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The Psilomelane Mineral of the Butte District, Montana

Logan E. Davis

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THE PSILOMELANE MINERAL
OF THE BUTTE DISTRICT, MONTANA

by

LOGAN E. DAVIS

A Thesis
Submitted to the Department of Geology
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science

MONTANA SCHOOL OF MINES
Butte, Montana
May 2, 1949
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THE PSILOMELANE MINERAL
OF THE BUTTE DISTRICT, MONTANA

by
LOGAN E. DAVIS

INTRODUCTION

During the last few years a great deal of research has been done in connection with the black manganese oxide minerals. This is especially true of the so called mineral psilomelane. It has been proven without a doubt that the name psilomelane has been used in the past to include a great variety of similar black manganese oxide minerals. By the use of X-ray equipment these minerals have been definitely identified. The name psilomelane has been retained, but it is now applied to a specific mineral with a definite X-ray pattern. To avoid confusion, the entire group of minerals are now considered to be of the "psilomelane type." This makes it unnecessary for an unreliable decision to be made in the field. The physical and chemical properties of the minerals are so similar that X-ray and chemical determinations are often necessary before a mineral can be identified with any degree of certainty.

The fact that manganese has become a strategic mineral for our economy has led to the recent work with the manganese oxide minerals. Since Butte and Philipsburg, Montana contribute a large portion of the supply of manganese for the United States consumption it is quite apparent that these deposits are of extreme importance.

The purpose of the work for this thesis is to determine the specific mineral or group of minerals in the Butte district
which have been, in the past, considered to be psilomelane. In addition, any other pertinent facts that may be determined will be included.

The author wishes to thank E. J. Bartzen of the Montana Bureau of Mines for the time and energy which he expended making chemical analyses for this paper, and Mr. William Joyce who was very cooperative about comparing data which he obtained from Philipsburg, Montana.

He wishes especially to express his appreciation for the advice and guidance contributed by Dr. Eugene S. Perry, without which, the work would have been exceedingly more difficult.
METHOD OF APPROACH

The logical method of approach for solving the problem seemed to consist of: (1) Collection of several samples of the psilomelane type mineral throughout the Butte district, (2) Preparation of samples for chemical analysis, and (3) Cutting and polishing the mineral for study under the microscope.

COLLECTION OF SAMPLES

Samples were taken from three different areas, as indicated on the included map of the Butte district, Montana. (See geologic map at the end of the report.) The areas sampled are: (1) Where the Emma lode crops out on the Star West claim south of Butte, (2) On the surface exposures of the outcrop of the Nettie vein west of Butte, and (3) Along the outcrop of the Black-Rock vein north of Butte, above Walkerville.

These represent three distinctly different veins about the periphery of the Butte mining district, and should therefore give a good cross section of the district. At this time, it is pointed out, that the psilomelane type mineral from the Star West and the Nettie have been derived by oxidation of manganese carbonate; whereas, the mineral of the Black-Rock vein has been derived essentially from manganese silicate. (5)
Plate No. I.

Outcrop of the Emma Vein on the Star West Claim.
PREPARATION OF SAMPLES
FOR CHEMICAL ANALYSIS

Several samples from each area were selected and sorted in an effort to secure the purest so called psilomelane mineral. The samples were then broken down and portions were placed in small vials and made ready for quantitative chemical analyses for: total Mn, total MnO₂, Fe, Ca, Mg, Ba, and K. The analyses were conducted by E. J. Bartzen in the Montana Bureau of Mines laboratory.

PREPARATION OF SAMPLES
FOR MICROSCOPIC STUDY

Forty-one different samples were cut with a diamond saw, ground, polished, and studied under the microscope. In addition, etch tests were conducted on all the above mentioned polished sections.

RESULTS OF CHEMICAL ANALYSIS

The most outstanding fact obtained is the absence of barium from all the samples tested. On the other hand, it was discovered that the samples did contain an appreciable amount of potassium. (See Plate II on page 7.) It is also quite noticeable that the potassium content of the ore derived from the manganese silicate is twice as large as it is in the ore derived from the manganese carbonate. The samples are further characterized by a high MnO₂ content and a low Fe content. When the quatra-valent and di-valent percentages of manganese were calculated,
<table>
<thead>
<tr>
<th>Location</th>
<th>Total Mn</th>
<th>Total MnO₂</th>
<th>Ba</th>
<th>K</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Star West</td>
<td>46.7</td>
<td>67.9</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Black Rock</td>
<td>42.6</td>
<td>66.5</td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Nettie</td>
<td>49.6</td>
<td>73.7</td>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td>1.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Plate No. II Table of average results of chemical analysis for Butte district.
it was found that the ore from the Black-Rock vein also has a low percentage of di-valent manganese as compared to the ore derived from the carbonate veins. This relationship may make possible the determination of the character of the primary manganese mineral in the Butte veins by chemical analysis of the outcrop material.

