

Manganese Investigation in Keweenaw County, Michigan

by

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ABSTRACT

Geological, geochemical, mineralogical and geophysical methods were used to investigate a manganese occurrence near Copper Harbor, Michigan, in Keweenaw County. Manganese oxides and silicates are present in calcite veins near the contact of the Portage Lake Lava Series and the overlying Copper Harbor Conglomerate. The deposits are small but very rich. Twelve hundred tons of ore mined from the Manganese Exploration south of Copper Harbor in the early 1880's assayed 55.7% manganese. Geophysical methods were not useful in identifying the manganese veins. Soil geochemistry proved to be the most promising method to identify the presence of the deposits using Mn, Cu, and V as indicator elements. Geochemical methods may be useful in finding other deposits, particularly if coupled with fracture analysis utilizing aerial photographs, as the manganese veins appear to be in fissures which cut the rock strata at steep angles.

TABLE OF CONTENTS

Abstract.....	1
Table of Contents.....	1
List of Figures	2
List of Tables.....	2
Introduction	2
Location and Accessibility	2
Acknowledgments	2
General Procedures	3
Local Mines and Mineralization.....	3
Previous Work.....	3
Geologic Setting.....	3
Regional Geologic Setting.....	3
Rock Units and Structures	3
Basalt.....	3
Conglomerate	3
Structure	4
Manganese Occurrences	4
Similar Deposits	4
Mineralogy and Chemistry of Rock Samples.....	4
Sampling	4
Procedures and Analysis	4
Mineralogy.....	4
Manganese Exploration.....	4
Ore Samples	5
Lake Manganese Vein.....	6
Chemistry	6
Soil Geochemistry.....	7
Introduction.....	7
Sampling and Analytical Procedures	7
Soil Chemistry Data Interpretations	7

Geophysics.....	8
Introduction.....	8
Procedures.....	8
Electromagnetic Survey.....	8
Self-Potential Survey.....	9
Magnetic Survey.....	9
Summary of Geophysical Methods.....	9
Conclusions on Manganese Potential and Prospecting Techniques.....	9
Recommendations.....	10
Appendix A.....	10
Appendix B.....	11
Appendix C.....	11
References.....	12

LIST OF FIGURES

Figure 1. Location map of the Manganese Exploration and the Lake Manganese Vein.....	2
Figure 2. Geologic map of the Manganese Exploration site.....	3
Figure 3. Probable paragenetic sequence at the Manganese Exploration and the Lake Manganese Vein.....	6
Figure 4. Surface plots of Mn, Cu, As, Sb, and V as determined for the A soil horizon.....	8
Figure 5. Surface plots of Mn, Cu, As, Strand V as determined for the B soil horizon.....	9

LIST OF TABLES

Table 1. Composition of manganese minerals.....	6
Table 2. Partial whole rock geochemistry.....	7
Table 3. Geochemical analyses of rock samples by Nuclear Activation Services.....	7

INTRODUCTION

Manganese is essential in the manufacture of steel and no substitute has been found. More than 90 percent of consumption in the United States is by the steel industry. The United States is completely dependent on foreign sources for manganese and imports all of its manganese from Brazil, Gabon, South Africa, France, and India. Deposits and reserves in the United States are small and economically unfeasible to mine at the present time.

This is a preliminary investigation of an unusual manganese occurrence in Keweenaw County, Michigan. This site has been mined and produced 1,200 tons of manganese ore. This investigation used geologic, geochemical, mineralogical, and geophysical methods to characterize this manganese occurrence. The characterization may be useful in finding other hidden manganese deposits of this type.

LOCATION AND ACCESSIBILITY

The Manganese Exploration is located near Copper Harbor, Michigan, south of Lake Fanny Hooe and Fort Wilkins State Park (Fig. 1). A vein of calcite containing manganese is found in the west bank of an outlet stream on the north shore of Lake Manganese, and is hereafter referred to as the Lake Manganese Vein. The Lake Manganese Vein is located .75 miles due west of the Manganese Exploration. The area of study is within the Lake Medora and Fort Wilkins quadrangles and includes the northern parts of sections 4 and 5, T58N, R28W.

Access by car is good south from the town of Copper Harbor. The Lake Manganese Vein is easily reached by a trail that follows the north shore of the lake. The Manganese Exploration can be reached with a 4-wheeled drive vehicle along a two-track road that is marked as part of the Copper Harbor cross-country ski trail. The trail runs along the base of the escarpment formed by the resistant Copper Harbor Conglomerate and the Portage Lake Volcanic Series.

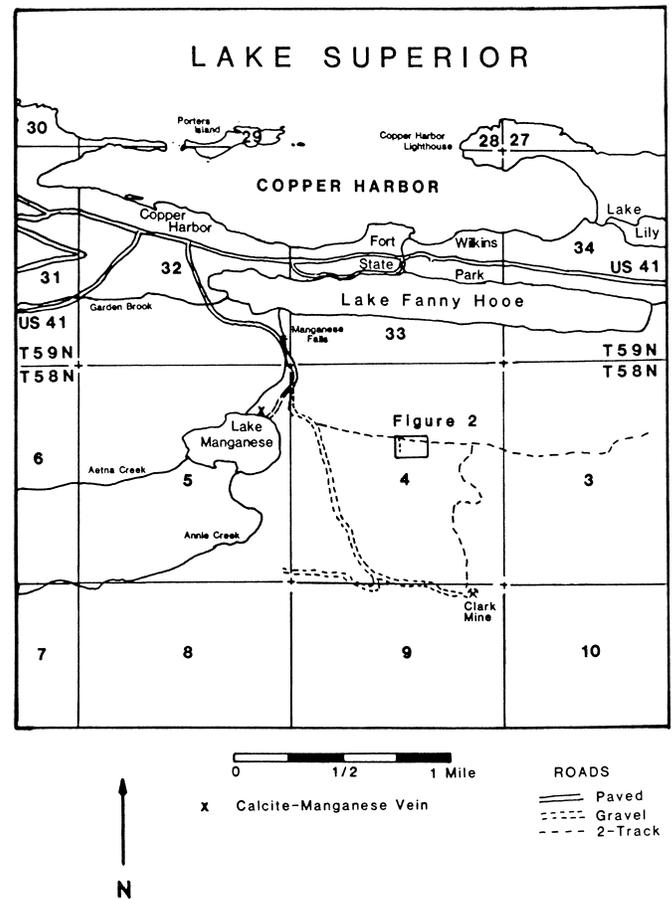


Figure 1.--Location map of the Manganese Exploration (area outlined as Figure 2) and the Lake Manganese Vein (X on north shore of Lake Manganese).

