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Manganese Oxide Deposits Near Butte and Development Since 1942

Emmett M. Gilmore

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MANGANESE OXIDE DEPOSITS NEAR BUTTE
AND
DEVELOPMENT SINCE 1942

by
Emmett M. Gilmore

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

Montana School of Mines
Butte, Montana
May 8, 1948
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MANGANESE OXIDE DEPOSITS NEAR BUTTE
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INTRODUCTION

Most conspicuous of the outcrop minerals in the Butte mining district are the black oxides of manganese. To the prospector this material is just "black" ore, but to the mineralogist a number of different kinds of manganese oxides are known. The writer has attempted to determine the various kinds of manganese oxides in the outcrop portion of some of the veins near Butte, and to ascertain whether or not unusual minerals, or unusual features of the common oxides are present. Development work since 1942 has been considered.

The manganese minerals occur in the peripheral zone of the Butte district with quartz in veins, which at depth contain galena and sphalerite closely associated with silver-bearing minerals. The manganese oxides are all oxidation products formed by weathering of primary rhodochrosite or rhodonite.

The area studied was restricted to the western portion of the Butte district within one to two miles of
the School of Mines and did not include the large, prominent lodes in the northern and northeastern parts of the district. Numerous mine roads, most of which are suitable for trucking, criss-cross this area; and the Butte, Anaconda, and Pacific Railroad crosses its southern edge. A loading ramp, and also the Domestic Manganese Plant where ores may be sold, are within two miles.

It was necessary to collect samples for study from vein matter 20 to 60 feet from the surface since deeper underground workings of mines in the area are inaccessible.

The writer wishes to express his appreciation to Dr. Eugene S. Perry, Professor of Geology at Montana School of Mines, for his advice and guidance in preparation of this report; to Mr. Curtis L. Graverson, Instructor of Metallurgy at the same school, and Mr. Robert E. Sullivan for their assistance in the X-ray examination of ore samples.

HISTORY

In 1871 the placer mines, which had been the first source of mining prominence in the area of Butte, were exhausted, and miners sought other fields.

In 1874, however, a group of claims were relocated by W. L. Forlin, and development of the black ledges near Big Butte began. Their wealth in silver
soon became known, and miners who had departed after the
gold decline returned to exploit the buried riches.  

The veins in this part of the Butte district
were first worked for their silver content. The Colorado
Mining and Smelting Company, which was organized in 1879,
owned and operated several mines known as the Burlington
group. The first in importance was the Nettie; the other
two were the Philadelphia and Burlington. Under the man-
agement of this Company the first large-scale mining was
done.

The ore in general was of milling grade, and
large quantities gave good results in concentrating, the
products containing a large proportion of manganese which
was a desirable smelting flux. Shafts were sunk 100 feet
yearly, 85 tons of ore were concentrated daily, and during
the year 1887, 6,000 tons of the concentrated products
were milled.

The Bluebird mine was another large and steady
producer of silver from its first production in 1885,
until it ceased operations in 1893. In 1888, approximate-
ly 37,000 tons of ore were mined, yielding 1,385,508
ounces of silver. An increasing percentage of zinc,
which was encountered at the depth of 600 feet, interfered
with the successful treatment of the ore in the silver
mill. In 1893, the losses from operation resulted in a
shut-down. Since then the mine has not been worked, but the vein has had sporadic development by lesarios.

Silver in the numerous veins lured prospectors who carried on small mining operations throughout the area. Their ore was milled and smelted by the larger companies. At depth the silver became too poor and too quartzose to pay for smelting, nor could many of the operations stand the losses and heavy milling charges which were approximately $30.00 per ton for chlorination and amalgamation which at early dates were the principal methods of recovering silver in Butte. 9/

The properties were mostly in the hands of small operators or miners who, individually, could not operate on a scale large enough to make their venture profitable; yet these people by holding the price at a prohibitive level barred the efforts of larger companies who might have successfully developed the area.

The period of active silver mining continued until 1892 when most mines of the area were closed due to the decline in the price of silver. The Nettie continued operations until 1896, and others worked at intervals, but none has been an active producer since then.

