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PARAGENESIS AND ORIGIN OF SEDIMENT-HOSTED MERCURY ORE AT THE MCDERMITT MINE, MCDERMITT, NEVADA

University of Nevada, Reno M.S. 1986

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Paragenesis and origin of sediment-hosted Mercury ore at the McDermitt Mine, McDermitt, Nevada

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Geology

by

John Kevin McCormack

September 1986
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University of Nevada

Reno

September 1986
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Undoubtedly, my greatest thanks go to my parents, Allanah and Red McCormack, for the unending support and encouragement they have given me during the five years it has taken me to complete this work. At times their interest in and enthusiasm for this project vastly outweighed my own, and I would have surrendered somewhere in the middle of it all without them. My advisor, Dr. Don Noble, and Ken Holtz, chief geologist at McDermitt Mine, have greatly improved my work through lengthy discussion and constructive criticism. Funding for this thesis was provided by McDermitt Mine, and support from McDermitt Mine staff made my work much easier. Additional thanks go to my advisory committee members Dr. Li Hsu and Dr. Ron Reitz, and to Dr. Frank Dickson, for improvements to my thesis resulting from their input. Brenda Keller and Paul Lechler of NMAL and Jim Sjoberg of the USBM gave generously of their time, ability, and facilities. Finally, someone told me at the start that they were sure I could do the job because they had faith in me. Saying thank you and being thankful here may not seem like much, but on being surrounded by so many such giants as these, it is the very best I can do.
Study of the paragenesis of sediment-hosted mercury ore at the McDermitt Deposit shows that the orebody formed by deposition from alkaline solutions advancing laterally through porous tuffaceous sediments. The intermediate argillic hydrothermal alteration mineral assemblage grades from high K'/H' ratio, high aSiO₂, to low K'/H', low aSiO₂-stable mineralogies from the southeast to the northwest, and indicates that precipitation of ore minerals was caused by cooling, oxidation, and drop in pH of the ore transporting solutions. Polished section study shows that pyrite and stibnite, then cinnabar, and finally silica were deposited from the solutions, and that the ore mineral corderoite was formed by secondary replacement of cinnabar. A previously unreported iodine-rich mercury phase occurs in the basal "opalite breccia", and native mercury occurring at the deposit formed by disintegration of cinnabar.
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I. INTRODUCTION

General

The McDermitt Mercury Mine is located in northern Humboldt County, Nevada, in the southern portion of the Opalite district, which straddles the Nevada-Oregon state line, and from which were produced more than 100,000 flasks of mercury from the presently inactive Opalite, Ruj一把, Bretz, and Cordero mines.

The Opalite district lies within the McDermitt caldera complex (Fig. 1), a composite collapse structure of Miocene age 45 km. (28 mi.) in maximum diameter, within which nested calderas were formed during the eruption of peralkaline rhyolitic volcanic rocks from 17.9 to 15.8 m.y.b.p. The complex is developed on a terrane of Cenozoic mafic and intermediate lavas varying from 150 m. (475 ft.) to 400 m. (1300 ft.) thick (Rytuba and Glanzman, 1979).

Open pit production at the McDermitt Mine began in 1975 with estimated reserves of 400,000 flasks (Roper, 1976), and it currently is the World's second largest mercury producer outside of Russia (L.R. Carrico, oral communication, 1985). The McDermitt Mine lies approximately 1000 m. (3000 ft.) north of the Cordero mine, which produced more than 100,000 flasks of mercury between 1941 and 1970. The Cordero mine is located on the
topographic rim of the caldera, whereas the McDermitt Mine lies well within the caldera. Miocene sediments that host the majority of the ore overlie a silicified layer that is generally referred to as the "opalite breccia".

Several geologic features indicate that the paleoenvironment of the McDermitt Mine pit area was of a variable depositional nature. Lymnaeid gastropods and small burrow features indicate a shallow water environment (J. B. Firby, oral comm., 1982). Preserved grasses, stems and reeds could have grown and been deposited either in a subaerial or subaqueous environment. However, eutaxitic structure and other volcanic textures and features could only have formed on dry land. A shoreline of a shallow lake is one possible depositional environment for the McDermitt Mine area.

The important ore minerals at McDermitt are cinnabar (HgS), which makes up approximately 75% of the ore being mined, and corderoite (Hg₃S₂Cl₂), which constitutes the remaining 25%. These minerals are finely disseminated throughout the ore body, and although average grade is 10 lbs. mercury per ton (0.5 wt%), lenses of rich ore are locally present.

Previous work

Bailey and Phoenix (1944) divided the quicksilver deposits in Nevada into eight geologic types based on host

Purpose of study

Because the hot-spring model developed by Roper (1976) inadequately explains many of the geologic features
exposed in the open-pit mine, this study was initiated by personnel of the McDermitt Mine with its primary objective being to determine a likely origin and paragenesis for ore emplacement in the sediment layer of the deposit, and as a secondary objective, to determine the method of formation of the ore mineral corderoite.

Field work

Most of the field work for this study was done during the summer of 1982, with additional field checking during the following school year. Over 700 half-pound sediment samples were taken along lines and grids in the pit floor and from vertical sections through the pit highwalls. The samples from the pit floor were taken at measured 25 foot intervals. All sample points were located using compass sightings on established mine survey stations. Cuttings from select drill holes were obtained, and numerous rock samples were taken. Samples were not taken in disturbed areas.

Geochemistry of mercury transport

Krauskopf (1951) concluded that most mercury ores are deposited from fluids at temperatures between $80^\circ$ and $250^\circ$ C and at pressures below 30 atmospheres, and that the only mechanisms capable of transporting geologically significant quantities of mercury under natural conditions
are transport in the vapor phase as the volatile chloride HgCl$_2$ or as elemental mercury, and transport as the complex ion HgS$_2$$^{2-}$ in sulfide solutions.

To illustrate, he showed that in the presence of H$_2$S, HgCl$_2$ vapor transport is possible if the equilibrium

$$\text{HgCl}_2(g) + \text{H}_2\text{S}(g) = \text{HgS}(s) + 2\text{HCl}(g)$$

is not displaced too far to the right. He stated that whereas this is geologically feasible, this method of transport is most effective if the transport fluid consists of vapor only. Because HCl is extremely soluble, if a liquid phase is present the HCl/H$_2$S ratio in the vapor will necessarily be low, forcing the reaction to the right.

In his work on vapor-phase transport of elemental mercury, Krauskopf showed that Hg$^0$ would have a vapor pressure of $2 \times 10^{-5}$ atms. at 227 degrees C. (This means that at 227 degrees C., 10 cubic meters of gas would contain one gram of mercury). He stated that although this is a small amount, over a period of time it could account for transport of considerable amounts of mercury. He further illustrated that vapor-phase transport of elemental mercury would not be greatly influenced by the presence of a liquid phase.

Additionally, he stated that the ideal mechanism for mercury transport is as the complex ion HgS$_2$$^{2-}$ in sulfide
solutions. He demonstrated that the solubility of HgS in water is so low that impossibly large volumes of solution would be required to transport small quantities of mercury. As stated by Krauskopf, Knox (1906) showed that HgS is appreciably soluble in alkaline sulfide solutions because the complex ion $\text{HgS}_2^{-2}$ is formed from HgS in the presence of excess sulfur according to the equilibrium:

$$\text{HgS} + \text{S}^{-2} = \text{HgS}_2^{-2}. \quad (2)$$

Krauskopf (1951) pointed out that these solutions would necessarily be neutral to alkaline because of the instability of the sulfide ion under lower pH conditions according to the equilibrium:

$$\text{HgS}_2^{-2} + 2\text{H}^+ = \text{HgS} + \text{H}_2\text{S}. \quad (3)$$

Krauskopf determined that chloride complexes are inadequate for transporting mercury in the presence of sulfur. Because of this, and because other complex-forming elements are scarce in ore-forming solutions, he concluded that no complex ion besides $\text{HgS}_2^{-2}$ is likely to play a role in mercury ore formation.

Dickson (1964) determined the saturation curves of HgS in the system HgS-Na$_2$S-H$_2$O at 50° to 250° C and one to 1800 bars. To summarize his findings: 1) at constant temperature and Na$_2$S concentration, increasing pressure decreases HgS solubility, 2) at constant pressure and Na$_2$S
concentration, increasing temperature reduces HgS solubility until it reaches a minimum at approximately 100 degrees C, from which point HgS solubility increases at an increasing rate, and 3) at constant temperature and pressure, increasing Na₂S concentration increases HgS solubility.