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by the Department of Geology and Geological Engineering and the Minerals Group of the Biosource Institute at Michigan Technological University. The work was supervised by Drs. Theodore Bornhorst, Allan Johnson, and Gordon Frantti. Mr. Jack VanAlstine was the project coordinator for the Geological Survey Division of the Michigan Department of Natural Resources. Dr. Johnson was also the project manager. The assistance of Eric Hepp and Christopher Williston in the field was greatly appreciated, as were the revisions made by Rodney C. Johnson.

GENERAL PROCEDURES

Geologic field work was conducted during the fall of 1986. Mapping was done at a scale of 1:500 by the compass and pace method. A grid for soil geochemistry and geophysics was taped in and stations flagged at 50 foot intervals (Fig. 2). Both A and B soil horizons were sampled. Rock samples were collected from outcrop for mineralogical, geochemical, and x-ray analyses. However, due to lack of outcrop the majority of rock and ore samples came from the mine dump surrounding the deposit. The geophysical field work was completed during the spring of 1987.

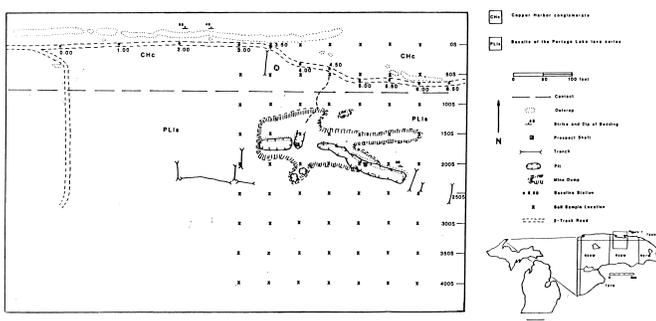
LOCAL MINES AND MINERALIZATION

Copper mines in the Copper Harbor area were small fissure deposits that proved largely unsuccessful.

The Hays exploration (now in Fort Wilkins State Park) mined a fissure in the Copper Harbor Conglomerate containing calcite and copper oxides. This occurrence is directly to the north of the Manganese Exploration.

Immediately to the south of the Manganese Exploration is the Clark mine. This mine was the largest in the area, and produced over 188,000 pounds of native copper from a fissure.

Figure 2.--Geologic map of the Manganese Exploration site showing geochemical sampling grid.



Numerous prospects dot the area. All are small and many are nothing more than exploration trenches.

Several calcite veins are found associated with vertical fissures in the area. These fissures cross the strike of the lava flows and conglomerate beds at high angles. Calcite was mined from one fissure (up to ten feet wide) for the manufacture of mortar during the mid 1800's.

According to one report, small amounts of manganese oxides were found at the East Exploration, a quarter mile to the east of the Manganese Exploration. These oxides were found intergrown with native copper.

Mines in this area were small and many contained unusual mineral assemblages. Manganese minerals and oxides of copper, which are rare in other parts of the Keweenaw Copper District, are locally abundant in this area.

PREVIOUS WORK

Based upon the literature search, this area has not received extensive geologic study. The most complete coverage was done by Butler and Burbank (1929, p. 59) who state:

"At the Manganese Mine, near Copper Harbor, it (manganite) occurs with other manganese minerals as a 'vein', essentially coinciding with an amygdaloid a short distance below the Great Conglomerate. The 'vein' was opened for a few hundred feet along the strike, and some ore was shipped from the mine."

"Pyrolusite (MnO₂) occurs at the Manganese Mine, near Copper Harbor."

Cornwall (1955) reports that 1200 tons of manganese ore assaying 55.73% manganese was shipped from the deposit between 1881 and 1883.

The manganese silicate minerals of this deposit were studied by Moore (et al., 1979), and a new species (macfallite) was reported.

GEOLOGIC SETTING

REGIONAL GEOLOGIC SETTING

The bedrock units of this area are all Middle Proterozoic in age. The rocks consist of basalts of the Portage Lake Lava Series and the Copper Harbor Conglomerate. The basalts are stratigraphically at the top of the Portage Lake Series. Outcrop is limited, and individual flows (if more than one does exist in the field area) cannot be distinguished.

ROCK UNITS AND STRUCTURES

Basalt

The basalts of the Portage Lake lava series found in the area are amygdaloidal flows that have been slightly altered. These rocks are brown to reddish in color and contain numerous vesicles. Nearly one half of these vesicles are filled with calcite and minor laumontite. The vesicles range in size from one quarter to one inch in diameter.

Conglomerate

The Copper Harbor Conglomerate is a red-brown pebble to boulder conglomerate, with small amounts of

MINERALOGY AND CHEMISTRY OF ROCK SAMPLES

SAMPLING

Rock samples were collected from the area for chemical and mineralogical analysis. Samples were taken from outcrop when available. Host rock samples were easily obtainable from outcrop, but in situ vein material was difficult to secure. One vein in basalt was uncovered on the south wall of the pit at the Manganese Exploration. With limited outcrop, the majority of the samples were collected from the mine dump. Samples were taken to represent each of the ore types that were seen.

The vein at Lake Manganese was also sampled for study.

PROCEDURES AND ANALYSIS

Eleven samples were selected for geochemical analysis. These samples were chosen to represent the differing ore types found. Two of these eleven samples were of basaltic flow top, which is the host rock at the Manganese Exploration site. Three of the samples were taken from the Lake Manganese Vein.

Geochemical analysis was determined by X-ray fluorescence following the method of Rose, et.al. (1986) and a suite of elements including silver were determined by Nuclear Activation Services. Thin sections were cut from these samples for mineralogical analysis. In addition to these eleven samples, several others showing variations in mineralogy and texture were chosen for thin sections, making 14 sections in all. Five polished mounts were prepared for identification of opaque minerals.