The great increase in the value of manganese in 1917 directed attention to the manganiferous gange of these
silver-zinc lodes, a material which, although formerly regarded as waste or fluxing material, now became under the high war time demand, a possible source of manganese.

Again mining began but was not of any magnitude because the competition was great from nearby sources, the carbonate ores of Butte and the Phillipsburg deposits.

It was not until 1942 that any large production took place.

GENERAL GEOLOGY

Rock Types

Quartz Monzonite

The common and characteristic rock of the district, the Butte "granite", occurs in a relatively minor quantity in this western area. It is more correctly a quartz monzonite, since the plagioclase and orthoclase occur in equal proportions and together amount to about 60 per cent of the mass. Quartz constitutes about 20 per cent of the rock and the mafic minerals, consisting principally of biotite and hornblende, range from 10 to 20 per cent. 3/

Aplite

In the western section of the Butte area, aplite occurs in unusual abundance, underlying large areas. It is a granular, siliceous granitic rock consisting of feldspar and quartz. It is white or cream-colored, medium-grained,
of sugary texture, and bears a superficial resemblance to sandstone.

The aplite has been intruded into the surrounding monzonite, most commonly in dikes and in irregular sheets. A large intrusion underlies the area studied, and is shown on the accompanying map. This mass of aplite is relatively shallow, and is underlain by monzonite at the depth of only a few hundred feet.

The aplite weathers much less readily than the Butte monzonite, and the intrusions therefore form conspicuous outcrops. The rock of the larger masses weathers into gentle slopes and bare, rounded surfaces. Usually the aplite is covered by a weathered crust which is loosely granular and easily reduced to coarse sand. 2/

Rhyolite

Two distinct varieties of rhyolite occur in this area: intrusive rhyolite which forms dikes and fills volcanic conduits; and extrusive or surface rhyolite which forms lava flows and surface breccias. This distinction is not shown on the map, since the boundaries are indefinite and not always recognizable where the two types overlap.

The rhyolite dikes are massive rocks of nearly uniform character. Microscopically both sanidine and plagioclase feldspars are distinguished, the former very greatly predominating. One of the longest of the dikes is near the
Nettie Mine, and it was encountered in the mine workings. The surface exposures range in width from 20 to 100 feet.

The extrusive rhyolites are less common in this area. They are usually recognized by their fragmental character. Near the Nettie mine and other mines of the western area they are generally but a few feet thick, and lie as a veneer upon the granite surface. The rocks are light colored with rusty red tones and form low rough masses.

Vein Systems

The veins of the area occur in both aplite and monzonite west and south of the School of Mines. They generally strike from east to west and have a relatively low southern dip. The outcrops are prominent in most places due to the contrast of the black manganese stain with the light color of the country rock, and also due to the presence of black stained quartz. In places, however, the veins are obscure. Walls of the veins are well defined, and perhaps 30 or more veins are found throughout the areas of aplite and granite.

The Nettie lode, one of the more important, consists of three closely associated veins extending westward about 2000 feet from the contact with the rhyolite body. They are broken and slightly displaced by three east-dipping cross faults, and are cut diagonally by a rhyolite dike which at depth is 200 feet thick. This dike narrows toward
the surface.

The main part of the Bluebird lode is a strong single vein whose dip is most irregular and which lies nearly horizontal for a considerable distance. It may be followed a distance of 2000 feet and has been mined to a depth of 600 feet. At this depth the vein was found to be on the contact between aplite and monzonite.

The Czarina lode due south of the School of Mines forms a conspicuous projecting outcrop of quartz, stained black by the manganese oxides. The lode has not been profitable in the western part of the district, but it presented an interesting problem in recent government development.

Other important veins are the Garibaldi group, which is 2000 feet south of the Nettie; the Germania, north of the Czarina; the Great Republic, and Moody & Sankey in the northwestern section; and the Mono vein, a westerly extension of the Nettie lode.