White (1981) discussed the importance of organic materials and vapors to transport of volatile mercury phases in hot-springs systems. He described a model whereby mercury deposits could form from a through-going CO₂ dominated vapor phase saturated with elemental and other volatile mercury phases.

Dickson stated that decrease in pressure probably does not play an important role in the precipitation of mercury ores because of the shallow nature of most mercury deposits. However, from Dickson (1964), Krauskopf (1951), Dreyer (1940), and White (1981) it is shown that precipitation of HgS can be caused by: 1) decreasing temperature in the range above 100° C, 2) decrease in pH, 3) dilution, and 4) oxidation.

Deposition temperature estimate for McDermitt

Although inexact, we can approximate the McDermitt deposits' temperature of formation. Learned et al. (1974) stated that most mercury ores were deposited at temperatures below 280 degrees C. Rytuba (1976)
presented fluid inclusion data from the McDermitt deposit indicating deposition at 200 +/−5°C, which as discussed later should be considered low. Within the resulting 200-280°C range, an estimated temperature of deposition of 215°C proves most reasonable.

Mine pit configuration

The open pit of the McDermitt Mine has an irregular outline and an average diameter of roughly 1000 m. (3000 ft.), and is deepest in the northwest, shallowest in the southeast (Fig. 2).

General geology of the McDermitt deposit

The McDermitt Deposit lies approximately one km. within a collapse caldera, the ore body being hosted by a layered sequence of gravels, sediments and volcanics. The beds exposed in the pit dip an average of five degrees to the northwest (Fig. 3).

The overlying gravels, which vary in thickness from 40 to 90 feet, post-date mineralization.

The Tertiary rhyolite volcanics that underlie the deposit are part of a thick volcanic base of andesites and rhyolites.

The zeolitic portion of the Miocene sediments, which at McDermitt is composed solely of clinoptilolite, is part of a zeolite-clay mineral zonation sequence shown by
FIG. 2. McDermitt Mine pit as it existed in June, 1982, showing local attitude of bedding. Topography shown is that of floor of pit.
FIG. 3. Idealized cross section along line A-A’, figure 2. Vertical exaggeration approximately 2x. Gravels are Quaternary, zeolitic sediments and "opalite breccia" are also Miocene.
Glanzman and Rytuba (1979) to exist within the McDermitt caldera. The zeolites are of diagenetic origin and are not related to the hydrothermal system that produced the McDermitt deposit.

The "opalite breccia" that underlies the Miocene sediments was considered by Roper (1976) to be a hydrothermal breccia formed during hot spring activity. Hetherington (1983), however, determined that the "opalite breccia" was formed by silicification of previously existing beds by hydrothermal solutions. She illustrated that typical breccia consists of silicified, partially welded to non-welded lithic-rich ash-flow tuff. In some locations it contains appreciable amounts of ore minerals.

The Miocene sediments unit is the economically most important unit of the McDermitt deposit, since this is the principal ore-bearing unit. It is referred to as sediments due to its high content of tuffaceous lacustrine and alluvial materials together with subordinate amounts of air-fall and ash-flow tuffs. Numerous conformable chalcedony lenses occur in the sediment sequence, and are also exposed in the surrounding countryside.

Ore body configuration

In order to delineate the configuration of the ore body at McDermitt, a Jerome Instruments mercury detector was used to analyze samples taken during the present
study. Due to the highly sensitive nature of the device, very small quantities of sample (average 1.5 mg.) were analyzed. Analysis of a standard (an average grade sample from the deposit) showed reproducibility well within 10% (the maximum reproducibility of the device). However, analysis of 110 samples failed to produce a distinguishable trend in ore distribution due to the very limited area of influence of such a small sample and the locally erratic nature of ore distribution within the deposit.

A second, and more successful attempt at the problem employed the compilation of data taken from mining "grids" developed by McDermitt Mine between 1980 and 1983. Mine personnel regularly sample on a "grid" for ore control wherein five pound samples taken at 25 foot centers are analyzed by atomic absorption methods.

For this study, all ore control grid samples with mercury contents of one pound mercury per ton (500 ppm) or higher were transferred to a map of the pit floor, and their elevations recorded. Many grids may be done in the same location (but at different elevations as work in the pit progressed), so that sample having the highest elevation was used in contouring. In all, 154 mining grids were utilized and 7015 points were evaluated to generate the contour map.

The contour map shows that the ore body has the same
general attitude as the beds of the deposit, dipping gently to the northwest (Fig. 4). From this evidence the ore body would appear to be stratigraphically controlled.
FIG. 4. Elevation of top of ore body as determined from ore control grids. Contours good where lines are solid, moderate where dashed, inferred where dotted.
II. MINERALOGY

ORE PETROLOGY

Introduction

A large portion of this study involved examination of two distinct yet intimately associated paragenetic aspects of the ore petrology of the McDermitt deposit, namely ore emplacement and corderoite formation. Reflected light microscopy was employed in the study of paragenetic textures and features in polished sections of ore specimens from the McDermitt Mine. Additional features were studied in thin section and by scanning electron microscopy. All phases were identified using standard X-ray diffraction techniques.

The following paragenetic sequence was established for the McDermitt deposit:

1) Coprecipitation of pyrite (FeS₂) and stibnite (Sb₂S₃),
2) Precipitation of cinnabar (HgS),
3) Beginning of formation of corderoite (Hg₃S₂Cl₂),
4) Silicification of the "opalite breccia".

Corderoite is the second most abundant ore mineral at the McDermitt Mine, constituting roughly 25% of the currently mineable ore. Corderoite is light pink on a freshly broken surface and is photosensitive, rapidly darkening to black on exposure to light. All corderoite
found at the deposit previous to this study had been extremely fine grained (less than 2 microns in diameter) making study of the mineral difficult.

The first published study of natural corderoite was carried out by Foord et al. (1974) on samples taken near the Cordero mine. Foord synthesized corderoite by allowing cinnabar to react with concentrated HCl or NaCl-H₂SO₄ solutions. His results and the occurrence of corderoite as replacements and rims on cinnabar led him to conclude that corderoite was formed by low temperature and/or supergene replacement of cinnabar. Information bearing on the formation of corderoite obtained to date has been of indirect nature, and in all cases has supported a low temperature and/or supergene origin.

Petrology

The bulk of the petrographic evidence presented here will be illustrated by photomicrographs taken of specimens from the McDermitt deposit. Pyrite and stibnite coexist in silicified material (Fig. 5). The paragenetic relationship between these two minerals is unclear, but lack of any definitive evidence placing precipitation of one mineral prior to the other leads me to conclude that the two minerals coprecipitated. In all cases where pyrite and cinnabar coexist, pyrite is enclosed in cinnabar (Fig. 6), indicating that pyrite formed before
FIG. 5. Pyrite (white-yellow) within and around stibnite (mottled grey-brown) in silica ("opalite", dark grey). Reflected light, uncrossed polars, field of view 0.87 mm. Location N 2,611,690 x E709,600.
FIG. 6. Pyrite (white-yellow) in cinnabar (dark grey with red internal reflections, pitted). Reflected light, uncrossed polars, field of view 0.35 mm. Location N 2,611,490 x E 709,250.
None of the polished sections studied contained coexisting stibnite and cinnabar. However, several sections contained both stibiconite \((\text{Sb}_3\text{O}_6\text{(OH)})\) and cinnabar. Stibiconite, which forms by the oxidation of stibnite (Dana, 1941), is pseudomorphic after stibnite at McDermitt (Fig. 7), and provides evidence on the paragenetic relations of stibnite and cinnabar at McDermitt. In all cases where the two minerals coexist, stibiconite is cross-cut by cinnabar (Fig. 8), indicating that stibnite formed before cinnabar.