MINERALOGY

Manganese Exploration

The host rock for this deposit is amygdaloidal basalt. The basalt is reddish-brown to brown in color with up to 25% vesicles by volume. The vesicles are filled with calcite and minor laumontite. The calcitic rock found on the dump contains altered fragments of basalt. These basalt pieces are reddish and grade into browner basalt with calcite vesicles. Some calcite in the brecciated areas shows a comb-structure around the basalt fragments.

Three samples were microscopically studied. FT-1 is a red-brown basalt with calcite vesicles. 550-1 is a brown basalt with vesicles, only one half of which are filled. FT-3 (a and b) are sections from the same sample of brecciated basalt with calcite cement. These samples represent the three varieties of basalt host rock.

Microscopically, the basalts show microlites of plagioclase (30-50%) set in a dark brown matrix of devitrified glass. The plagioclase microlites are "dirty"

sandstone. The clasts are mainly rhyolite and rhyolite porphyry, are well rounded and range in size from 1 to 8 inches in diameter. The matrix is sand derived from the same source as the pebbles. Calcite cement can be found in some places around and between the clasts. Pink laumontite is sometimes associated with the calcite. Sand lenses and beds up to 6 inches thick are present. The rock is well indurated.

Structure

There are no major structures to be found in the area. The rock units strike E-W and dip to the north at 40 degrees.

MANGANESE OCCURRENCES

There are two occurrences of manganese minerals in the area of this study (see Fig. 1). The first and most important is the Manganese Exploration. Here, the manganese minerals are found in calcite veins in the amygdaloidal tops of the basalt flows. The manganese minerals have replaced calcite. Details of the mineralogy and paragenesis will be discussed later.

The second occurrence of manganese mineralization is on the north shore of Lake Manganese. At this location manganese minerals are found in a calcite vein at the base of the Copper Harbor Conglomerate. The vein is 12 inches thick and appears to be conformable with bedding in the outcrop. Detailed descriptions of these features are presented in a later section of this report.

SIMILAR DEPOSITS

The mineral assemblages and associations found in these veins are unique, but deposits showing similarities are known.

The manganese deposits of the Olympic Peninsula of Washington are also found in basalt (Lee, 1976 and Park, 1946 and 1942). These deposits cross-cut limestone beds associated with the basalt. Manganese mineralogy is somewhat similar and is also associated with copper.

The manganese deposits of the Oriente Province, Cuba, are similar in mineral assemblage. (Simons and Straczek, 1958). These deposits are found in large volcanic piles of latitic tuffs. Mineral assemblages are low temperature and hypogene in nature.

Vein deposits in the Southwestern United States also show similarities to this deposit. (Hewett, 1964). These deposits contain manganese oxides and are found in a wide variety of rock types. Some deposits are calcite rich. All deposits are low temperature and are classed as hypogene occurrences.

and some appear to be altered to calcite. Most of the plagioclase microlites are turbid and appear to have been altered to a fine grained gray-tan material, usually surrounding tiny remnants of unaltered plagioclase. Some plagioclase crystals show cores with opaque dust.

The vesicles in these basalts contain clear calcite crystals. Some vesicles have rims of tiny quartz(?) crystals. Calcite fills the rest of these vesicles. The dark matrix of these rocks show many opaques. Some of these opaques show red edges, suggesting hematite.

Ore Samples

Most of the ore samples were collected from the mine dump found around the old workings of the Manganese Exploration. The host rock here is the basalt described earlier. However, two samples were collected in place; these are identified as 450-2Cu and 450-V, and were collected from the same outcrop of calcitic material found along the south wall of the pit.

Heinrich (1974) outlined four categories of manganese ore from this deposit. These divisions are useful in this study. They include:

- 1) Calcite with grain boundary veinlets of black manganese oxide minerals. Some calcite becoming black due to replacement by dusty manganese minerals.
- 2) Black and white ore. 50% each of calcite and black manganese minerals by veining and replacement of calcite.
- 3) Red and white ore. Similar to 2 but with red-brown manganese silicates instead of black manganese oxides.
- 4) Black ore. Minor calcite remnants in a black, massive, fine grained mixture of manganese oxides and radial fibrous aggregates of silicates.

Samples were chosen to represent each of these ore types. Eight samples were studied microscopically to determine mineralogy and paragenetic sequence.

Samples MD-12 and MD-14 represent the calcite grain boundary veinlet category. These specimens show relatively large calcite crystals and black manganese oxides. The manganese minerals grew along grain boundaries and along cleavage traces inside individual grains. Dendritic growths and radiating sprays of brown manganese silicates are associated with the oxides. The black opaque found in these samples is braunite. These samples represent early stage replacement of calcite by the manganese minerals.

Black and white ore is represented by samples MD-15 and MD-19. More advanced replacement can be seen in these samples. Oxide minerals (braunite, pyrolusite) and silicates (macfallite, orientite) have replaced up to one half of the calcite in the samples. Replacement is from the grain boundaries inward, with knots of silicate minerals and intergrown oxides up to 10mm in diameter. Needles of pyrolusite project in towards the centers of

calcite crystals. Pyrolusite needles have grown from black masses of braunite grains, suggesting that the pyrolusite formed later than the braunite. MD-15 shows large (3-5 mm) sprays of pyrolusite and manganite. These minerals have replaced large calcite crystals with cleavage faces up to 40mm across. Small amounts of braunite are associated with the pyrolusite, which has replaced manganite. Calcite crystals are now becoming severely eroded, representing advanced replacement by the manganese minerals.

Red and white ore is similar to black and white ore. Red-brown silicate minerals are found instead of black oxides. Sample 350-2A shows dendritic and radiating knots of orientite and macfallite replacing calcite grains. Growth is most intense along calcite grain boundaries, but the interiors are also replaced. Braunite and pyrolusite are also associated with these silicates.

The black ore is the richest type found. Samples MD-20 and 450-V represent this category. Nearly complete replacement of the calcite has occurred with only remnant cores of calcite occasionally found. This ore type features complexly intergrown pyrolusite, manganite, braunite and manganese silicates. The silicates are found as knots surrounded by black oxides. Colloform pyrolusite growths and felted masses are found around some of the knots.