Rhyolite invariably cuts off the veins. It is not mineralized except where oxidized iron or manganese minerals have been formed by recent surface waters.

The veins are remarkable persistent from one end of the mines to the other and their dip is generally constant. They always occur in the aplite and granite, and vary in width from perhaps 1 inch to 25 feet. The vein filling, like that of all the silver-bearing veins of the camp, consists of quartz with associated silicate and car-
bonate of manganese, and the usual sulphides of lead, zinc, and iron; probably argentite and proustite also are present.

The Nettie vein which is the northerly one of the Nettie lode, had a conspicuous outcrop, but is said not to be workable below a depth of 300 feet due to low grade of ore. The middle vein has a well-defined and strong outcrop, and has been worked to a depth of 500 feet, but has not proved particularly profitable. The south vein, the Philadelphia, has an ill-defined outcrop, but has proved very productive in the lower levels to approximately 700 feet. It narrows westward and widens to the east.

Fractures

The mine workings show at least three periods of ground movement. The first produced a series of parallel joint fissures which sheeted the aplite, and along these fissure planes mineralization took place, forming the veins. Subsequent to this a series of northwest-southeast fault fractures were formed, faulting the veins and forming lines of weakness, along which the rhyolite was injected. There is no dislocation of the veins parallel to this plane of movement.

The last period of fracturing resulted in displacements, producing three well-defined persistent left-thrown faults, which cross the veins at right angles and throw their eastward extensions up to 150 feet northward.
This was shown on the 550-foot level of the Nettie mines.

At the western edge of the area a strong north-trending fault, known as the Rocker fault, has cut the east-west veins. Westward the surface is underlain by several hundred feet of lake deposits.

GENERAL MINERALOGY OF MANGANESE OXIDES

Pyrolusite

Pyrolusite, the most common manganese ore, is widespread in its occurrence and although it has a variety of modes of occurrence, in all cases it is a secondary mineral. Rarely it occurs in well-developed crystals; usually it occurs in radiating fibers or columns, in reniform coats, dendritic shapes, and also in granular masses.

Dendritic coatings of this mineral are frequently observed on the surfaces of fractures, and coating pebbles. Beds of pyrolusite are found inclosed in residual clays derived from the decay of manganiferous lime-stones. It is also found in veins near the surface with quartz.

Pyrolusite is diagnostically characterized by its low hardness (1 - 2 by the Mohs' scale of hardness), which often causes soiling of fingers. When intergrown with quartz a false hardness is developed. Its specific gravity is 4.7. The luster is metallic, submetallic, or earthy. The composition if manganese dioxide, MnO₂, and
it contains about 63 per cent manganese and 36 per cent oxygen, commonly with small amounts of water.

Psilomelane

This ore of manganese occurs usually with pyrolusite, and its origin and associations are similar to those of that mineral. It is massive and botryoidal, but unlike pyrolusite it is amorphous. Psilomelane possesses a black color, with a peculiar blue cast to the blackness. Its luster is submetallic. It is diagnostically characterized and distinguished from other manganese oxides by its superior hardness of 5 to 6, its lack of crystal structure, and the presence of the blue cast of color.

The ideal chemical formula is $H_4R_2Mn_6O_{20}$, where $R$ is chiefly barium but also includes manganese, magnesium, calcium, nickel, cobalt and copper in traces.

Psilomelane contains varying amounts of barium, but from analyses studied the amount never exceeds 17 per cent barium oxide. Impurities present in most psilomelanes account for a wide range in the barium content. Psilomelane in its pure form has a definite chemical formula, and it has been suffested that the name psilomelane be applied to those manganese minerals which contain 17 per cent barium oxide. 8/

It has also been suggested that psilomelane be used as a group name, rather than one definite mineral
name. Such a series has not been made available in literature.

Wad

The convenient name of Wad is given to black manganese ore composed of a mixture of hydrous manganese oxides, commonly earthy and impure due to the presence of clay or iron oxide.

Manganite

Manganite is a minor ore of manganese found associated with other manganese oxides and, likewise, has a similar origin. It commonly alters to pyrolusite. It may be found in veins associated with the granitic igneous rocks, both filling cavities and as a replacement of the surrounding rocks.