After examination of the pertinent literature (Foord et al., 1974; Vasil'yev and Grechishchev, 1979; Hetherington, 1983; Roper, 1976), it was not unexpected to find that in all cases, textures relating cinnabar and corderoite showed corderoite to be a replacement mineral of cinnabar. Common replacement textures as viewed in McDermitt ore samples include sharp and irregular boundaries between replaced and replacing minerals along fractures and grain boundaries (Craig and Vaughan, 1981). In particular, "caries" texture results when a replacing mineral forms a series of cusp-shaped embayments in the replaced mineral (Ramdohr, 1980). Textures such as these are common in the McDermitt ore samples (Figs. 9-13), and are prima facie evidence for corderoite formation by replacement of cinnabar.
FIG. 7. Stibiconite (grainy, medium grey blades) pseudomorphs after stibnite in silica ("opalite", darker grey). Reflected light, uncrossed polars, field of view 0.87 mm. Location N 2,611,680 x E 709,700.
FIG. 8. Cinnabar (pink) veinlet cutting stibiconite (fibrous, white) in silica ("opalite", darker grey). Reflected light, uncrossed polars, field of view 0.35 mm. Location N 2,611,680 x E 709,700.
FIG. 9. Reflected light photomicrographs of corderoite replacement rim on cinnabar in silica ("opalite"). A: uncrossed polars, cinnabar is pink, corderoite is medium grey, silica is darker grey. B: crossed polars, cinnabar is red, corderoite is clear, silica is white. Field of view is 0.35 mm. Location N 2,610,720 x E 709,880.
FIG. 10. Reflected light photomicrograph of corderoite replacement rim on cinnabar in silica ("opalite"). A: uncrossed polars, cinnabar is pink-white, corderoite is medium grey, silica is darker grey. B: crossed polars, cinnabar is red, corderoite is clear-yellow, silica is white. Field of view is 1.7 mm. Location N 2,610,690 x E 709,870.
FIG. 11. Reflected light photomicrograph of corderoite replacement rim on cinnabar in silica ("opalite"). A: uncrossed polars, cinnabar is pink-white, corderoite is medium grey, silica is darker grey. B: crossed polars, cinnabar is red, corderoite is clear-yellow, silica is white. Field of view is 1.7 mm. Location N 2,610,740 x E 709,750.
FIG. 12. Reflected light photomicrograph of corderoite replacing cinnabar on rims and along fractures. A: uncrossed polars, cinnabar is white, corderoite is medium grey, silica is darker grey. B: crossed polars, cinnabar is red, corderoite is clear-yellow, silica is white. Field of view is 0.87 mm. Location N 2,610,800 x E 709,700.
FIG. 13. Reflected light photomicrograph of corderoite replacing cinnabar on rims and along fractures. A: uncrossed polars, cinnabar is white, corderoite is medium grey, silica is darker grey. B: uncrossed polars, cinnabar is red, corderoite is clear-yellow, silica is white. Note well developed "caries" texture. Field of view is 0.87 mm. Location N 2,610,700 x E 709,750.
The crystal morphology of the two ore minerals also provides paragenetic information. Cinnabar is hexagonal, commonly forming hexagonal and rhombohedral crystals. Corderoite is cubic, and the only previously described naturally occurring crystals are rhombic dodecahedrons from the Arzak deposit in Russia (Vasil'yev and Grechishchev, 1979).

Corderoite crystals at McDermitt occur as anhedral grains, crudely crystalline grains of variable morphology, or as six-sided grains. Figure 14 is a photomicrograph of a hexagonal cinnabar grain as seen in thin section. This morphology is common for cinnabar at McDermitt. Figure 15 is a photomicrograph of a six-sided corderoite grain in thin section. Many such corderoite grains have cinnabar cores (Fig. 16). Corderoite crystals such as these provide evidence for corderoite replacement of cinnabar, although optical methods are not the optimum tool in a morphological study because they allow for only a two-dimensional view of the mineral in question.

The scanning electron microscope allows for a three-dimensional view of materials. A sample of the same argillized material used for the thin sections described above was examined using the SEM. Distinguishing between mercury phases was done using the SEM's microprobe attachment, based on the fact that corderoite contains chlorine whereas cinnabar does not.
FIG. 14. Cinnabar hexagonal plate in matrix of argillized volcanic glass. Transmitted light, uncrossed polars, field of view is 0.29 mm. Location N 2,611,590 x E 709,630.
FIG. 15. Six-sided plate of corderoite pseudomorphous after cinnabar in matrix of argillized volcanic glass. Transmitted light, uncrossed polars, field of view is 0.87 mm. Location N 2,611,590 x E 709,630.
FIG. 16. Six-sided plate of corderoite with cinnabar core in matrix of argillized volcanic glass. Transmitted light, uncrossed polars, field of view is 0.87 mm. Location N 2,611,590 x E 709,630.
Figure 17 is a scanning electron microscope photomicrograph of a hexagonal plate of corderoite. Figure 18 is another of a more elongate (possibly twinned) hexagonal crystal of corderoite. These photos clearly demonstrate pseudomorphic replacement of cinnabar by corderoite.

In all nine polished sections studied that contain coexisting cinnabar and "opalite breccia" silica, the silica encloses and crosscuts cinnabar (Fig. 19), indicating that cinnabar was deposited before silicification of the "opalite breccia". Figure 20 illustrates silica of the "opalite breccia" cross-cutting cinnabar that had been partially replaced by corderoite, indicating that silicification of the "opalite breccia" was not only later than cinnabar precipitation, but also later than the onset of corderoite formation.

Figures 21-24 illustrate textures common in materials from the McDermitt Mine that establish paragenetic relationships between ore minerals and the host rocks. The more obvious textures include ore minerals following fractures or cross-cutting bedding features, infilling by ore minerals in host materials, and ore mineralization following features having higher porosities or permeabilities than surrounding materials. The resultant textures are all transgressive, indicating that ore minerals were deposited epigenetically in preexisting
FIG. 17. Scanning electron microscope photograph of corderoite grains in matrix of argillized volcanic glass. Grain in upper right has well developed six-sided plate morphology. Bar scale is 100 microns in length. Location N 2,611,590 x E 709,630.
FIG. 18. Scanning electron microscope photograph of corderoite grains in matrix of argillized volcanic glass. Large grain has elongate six-sided plate morphology. Bar scale is 10 microns in length. Location N 2,611,590 x E 709,630.
FIG. 19. Reflected light photomicrograph of silica ("opalite", dark grey) cross cutting cinnabar (white). Uncrossed polars, field of view is 3.5 mm. Location N 2,610,750 x E 709,900.
FIG. 20. Reflected light photomicrograph of silica ("opalite") cross cutting cinnabar that had been partly altered to corderoite. A: uncrossed polars, cinnabar is white, corderoite is medium grey and forms rims on grain boundaries and along fractures, silica is dark grey. B: crossed polars, cinnabar is red, corderoite is clear, silica is white. Field of view is 3.5 mm. Location N 2,610,740 x E 709,920.
FIG. 21. Dark red-brown cinnabar impregnating very fine grained siltstone, following fractures as well as primary bedding planes. Coin is 1.75 cm. in diameter. Location N 2,611,540 x E 709,270.
FIG. 22. Red cinnabar and later white silica filling fracture in host rock. Width of fracture is 1.5 mm. Location N 2,610,720 x E 709,800.
FIG. 23. Dark red-brown cinnabar impregnating coarse grained sandy layer. Coin is 1.75 cm. in diameter. Location N 2,611,450 x E 709,530.
FIG. 24. Cinnabar (red) impregnating coarser grained, more porous and permeable layer in argillized sandy groundmass. Transmitted light, uncrossed polars, field of view is 8.6 mm. Location N 2,611,450 x E 709,530.
rocks. A less obvious texture involves the presence of cinnabar in and around devitrification spherulites. In an intercaldera environment, spherulites such as these (Fig. 25) commonly form in densely welded volcanic materials. In peralkaline tuffs, this welding takes place at temperatures above 600 degrees C, commonly at 800+ degrees C. If these spherulites were formed from densely welded glassy volcanic materials, then this texture also indicates that the ore mineralization was deposited epigenetically, because welding temperatures are far in excess of the maximum temperature at which cinnabar is stable.