Some unusual minerals are found in samples 450-2Cu and OR-1. 450-2Cu was found in situ in a vein, and was selected for study because it contains native copper. The copper is found as small pieces with associated green copper alteration minerals. Surrounding the copper are fine grained zeolites which occur as laths and appear to have formed at the same time as the calcite. Manganese silicates are seen rimming the calcite grains and growing in the zeolites. Dusty black opaques are also found in some of the zeolites.

A brown platy mineral was found in OR-1 that proved to be unusual. This material is light pinkish-brown and very fine grained. Microscopically, it turned out to be dirty quartz aggregates. The "plates" were formed by the removal of some unknown mineral after the formation of the quartz, leaving the quartz plates as casts. The quartz pre-dates the manganese minerals, because oxides and silicates can be seen replacing both the calcite and the quartz in the sample.

Thin section, polished section, and hand specimen observations were used to establish a paragenetic sequence. Appendix A contains microscopic identification notes for the samples. Figure 3 gives the paragenesis. There is much overlap in the sequence of the crystallized phases. Fissure calcite is obviously first. Orientite, braunite, manganite, and macfallite all appear to have formed at the same time. Clear, replacement calcite appears to have formed slightly before these minerals. Pyrolusite appears to be late. It is not completely clear where the zeolites, native copper, and quartz belong to this sequence. It seems probable that these minerals formed at the same time. They are put

into the paragenetic sequence based on limited observations.

Brown manganese silicates were chosen from two different samples for x-ray diffraction analysis. Both were identified as macfallite. Macfallite appears to be much more abundant in this deposit than orientite. Macfallite is a new species (Moore, 1979) and the only known locality of this mineral is at this deposit, where it is quite abundant. Table 1 lists the compositions of the manganese minerals found in this occurrence.

Figure 3.--Probable paragenetic sequence at the Manganese Exploration and the Lake Manganese Vein.

Early	Fissure (coarse) calcite - zeolites - native Cu - quartz orientite - braunite replacement calcite macfallite - manganite
Late	pyrolusite

Based on the mineral relationships, the deposit was formed by replacement of calcite by manganese minerals. Manganese bearing solutions reacted with the calcite, producing calcium-manganese silicates and manganese oxides. These fluids probably represent late stage copper mineralization activity, but the exact timing relationships is not known.

Lake Manganese Vein

The vein at Lake Manganese consists of calcite and manganese minerals in Copper Harbor Conglomerate. This vein is approximately one foot thick and follows what appears to be bedding in the outcrop. Three samples were studied from this location; V-4, V-3, and V-3Top.

V-3Top was taken from the upper part of the vein. This sample contains large calcite crystals up to one inch long. These large crystals are zoned and are "dirty" or turbid under the microscope. A zone of pinkish, fine grained, clean calcite cuts the large calcite grains. Remnant pieces of "first stage calcite" (large crystal) can be found in the "second stage calcite" (pink, fine grained). Small stringers and "trains" of minute opaque crystals are found in the pink calcite. This pinkish calcite formed after the main fissure calcite.

Sample V-3 was collected immediately below V-3Top. This specimen contains calcite with brown layers. These layers are not separate, but consist of brownish areas within the calcite. The calcite in this sample is the same as the "first stage calcite" in V-3Top. Microscopically, these brown layers are caused by dendritic growths in the large calcite grains. The dendrites are composed of a very fine grained, unidentified material.

The center section of the vein contains stringers of black dust in calcite. Sample V-4 is from this section. This rock contains the same coarse grained "first stage calcite" seen in the two previous samples. The black mineral is forming along the calcite grain boundaries. This mineral was identified as braunite using reflected

light. Minor amounts of pyrolusite are found replacing the braunite. Quartz is found in very minor quantities in all of these samples.

Table 1. Composition of manganese minerals encountered at the Manganese Exploration and the Lake Manganese Vein.

Mineral	Composition
Braunite	$Mn^{+2}Mn_6^{+3}SiO_{12}$
Macfallite	$Ca_2Mn_3^{+3}(SiO_4)(Si_2O_7)(OH)_3$
Manganite	$MnO(OH)$
Orientite	$Ca_2Mn^{+2}Mn_2^{+3}Si_3O_{10}(OH)_4$
Pyrolusite	MnO_2

The manganese minerals and fine grained calcite appear to have formed at the same time. The brown dendritic fine grained mineral found in the calcite was identified as orientite by Moore (1979, p. 326). These minerals formed after, and began to replace, the coarse grained fissure calcite.

CHEMISTRY

Eleven rock samples were prepared for chemical analysis. Quantitative measurements of major and trace elements were made using x-ray fluorescence (XRF) techniques, except Ag which was determined by Nuclear Activation Services (Table 2).

Trace elements were chosen on the basis of late-stage, low-temperature formation of the deposit. These elements also gave insight for analysis of soil samples.

In addition to these analysis, all rock samples were sent to Nuclear Activation Services for silver determinations. Samples MD-14, MD-19, and MD-20 were sent for quantitative determinations for a suite of elements (Table 3).

The ore samples show low levels of Mg and Fe. This reinforces the idea that the calcite is pure, and there is almost no Fe in the system. The analyses of amygdaloidal basalt show slight depletion of MgO when compared to average compositions of the Kearsarge and Scales Creek flows. Other major element compositions compare well with these Cu bearing Keweenaw lava flows.

Crustal abundances of Mn average about 0.16 wt. % in mafic rocks and 0.06 wt. % in felsic rocks. Ore grade deposits must contain between 25 and 50 wt. % manganese. The samples of "black ore" are high in manganese. Samples MD-20 and MD-19 contain 55.17 wt. % MnO and 21.90 wt. % MnO respectively. Other samples contain between 8 and 10 wt. % MnO. Averaging the manganese content of the 6 ore samples, the deposit contains an average of 17.42 weight percent MnO. However, some of the Mn is tied up in silicate minerals, where it would be difficult if not impossible to extract.

Table 2.--Partial whole rock geochemistry.

