.6643. The correct value is 1:1.6534. Although the crystals appear quite perfect on casual examination, the faces often give multiple images on the reflecting goniometer, due to vicinal

development. A coarse lineage structure is commonly present. The six crystals measured by the writer gave ρ values for $\{101\}$ ranging between $58^{\circ}44'$ and $59^{\circ}30'$. The average of the best values was $59^{\circ}6'$, for which $a:c = 1:1.6709$. The ratio of the structural cell is $a_0:c_0 = 1:1.695$ for which the calculated ρ angle of $\{101\}$ is $59^{\circ}28'$. An angle table, based on the elements of the structural cell is given in Table 1. The morphological development is of little aid in fixing the crystal class. Four classes are possible, if it is assumed that the lower and upper planes are geometrically and structurally identical. These are $4/m \ 2/m \ 2/m$, $4 \ 2 \ 2$, $\bar{4} \ 2 \ m$ and $4/m$ (see Table 3).

TABLE 1. ANGLE-TABLE FOR PARAMELACONITE

Tetragonal; ditetragonal-dipyramidal— $4/m \ 2/m \ 2/m$				
$a:c = 1:1.695$; $p_0:r_0 = 1.695:1$				
Forms	ϕ	ρ	A	\bar{M}
<i>c</i> 001	—	—	90°00'	90°00'
<i>a</i> 010	0 00	90°00'	90 00	45 00
<i>d</i> 011	0 00	59 28	90 00	52 29

Etch-Figure Symmetry. Satisfactory etch figures were obtained only after lengthy experimentation. The best results were obtained from a solution about 0.001N H_2SO_4 and 0.3N NH_4Cl . Etch pits appeared on the crystals after standing in the solution for a few hours. No change in the shape of the pits took place after standing for several days. The shape and orientation of the etch pits and etch hillocks is shown in Fig. 4. The pits on $\{001\}$ were large, deep four-sided pyramidal depressions with rounded and terraced sides. The base of the figures had a square but somewhat irregular or rounded outline oriented at 45° to $[100]$. Etch hillocks were obtained on $\{101\}$. These were tooth-shaped with the sharp end pointing upward. The hillocks on all four upper faces of $\{101\}$ were identical. Minute canoe-shaped pits were formed on $\{100\}$. The pits were identical in shape and orientation on all four faces of this form. The hillocks on $\{101\}$ and the pits on $\{100\}$ were sensibly symmetrical about a line representing the trace on these forms of vertical axial planes. The observed etch effects are consistent with the existence of a vertical four-fold symmetry axis, together with vertical axial and diagonal planes of symmetry and a horizontal plane of symmetry. Horizontal axial and diagonal two-fold axes of symmetry, and a center of symmetry are required by these operations. The crystal class is thus uniquely fixed by the etch symmetry as ditetragonal-dipyramidal ($4/m \ 2/m \ 2/m$).

The velocity of chemical attack is markedly greater along $[001]$ than perpendicular thereto. The $\{001\}$ face on a crystal left in the etching solu-

tion for a period of days was completely hollowed out to a depth of about 0.3 mm. leaving the lateral {101} faces standing up as thin walls. The {100} faces at the same time were only pitted locally and for the most part still maintained their original smoothness and luster. The pronounced elongation of the pits on {100} also indicates the greater rate of

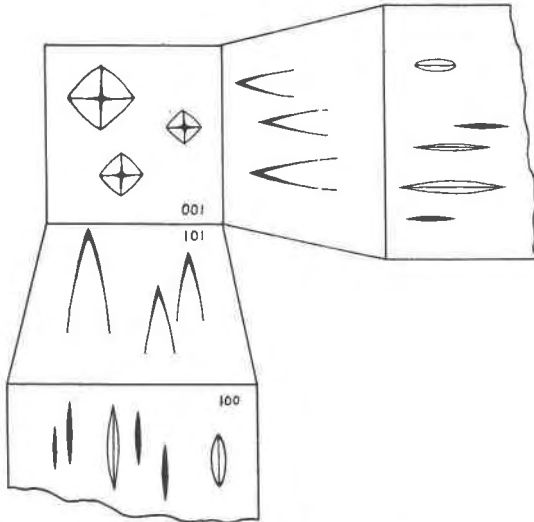


FIG. 4. Etch figures and hillocks on {001}, {100} and {101} of paramelaconite. Produced in 8 hours by $\text{NH}_4\text{Cl} + \text{H}_2\text{SO}_4$ solution. The absolute and relative sizes of the figures are greatly exaggerated.

attack along [001]. Similar shell-like solution forms have been obtained by the action of H_2SO_4 on {001} of apophyllite crystals.