Conclusions

Laboratory study by Foord together with the direct physical evidence of replacement textures common in polished sections of ore specimens, and corderoite pseudomorphs of cinnabar visible in thin section and under the scanning electron microscope provide overwhelming evidence for corderoite genesis by replacement of cinnabar. Additional textures visible in hand specimen and under the microscope provide ample evidence that ore minerals at McDermitt were emplaced epigenetically in preexisting rocks.
FIG. 25. Cinnabar (red) in and around argillized devitrification spherulites. Transmitted light, uncrossed polars, field of view is 0.35 mm. Location N 2,611,590 x E 709,630.
NATIVE MERCURY

Small amounts of native mercury occur at the McDermitt deposit in the form of isolated blebs and globules. The native mercury is in all cases associated with extremely rich corderoite-cinnabar ore, and calomel and eglestonite are in all cases present in the same localities. Although the native mercury has been attributed to vapor-phase transport and deposition (Roper, 1976), it more likely formed in place by supergene decomposition of cinnabar, because vapor-phase deposition of the metal has been noted to produce extensive zones containing uniformly dispersed small globules of native mercury (Fedorchuk, 1958) rather than the isolated occurrences observed at McDermitt.

Fedorchuk (1958) noted that hypogene, vapor-phase native mercury contained all the principle constituents of low-temperature ore-bearing solutions including hundreds of ppm silver. His premise was that if native mercury were present in the vapor-phase during active ore transport and deposition, it should contain significant amounts of dissolved metals. Following that premise, atomic absorption analyses of a five gram sample of native mercury and a sample of cinnabar collected at the McDermitt mine are given on table 1. Of the elements analyzed, those marked with an asterisk have atomic radii within 15% of the atomic radius of mercury and should dissolve easily in native mercury (Tunell, 1969). Only
Table 1. Atomic Absorption Analyses of Native Mercury and Cinnabar from the McDermitt Mine.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
<th>Native Mercury</th>
<th>Cinnabar</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Cu</td>
<td>&lt;3</td>
<td>&lt;28</td>
<td></td>
</tr>
<tr>
<td>*Co</td>
<td>&lt;13</td>
<td>&lt;24</td>
<td></td>
</tr>
<tr>
<td>*Fe</td>
<td>8</td>
<td>2423</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;5</td>
<td>1785</td>
<td></td>
</tr>
<tr>
<td>*Ni</td>
<td>2</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>*Ag</td>
<td>9</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>*Pb</td>
<td>2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>*Zn</td>
<td>3</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>*Sb</td>
<td>25</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

* Denotes Element that Dissolves Easily in Native Mercury.

Analyses by John McCormack, at Nevada Bureau of Mines and Geology Laboratory.
copper and lead will commonly substitute for mercury in cinnabar according to Pauling's rules for substitution. The high iron content of the cinnabar sample is probably due to pyrite inclusions similar to those described in the ore petrology section of this study and should be disregarded. The accompanying high manganese content may be related to the high iron content and should also be disregarded.

The native mercury at the McDermitt mine shows no particular enrichment in other metals. Lead, zinc, antimony, and nickel have somewhat higher concentrations in the cinnabar than in the native mercury. Silver in the native mercury is an order of magnitude lower in concentration than the hundreds of ppm noted by Fedorchuk in hypogene, vapor-phase native mercury. Thus, the low content of other metals suggests a supergene origin for the native mercury at McDermitt. The cinnabar, in contrast, has higher metal contents because of its hypogene origin.

The mineral calomel most commonly occurs as a product of the alteration of cinnabar, and eglestonite is most commonly formed by the oxidation of calomel (Dana, 1951). Cinnabar can be oxidized by solutions containing ferric sulfate, and this oxidation is accelerated by the presence of sodium chloride, as illustrated by the reaction
HgS + Cl⁻ + Fe³⁺ = HgCl + S⁰ + Fe²⁺.

Solutions containing these components may react with cinnabar, producing native mercury, calomel, and oxychlorides (Tunell, 1969). This is well illustrated in figure 26, which shows calomel and native mercury rimming and replacing cinnabar. This feature likely formed as a result of processes similar to those described above. The isolated distribution of the native mercury, its association with calomel and eglestonite, and the low concentrations of dissolved other metals provide strong evidence supporting a supergene origin by decomposition of cinnabar for the native mercury at the McDermitt deposit, rather than transport as elemental mercury vapor or liquid.
FIG. 26. Native mercury droplets (silver, slightly out of focus) on calomel (brown-grey) replacement rim on cinnabar (white) in silica ("opalite", dark grey). Note pronounced embayments of calomel into cinnabar at boundary. Reflected light, uncrossed polars, field of view is 0.87 mm. Location N 2,610,860 x E 710,100.
ALTERATION

Introduction

The mineralogy of altered rocks at the McDermitt mine was established by using standard X-ray diffraction techniques to identify minerals in 355 samples taken from the pit floor and highwalls (Fig. 27). The pit floor conforms to the bottom of the ore body, that is, it dips to the northwest, and the ore body is conformable to the stratigraphy as previously discussed. As a result, the samples taken from the floor of the pit for this study are generally from one horizon.

The alteration minerals identified are montmorillonite, quartz, clinoptilolite and alunite, with smaller amounts of adularia, kaolinite, and cristobalite. Clinoptilolite is found in the northernmost third of the pit area, overlying all other materials. Alunite occurs rarely, having its greatest number of occurrences in the northwestern portion of the pit. Montmorillonite and quartz are essentially ubiquitous throughout the pit area whereas kaolinite and cristobalite have their greatest number of occurrences in the northwestern third of the pit, with minor showings elsewhere. Adularia has its greatest number of occurrences in the southeastern third of the pit, with minor occurrences elsewhere. With the exception of clinoptilolite, there is no vertical
FIG. 27. Location of samples analyzed by X-ray diffraction methods.
component to the alteration pattern.

Hydrothermal alteration at McDermitt was contemporaneous with ore deposition. Direct evidence for this is provided by adularia crystals that contain cinnabar deposited conformable to crystal growth structures (Fig. 28), indicating that the two minerals formed together.

Clinoptilolite

As illustrated in figure 3, clinoptilolite occurs in a discreet layer overlying the orebody. The clinoptilolite is part of a zeolite-clay mineral sequence shown by Glanzman and Rytuba (1979) to exist within the McDermitt caldera complex. Their work showed that clinoptilolite is present as a continuous unit as far as 4 km. from the deposit, as well as in several other localities in various parts of the caldera complex. Although no adequate evidence has been found that would place clinoptilolite formation chronologically before or after hydrothermal alteration of the deposit, the fact that clinoptilolite exists throughout the caldera rather than being restricted to those areas immediately surrounding the ore deposits of the caldera indicates that it is of diagenetic rather than hydrothermal origin. Fisher and Schmincke (1984) illustrated that tuffaceous glass in saline alkaline lake deposits typically undergoes diagenetic alteration.
FIG. 28. Cinnabar (small dark red blebs) in adularia crystals. Note "bow tie" structure of adularia grain. Transmitted light, uncrossed polars, field of view is 0.35 mm. Location N 2,611,705 x E709,665.
resulting in a zoned pattern wherein the glass changes laterally through various zeolite phases into a final potassium feldspar phase. This pattern is virtually identical to that zeolite zonation pattern presented by Glanzman and Rytuba (1979). Clinoptilolite commonly forms diagenetically from pyroclastic materials (Mumpton, 1960), and this occurrence within the McDermitt caldera is not unusual.

Alunite

Alunite occurs as very fine grained, white, chalky material, commonly as balls 1" to 4" in diameter (Fig. 29). Alunite, identified by x-ray methods in 15 samples, has a random, spotty distribution throughout the mine, although it has its greatest number of showings in the northwestern portion of the pit floor. Alunite exhibits no preferential association with any other mineral.

Hypogene deposition of alunite, which is stable under conditions of high activities of $K^+$, $H^+$, and $SO_4^{-2}$ (Hemley et al., 1969), would call for radical changes in the alkaline nature of the system responsible for mercury transport. No evidence for such changes has been observed. This lack of chemical compatibility, the fine grained nature of the alunite, its random distribution, and the lack of any association with the rest of the mineralogy at the deposit indicates that the alunite is of
FIG. 29. "Potatoid" white alunite balls from the McDermitt deposit. Coin is 2.45 cm. in diameter. Location N 2,612,070 x E 709,580.
supergene origin.