	MD-20	550-1	MD-14	450-2CU	MD-19	U-4	350-2R	FT-1	MD-12	V3TOP	U3
MgO	0.12	2.89	0.18	4.47	0.44	0.13	0.12	5.08	0.10	0.02	0.11
Fe2O3	0.42	12.61	0.03	3.45	1.06	0.00	0.07	10.57	0.02	0.00	0.09
MnO	95.17	0.35	8.22	0.45	21.90	0.66	8.97	0.21	9.81	0.03	0.04
SiO2	10.48	47.33	1.05	18.69	14.92	1.09	7.35	37.98	1.92	0.76	1.07
CaCO3	14.91	8.74	68.41	58.33	51.45	70.90	66.68	22.06	68.87	71.22	71.15
Hr	427000	2680	63700	3540	170000	5090	69400	1660	76000	341	407
S	680	63	172	131	778	347	855	88	332	1306	963
As	1	17	4	10	8	10	12	7	18	5	5
Pb	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cu	1880	34	496	663	4230	64	1280	5	2670	5	5
Ni	15	76	16	42	23	15	20	105	17	15	15
Sb	16	9	45	56	25	35	38	24	39	47	35
V	638	336	8	57	494	0	148	314	56	2.5	2.5
Total	81.38	71.92	77.89	85.45	90.17	72.68	83.37	76.08	81.02	72.13	72.55

Table 3.--Geochemical analyses of rock samples by Nuclear Activation Services.

	MD-19	MD-20	450-2CU
Wt. %			
Na2O	<0.05	<0.05	0.29
TiO2	0.12	0.045	0.34
P2O5	0.02	0.01	0.04
ppm			
Ba	200	700	300
Br	<5	<5	<5
Cd	1	1	<1
Cr	80	90	80
Cs	<2	<2	<2
Hf	<1	<1	<1
Hg (ppb)	36	44	28
Mo	30	100	<5
Pb	<2	6	2
Rb	<30	<30	<30
Sc	4.2	1.3	13.5
Se	<5	<5	<5
Sr	<1000	<1000	<1000
Ta	<1	<1	<1
Th	0.5	<0.5	1.7
U	1.9	2.8	1.2
Zn	22	50	46
La	8	6	16
Se	9	9	21
Nd	<10	<10	10
Sm	0.8	0.8	1.8
Eu	0.4	<0.2	0.7
Yb	0.4	0.7	1.2
Lu	0.1	0.11	0.18
Ir (ppb)	<20	<20	<20

SOIL GEOCHEMISTRY

INTRODUCTION

Geochemical prospecting for Mn is difficult at best as it is widespread in the earth's crust, and background contents in rocks and soils are high and variable. Mn is immobile under most surface conditions. Oxides of manganese are commonly precipitated under surface weathering conditions, are insoluble, and these precipitates are known to scavenge mobile elements from the environment.

In areas of residual soils, Mn anomalies may lead to geochemical prospecting successes because of the insolubility of Mn oxides. Where the soil has been transported, there may be no surface sign of the deposit below. Due to the fact that manganese is easily

precipitated under surface conditions, positive anomalies are very often misleading.

SAMPLING AND ANALYTICAL PROCEDURES

During the fall of 1986, a grid network was established over the known location of the manganese deposit (see Fig. 2). This grid was taped in, and stations were flagged at 50 foot intervals. This grid covered an area 300 feet by 400 feet. Seven north-south traverses were taken along an east-west baseline. Along each of these traverses, nine stations were marked at 50 foot intervals, beginning with 0 feet south (0S) and ending with 400 feet south (400S) (see Figure 2).

At each station, a hole was dug to bedrock when possible, or until no change was seen in the soil. If the sampling station was on or near a mine dump, the hole was located to minimize the effects of the disturbed ground. Some stations were on rock piles (from the mining activity) so no soil samples were collected.

Two samples were collected from each hole. The first sample was from the B horizon. This was sampled first to remove contamination from the A-horizon, which was sampled second.

Samples were chosen from traverses 3+00, 4+00, 5+00, and 6+00 for A-horizon analysis. Where gaps existed in the traverses due to mine dump interference, samples from adjacent traverses (3+50, 4+50, 5+50) were substituted. In all, 32 samples were analyzed from the A-horizon. Two traverses (4+00 and 5+00) from the B-horizon were selected, producing 14 samples.

In addition to the XRF analysis, the A-horizon soils were analyzed for total volatiles by Loss on Ignition (LOI) by heating at 100°C for 12 hours (overnight) followed by heating at 1,000°C for two hours.

Both the A and B horizon soil samples were analyzed for Mn, Cu, As, Sb, and V (see appendices A and B). Four samples from each horizon were sent to Nuclear Activation Services for silver analysis. All of the silver values were below the detection limit for that element. As and Sb were chosen for analysis because of their association with low-temperature, hot spring type deposits.

SOIL CHEMISTRY DATA INTERPRETATIONS

Correlation coefficients, a measure of the linear relationship between variables, were calculated for the data to check for intervariable correlations. Correlations between Mn and Cu and between Mn and LOI were high in the A-horizon data. In the B-horizon, Mn was well correlated with Sb and V.

Surface plots were made for the A and B-horizon soils (Fig's. 4 and 5). In areas of missing data, due to mining interference, data points were filled in from adjacent

traverses. Fill-in data points came from the 3+50, 4+50, and 5+50 traverses. One station, 5-150, had exceptionally large anomalous values of Mn and Cu in both the A and the B horizons. This station was reviewed in the field notes, and was found to be located on the edge of a mine dump. Therefore, the data for this station was dropped.

In the A (Fig. 4) and B-horizon soils (Fig. 5), amounts of all surveyed elements (Mn, Cu, As, Sb, V) were low at the north end of the traverses. This end of the sampled area is underlain by the Copper Harbor Conglomerate. Upon crossing over to the basalt and manganese deposit, numbers were generally higher, but also showed much variability. In general, the elemental values were higher over the deposit. The quantities seemed to level off to the south, away from the deposit.

Mn, Cu, and V indicate increased values immediately over or slightly to the south of the known location of the mineralized vein. While the plot of Sb exhibits a similar distribution, the plotted values are all below or close to detection limits for this element. Although Cu showed an anomaly over the ore zone the use of Cu alone would be confusing in the Keweenaw as an indicator of manganese deposits.