X-RAY STRUCTURAL CELL

A Weissenberg x -ray study was made of small cut sections and crystals. Cu radiation was employed. Rotation photographs were taken about [001], [100] and [110], together with 0- 1- and 2-layer-lines about [100], 0-, 1-, 2-, 3- and 4-layers about [001], and a 0-layer about [110]. The n -layers were filtered with Ni. The rotation photographs about the vertical and horizontal axes exhibited a very pronounced pseudo-cell of one-half the dimensions of the true cell. It was necessary to take long exposures (40 to 60 KWH at 12 ma. and 55 KV) in order to record the odd-layer lines.

Centro-Symmetry of the Weissenberg Films. The 0-layer and n -layer Weissenberg films taken about [001] revealed a four-fold axis of symmetry, with planes of symmetry at 45° . The 0-layer and n -layer films about [100]

and the 0-layer film about [110] revealed a two-fold axis of symmetry, with planes of symmetry at 90°. Paramelaconite is, therefore, tetragonal, and the apparent point symmetry is $4/m\ 2/m\ 2/m$. The actual point symmetry of the mineral may be either $4/m\ 2/m\ 2/m$, or that of any other crystal class the symmetry of which, by introduction of a center, can be raised to $4/m\ 2/m\ 2/m$. These crystal classes are indicated in Table 3.

TABLE 2. CATALOGUE OF OBSERVED X-RAY REFLECTIONS

[001] axis	[100] axis
0-layer $\begin{cases} h00 \text{ when } h \text{ is even} \\ hk0 \text{ when } h \text{ and } k \text{ are even} \\ hh0 \text{ when } h \text{ is even} \end{cases}$	0-layer $\begin{cases} 00l \text{ when } l=4n \\ h00 \text{ when } h \text{ is even} \\ h0l \text{ when } h+l \text{ is even} \end{cases}$
1-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hhl \text{ all absent} \\ hkl \text{ when sum is even} \end{cases}$	1-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hk0 \text{ all absent} \\ hh0 \text{ all absent} \\ hkl \text{ when sum is even} \end{cases}$
2-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hhl \text{ all absent} \\ hkl \text{ when } h, k \text{ and } l \text{ are even} \end{cases}$	2-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hk0 \text{ when } h+k \text{ is even} \\ hh0 \text{ when } h \text{ is even} \\ hkl \text{ when sum is even} \end{cases}$
3-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hhl \text{ all absent} \\ hkl \text{ when sum is even} \end{cases}$	
	[110] axis
4-layer $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hhl \text{ when } h \text{ is even} \\ hkl \text{ when } h, k \text{ and } l \text{ are even} \end{cases}$	0-layer $\begin{cases} hh0 \text{ when } h=2n \\ 00l \text{ when } l=4n \\ hhl \text{ with sum}=4n \end{cases}$

Space-Lattice Type and Space Group. The observed x-ray diffraction effects on the Weissenberg films taken about [001], [100] and [110] are given in Table 2. These data require the space-lattice type to be body-centered. The systematic omissions indicate the presence of an axial glide along [100] in the horizontal plane {001}, and of a diagonal glide in the vertical plane {110}. The space group is uniquely fixed by these operations as $D_{4h}^{19} = I4/am\bar{d}$. This finding confirms the crystal class as ditetragonal-dipyramidal. The evidence bearing on the symmetry of paramelaconite is summarized in Table 3. Additional, apparently systematic, omissions are also present in the 2- and 4-layer Weissenberg photographs taken about [001]. These are without significance for purposes of space group determination, and presumably are due to special properties of the structure, as indicated beyond.