No full explanation for the round morphology of the alunite at McDermitt has been found. Formation of the balls by replacement of lithophysae is highly unlikely because all spherulites found at McDermitt that have not been silicified have been altered to montmorillonite, and lithophysae are essentially large spherulites. The chemical makeup of lithophysae and spherulites that formed from the same materials should be very similar. To suggest that in this instance that the size of the materials involved was the controlling factor that determined which of two completely different phases was formed during alteration of the materials is wholly unfounded.

The alunite balls at McDermitt may have formed by replacement of some previously round feature. Ashy, glassy, crystal-bearing balls of comparable size (Fig. 30) have been found in tuffaceous sediment layers in the vicinity of the Bretz mine. It is possible that the alunite balls at McDermitt formed by alteration of similar materials.

It is also possible that these balls may be alunite concretions. Where unlike materials having differing surface energies occur, free energy is reduced by the formation of concretions which reduces surface area (Pettijohn, 1975). Other sulfate minerals such as barite
FIG. 30. Light green, ashy, glassy balls from a unit of bedded tuff within the McDermitt caldera complex. Coin is 2.45 cm. in diameter. Location approximately 4 km. west of the Bretz mine.
and gypsum have been noted to form concretions, and the McDermitt deposit may be the first locality at which alunite concretions have been recognized.

Montmorillonite and quartz

Formation of montmorillonite, a common alteration product in hydrothermal ore deposits, is favored by an alkaline environment (Rose and Burt, 1979). Quartz is a common gangue mineral of hydrothermal systems, and the development of both minerals in tuffaceous materials subjected to alkaline hydrothermal solutions is not unusual.

Both minerals are ubiquitous at McDermitt, very rarely being absent in concentrations identifiable by X-ray diffraction methods. Although montmorillonite and quartz are the dominant alteration minerals at McDermitt, their presence throughout the pit does not allow for any inference of alteration trends or patterns to be made. As such they are removed from present discussion so that more informative alteration trends may be considered.

Kaolinite, cristobalite, and adularia

Although present only in accessory amounts, kaolinite, cristobalite, and adularia are the only alteration minerals having variable distributions at the McDermitt mine. Kaolinite and cristobalite have their greatest
number of occurrences in the northwestern third of the pit, with minor showings elsewhere, whereas adularia has its greatest number of showings in the southeastern third of the pit, with minor showings elsewhere. The generalized distributions of these minerals are shown on figure 31.

The vertical sections on the highwalls of the pit and the drill holes outside the pit area that were studied established that, with the exception of clinoptilolite-bearing sediments overlying the ore body, vertical patterns or trends in alteration mineralogy did not exist. The vertical sections themselves merely occupied a position within the lateral alteration pattern identified in the pit, for instance, those sections in the southeast portion of the pit had a greater number of showings of adularia whereas those sections in the northwest portion of the pit had a greater number of showings of kaolinite and cristobalite.

Conclusions

The ubiquitous presence of montmorillonite, the adularia-kaolinite reaction

\[ 2\text{KAlSi}_3\text{O}_8 + 2H^+ + \text{H}_2\text{O} = \]

\[ \text{Al}_2\text{Si}_2\text{O}_5(OH)_4 + 2\text{K}^+ + 4\text{SiO}_2, \]  

and the alteration pattern at McDermitt (Fig. 31) indicate
FIG. 31. Generalized map showing pattern of hydrothermal alteration at McDermitt. Patterned areas illustrate areas where cristobalite, kaolinite, or adularia have their greatest number of occurrences. None of the three minerals have a great number of occurrences in the unpatterned area. Quartz and montmorillonite are ubiquitous.
that neutral to alkaline ore-forming solutions moved laterally through the host materials from the southeast to the northwest, cooled as they traveled, and underwent significant changes in $aK^+/aH^+$ and $aSiO_2$. 
III. DISCUSSION

ORE MINERALOGY

Foord (1974) synthesized corderoite by allowing cinnabar to react with concentrated HCl or NaCl-H_2SO_4 solutions. Foord's experiments and the abundance of iron oxides in the McDermitt mine pit led Speer (1977) to propose that H_2SO_4 produced by the oxidation of pyrite at McDermitt was responsible for corderoite formation. This mechanism is unlikely because the equilibrium

\[ 3\text{HgS} + 2\text{Cl}^- + 2\text{O}_2 = \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{SO}_4^= \]  

(5)

illustrates that a high aSO_4 would force the reaction towards the field of cinnabar stability. Additional evidence against this possibility comes from the polished sections of "opalite" containing pyrite and corderoite (Figs. 5, 20). The figures show pyrite preserved in "opalite", which indicates that oxidation of pyrite at McDermitt took place after silicification of the "opalite". The polished section work also clearly illustrates that corderoite formation began before silicification of the "opalite" took place. Therefore, oxidation of pyrite at McDermitt took place after corderoite formation began, or in other words, pyrite was stable during corderoite formation, and the abundant iron oxides at the deposit formed extremely late.
A pH-aO₂ diagram (Fig. 32) showing generalized stability fields of cinnabar vs. corderoite was constructed using equations five through nine:

\[
3\text{HgS} + 2\text{Cl}^- = \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{S}^- + \text{H}^+ \quad (6)
\]

\[
3\text{HgS} + 2\text{Cl}^- + \text{H}^+ = \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{HS}^- \quad (7)
\]

\[
3\text{HgS} + 2\text{Cl}^- + 2\text{H}^+ = \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{H}_2\text{S} \quad (8)
\]

\[
3\text{HgS} + 2\text{Cl}^- + \text{H}^+ + 2\text{O}_2 = \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{HSO}_4^- \quad (9)
\]

These reactions and the diagram illustrate that corderoite is the stable phase under conditions of low pH and/or high aO₂, and increasing aCl⁻ increases the stability field of corderoite.

Because pyrite was stable during corderoite formation, an additional constraint can be placed on the above diagram by including the corresponding stability fields of pyrite vs. hematite. The pyrite-hematite equilibrium reaction

\[
2\text{FeS}_2 + 7.5\text{O}_2 + 4\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 8\text{H}^+ \quad (10)
\]

illustrates that high aO₂ conditions would make hematite the stable iron phase. Therefore, reactions such as numbers seven and eight above would likely have been the most important in triggering the cinnabar to corderoite
FIG. 32. A log $aO_2$ vs. pH diagram illustrating generalized stability fields (heavy dashed lines) of corderoite ($Hg_3S_2Cl_2$) and cinnabar ($HgS$). Variations in stability fields due to change in $Cl^–$ concentration given for hypothetical activities $10^{-2}X$, $10^{-1}X$, $10^{0}X$, and $10^{1}X$. PY = pyrite, HEM = hematite, MAG = magnetite, PO = pyrrhotite. Temperature = 200°C, total sulfur = 0.01 mol/kg., unit activities for all solid phases and H$_2$O. Base diagram modified from Henley et al. (1984), assuming $fO_2 = aO_2$. 
transition because they are pH dependent and could take place without disturbing pyrite stability. Other reactions such as numbers five and nine which involve significant \( aO_2 \) would necessitate conditions wherein hematite was the stable iron phase. Although all reactions listed could have been responsible for corderoite formation, pyrite stability during corderoite formation indicates that the cinnabar to corderoite transition was dominantly pH dependent.

Finally, it should be noted that from all reactions listed, decrease in total sulfur in the system will promote corderoite formation.

Late silicification of the "opalite breccia" is the reason why all mineralized "opalite breccia" darkens rapidly on exposure to sunlight. Corderoite formation could not have taken place in the "opalite breccia" if silicification took place contemporaneously with cinnabar precipitation or prior to corderoite formation, because the silica would have protected the enclosed cinnabar from the corderoite-forming solutions. If that had happened, there should be present at McDermitt a considerable quantity of mineralized "opalite breccia" that is not photosensitive, and this is not the case. This field relationship supports the laboratory work that indicates that silicification of the "opalite breccia" took place after corderoite formation began.
It is likely that silicification of the "opalite breccia" arrested corderoite replacement of cinnabar in that unit. However, the replacement process probably continued in the overlying non-silicified sediments because the cinnabar from the sediments is visually more thoroughly altered to corderoite than is the cinnabar from the "opalite breccia".

Corderoite probably occurs at other mercury deposits within the caldera. Yates (1942) describes "cinnabar" at the Bretz mine that darkens rapidly when exposed to sunlight. If this cinnabar is actually corderoite, then corderoite formation is a result of some process that took place in many parts of the McDermitt Caldera Complex.