Profiles from traverse 5+00 were unique. The values for each element were high near the deposit, but the peaks were all on the south side of the deposit. Some profiles from other traverses showed similar behavior. This may be due to glacial action. Movement of the Pleistocene glaciers in this area was from the north, and this may have transported material from the deposit and left it on the southern side. However, a more probable cause is that the concentrations are greater because basalt is the bedrock, and the influence from the conglomerate is becoming progressively diluted.

In conclusion, none of the elements show obvious anomalies in the profiles. When used in conjunction with each other Mn, Cu, and V may be of value in indicating deposits of this type. Extension of the traverses to the north and south may further help to define the background and anomalous values of Mn, Cu, and V in the immediate vicinity.

GEOPHYSICS

INTRODUCTION

The Mn-oxide deposit under investigation appears to have no outstanding diagnostic geophysical characteristics that would prove useful in finding similar concentrations of the metal. Mn-oxide deposits are non-magnetic except possibly for a rare associated magnetic mineral. The relatively high specific gravity of manganese minerals may make gravimetric techniques useful, especially if the deposit does not contain voids or depleted areas within the ore body. There is not much information in the literature to suggest appropriate methods for geophysical evaluation methods.

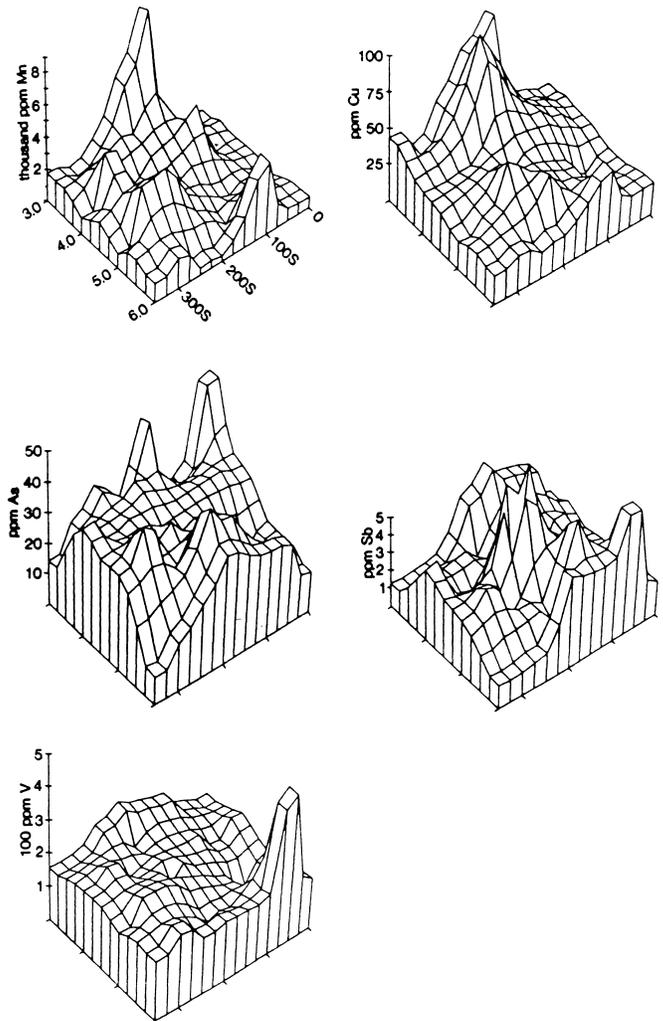


Figure 4.--Surface plots of Mn, Cu, As, Sb, and V as determined for the A soil horizon. Note that Sb values are near or below detection limit (3ppm) for XRF.

PROCEDURES

After discussions with geophysicists in the Department of Geology and Geological Engineering at M.T.U. concerning possible geophysical methods, three techniques were decided upon. Very Low Frequency Electromagnetics (VLFEM), Self-Potential (SP), and magnetic surveys were selected for trial in the field. The surveys were run over the grid established for geochemical sampling. This work was done in the spring of 1987.

Electromagnetic Survey

The electromagnetic survey was done with a Geonics EM-16 instrument. The survey was run over traverses 3+00, 4+00, 5+00 and 6+00. Readings were taken every twenty feet along the traverses. The data show a maximum dip angle range of only 4 degrees. These readings lie within the range of error of the instrument and therefore do not define a conductive body. Thus, VLFEM is not a promising method for vein-type Mn-oxide deposits.

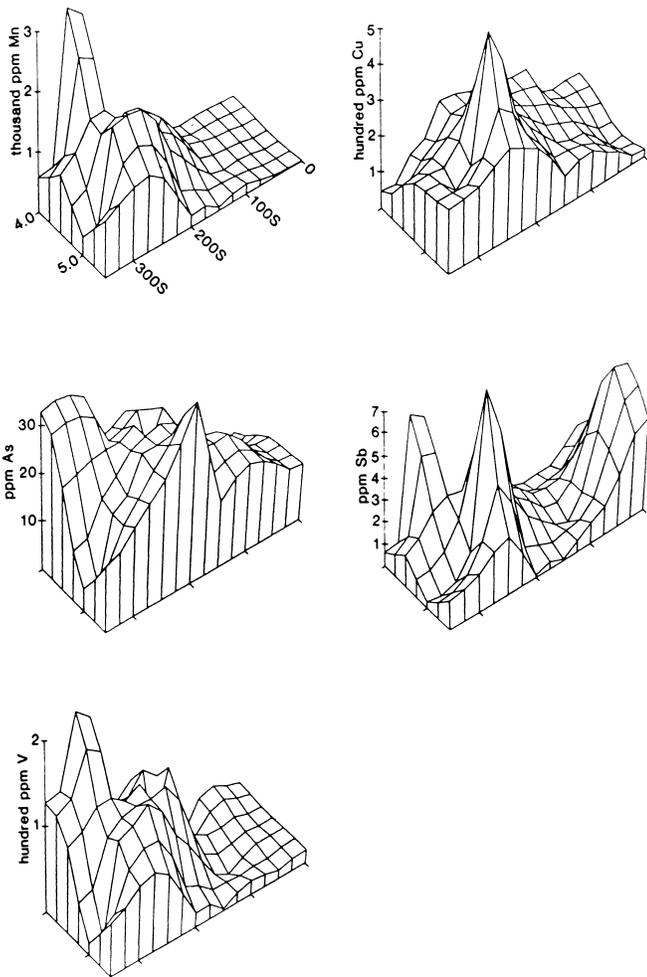


Figure 5.--Surface plots of Mn, Cu, As, and V as determined for the B soil horizon. Note that Sb values are near or below detection limit (3ppm) for XRF.