TABLE 3. SYMMETRY OF PARAMELACONITE

Crystal class	Morpho-logical symmetry	Etch symmetry	Weissen-berg film symmetry	Space group symmetry
Ditetragonal-dipyramidal = $4/m\ 2/m\ 2/m$	*	*	*	$I4/amd$
Tetragonal-trapezohedral = $4\ 2\ 2$	*		*	
Ditetragonal-pyramidal = $4\ m\ m$			*	
Tetragonal-scalenohedral = $\bar{4}\ 2\ m$	*		*	
Tetragonal-dipyramidal = $4/m$	*		*	
Tetragonal-pyramidal = 4				
Tetragonal-disphenoidal = $\bar{4}$				

Pseudo-Cell and Structural Relations. The rotation photographs indicate a marked pseudo-cell with both a_0 and c_0 halved. The intensity of the reflections on the even-layer Weissenberg photographs about both [001] and [100] is for the most part either very strong or weak. A catalogue of the strong reflections is given in Table 4.

TABLE 4. CATALOGUE OF OBSERVED (STRONG) REFLECTIONS IN THE PSEUDO-CELL

[001] axis	[100] axis
0-layer (=0-layer of true cell) $\begin{cases} h00 \text{ when } h \text{ is even} \\ hk0 \text{ when } h+k \text{ is even} \\ h00 \text{ all present} \end{cases}$	0-layer (=0-layer of true cell) $\begin{cases} 00l \text{ when } l=2n \\ h00 \text{ when } h \text{ is even} \\ h0l \text{ when } h+l \text{ is even} \end{cases}$
1-layer (=2-layer of true cell) $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hhl \text{ all absent} \\ hkl \text{ when } h+k+l \text{ is even} \end{cases}$	1-layer (=2-layer of true cell) $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hk0 \text{ when } h+k \text{ is even} \\ hhl \text{ when sum is even} \\ hkl \text{ when sum is even} \end{cases}$
2-layer (=4-layer of true cell) $\begin{cases} h0l \text{ when } h+l \text{ is even} \\ hkl \text{ when } h+k \text{ is even} \\ hhl \text{ all present} \end{cases}$	

These data indicate that the pseudo-cell is based on a body-centered lattice and is without special symmetry operations. Accordingly, the space group is $I4/mmm$. The pseudo-cell probably represents the essential structural make-up of the substance, and the true cell, as described above, may then define a super-structure originating in an ordering of the cuprous ions or of the oxygen-defect positions, as described beyond. Neither the true cell nor the pseudo-cell appears to stand in a close dimensional relation to either cuprite or tenorite. A comparison with some other compounds of the AX type is given in Table 5. Structurally, paramelaconite

probably is based on a square coordinated grouping of oxygen atoms about a central copper atom, analogous to the structure of cooperite, PtS. Such a structure would present analogies to the structure of the monoclinic cupric oxide, tenorite, analyzed by Tunell, Posnjak and Ksanda (1935), in which essentially square coordinated groups of O atoms about Cu atoms are unsymmetrically distorted.

TABLE 5. COMPARISON OF SOME COMPOUNDS OF THE AX TYPE

	Space group	Cell contents	a_0	c_0	
Paramelaconite (true cell)	$I4/amd$	"Cu ₁₆ O ₁₆ "	5.83	9.88	
Paramelaconite (pseudo-cell)	$I4/mmm$	"Cu ₂ O ₂ "	2.915	4.94	
PbO (red or α -PbO)	$P4/nmm?$	Pb ₂ O ₂	3.99	5.01	
PdO	$P4/nmm?$	Pd ₂ O ₂	3.00	5.20	
SnO (α -SnO)	$P4/nmm?$	Sn ₂ O ₂	3.80	4.81	
Cooperite (Pts)	$P4/mmc$	Pt ₂ S ₂	3.47	6.10	
Tenorite (CuO)	$C2/c$	Cu ₄ O ₄	4.653	5.108	$b_0 = 3.410$ $\beta = 99^\circ 29'$
Cuprite (Cu ₂ O)	$Pn3m$	Cu ₄ O ₂	4.26		

Cell Dimensions. Powder Diffraction Data. The edge-lengths of the unit cell as calculated from high order axial reflections on the 0-layer Weissenberg photographs about [001] and [100] are

$$a_0 = 5.83. \quad c_0 = 9.88. \quad a_0 : c_0 = 1 : 1.695.$$

The values calculated from the rotation photographs were $a_0 = 5.81$, $c_0 = 9.87$, [110] period = 8.14. The powder diffraction data are summarized in Table 6. The powder photograph of paramelaconite is shown in comparison with those of tenorite and cuprite in Fig. 5.