Crystals are commonly grouped in bundles, or in radiating masses. It is intermediate in hardness between pyrolusite and psilomelane. Its luster is metallic or submetallic, and it has a steel-gray to iron-black color.

It is diagnostically characterized by its black color, acicular crystals, intermediate hardness, and brown streak. The chemical composition is given as MnO (OH), containing 62.4 per cent manganese, and 27.3 per cent oxygen, and 10.3 per cent water.

MINERALOGY OF THE MANGANESE OXIDES AT BUTTE

Origin and General Characteristics

Manganese oxides associated with more or less
quartz are found in the upper parts of the lodes. Few of the veins are less than 3 feet wide, most are 6 feet or more, and several range from 40 to 100 feet. Manganese minerals are scarce in the copper veins and are not found in the central copper zone.

The depth of oxidation in the manganiferous area ranges from 60 to 200 feet or more. The lower limit is sharp and the change from oxidized to unoxidized material is abrupt. In the process of oxidation all the vein materials were dissolved except quartz, and the manganese was transported and redeposited as oxides, chiefly in cracks or other open spaces cementing loose material.

Oxidation, it is believed, caused but little change in the manganese percentage in the lodes. Doubtless a considerable enrichment has been caused by the solution and removal of other materials, such as the silica of rhodonite, and the carbon dioxide of rhodochrosite, and also sulphide minerals. In part this enrichment is offset by the scattering of the oxides by transportation away from the vein.

Manganese oxide minerals present in the area are: pyrolusite, psilomelane, manganite, and wad.

Pyrolusite in the Butte Veins

Pyrolusite, most abundant of the oxides, occurs plentifully throughout the oxidized zone. In places it forms solid masses, but more often it is found disseminated
through the veins.

Polished sections studied reveal the light gray color, and hydrochloric acid is the most convenient reagent to give a positive etch test. It reacts vigorously, and gives a brown color to the solution. Its hardness in polished surfaces is intermediate, and a black powder is obtained when it is scratched with a needle.

Since it is the softest of the manganese minerals, it clearly shows the highest polish upon microscopic study with reflected light. Fractured quartz is often found cemented with pyrolusite. The pyrolusite commonly forms an irregular pattern around the quartz grains, and while it is distinct from the quartz, there is a suggestion of replacement.

Psilomelane in the Butte Veins

General Character

This complex oxide of manganese is found as concretionary masses and crusts. On freshly fractured surfaces it displays a typical blue cast of color with a submetallic luster. It is often found lining cavities or vugs which are abundant in the oxidized zone. It cements breccias. It is intimately associated with pyrolusite for which it is often mistaken due to the false hardness given to a specimen containing it by fine-grained quartz which it has either coated or cemented and stained black.
X-Ray Analysis

The use of X-ray diffraction methods for analysis of minerals has been recognized for many years as an accurate means of determining the various constituents of a mineral. Depending upon the complexity of mineral composition, intensive study and experimentation are necessary to determine an applicable procedure. It was the opinion of the writer that by the application of X-ray diffraction it would be possible to obtain positive information concerning mineralogical composition of psilomelane occurring in the Butte area.

There were two main reasons for choosing this method of analysis in preference to spectroscopy: the successful use of X-ray diffraction by previous investigators in their studies of psilomelane, and the fact that X-ray diffraction indicates not only elements present but also the form in which these elements occur in a certain compound. Therefore, it can be readily understood that the application of X-ray diffraction to the study of minerals results not only in an indication of elemental composition but also of mineralogical composition.