RESULTS OF MICROSCOPIC STUDY

PHYSICAL TESTS

Upon observation of physical characteristics it was seen that there were at least two different minerals present, or in any event, two apparently different psilomelane minerals; one with a gun-metal blue shiny luster and a hardness of 6-6 ½; the other with a dark dull luster and a hardness of approximately 2. Of course, there is also the crystalline variety of pyrolusite. In some specimens a definite banded effect in the psilomelane could be seen, with the bands being formed of the hard and soft minerals in concentric rings.

The lighter of the two minerals appears to be isotropic under the microscope, whereas the darker softer mineral is strongly anisotropic. The composite sample is steel gray to bluish gray on a fresh surface and breaks with a definite conchoidal fracture. The specimens soil the hands almost immediately, which must be due to the rubbing off of the softer of the two minerals. Quite commonly small quartz veinlets were observed traversing through the minerals, especially in the Star West and Nettie districts.
Plate No. III.

Manganese Oxide Outcrop
at the Nettie Mine,
Butte, Montana
ETCH TESTS

A number of different reagents were tried in an attempt to secure an etch test which would separate the two observed minerals. H₂SO₃, HNO₃, HCl, FeCl₃, and HgCl₂ were some of the reagents experimented with. It was found that by using concentrated HCl for 90 seconds on an apparently homogeneous surface, an etch pattern could be discerned. In fact, the etch brought out a concentric banded effect similar to the one mentioned in the previous section. (See Plate IV, B.) Apparently one mineral reacted more readily with the hydrochloric acid than the other, and ridges of the resistant mineral were separated by troughs left by the less resistant material. The liberation of free chlorine was indeed noticeable.

S. R. Cooke, (1:211) while working with manganese ore in the iron ranges of Minnesota, found that by using a solution of sulphurous acid he could separate pyrolusite from psilomelane minerals in an etch test on a polished section. The pyrolusite would be attacked more intensely than the psilomelane mineral, and would become a dull black in color, whereas, the psilomelane mineral would not be attacked quite as much, and would remain much lighter in color than the pyrolusite.

Suspecting that the softer of the two minerals exhibited in the specimens from the Butte district might be pyrolusite, the author etched several polished sections with sulphurous acid for 90 seconds. The results were the same as those obtained by S. R. Cooke. (See Plate IV, A.)
A. Separation of cryptomelane and pyrolusite with a 90 sec. etch with H$_2$SO$_3$.

B. Banding of cryptomelane and pyrolusite. 90 sec. etch with conc. HCl.

C. Cryptomelane forming bands with pyrolusite in the Black-Rock vein. 90 sec. etch with conc. HCl.

Plate No. IV. Photographs of Manganese Oxide Minerals Under a Microscope. All Magnifications are 10 X.
For convenience, a chart has been set up to illustrate the reactions of the different reagents on the manganese oxide samples. (See figure 5.)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Hard Steel-blue Mineral</th>
<th>Soft Dark Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₃</td>
<td>Darkens with sorbic pattern</td>
<td>Darkens rapidly; deeply etched.</td>
</tr>
<tr>
<td>HCl</td>
<td>Tarnishes</td>
<td>Deeply etched</td>
</tr>
<tr>
<td>HNO₃₃</td>
<td>Light brown tarnish</td>
<td>Negative</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>Negative</td>
<td>Negative</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>Negative</td>
<td>Negative</td>
</tr>
</tbody>
</table>

Figure No. 5. Etch results on manganese oxide minerals

PRESENT CLASSIFICATION OF MANGANESE OXIDE MINERALS

The basis for classification that is used by the author was set forth in 1943 by Michael Fleischer and Wallace E. Richmond (10 : 272) of the U. S. Geological Survey in their preliminary report on the manganese oxide minerals. (See Plate No. VI.) Their classification is based upon results obtained from X-ray and chemical analyses.

It will be noticed that in the list of minerals in Plate No. VI that there are four minerals listed with chemical formulas that are new and subject to revision. Each of these minerals
Plate No. V.

Outcrop of the Black-Rock Manganese Oxide Vein at Butte, Montana
has a definite X-ray photo pattern, but the chemical formulas are largely empirical. The elements listed are correct, but there seems to be a slight variation in the amounts present in various samples. Consequently, the four formulas listed are not exact, but they should be very close approximations.

CLASSIFICATION FOR THE BUTTE DISTRICT

Based upon the results of both the microscopic study and the chemical analysis, the author concludes that the psilomelane mineral of the Butte district is not psilomelane, but is an intimate mixture of cryptomelane and pyrolusite. In the Star West and Nettie areas, approximately one-third of the total manganese present in the oxide ore is cryptomelane and two-thirds is pyrolusite. In the Black-Rock area cryptomelane comprises roughly two-thirds of the manganese oxide mineral and pyrolusite comprises the other one-third.