TABLE 6. X-RAY POWDER DIFFRACTION DATA FOR PARAMELACONITE
Cu radiation. Camera radius = 57.26 mm. (uncorr.)

No.	d	I	Index	No.	d	I	Index
1.	4.027	vw	110	12.	1.233	w	008
2.	3.115	vw	112	13.	1.056	w	228
3.	2.888	w	200	14.	1.025	vw	440
4.	2.490	vs (1)	202	15.	1.017	w	426
5.	2.464	w	004	16.	0.949	w	600
6.	2.050	m	220	17.	0.939	w	444
7.	1.874	vw	204	18.	0.935	w	408
8.	1.575	s (2)	224	19.	0.916	vw	620
9.	1.449	m	400	20.	($\alpha_1\alpha_2$) 0.859	w	624
10.	1.430	m	206	21.	($\alpha_1\alpha_2$) 0.832	w	606
11.	1.251	s (3)	404	22.	($\alpha_1\alpha_2$) 0.821	vw	00.12

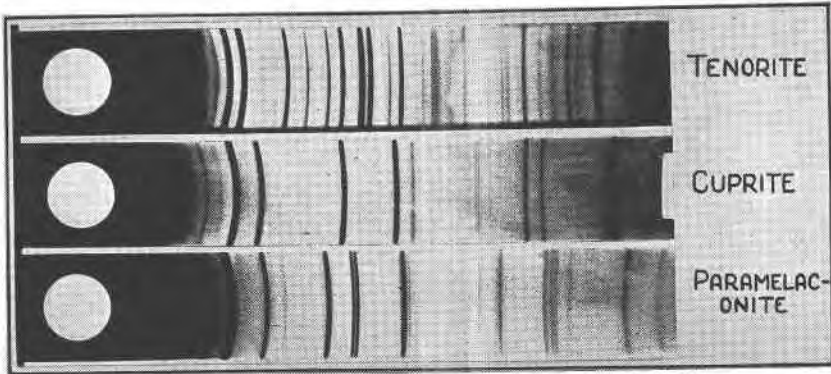


FIG. 5. X-ray powder photographs of tenorite, cuprite and paramelaconite. Cu radiation. Some faint lines do not show in the reproduction of the patterns, and the relative intensity of the stronger lines is not accurately represented.

PHYSICAL PROPERTIES

Cleavage is lacking. The fracture is flat conchoidal. The mineral is brittle. It is scratched with difficulty by apatite and scratches fluorite (contrary to the statement of Koenig that the hardness on {001} is equal to that of apatite) so that the hardness is $4\frac{1}{2}$. The specific gravity is 6.04. This value represents three identical determinations made on separate grains on the Berman microbalance. The value 5.833 for the specific gravity given by Koenig is in error and probably was obtained on a sample mixed with massive tenorite. The luster of paramelaconite is brilliant metallic-adamantine. The color on fracture surfaces is pitch-black. The color on the natural crystal faces is black with a faint purple tone of color. The streak is brownish-black. It is opaque.

In polished section, the mineral is white with a faint pinkish-brown tint of color. The color resembles that of tenorite but is much whiter. The mineral is weakly pleochroic in white to pinkish-brown, and is strongly anisotropic. Internal reflections were not observed in strong oblique illumination. The substance is etched by FeCl_3 , KCN, HCl and HNO_3 , but is almost or entirely negative to KOH. It is strongly tarnished by HCl or HNO_3 fumes. The above observations were made on sections approximately parallel to [001]. No evidence of twinning or of zonal growth was observed, and the mineral appeared to be entirely homogeneous.