A Hayes X-ray machine equipped with a powder-type camera was used in this particular investigation. This machine has a kilovolt range from zero to fifty-nine, and a milliamperc range from zero to fifty. The number of kilovolts and milliamperes which may be used
in any specific determination is limited by the type of X-ray tube being used. All X-ray tubes have a definite maximum power input which they can withstand. Any combination of voltage and amperage which does not exceed this limiting power rating can be used. The two tubes used in this investigation were copper and cobalt and can safely be used up to a power input of 800 watts. 15/

The samples tested were in either the powdered or solid form and were mounted on special steel specimen holders in the powder camera. A variety of holders which allowed samples to be tested in various positions were employed. The powdered samples were ground through 100 mesh. This material was then sprinkled on a narrow strip of cellophane and held in place by Canada Balsam. The reason for using Canada Balsam as a cementing agent was that this substance is amorphous and hence does not interfere with the diffraction pattern which is obtained on the photographic film. The cellophane strip was secured to a Y-shaped specimen holder and placed in the camera. A number of tests were made using this procedure and varying the time, amperage, and voltage elements, but no positive results were obtained.

In this case the reason for negative results could be due to too short a time, the inability to obtain a close compact concentration of psilomelane on the strip, and the type of X-ray tube used. An important factor affecting
X-ray analysis is the type of target used in the X-ray tube. Depending upon the material being analyzed and the X-ray absorption coefficients of the components of this material a specific type of tube should be used. In other words to obtain a satisfactory diffraction pattern it is necessary to use different targets for different elements. The use of the wrong type of tube might possibly result in the inability to obtain any diffraction pattern.

The next step consisted of making a mixture of powdered psilomelane and flour and placing this mixture in a capillary glass tube. Again the reason for using flour was the same as that previously stated for the Canada balsam. The glass tube was then secured to a platform-type specimen holder, placed in the powder camera and rotated through 360 degrees for the duration of the X-ray exposure. Several tests were made employing this procedure varying the aforementioned factors, and also the concentration of psilomelane in the mixture.

Again negative results were obtained and this was possibly due to the wall thickness of the capillary tube which was approximately one-tenth millimeter. Thinner wall thicknesses were impossible to obtain with the equipment which was available. Therefore further testing employing this procedure was impossible.

The third method consisted of placing a paste composed of the mineral-flour mixture in a wedge type speci-
men holder and allowing the mixture to solidify in place. This method also proved unsatisfactory due to the thickness of samples. As a result of these tests it was assumed that no satisfactory results could be obtained using powdered samples and the equipment available. Therefore the next step was to experiment with the sample in a solid state.

Several solid samples were made in various shapes and thicknesses. These samples were then mounted on the various specimen holders and numerous tests were made varying the time, amperage, and voltage. Positive results were not obtained probably due to the inability to obtain a solid specimen of desirable thickness. In other words it was impossible to obtain a plate of psilomelane which was thin enough.

The thickness of material analyzed has a direct bearing on whether or not a diffraction pattern will be obtained because if material is too thick and the absorption coefficient composing this material is too high the X-rays will be absorbed by those elements and will not be reflected off the crystal faces which is necessary for formation of a diffraction pattern. 15/

The tests which were made and conditions under which they were made are shown in the following table.
<table>
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<tr>
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<td>Tube</td>
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<tr>
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It is the belief of this writer that however adverse these results may be it would be possible to obtain positive, accurate results by further experimentation with other types of X-ray tubes and numerous tests varying the time, amperage, and voltage. The time element is an important consideration in all X-ray work because on this factor may hinge the success or failure of an analysis. It should be made clear that the absorbing power of the specimen being analyzed has a very important effect upon the period of exposure of the specimen to the X-rays. This time, depending upon the elemental composition of the sample may vary from five minutes to as high or higher than 48 hours. 15/
Polished Sections

Studies of polished sections revealed that at least three distinct manganese minerals are present in some specimens. These minerals are so very similar in polished surfaces that it is difficult to distinguish them. The lighter shade of gray differentiates pyrolusite from psilomelane, but it is believed that impurities present with this mineral give variety to the gray color.

Psilomelane has a light gray color in reflected light. On a polished surface it possesses an intermediate hardness which can barely be scratched by a needle. Anisotropism was feebly displayed on a few specimens, and most were isotropic.

The reagents employed in conducting etch tests were those recommended by M. N. Short. They included nitric acid, hydrochloric acid, potassium cyanide, ferrous chloride, potassium hydroxide, aqua regia, and hydrogen peroxide.