CRYPTOMELANE

The mineral cryptomelane has been identified for several years. Early investigators (7: 146) found that psilomelane sometimes contained either the element barium or potassium. However, if the mineral contained one element then it did not contain the other.

L. S. Ramsdell (7: 145) was the first worker to separate the potassium bearing mineral from the barium bearing mineral. He called the potassium bearing mineral "true psilomelane."
Fleischer and Richmond, in their recent work have introduced the name cryptomelane as the name for Ramsdell's (9:608) "true psilomelane", and have restricted the name psilomelane to the barium bearing mineral. This nomenclature has been accepted in the literature, and will also be accepted for this report. With the exception of pyrolusite, cryptomelane is probably the most commonly occurring manganese oxide mineral.

Cryptomelane has the formula $\text{K}_8\text{O}_{16} \quad (?) \quad \text{R}^- \quad \text{Mn}^{IV}$ chiefly, also $\text{Mn}^{II}$, $\text{Zn}$, and $\text{Co}$. This means a manganese oxide with considerable quadra-valent manganese, some potassium, some divalent manganese and small amounts of $\text{Zn}$ and $\text{Co}$ may be present.

Most samples contain 2 to 4 per cent nonessential water. The mineral is tetragonal, steel gray to black in color, black when tarnished, has a dark brownish black streak, hardness of 6 to $6\frac{1}{2}$, and a specific gravity of approximately 4.3. The mineral has a number of habits of occurrence: (1) Most commonly as a very fine grained steel-gray dense compact masses with a conchoidal fracture. (2) Less commonly as botryoidal masses. (3) Uncommonly as coarse cleavage masses that would not ordinarily be labeled "psilomelane type". (4) Rarely as distinct crystals. (10:273)

Observed under the microscope, some areas appear anisotropic and other areas appear isotropic. $\text{HNO}_3$ stains light brown. $\text{HCl}$ stains brown to black with a more intense action than that of $\text{HNO}_3$. $\text{KCN}$ negative. $\text{FeCl}_3$ stains some specimens light brown and on other specimens is negative. $\text{KOH}$ and $\text{HgCl}_2$ negative. $\text{H}_2\text{O}_2$ effervesces vigorously without etching. Polished surfaces commonly show concentric banding. $\text{H}_2\text{SO}_3$ etches with a sorbic pattern.
Manganese Oxide Minerals
by
Fleischer and Richmond (10: 272)

Bixbyite—(Mn, Fe)$_2$O$_3$.

*Braunite—3(Mn, Fe)$_2$O$_3$.MnSiO$_3$.

Cesarolite—PbMn$_3$O$_7$.H$_2$O Rare.

Chalcophanite—(Mn, Zn)Mn$_2$O$_5$.2H$_2$O Rare.

Coronadite—Pb$_8$O$_{16}$ (?), R=Mn$^{IV}$ chiefly, also Mn$^{II}$, Cu, Zn.

Crednerite—CuMn$_2$O$_4$ Rare.

*Cryptomelane—K$_8$O$_{16}$ (?), R=Mn$^{IV}$ chiefly, also Mn$^{II}$, An, Co.

Galaxite—(Mn$^{II}$, Fe$^{II}$) (Al, Fe$^{III}$)$_2$O$_4$ Rare.

Hausmannite—MnMn$_2$O$_4$.

Hetaerolite—ZnMn$_2$O$_4$.

Hollandite—Ba$_8$O$_{16}$ (?), R=Mn$^{IV}$ chiefly, also Fe$^{III}$, Mn$^{II}$, Co.

Jacobsite—(Mn$^{II}$, Fe$^{II}$, Mg) (Mn$^{III}$, Fe$^{III}$)$_2$O$_4$.

Lithiophorite—Li$_2$(Mn$^{II}$, Co, Ni)$_2$Al$_8$Mn$^{IV}$10$^0_{35.14}$ H$_2$O (?).

Manganite—MnO(OH)—Mn$_2$O$_3$.H$_2$O.

Manganosite—MnO Rare.

Poliianite—Pyrochroite. The name poliianite should be dropped.

*Psilomelan—Ba$_9$O$_{18}$.2H$_2$O (?), R=Mn$^{IV}$ chiefly, also Mn$^{II}$, Co.

Pyrochroite—Mn(OH)$_2$ Rare.

*Pyrochroite—MnO$_2$.

Queenselite—Pb$_2$Mn$_2$O$_5$.H$_2$O Rare.

Ramsdellite—MnO$_2$ (dimorph of pyrochroite).

Rancieite—(Ca, Mn$^{II}$) Mn$^{IV}$4.9$.3H$_2$O (?).

Sitaparite=Bixbyite. The name sitaparite should be dropped.