CHEMISTRY

Qualitative Reactions. Splinters of paramelaconite are rounded at the edges in a strong oxidizing flame. The mineral melts easily and yields metallic copper in the reducing flame. The powder is readily soluble in cold

dilute mineral acids. Fragments are attacked by extremely dilute HCl (a few drops of acid in 50 cc. of water) with the formation of a surface coating of cupric oxide and cuprous chloride. Extremely dilute HNO₃ or H₂SO₄ causes the formation of a loose flaky coating of metallic copper and cupric oxide. The action of the oxidizing agent HNO₃ in forming metallic copper from cuprous oxide is well known (see Mellor (1923)). The powder is easily soluble without the formation of metallic copper or cupric oxide in cold dilute NH₄Cl or NH₄OH solution. The color of these solutions is blue. Fragments are not appreciably attacked over a period of hours in cold dilute acetic acid.

Homogeneity. Analyses. Spectrographic Data. Koenig (1891) stated that inclusions of cuprite were present in the sample analyzed by him. He found (column 1, Table 7) that the mineral was an oxide of copper, with an excess summation of 1.32 per cent when the total copper, determined as Cu₂S, was expressed as CuO. The excess was taken to represent oxygen and was calculated as Cu₂O, to the amount of 11.70 per cent. The Cu₂O was then ascribed to the admixed cuprite, and the true composition of the mineral was considered to be CuO, like tenorite.

TABLE 7. ANALYSES OF PARAMELACONITE

	1.	2.	3.	4.	5.
Cu			[81.68]	81.80	81.95
O			[18.32]	[18.20]	18.05
Cu ₂ O	11.70	19.45	19.97	[21.38]	[23.07]
CuO	87.66	77.94	80.03	[78.62]	[76.93]
Fe ₂ O ₃	0.64	2.70		0.00	
Total	100.00	100.09	100.00	[100.00]	100.00

1. Analysis by Koenig (1891). Made on 0.2031 gram sample. Cu₂O and CuO calculated from excess summation (=101.32 per cent) of total Cu taken as CuO and determined as Cu₂S.

2. Analysis by F. A. Gonyer (January, 1940) on 0.5 gram sample. Cu₂O and CuO determined directly by the KNa tartrate method.

3. Analysis 2 recalculated to 100 per cent after deduction of Fe₂O₃. Total Cu and O calculated from Cu₂O and CuO.

4. Analysis by F. A. Gonyer (March, 1941) on 0.4 gram sample. Total Cu determined directly by electrolytic method. Cu₂O and CuO calculated from excess summation (102.39 per cent) of the total Cu taken as CuO.

5. Calculated composition for Cu₆Cu₂O₇.

Koenig's interpretation of the composition is in error, because pure grains of the mineral give strong qualitative tests for cuprous copper. Two samples were prepared for new analyses. Special care was taken to ensure the entire homogeneity of the samples. For the first sample several

single crystals were removed from the specimen and were broken down to a coarse powder. It was observed that the portions of the crystals at their attached ends locally had a dull and coal-like appearance, with a rather uneven fracture. Open lineage cracks in these portions were filled by a soft black material which proved on x -ray powder examination to be tenorite. The remainder of each crystal afforded lustrous grains with a flat conchoidal fracture. The sample, when handpicked for impurities, was free from transparent material under the microscope and an x -ray powder photograph showed no evidence of admixture. An analysis of this sample was undertaken by Mr. F. A. Gonyer and the results are reported in column 2 of Table 7. The cuprous and cupric copper were separated by precipitation from a Rochelle-salt solution, and the Cu_2O and CuO in the filtrate and precipitate were determined by electrolytic determination of the copper. The surprisingly large amount of Fe_2O_3 reported undoubtedly represents admixed finely divided iron oxide, in light of the observations of Koenig and of the further analysis reported beyond.

After the completion of the foregoing analysis, a sample was prepared entirely from the lustrous, flat conchoidal material from the apical portion of a single crystal. An x -ray powder photograph of the sample showed no evidence of admixture. The results of this analysis are tabulated in column 4 of Table 7, and are considered to represent very accurately the composition of the mineral. The total copper was determined electrolytically, and the relative amounts of the Cu_2O and CuO were calculated from the excess summation taken as oxygen (=2.39 per cent) when the total copper is calculated as CuO . Fe_2O_3 and heavy metals other than copper were absent.