Self-Potential Survey

Self-potential (SP) measures spontaneous electrical potentials caused by electrical reactions associated with mineral deposits. SP traverses were run over lines 4+00, 5+00, and 6+00, with readings taken at 25 foot spacings. Readings were taken in millivolts between two porous pot electrodes. The electrodes were placed in contact with moist soil to insure good electrical connection. One porous pot was maintained at the zero station for every reading, while the second electrode was moved to successive stations. Four measurements were taken at each station and the average value was recorded. The SP data appear to be random with values ranging from -17 to +7 millivolts.

Magnetic Survey

A magnetic survey was performed along traverse 4+00. The total field was measured using a proton precession magnetometer. Three readings were taken and averaged at each of the stations at twenty five foot spacing. No correction was needed on the data since the entire survey was completed in a very short period of time on the small grid.

The magnetic profile shows a gradient increasing to the south. The gradient in the data is probably due to the contact between the conglomerate and the basalt. This contact lies between stations 50S and 100S. The basalt (to the south) should produce a higher magnetic background, which is the case. There are no large peaks in the data, the highest being 75 gammas at one station. This small peak could be caused by stray objects containing iron such as a relic from old mining activity.

SUMMARY OF GEOPHYSICAL METHODS

The geophysical techniques used were not capable of defining useful anomalies at the Manganese Exploration site. This Mn-oxide deposit is non-magnetic and non-conductive, ruling out several geophysical methods. Also, the small size and mineralization type (in calcite) makes normal gravity techniques unfeasible. It is possible that a micro-gravity survey at very close station spacing could define the vein area. It is also possible that selected IP (induced potential) electrical methods might be useful. The limited extent of the geophysical portion of this study is inadequate to support definitive conclusions about the potential usefulness of geophysics in manganese exploration in this area.

CONCLUSIONS ON MANGANESE POTENTIAL AND PROSPECTING TECHNIQUES

1. Manganese deposits of this type are believed to have formed by the replacement of calcite by Mn-oxides (manganite and pyrolusite) and Mn-silicates (braunite, macfallite, and orientite). This deposit could have originated from late stage, low temperature hypogene fluids entering a near-surface environment. The source of the manganese and its relationship to volcanism is not known, although similar occurrences are reported in other volcanic areas. A fumarolic origin has been proposed for the assemblage (Moore, 1979). Timing of emplacement of this deposit with respect to the Keweenaw copper deposits is not known, but it was obviously formed after the deposition and lithification of the Copper Harbor conglomerate.
2. Mn mineralized calcite veins are often associated with fissures which cut the local stratigraphy at steep angles.
3. The two known occurrences of Mn mineralization are found along strike and on both sides of the contact between the Copper Harbor conglomerate and the Portage Lake lava series. The reported occurrence at the East Exploration (.25 miles east of the Manganese Exploration) is also in a similar stratigraphic position.
4. The area between the Lake Manganese Vein and the Manganese Exploration (.75 miles) holds the most promise for similar deposits. Outcrop between the two occurrences is entirely absent, except for small

exposures of Copper Harbor Conglomerate. Areas to the east of the Manganese exploration may also prove promising, but the likelihood of finding another deposit is probably best between the two occurrences.

5. The best exploration method determined from this work is soil geochemistry. The elements Mn, Cu, and V are most promising.

6. Outcrop is virtually non-existent, and geophysical techniques used have been shown to be inconclusive. However, micro-gravity, induced potential, and shallow seismic reflection may have promise.

7. Although the deposits appear to be small (from the surface exposures) they are very rich. The possibility of additional occurrences should not be ruled out.

RECOMMENDATIONS

1. The sampling grid should be extended for both geochemical and geophysical evaluation, so that non-anomalous areas are included for comparison.
2. Because, soil geochemistry was the best method to define the Manganese Exploration site, soil sampling at the bedrock interface should be considered for use, particularly where overburden thickness is great.
3. Because other deposits of this type are not known in the copper district, more elemental analyses should be performed on the richer manganese ore (black ore).
4. Fracture analysis using aerial photographs and, perhaps, satellite imagery should be considered as a possible method to find other fissure deposits in conjunction with geochemical methods.
5. Antimony should be reevaluated as a geochemical pathfinder with other analytical methods capable of a lower detection limit, such as instrumental neutron activation analysis (INAA).
6. More detailed geophysical surveys should be carried out to evaluate micro-gravity, induced potential, and shallow seismic reflection methods.

APPENDIX A

Brief Petrographic Descriptions

Sample: V-3Top

Megascopic Description: Coarse grained calcite. Crystals up to 20 mm. long. Some crystals show zoning. Fine-grained, pinkish calcite in veinlet up to 10 mm. wide cutting coarse calcite.

Microscopic Description: Large-grained calcite (80%), dirty. Pink calcite (20%), fine-grained, replacing large calcite grains. Very minor opaques with fine-grained calcite.

Sample: V-3

Megascopic Description: Coarse-grained calcite. Similar to V-4. Some crystals are zoned. Brown layers in calcite.

Microscopic Description: Brown dusty material in calcite grains. Some forming dendrites, very small.

Sample: V-4

Megascopic Description: Coarse-grained calcite. Crystals up to 15 mm. across. Black veinlets and dark dusty areas in the calcite.

Microscopic Description: Calcite: (95%), large grains, many cleavage traces. Opaques: (5%), small grains and masses growing around calcite grains (identified as braunite with reflected light). Quartz: (<1%), very minor filling in calcite.

Sample: 550-1

Megascopic Description: Brown, aphanitic, amygdaloidal basalt. Vesicles 20% of rock, half of vesicles filled.

Microscopic Description: Plagioclase: (25%), microlites, appear altered. Vesicles: (20%), filled with calcite, some rimmed by quartz. Opaques: (10%), black, some with red edges (hematite?). Brown groundmass: (45%), devitrified glass.