(?) New and subject to revision
* Most common minerals

Plate No. VI. Manganese oxide minerals

-16-
PYROLUSITE

The most common manganese oxide mineral, pyrolusite has a chemical formula MnO₂. It commonly has a little non-essential water. The mineral is tetragonal, iron-gray to black in color, has a dead black streak, a hardness of nearly always 2-2½ but in some specimens higher even up to 6½, and a specific gravity of 4.9 to 5.0 for pure samples and 4.7 to 4.8 for most specimens. It occurs as (1) Compact fine-grained dense masses with a conchoidal fracture. (2) Massive friable with the grain size usually somewhat larger than the compact variety and easily broken down with the fingers. (3) Botryoidal, and in many finely banded specimens composed of harder and softer bands, the softer portion is pyrolusite and the harder portion may be pyrolusite, cryptomelane, or psilomelane. (4) Rarely does it occur as crystals. (10 : 275)

Observed under the microscope the mineral is strongly anisotropic. HNO₃ negative. HCl etches deeply and colors brown. KCN, FeCl₃, KOH, and HgCl₂ negative. H₂O₂ causes vigorous effervescence, but the surface does not stain. Perfect prismatic cleavage. Most specimens stain the fingers black. The apparently amorphous variety appears to be a mat of tiny interlocking needles. When reacting with HCl, pyrolusite liberates a great deal of chlorine.
DISCUSSION

The hard gray to gun-metal-blue mineral has been classified as cryptomelane: (1) Partly because of the physical and optical properties and (2) Mainly on the basis of the results of the chemical analyses. The fact that no trace of barium was found in any of the samples analyzed definitely established the fact that the psilomelane type mineral of the Butte district is not psilomelane. The presence of potassium, however, does establish the fact that the mineral is cryptomelane.

Perhaps the greatest argument against this might be that it is possible that the samples analyzed were not pure. Perhaps there was enough orthoclase from country rock in the specimens to account for the potassium content. It is a know fact that these manganese minerals may contain a certain amount of country rock even when they appear pure under the microscope.

However, the author notes that the K₂O content of the quartz-monzonite country rock in which the veins occur is 4.1% (5 : 169). This gives a potassium content of 3.6%. Even when all the rest of the sample not accounted for in the chemical analysis is considered to be country rock there is not enough potassium present to account for the amount in the analysis. On this basis the maximum possible potassium content for the Star West would be 1%, for Black-Rock 1.1%, and for the Nettie 0.9%. By reference to Plate No. II, it can readily be seen that in all cases these values are less than the actual amount present.

In all probability the percentage of country rock is not as
high as indicated for at least 5% to 10% of the samples are composed of veinlets of quartz, but the extreme case was taken in order to show that potassium from orthoclase impurities could not account for the amount of potassium present. Therefore, potassium must be present in the crystal lattice, which is proof enough that the mineral is cryptomelane. Cryptomelane is the only manganese oxide mineral that does contain potassium.

The soft dark mineral which is intermixed in bands with cryptomelane has been classified as pyrolusite: (1) partly because of the physical and optical properties, (2) partly on the results of the etch test, (3) partly on the fact that other workers have commonly found pyrolusite and cryptomelane occurring together to give a banding effect, and (4) because of an excess of MnO₂ that could not be accounted for by the cryptomelane. Particular emphasis was placed upon the results of the various etch tests, especially the HCl and H₂SO₃ etches.

Because of the similarity of the manganese oxide minerals, classification upon any one physical property would be extremely presumptive. However, when several physical properties are used in conjunction with optical and chemical results, they can be used to help classify the mineral. In the case of the pyrolusite the etch tests are reliable. They will not separate the psilomelane minerals, but according to S. R. Cooke, Warren Howes, and A. H. Emery, the HCl and especially the H₂SO₃ etch tests are reliable for separating pyrolusite from the psilomelane minerals.
CONCLUSIONS AND SUMMARY

As a result of the study and interpretation of the facts derived from the present work, the author has reached the following conclusions:

(1) There is no psilomelane in the Butte district, Montana.

(2) The "psilomelane type" mineral of the area is cryptomelane.

(3) The mineral that appears to be a "psilomelane type" mineral in the hand specimen is actually an intimate mixture of pyrolusite and cryptomelane.

(4) The fact that the manganese oxide ore derived from the manganese silicate contains twice as much potassium, and consequently twice as much cryptomelane, as does the ore derived from manganese carbonate, may indicate a relationship between the origin of the mineral and the potassium content.

The author feels that the problem for this thesis has been greatly cleared. The study of the manganese oxide minerals is very interesting as well as perplexing. The similarity of the minerals makes their classification difficult, and to add to this, the greatest amount of work has been done so recently that it is hard to find published literature concerning the work. The author hopes that this work will contribute to the knowledge of the manganese oxide minerals of the Butte district.
BIBLIOGRAPHY