A spectrographic examination was made on a Baird two meter grating instrument of part of the sample used in the first chemical analysis. The results of this examination are tabulated below. The writer is indebted to Mr. Rockwell Kent, III, for contributing these data.

<0.001%	= Sn, V
<0.01%	= Ca, Pb, Zn, Mo, Ti, Zr
<0.1%	= Al, Mn, Si, Mg, Ba
>1%	= Fe

Composition. The chemical constitution of paramelaconite presents an interesting problem. The atomic contents of the unit cell are derived and itemized in Table 8. Two alternative interpretations of the composition can be made: (1) That some of the oxygen positions in the structure are vacant. (2) That there is not a defect structure and the composition is $\text{Cu}_{12}\text{Cu}_4\text{O}_{14}$.

TABLE 8. OBSERVED ATOMIC CONTENTS OF THE UNIT CELL OF PARAMELACONITE

1.	2.	3.	4.	5.
Analysis No. 4	Molecular quotient	Atomic quotient	Observed cell contents. Mol. wt. of cell=1230	Observed cell contents adjusted to 16 total Cu atoms
CuO = 78.62 Cu ₂ O = 21.38 <hr/> 100.00	0.9888 0.1494	Cu ² =0.9888 Cu ¹ =0.2987 O = 1.1382	= 12.16 = 3.67 = 14.00 } 15.83	= 12.29 = 3.71 = 14.15 } 16

(1) *Oxygen-Defect Structure.* On this basis, the *ideal* cell contents must be either $\text{Cu}_{16}\text{O}_{16}$ or $\text{Cu}_{14}\text{Cu}_2\text{O}_{15}$. The latter formulation is excluded because arrangements of this number of atoms can not be found which conform to the geometry of the space group. Accepting the ideal cell contents as $\text{Cu}_{16}\text{O}_{16}$, the actual cell contents of the defect structure may be written $(\text{Cu}_{16-2x}, \text{Cu}_{2x})\text{O}_{16-x}$. The value of x in this formula is fixed by analysis no. 4, Table 7, as 1.85. The simplest formula is $(\text{Cu}_{1-2x}, \text{Cu}_{2x})\text{O}_{1-x}$, where $x=0.116$. In this view, paramelaconite may be described as a cupric oxide CuO , with an oxygen-defect structure in which the valence change accompanying the omission of oxygen atoms is compensated by the appearance of cuprous ions in place of some of the cupric copper. The cuprous copper is then proper but not essential to the crystal. Geometrical arrangements of the ideal cell contents $\text{Cu}_{16}\text{O}_{16}$ can be found in both the space group of the true cell, $I4/amd$, and of the pseudo-cell, $I4/mmm$. The calculated specific gravity of the adjusted defect cell is 6.106, and the calculated specific gravity of the ideal cell is 6.25. Support for the validity of this interpretation of the composition would be afforded if additional occurrences of paramelaconite were found in which the postulated formulation was satisfied with different values of x . Definite proof, however, must await an analysis of the structure.

Defect structures with omissions among the anions are quite unusual. Ordinarily, the anions act as the "structure-supporters" and the omissions occur among the cations. Oxygen-defect structures, however, have been reported by Sillén and Aurivillius (1939) in the systems $\text{PbO}-\text{Bi}_2\text{O}_3$ and $\text{SrO}-\text{Bi}_2\text{O}_3$. Anion-defect structures also occur between yttrifluoride and fluorite, and between the Sr and La analogues of these substances.

(2). *Non-Defect Compound, $\text{Cu}_{12}\text{Cu}_4\text{O}_{14}$.* Paramelaconite also may be represented as an oxide with both essential cuprous and cupric copper in definite ratio. The indicated formula is $\text{Cu}_{12}\text{Cu}_4\text{O}_{14}$. Cell contents with less or more than a total of 16 copper atoms or 14 oxygen atoms must be

excluded because of the marked differences then appearing between the observed and calculated specific gravities, as seen from Table 9.