Sample: FT-1

Megascopic Description: Brown amygdaloidal basalt. Vesicles filled with calcite. Plagioclase microcrystals seen in hand specimen.

Microscopic Description: Vesicles: (20%), filled with calcite. Plagioclase: (35%), up to 1 mm. long, altered to straw colored, fine-grained material. Opaques: (10%).

Sample: FT-3 (a and b; b is a fragment)

Megascopic Description: Brecciated amygdaloidal basalt. Breccia fragments up to 30 mm. cemented by calcite.

Microscopic Description: Calcite: (50%), fine-grained, clear calcite grains. Fragments: amygdaloidal basalt similar to FT-1 and 550-1. Brown dusty material in calcite.

Sample: MD-12 (Net Vein Ore)

Megascopic Description: Calcite with "vein net" of black minerals surrounding grains. Aggregates of fine-grained dusty brown and black manganese minerals.

Microscopic Description: Calcite: two phases, coarse-grained dirty and fine-grained clear calcite. Opaques: braunite and minor pyrolusite growing along grain boundaries. Mn-silicates: brown radial sprays associated with oxides, also, dusty dendritic growths in calcite grains.

Sample: MD-14

Megascopic Description: Coarse-grained calcite, up to 20 mm. with veinlets and aggregates of dark, fine-grained Mn-oxide minerals.

Microscopic Description: Calcite: (80%), coarse-grained. Braunite: (20%), replacing calcite along grain boundaries, some radiating (pyrolusite?) crystals. Mn-silicates: minor radiating brown, fine-grained, fibrous, dendritic aggregates in calcite crystals.

Sample: MD-19 (Black and White Ore)

Megascopic Description: Dark Mn minerals (oxides and minor silicates) composing 50% of rock. Remainder is calcite. Some calcite cleavage faces dark due to dusty Mn minerals.

Microscopic Description: Calcite: (50%), grains strongly replaced by manganese minerals, most replacement along grain edges. Opaques: rounded aggregates and stringers of braunite and hair-like growths of pyrolusite, with radiating clots and masses of Mn-silicates.

Sample: 350-2A (Red and White Ore)

Megascopic Description: Brown Mn-silicates in calcite. Some aggregates dendritic.

Microscopic Description: Calcite: (50%). Mn-silicates: (50%), aggregates replacing calcite around grains and in grain interiors, masses and clots up to 2 mm. in diameter, minor opaques and dusty material.

Sample: MD-20 (Black Ore)

Megascopic Description: Dense, heavy, dark Mn minerals. Vuggy areas with radiating growths of pyrolusite and "islands" of brown Mn-silicates.

Microscopic Description: Clots of orientite and macfallite surrounded by pyrolusite and braunite. Calcite entirely replaced. Reflected Light: Pyrolusite: felted masses of intergrown blades and sprays, remnants of manganite, colloform textures seen in pyrolusite surrounding silicate clots.

Sample: 450-2Cu

Megascopic Description: Comb structure calcite with Mn-silicates. Fine-grained brown material surrounding crystals of calcite. Some native Cu. Clast of Amygdaloidal basalt surrounded by calcite.

Microscopic Description: Calcite: (50%), coarse, euhedral grains. Zeolites: (30%), fine-grained laths, as masses between calcite crystals. Mn-silicates: (20%), brown radiating masses in zeolites and rimming calcite grains.

Appendix B.--Elemental determinations for A horizon.

Sample	Mn (ppm)	Cu (ppm)	As (ppm)	Sb* (ppm)	V (ppm)	Total Volatiles (wt. %)
3-0-A	185	23	44	1.5	111	11.46
3-50-A	137	27	16	4	125	5.06
3-100-A	256	22	13	4	177	13.76
3-150-A	8300	93	42	5	184	30.07
3-200-A	4570	71	16	4	214	14.97
3-250-A	1780	47	29	1.5	187	15.28
3-300-A	792	22	22	1.5	139	13.05
3-350-A	1540	43	13	1.5	140	9.47
3, 5-200-A	2130	90	30	1.5	133	11.30
4-0-A	508	25	25	1.5	152	10.12
4-50-A	243	33	27	3	105	7.91
4-100-A	3540	41	26	1.5	152	9.55
4-250-A	624	29	27	1.5	134	8.00
4-300-A	4080	27	25	1.5	197	19.15
4-350-A	647	28	32	4	163	14.74
4, 5-200-A	850	32	21	10	182	8.69
5-0-A	108	20	17	1.5	114	4.29
5-50-A	876	34	13	7	102	17.59
5-100-A	424	29	28	4	122	14.90
5-150-A	63400	1050	20	6	231	17.97
5-250-A	3900	54	17	1.5	197	15.64
5-300-A	4080	28	39	4	205	9.87
5-350-A	531	19	28	3	138	8.83
5, 5-150-A	345	30	34	6	123	16.10
5, 5-200-A	1340	51	40	1.5	116	12.98
6-0-A	658	24	13	1.5	114	5.60
6-50-A	576	21	27	7	436	10.72
6-100-A	4570	51	26	4	133	19.53
6-200-A	239	20	32	5	162	4.01
6-250-A	144	17	22	1.5	147	4.10
6-300-A	1940	27	16	1.5	206	12.48
6-350-A	992	21	9	1.5	154	10.08

* Values less than detection limit have arbitrarily been assigned the value of 1.5 ppm.

Appendix C.--Elemental determinations for the B horizon.

Sample	Mn	Cu	As	Sb*	V
4-50-B	268	24	9	1.5	116
4-100-B	249	39	20	1.5	94
4-250-B	316	45	23	1.5	127
4-300-B	3080	30	33	7	213
4-350-B	420	20	33	1.5	157
4, 5-200-B	1060	41	30	3	178
5-0-B	170	16	18	6	105
5-100-B	207	27	24	1.5	95
5-150-B	18500	520	16	12	180
5-250-B	1690	87	28	8	166
5-300-B	1840	30	22	1.5	159
5-350-B	244	39	11	1.5	93
5, 5-150-B	204	27	19	1.5	96
5, 5-200-B	304	44	36	1.5	103

* Values less than detection limit have been arbitrarily assigned the value of 1.5 ppm.

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