Although low pH and/or low total sulfur and/or high $aO_2$ allow for stable formation of corderoite from cinnabar, these conditions are met at numerous mercury deposits throughout the world that contain no corderoite, indicating that a relatively high $aCl^-$ is the controlling factor in the process of corderoite formation.

A simple $aCl^-$ vs. pH diagram illustrating the relative stability fields of corderoite vs. cinnabar was constructed using equation 7 above (Fig 33), and it illustrates that corderoite is stable under conditions of high $aCl^-$ and low pH, whereas cinnabar is stable under low $aCl^-$, high pH conditions.

It is very possible that within the McDermitt caldera,
FIG. 33. Generalized log $a$ Cl$^-$ vs. pH diagram illustrating relative stability fields of corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$) vs. cinnabar ($\text{HgS}$). Corderoite is stable phase under high Cl$^-$, low pH conditions while cinnabar is stable at low Cl$^-$, high pH conditions. This is a graphic representation of equation 7.
an unusually high salinity and resulting high concentration and activity of Cl\(^-\) in the original ore bearing/transporting solution was the key factor resulting in corderoite formation on arrival at the site of deposition.

Evidence to indicate that the reaction of cinnabar to corderoite took place during cinnabar precipitation would include textures showing alternating cinnabar and corderoite layering in the same specimen or other textures indicating contemporaneous formation of the two minerals. No such textures have been found; in fact in all cases textures relating the two minerals show that corderoite replaces cinnabar. The low pH and/or low total sulfur conditions favorable for corderoite formation would provide an ideal environment for cinnabar deposition. Lack of textural evidence for contemporaneous formation of the two minerals indicates that corderoite formation began after cinnabar deposition had ended.

The possibility of a secondary remobilization of cinnabar at McDermitt that could have been responsible for the transgressive ore textures observed is very unlikely because of several chemical and physical restrictions. As previously discussed, the only mechanism capable of transporting significant amounts of Hg is transport as the complex ion HgS\(_2\)^{-2} in hot, alkaline reduced solutions (Krauskopf, 1951; Dickson, 1965). Cooling, drop in pH, or
oxidation of such solutions would force precipitation of HgS, and remobilization of precipitated HgS would require a return to the original transporting conditions. The near-surface environment of the McDermitt deposit would prohibit reheating and reduction of cooled, oxidized conditions. More importantly, formation of the mineral corderoite indicates that there was a change from the alkaline conditions required for HgS transport to the lower pH and/or lower total sulfur conditions necessary for corderoite formation.

This study has shown that corderoite formed from cinnabar and that corderoite formation began before the silicification of the "opalite breccia". There is no evidence for a prolonged time gap between cinnabar deposition and silicification of the "opalite breccia", indicating that conditions necessary for corderoite formation developed rather quickly. The development of these lower pH and/or lower total sulfur conditions essentially prohibited a secondary remobilization of cinnabar at McDermitt.

ALTERATION MINERALOGY

The alteration pattern at McDermitt indicates that while alkaline solutions moved laterally through the host rocks, the stability of the alteration minerals observed was dependent upon the log $aK^+/aH^+$ and the $aSiO_2$ of
The ubiquitous presence of montmorillonite indicates that the mercury transporting solutions were alkaline in nature, otherwise a low pH-stable phase such as kaolinite would have been the dominant alteration mineral.

The distributions of the accessory alteration minerals kaolinite, cristobalite, and adularia are best explained by lateral movement of mercury transporting solutions and accompanying changes in activities of $K^+$, $H^+$, and $SiO_2$. The equilibrium constant

$$K = \frac{a(K^+)^2 \cdot a(SiO_2)^4}{a(H^+)^2}$$

(10)

for the adularia-kaolinite reaction

$$2KAlSi_3O_8 + 2H^+ + H_2O =$$

$$Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_2(aq)$$

(4)

illustrates that the adularia-kaolinite reaction is to a major extent dependent on the silica activity of the system, and to a lesser extent dependent on the $aK^+/aH^+$ ratio of the system. Figure 34, which was modified after Bürt (1976) using equation 4, the adularia-muscovite reaction

$$1.5KAlSi_3O_8 + H^+ = 0.5KAl_3Si_3O_10(OH)_2 + K^+ + 3SiO_2$$

(11),

and the muscovite-kaolinite reaction
FIG. 34. Schematic H₂O vs. K⁺/H⁺ diagram illustrating relative stability fields of kaolinite, K-spar, and muscovite. Dashed line illustrates expanded stability field of K-spar corresponding to a 0.5 increase in activity of silica in aqueous solution. Modified after Burt (1976).
illustrates that fluctuations in silica activity can produce major changes in the stability field of adularia while other conditions remain unchanged, and that a high silica activity would force the stability of adularia. The silica concentration and resulting silica activity of a solution is directly proportional to temperature (Holland and Malinin, 1979).

At McDermitt, the adularia-kaolinite-cristobalite zonation pattern was produced by solutions traveling through the host rock environment from the southeast to the northwest. Solutions entering the Miocene sediments in the southeast were initially hotter and had a higher silica concentration and activity which forced the stability of adularia. As solutions moved to the northwest they cooled, forcing the precipitation of cristobalite, which lowered the silica concentration and activity of the solution and made kaolinite the stable phase. Additionally, precipitation of adularia in the southeast removed potassium from the system and lowered its $aK^+/aH^+$ ratio, which further enhanced kaolinite stability as solutions moved to the northwest. In summary, the alteration pattern observed at McDermitt is one of high $aSiO_2$, high $aK^+/aH^+$-adularia-stable conditions in the
southeast grading laterally into conditions of low aSiO₂, low aK⁺/aH⁺-kaolinite+cristobalite-stable conditions in the northwest.

The alteration assemblage at McDermitt classifies as intermediate argillic (Rose and Burt, 1979). This classification and the lack of a vertical component in the hydrothermal alteration pattern indicates that the deposit was formed beneath the water table.

DEPOSIT PARAGENESIS

The Cordero mine is located on the ring fracture system whereas the McDermitt deposit is situated well within the caldera (Fig. 35). Because the hydrothermal alteration pattern is so well developed within the pit area, it is likely that the McDermitt deposit had its own feeder system independent of, although probably related to, the Cordero deposit.

Ore transporting solutions entered the host rocks of the McDermitt deposit via this feeder system, then moved laterally downhill because these host rocks were the first highly permeable units the solutions encountered. The zeolitic sediment layer has a uniformly low (50-100 ppm) mercury concentration, although mercury values as high as 1,150 ppm have been reported, indicating that this layer had poor permeability which restricted the ore solutions from moving upwards into the overlying sediments.
FIG. 35. Schematic diagram illustrating relative positions of the Cordero and McDermitt orebodies. Vertical exaggeration approximately 4X.
The sulfides were deposited and corderoite formation began, then silicification of the "opalite breccia" took place. Because silica was deposited later than the sulfide minerals, silica was probably deposited from a cooler solution than were the earlier sulfides. Silicification did not significantly extend into any unit other than the lithic ash-flow tuff unit that became the "opalite breccia" due to that unit's highest permeability, perhaps also being restricted to that unit because of a later, cooler nature of the silicifying solution.

White's (1981) model of mercury transport as a major constituent in a CO₂-rich vapor fails to satisfy evidence presented from the McDermitt mercury deposit. Initially, his model requires transport solution temperature to fall below 100°C to insure condensation and deposition of mercury from vapor. As mentioned earlier, Rytuba (1976) studied fluid inclusions in fine grained quartz occurring in fractures and lining cavities within "opalite breccia" from the McDermitt deposit having homogenization temperatures indicating deposition at 200±5°C. As presented in this study, the silicification of the "opalite breccia" took place later than cinnabar deposition. The materials used by Rytuba in his fluid inclusion study are therefore very late, and temperatures derived from these materials may not have a significant relationship to ore mineral deposition. At best, these
temperatures should be considered low, since most ore
depositing systems cool down with time. For this reason,
200°C should be considered a minimum deposition
temperature for McDermitt, and this temperature is fully
100°C higher than the maximum deposition temperature for
White's model. Additionally, this study indicates that
ore-forming fluids at McDermitt moved laterally downhill
through tuffaceous sediments beneath the water table. A
vapor phase would travel upward through saturated
sediments unless a considerable force pushed it downhill.
Therefore, for vapor-phase transport of mercury to apply
to the McDermitt deposit, a strong force capable not only
of pushing a vapor down into a saturated environment but
also able to force individual gas bubbles through
sediments (as opposed to a highly permeable fractured zone
or open space) must have been exerted on the system, and
this is not likely. Finally, this study indicates that
the native mercury present at McDermitt was not deposited
from a vapor phase. Clearly, evidence presented makes
vapor-phase transport and deposition of mercury highly
unlikely at McDermitt, and strongly favors mercury
transport and deposition from a solution.