TABLE 9. RELATION BETWEEN ATOMIC CONTENTS OF UNIT CELL AND CALCULATED SPECIFIC GRAVITY

Total Number of Copper Atoms	12	13	14	15	16	17	18	26
Corresponding No. of Oxygen Atoms	10.61	11.49	12.38	13.26	14.15	15.03	15.91	22.99
Calculated Specific Gravity	4.37	4.96	5.34	5.72	6.106	6.49	6.87	9.92
Total Number of Oxygen Atoms	12	13	14	15	16	17	18	23
Corresponding No. of Copper Atoms	13.57	14.71	15.84	16.97	18.10	19.23	20.36	26.02
Calculated Specific Gravity	5.18	5.61	6.04	6.48	6.91	7.34	7.77	9.92

Evidence bearing on the validity of this interpretation may be mentioned. The content of atoms in the cell must be that of whole numbers, within the experimental error. If the content is irrational the present interpretation must be denied. (The necessity for a whole number ratio of the cupric and cuprous ions would be obviated if these ions were structurally equivalent, but there would then appear to be no reason for maintaining the definite ratio between these ions required in the present case by the fixed number of oxygen atoms in the formula. Variation in the cuprous:cupric ratio would vary the total number of oxygen atoms and the case would become that of (1), previously discussed.) The observed number of cuprous atoms in the cell is only 3.71, but it is not entirely certain that this departure from the whole number 4 is beyond the experimental error. The per cent of copper in $\text{Cu}_6\text{Cu}_2\text{O}_7$ is 81.95, which agrees quite closely with the directly determined value of 81.80. (See Table 7, columns 4, 5.) This difference is considered by the analyst to be beyond the limit of error of the determination in the present especially favorable case, but direct test of the accuracy in the way of duplicate determinations is lacking.

Geometrical arrangements of the cell contents $\text{Cu}_{12}\text{Cu}_4\text{O}_{14}$ can not be found in the space group, $I4/amd$, of paramelaconite. It is assumed that the copper and oxygen atoms are non-equivalent. The only possible arrangements of the postulated cell contents in a ditetragonal-dipyramidal space group is in $I4/mmm$. This is the space group of the pseudo-cell, but this cell, which has one-eighth the volume of the true cell, could accommodate only fractional atoms. It appears, therefore, that the present basis of interpretation must be excluded and the mineral be represented

as an oxygen-defect cupric oxide. Interpretations based on interstitial solid solution, or on omissions in the copper positions, also must be discarded for reasons already indicated.

Thermal Behavior. Powdered paramelaconite was heated in evacuated Pyrex capsules in an electric furnace. Material from the sample used for analysis 4, Table 7, was employed for the purpose. The cooled product was examined by the *x*-ray powder method. An immediately reversible transformation would of course go unrecognized in this method. Material held at 365° C. for 2 hours gave the pattern of tenorite with a distinct superimposed pattern of cuprite and traces of the strongest lines of paramelaconite. Material held for 1 hour at 300° C. and another sample held for 5 hours at 240° C. gave a strong pattern of paramelaconite with a faint superimposed pattern of tenorite and traces of the strong lines of cuprite. A sample held for 40 hours at 190° C. gave superimposed patterns of about equal intensity of tenorite and paramelaconite with a faint pattern of cuprite. As far as could be judged the relative amounts of tenorite and cuprite in all of the above preparations was the same. The breakdown seemingly represents a simple dissociation of the cuprous and cupric copper of the original homogeneous oxide phase into admixed CuO and Cu₂O. Paramelaconite of ideal composition (CuO), without vacant oxygen positions, presumably would break down to tenorite alone. A somewhat similar behavior has been found by Goldschmidt and Thomassen (1923) for the compound UO₂ (uraninite). The natural material is more or less oxidized to UO₃ but still maintains the original, fluorite-type, structure. The extra oxygen is thought to be in interstitial solid solution, occupying vacant NaCl-types positions in the structure. On heating, unoxidized UO₂ remains unchanged, but the oxidized material may break down in part to U₃O₈.