Most of the oxides of manganese were chemically inert to the reagents suggested. A concentrated solution of hydrochloric acid, however, placed on an apparently homogenous surface developed a pronounced etch which after washing revealed a peculiar pattern of two minerals irregularly and intimately arranged. One mineral which possessed a brown surface stain was perhaps pyrolusite, while the other with a gray surface stain was psilomelane. Dilute (1:1 and 1:10) solutions gave the same reaction but were less pronounced.
and the time of reaction was longer.

A three per cent commercial solution of hydrogen peroxide when applied to a polished surface effervesced vigorously but when washed after one minute left no stain. Although washing was prolonged until five minutes a stain failed to remain.

From the observations made on the etch tests it is thought that perhaps more minerals are present, but the slight contrast and minute size of crystals do not allow them to be distinguished.

RECENT DEVELOPMENTS

The great need for manganese during World War II directed attention to the manganiferous deposits of the Butte area. Excluding the carbonate ores, the manganese oxides found in the upper portions of the veins have proved a worthy source of the metal.

Although the great bulk of the material had been extracted previously as a gangue of silver ores and used as a smelting flux, the recent mining of abandoned small outcrops and deposits produced a substantial tonnage. Undeveloped portions of the north Nettie vein were exploited. At one point an inclined shaft was sunk to sixty feet; at another the outcrop was gouged along the strike to a depth of 100 feet.

The reopening of the Burlington vein also resulted
in the successful production of manganese, and encouraged
the present development of silver-bearing deposits. Fur-
thermore, a dozen small operations were carried on in the
monzonite area. Although it was impossible to determine
the exact tonnage or procure figures regarding tonnage of
the individual leases, the wartime activity in the area
indicated that the combined output was satisfactory.

The Domestic Manganese Plant in Butte which operated
in conjunction with the Office of Metals Reserve, a Federal
project, bought and processed the "black" manganese. This
convenient arrangement stimulated interest in the mining of
manganese ores. From the later months of 1942 until early
1944 mining in this area received its greatest impetus. Be-
tween 30,000 and 40,000 tons of ore were mined and stock-
piled at the Domestic Manganese Plant.

This unimpressive tonnage does not truly portray the
picture. Mining was carried on by crude methods; and the
individual temporary operations, speedily undertaken with
small hoists, fragile head frames and a minimum amount of
timbering, were not conducive to a large production. Never-
theless, because of the efforts of enterprising miners,
this abandoned unpopulated portion of the "richest hill on
earth" did contribute in its small way to the production
of a strategic metal of which the United States was in
great need.
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10. Weed, Walter H., Geology and Ore Deposits of the Butte District, Montana, U. S. G. S. Professional Paper 74
PHOTOMICROGRAPHS OF POLISHED SECTIONS OF MANGANESE OXIDE MINERALS

Showing concretionary banding.  x 16
PHOTOMICROGRAPHS OF POLISHED SECTIONS OF MANGANESE OXIDE MINERALS

A. Botryoidal structure of psilomelane. x 2

B. Quartz and pyrolusite veinlets in a psilomelane matrix. x 16

C. Pyrolusite surrounding a cavity left by quartz. x 2

D. Quartz inclusions in psilomelane. x 16
A. View showing a portion of the area: The Nettie dumps in the foreground; the Orphan Girl mine, and the Montana School of Mines. Looking southwest from the Hibernian

B. View showing the Czarina outcrop. Looking south.

VIEWS OF THE WESTERN PORTION OF THE BUTTE DISTRICT
Views showing active development of the north vein of the Nettie Group. Looking northeast.
Plate V

Views of the Burlington workings, showing well-defined vein walls.

Looking west.
A. View showing the surface of the Minnie Jane Mine, the largest of recent producers. Looking west.

B. View showing a typical small lease, with inclined shaft following the dip of the Mono vein. Looking west.

VIEWS OF PROPERTIES IN THE WESTERN SECTION OF THE BUTTE DISTRICT