Numerous studies (Krauskopf, 1951; Dickson and Tunell,
1968; Tunell, 1970) clearly illustrate that mercury is
easily transported as a complex sulfide ion in alkaline
solutions. Application of such a transporting model would
explain formation of the montmorillonitized McDermitt orebody.

Precipitation of cinnabar at McDermitt was likely forced by cooling of the mercury transporting solutions as reflected by the lateral hydrothermal alteration pattern discussed above. Because the deposit formed beneath the water table, the hotter, alkaline ore transporting solutions were undoubtedly affected by mixing with cooler, neutral meteoric water of the host rock environment. In summary, precipitation was caused by cooling and drop in pH (from alkaline to neutral) of the mercury transporting solution when it mixed with the meteoric waters of the host rock environment.

A paragenetic diagram relating primary and alteration mineralogy at McDermitt is shown in figure 36. Silica is illustrated as shown to include the quartz and cristobalite from the hydrothermal alteration of the deposit with sulfide deposition and yet still illustrate the late silicification of the "opalite breccia". The diagram also illustrates that during the entire deposit-forming process, the ore-transporting solutions underwent a change from sulfide deposition to silica deposition.

Chalcedony is included with host rock materials that were deposited prior to mineralization of the deposit. Chalcedony occurs throughout the McDermitt caldera, indicating that it was emplaced by a regional rather than
FIG. 36. Paragenetic diagram for materials deposited at the McDermitt Mine. Host rock materials include all tuffaceous, lacustrine, and alluvial materials at the mine.
local process. Evidence placing chalcedony prior to mineralization is illustrated by figure 37 in which cinnabar-bearing adularia crystals are deposited in a veinlet that cuts across chalcedonic host rock, figure 38 wherein chalcedony clasts are recemented by later cinnabar, and by figure 39 wherein cinnabar is deposited in fractures in chalcedony.

The laterally trending intermediate argillic hydrothermal alteration pattern observed at the McDermitt mine provides strong evidence against surficial, syngenetic ore mineralization by hot springs mechanisms. Epigenetic, subsurface mercury deposition from laterally advancing alkaline solutions provides comprehensive explanation for the hydrothermal alteration pattern and the transgressive ore textures observed at the deposit.

Additional evidence against Roper's (1976) hot-spring mineralization model includes post-mineralization silicification of those rock materials collectively referred to as the "opalite breccia". Hetherington (1983) identified the silica phase present in the "opalite breccia" as alpha quartz, which extensively replaced all host materials it encountered. Silicification of the "opalite breccia" took place after ore mineralization, as previously discussed. Late replacement of host rock materials by silica was cited by Yates (1941) as evidence against a hot-spring genesis model for other similar
FIG. 37. Dark brown cinnabar-bearing adularia crystals of figure 27 in veinlets cross-cutting feathery, radiating chalcedony. Transmitted light, crossed polars (section slightly thick), field of view is 8.6 mm. Location N 2,611,705 x E 709,665.
FIG. 38. Angular white chalcedony clasts recemented by massive dark purple and red cinnabar. Coin is 1.75 cm. in diameter. Location N 2,612,210 x E 709,910.
FIG. 39. Red cinnabar deposited in fracture in chalcedony. Coin is 1.75 cm. in diameter. Location N 2,610,700 x E 710,190.
deposits of the Opalite District. In the same manner, late replacement of host rock materials by silica at the McDermitt deposit is cited as additional evidence against a syngentic hot-spring mineralization for the deposit.

Roper (1976) stated that the interpretation of the McDermitt mine as a surficial, syngentic hot springs deposit may not provide adequate explanation for the genesis of the McDermitt deposit as excavation and investigation of chemical processes continued. Since publication of that earlier model, extensive pit development and laboratory work have illustrated serious shortcomings in the surficial, syngentic hot springs genesis model and favor an epigenetic, epithermal genesis for the deposit. Although there are many megascopic features of the deposit that individually could mistakenly be interpreted as evidence for hot springs deposition, the textures and features of the deposit when taken on the whole can only adequately be explained by epigenetic, epithermal deposition. The hot-spring deposition model for the formation of the McDermitt deposit is no longer viable and should be abandoned.
IV. CONCLUSIONS

Hot, reduced, alkaline solutions moving laterally from the southeast to the northwest through tuffaceous sedimentary rocks deposited first pyrite and stibnite, then cinnabar, and finally silica, beneath the water table forming a disseminated deposit having local high concentrations of mercury. Precipitation was caused by cooling and drop in pH (from alkaline to neutral) of the ore transporting solution when it mixed with the meteoric waters of the host rock environment.

Corderoite forms as a replacement mineral by the chlorination of cinnabar under low pH, low total sulfur conditions. A high Cl$^-$ activity is the key controlling factor in corderoite formation. The near-surface environment of the McDermitt deposit provided the necessary low pH, low total sulfur conditions, and an unusually high salinity (and resulting high concentration and high activity of Cl$^-$) of the ore forming/transporting solution was perhaps the key factor resulting in the formation of corderoite there.
V. ADDITIONAL STUDIES

Mineralogy

The mineral kleinite (mercury nitride chloride sulfate, exact chemical composition unknown) occurs at McDermitt, commonly associated with gypsum in fractures in the "opalite breccia". Roper (1976) attributed its formation to precipitation from a vapor phase. However, this study illustrates that silicification of the "opalite breccia" took place later than cinnabar mineralization, and the occurrence of kleinite in fractures in the breccia indicates that kleinite formation took place well after the end of any ore-depositing process. Kleinite likely formed by late reaction of cinnabar with oxidized meteoric water, from which kleinite derives its nitride content. This formation of kleinite as a very late phase indicates that the system had a significant chlorine content even in its latest stages. This also implies that the ore deposit was still beneath the water table during the formation of kleinite.

Calomel (Hg₂Cl₂) has been identified during the course of this study, and in all cases is associated with eglestonite (Hg₆Cl₃O₂H) and native mercury. Dana (1951) describes calomel as a secondary mineral, formed by the alteration of cinnabar.

A mineral tentatively identified as mosesite
(Hg₂N(SO₄,MoO₄,Cl)H₂O) occurs in sediments in the north-central portion of the pit. Physical description of samples analyzed agrees with that of given in Dana (1951). However, due to contamination from gangue and a very limited concentration of the mineral, very poor X-ray diffraction patterns were obtained and a positive identification could not be made.

Chapmanite (SbFe₂(SiO₄)₂(OH)) has also been identified, occurring as veinlets in the softer lake sediments, deposited both conformably and nonconformably to bedding. Cech (1964) describes it as a probable hydrothermal mineral, and the field relationships wherein chapmanite veinlets cross-cut bedding planes support a primary hydrothermal paragenesis for the mineral.

Framboidal pyrite has been observed rarely in polished sections of silicified material.