A small solid grain of paramelaconite was brought rapidly to dull red heat in air and immediately quenched. This grain gave a mixed *x*-ray pattern of tenorite and cuprite, identical in relative intensity with that of the material heated in vacuo. No lines of paramelaconite were found in this sample. It may be noted that the rate of breakdown increases very markedly with increasing temperature. If the fine powder is held at temperatures above dull red heat for an hour or so, a pronounced increase in the amount of admixed cuprite is observed. This effect probably is due to the dissociation of the CuO generated in the initial breakdown, since the reaction $4 \text{CuO} \rightleftharpoons 2 \text{Cu}_2\text{O} + \text{O}_2$ goes to the right with increasing temperature. At ordinary pressure the reaction is said to go to completion at about 1050° C. It was found in this connection that ignited samples containing cuprite when left to stand in contact with air for a day or so completely oxidized to tenorite.

Wöhler and Foss (1906) contended that the Cu_2O , formed as the reaction $4\text{CuO} \rightleftharpoons 2\text{Cu}_2\text{O} + \text{O}_2$ proceeds to the right, enters a solid solution with the CuO as a single phase. A later thermal study by Smyth and Roberts (1920) of this system showed that solid solubility between Cu_2O and CuO was non-existent or negligible. This conclusion is supported by the present x -ray observations. Paramelaconite could be interpreted as a solid solution of CuO and Cu_2O in the sense of these writers, on the basis of an oxygen-defect structure, but the mineral has of course been formed in a very different system and temperature range. The present observations also indicate that tenorite does not form an oxygen-defect structure over the temperature range investigated to an extent comparable to that of paramelaconite.

The crystallites of tenorite and cuprite formed in the breakdown are randomly oriented with respect to each other and to the original paramelaconite. X -ray rotation photographs taken about [001] and [100] of two heated single-crystals gave complete powder pictures of tenorite and cuprite with no evidence of layer-periodicities. A third crystal, heated briefly at about 400°C ., broke down only partially and gave definite layer-periods of paramelaconite with superposed powder patterns of tenorite and cuprite.

OCCURRENCE AND ASSOCIATION

The matrix of the specimens consists of goethite with a small amount of admixed cuprite and native copper. Upon this base is a thin botryoidal coating of radially fibrous goethite, which in part is overlain by black massive tenorite. Deposited directly upon this crust are the crystals of paramelaconite, which in turn support, and in part enclose, long prismatic crystals of connellite. Elsewhere the connellite rests directly upon the tenorite or goethite crust. Small crystals of cuprite are sometimes found completely embedded in the paramelaconite. It is clear that paramelaconite, connellite and cuprite were deposited contemporaneously for a brief period at least, and that the deposition of the connellite continued after the cessation of crystallization of the paramelaconite. The mineral succession was closed by the deposition of light greenish or silvery white felted flakes of a mineral identified by its x -ray pattern as malachite. The mineral succession may be summarized as:

(Matrix = goethite, cuprite, native copper) \rightarrow goethite \rightarrow tenorite \rightarrow paramelaconite (with minor cuprite and connellite) \rightarrow connellite \rightarrow malachite

X -ray powder photographs were taken of specimens of the pulverulent or pitch-like black massive varieties of cupric oxide, usually termed melaconite, melanochalcite or copper pitch-ore, in hope of finding further

occurrences of paramelaconite. Of twelve specimens from seven localities, nine were found to consist of tenorite, and three to consist of delafossite. One of the occurrences of delafossite, from Eureka, Nevada, is new. The identity of melanochalcite and of copper pitch-ore in general with tenorite was urged by Hunt and Kraus (1916) and by Guild (1929) on optical and chemical grounds, and this view is here confirmed. Koenig, in the original description of paramelaconite, reported a second occurrence of the mineral as an impregnation of black crystals in a coarse sandstone. The locality was given only as Arizona. One of the two original specimens of this material was examined and proved to be tenorite.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Professor Harry Ber-
man for his interest and aid throughout the investigation, to Dr. C. W.
Wolfe for a discussion of the crystallographic and x -ray data, and to Dr.
George Tunell, of the Geophysical Laboratory, Washington, D. C., for
reading the manuscript. The writer also has had the opportunity to dis-
cuss aspects of the problem with Professor M. J. Buerger of the Massa-
chusetts Institute of Technology.

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