Table 2 is a complete listing and paragenetic classification of minerals known to occur at the McDermitt Mine. In addition, a previously unreported mercury phase containing major amounts of iodine occurs with corderoite and cinnabar in the basal "opalite breccia" layer of the deposit. Samples of "opalite" that contain the iodine phase are bright yellow-orange and are photosensitive, rapidly darkening to black on exposure to sunlight. Polished sections viewed in reflected light show that the phase is a brilliant canary yellow, and exhibits abundant
Table 2. Minerals present at the McDermitt Mine, with parageneses.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hg Minerals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
<td>Primary Hydrothermal</td>
</tr>
<tr>
<td>Corderoite</td>
<td>Hg₃S₂Cl₂</td>
<td>Hydrothermal Replacement</td>
</tr>
<tr>
<td>Calomel</td>
<td>Hg₂Cl₂</td>
<td>Secondary</td>
</tr>
<tr>
<td>Eglestonite</td>
<td>Hg₆Cl₃O₂H</td>
<td>Secondary</td>
</tr>
<tr>
<td>Kleinite</td>
<td>Hg₃N₃Cl₂SO₄</td>
<td>Secondary</td>
</tr>
<tr>
<td>Schuetteite</td>
<td>Hg₃(SO₄)₂</td>
<td>Secondary</td>
</tr>
<tr>
<td>Mosesite (?)</td>
<td>Hg₂N(SO₄,MoO₄,Cl)·H₂O</td>
<td>Secondary</td>
</tr>
<tr>
<td><strong>Sb Minerals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stibnite</td>
<td>Sb₂S₃</td>
<td>Primary Hydrothermal</td>
</tr>
<tr>
<td>Chapmanite</td>
<td>SbFe₂(SiO₄)₂(OH)</td>
<td>Primary Hydrothermal</td>
</tr>
<tr>
<td>Stibiconite</td>
<td>Sb₃O₆(OH)</td>
<td>Secondary</td>
</tr>
<tr>
<td>Tripuhyite</td>
<td>FeSb₂O₆</td>
<td>Secondary</td>
</tr>
<tr>
<td><strong>Fe Minerals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>Primary Hydrothermal</td>
</tr>
<tr>
<td>Limonite</td>
<td>FeO(OH)</td>
<td>Secondary</td>
</tr>
<tr>
<td>Jarosite</td>
<td>KFe(SO₄)₂(OH)₆</td>
<td>Secondary</td>
</tr>
</tbody>
</table>
Table 2, continued.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>$(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$</td>
<td>Hydrothermal Alteration</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$</td>
<td>Hydrothermal Alteration</td>
</tr>
<tr>
<td>Adularia</td>
<td>$\text{KAlSi}_3\text{O}_8$</td>
<td>Hydrothermal Alteration</td>
</tr>
<tr>
<td>Quartz</td>
<td>$\text{SiO}_2$</td>
<td>Hydrothermal Alteration</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>$\text{SiO}_2$</td>
<td>Hydrothermal Alteration</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>$(\text{Na,K,Ca})_{2-3}\text{Al}<em>3(\text{Al,Si})<em>2\text{Si}</em>{13}\text{O}</em>{36} \cdot 12\text{H}_2\text{O}$</td>
<td>Diagenetic</td>
</tr>
<tr>
<td>Alunite</td>
<td>$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$</td>
<td>Secondary</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>Secondary</td>
</tr>
</tbody>
</table>
bright yellow internal reflections (Fig. 40). X-ray
diffraction scans of slide-mounted samples using Cu K-
alpha radiation gave the d-spacings and intensities listed
in table 3, the reflections of cinnabar and quartz being
included in case of overlap with the iodine phase.
Preliminary energy-dispersive microbeam analysis gave the
approximate chemical composition listed on table 4 and the
possible stoichiometric formula $\text{Hg}_5(\text{S, O})_4(\text{I, Cl})_2$. The
unusually high iodine content of this phase indicates that
it is a new mineral. This study has shown that at
McDermitt the mineral corderoite formed by replacement of
cinnabar under low pH and/or high $\text{Cl}^-$ conditions. The
fact that the new iodine phase occurs intimately
associated with both cinnabar and corderoite indicates
that the phase may have formed by similar processes under
similar chemical conditions.

Fluid Inclusions

Because Rytuba's (1976) fluid inclusion study was made
on very late materials, an attempt was made to obtain
fluid inclusion data from samples of colloform, open-space
filling cinnabar from McDermitt. Preparation and study of
four samples failed to reveal any fluid inclusions in the
cinnabar. Due to the opacity of the cinnabar, the samples
had to be ground thinner than normal to allow ample
transmission of light. No interference figures could be
FIG. 40. Brilliant yellow iodine-bearing phase with cinnabar (red) in silicified matrix. Reflected light, crossed polars, field of view is 0.87 mm. Location N 2,610,670 x E 709,950.
Table 3. X-Ray Powder Data for Iodine-Bearing Phase.

<table>
<thead>
<tr>
<th>d(Å)</th>
<th>I</th>
<th>d(Å)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.48</td>
<td>7</td>
<td>2.59</td>
<td>17</td>
</tr>
<tr>
<td>6.33</td>
<td>5</td>
<td>2.54</td>
<td>8</td>
</tr>
<tr>
<td>4.99</td>
<td>5</td>
<td>2.47</td>
<td>10 Q</td>
</tr>
<tr>
<td>4.25</td>
<td>26 Q</td>
<td>2.28</td>
<td>12 Q</td>
</tr>
<tr>
<td>4.15</td>
<td>9</td>
<td>2.23</td>
<td>8 Q</td>
</tr>
<tr>
<td>3.89</td>
<td>16</td>
<td>2.12</td>
<td>8 Q</td>
</tr>
<tr>
<td>3.73</td>
<td>10</td>
<td>2.07</td>
<td>6</td>
</tr>
<tr>
<td>3.65</td>
<td>10</td>
<td>1.98</td>
<td>8 Q</td>
</tr>
<tr>
<td>3.34</td>
<td>100+ Q,C</td>
<td>1.97</td>
<td>7</td>
</tr>
<tr>
<td>3.16</td>
<td>7 C</td>
<td>1.97</td>
<td>5</td>
</tr>
<tr>
<td>2.96</td>
<td>11</td>
<td>1.82</td>
<td>11 Q</td>
</tr>
<tr>
<td>2.86</td>
<td>17 C</td>
<td>1.81</td>
<td>8 Q</td>
</tr>
<tr>
<td>2.71</td>
<td>11</td>
<td>1.64</td>
<td>7 Q</td>
</tr>
<tr>
<td>2.64</td>
<td>21</td>
<td>1.54</td>
<td>10 Q</td>
</tr>
</tbody>
</table>

Q = Quartz, C = Cinnabar
Copper K-alpha Radiation
25 kilovolts, 15 milliamps
### Table 4. Chemical composition of Iodine-bearing phase.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>Atoms in unit cell, Hg = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>122.05</td>
<td>76.36</td>
<td>1.00</td>
</tr>
<tr>
<td>S</td>
<td>12.27</td>
<td>7.68</td>
<td>0.63</td>
</tr>
<tr>
<td>Cl</td>
<td>3.57</td>
<td>2.23</td>
<td>0.17</td>
</tr>
<tr>
<td>I</td>
<td>20.49</td>
<td>12.83</td>
<td>0.27</td>
</tr>
<tr>
<td>O (calculated)</td>
<td>1.46</td>
<td>0.91</td>
<td>0.15</td>
</tr>
<tr>
<td>Total</td>
<td>159.84</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Ideal formula: \( \text{Hg}_5\text{S}_{3.25}\text{O}_{0.75}\text{I}_{1.25}\text{Cl}_{0.75} \)

or \( \text{Hg}_5(\text{S,O})_4(\text{I,Cl})_2 \)

Weight Percent:  
- Hg = 77.4  
- S = 8.0  
- Cl = 2.0  
- I = 12.2  
- O = 0.3  

Total = 99.9

A: Original energy-dispersive analysis.

B: Analysis calculated to 100% including sufficient oxygen to obtain charge balance assuming mercury is in the +2 state and sulfur is in the -2 state.
obtained, however, these cinnabar chips showed a maximum of second order red interference colors under the polarizing microscope. If the samples were oriented to produce maximum birefringence, then knowing that the birefringence of cinnabar is 0.351, the estimated thickness of the samples is three microns. This fluid inclusion study was made impossible because the samples had to be ground thinner than the diameter of any resolvable fluid inclusions.
VI. SUGGESTIONS FOR FUTURE STUDY

Additional fluid-inclusion studies should be conducted if proper materials could be found because the expense of such a study would be minimal compared to information on transport and deposition temperatures and salinities that could be obtained.

Examination of the iodine-bearing phase and confirmation of its mineral status is imperative because knowledge gained from its study may have great bearing on the geochemistry of the McDermitt deposit.

Alteration studies of the other orebodies of the Opalite district should be conducted in order to establish a complete model for mineralization within the McDermitt caldera complex.

Further study of the paragenesis of the alunite balls would likely result in a more thorough understanding of the importance of the mineral at other deposits.
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