UNIVERSITY OF NEVADA, RENO

Depositional Modes of Manganese Oxides at Artillery Peak, Mohave County, Arizona

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

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4/15/2012

By

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Abstract ~

Economically significant manganese oxides deposits within Southwestern North America share many commonalities regarding alteration, depositional environment/mode, relative age, and mineralogy. These deposits can be broadly divided into two categories; terrestrial vein – type deposits (volcanogenic or hydrothermal) and terrestrial sedimentary rock – hosted stratiform – type deposits. Original depositional environments for stratiform deposits are interpreted as soils and bogs with hydrothermal enrichment or as a detrital component of a hot springs system redeposited into lacustrian basins. Vein – type manganese is believed to be a product of mineralizing aqueous fluids undergoing Eh – pH changes during ascent through near surface host rock or sediments (Roy, 1992). Manganese ions are naturally mobile at the earth's surface due to weathering, and manganese is the second most abundant transition metal at the earth surface. Reworking of manganese readily occurs due to late fluid influences within a wide range of temperature and chemical settings. As a result, some economically viable manganese oxide deposits are a combination of the aforementioned deposit styles. The mineral resource under development near Artillery Peak, AZ can be classified as a syngenetic stratiform manganese oxide deposit (Lasky and Webber, 1949). Recent evaluations of mineral deposits in western Arizona have led to the proposal of a new overall model for the Artillery Peak Manganese district as being a Detachment Fault Related Deposit. (Long, 2004) This deposit type is distinguished by a unique suite of precious and base metals, alteration gangue mineralogy, salinity, temperature, and structural setting. Resources at Artillery Peak exist in large stratabound manganese – rich sediments ranging from clays to coarse sands. Apparent vein - type manganese deposits are also

present at the locality and are known to have formed approximately 5 Ma after the emplacement of the stratiform manganese (Spencer, 1989). Fissures associated with local parallel faults striking northwest through the area are known to contain dense manganese chemically similar to stratiform manganese, but with highly elevated manganese and potassium. Manganese oxide mineralogy present at the site is dominantly hydrated manganese oxides (wad); ancillary minerals include romanechite – psilomelane $((BaH_2O)_2(Mn,Mn)_5O_{10})$, pryrolusite (MnO_2), ramsdellite (polymorph MnO_2), coronadite $((Pb\ (Mn,Mn)_8O_{16}))$, hollandite $((Ba(Mn,Mn)_8O_{16}))$, cryptomelane $((K(Mn,Mn)_8O_{16}))$, and other high oxide manganese minerals. Anomalous amounts of strontium, barium, and arsenic are associated with both vein – type and stratiform – type manganese. Presently there has not been any in – depth investigation of so called vein – type of manganese origin. Current commercial technical reports and past authors from various federal and state agencies propose conflicting theories regarding origin of so called vein – type manganese. The current Artillery Peak 43-101 argues for the deposition of hydrothermal vein type manganese associated with mid – Miocene volcanism (Tribe, 2010). Other authors have proposed migration and concentration of stratiform - type manganese via chemical interaction with alkalic fluids as a source for so called vein – type manganese (Spencer, 1991). Other evidence indicating that veins may have been derived from stratiform deposits includes; close spatial relationships of modal types and alkalic basalt flows and a high degree of similarity between low - temperature hydrous minerals, textures, and geochemistry in altered sections of stratiform – types and vein – type. Such remobilization via alkalic fluids has been noted in other Miocene manganese deposits of the southwestern US and Mexico.

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Chapter 1 ~ *Introduction*

This paper discusses the mineralogical and modal aspects of manganese oxide deposits within the Artillery Peak manganese district. Field work and mapping is focused on the western most down dropped fault block of three along a northwest – southeast trend, known as the Sandtrap Wash and Maggie Canyon. Mineralization in this basin is confined almost entirely to so called fissure and vein – type manganese. Units within this block are stratigraphically higher than the Chapin Formation which contains the principal volume of known stratiform – type manganese. Old workings at several sites and historic information from USBM show that vein – type manganese oxides within the study area experienced short lived production during the 1940's in the interest of developing strategic resources for raw steel (Lasky and Webber, 1949). Exposures of dense manganese veins, 1 – 3m in width, and veinlets as well as apparent fault breccias with dense manganese infill are associated with later and potentially syngenetic calcic and silicic events. Several authors have published work focusing on characteristics and mineralogy of sites in the eastern half of the district outlined hereafter. Publications and mapping initiatives by the Arizona Geologic Survey outline basic elements of geology, structure, and deposit typology.

Thesis Proposal ~

My proposal to update the most recent geology map from USBM Bulletin 936 Plate 82 focusing on unmapped fissure deposits in the Northwestern Maggie and Sandtrap Wash is complete. The primary goal is to illustrate a more accurate extent of the individual deposits, associated structural controls, and their collective depositional area which was completed through ongoing work digitizing outcrop mapping with associated optical and geochemical summaries of deposit localities. Mineralogy and depositional modes of vein – type manganese are not well studied or documented. Establishing mineralogy and paragenetic relationships at sample localities is an additional primary goal.

Further data collection focusing on fluid inclusion salinity and geochemistry will continue in order to develop a more robust data set. Comparisons of recently collected samples from new localities with those of previous studies will better demonstrate aspects of fluid salinity and geochemistry. There is strong evidence to suggest that the deposition of vein – type manganese has occurred in multiple short term episodes. Experimental dating techniques may be available to establish if there is a relationship between the relative ages of various events, to determine the sequencing of late vein events but will not be included in this discussion. In pursing these goals I intend to outline a preliminary model for the deposition of manganese oxides at the study site.

Method Definition ~

A geologic field mapping program, using GPS survey and illustrated via Arc GIS, expanding on Bulletin 936, Plate 63, was completed and includes new manganese oxide deposits within the map area. A cross section based on this mapping and recent drill logging is included in the appendices. A 3d model of all known manganese resources is being developed from drill logs, using Leapfrog 3d modeling software.

Methods being used to determine mineralogy, paragenetic relationships include ongoing petrographic work, scanning electron microprobe backscatter mapping, standard X – ray diffraction, and X – ray fluorescence analysis.

Analytical Techniques ~

Optical analytical techniques provided some identification of manganese oxides. A standard petrographic microscope, using reflected and transmitted light, was used to analyze 48 thin sections. However, poor crystallinity and the general similarity in optical characteristics of manganese oxides as a mineral group required further analysis to confirm primary identification. X – ray diffraction analysis was used to confirm mineralogy at 12 sites. Analysis was conducted using the XRG 3100 X – ray generator and XRD unit at UNR. Angle count per location was 2 analyzing from 50 to 90°. Wet samples were produced by pulverizing crystalline manganese in acetone and placing the resulting material on a standard slide. SEM samples from 8 thin section specimens were examined using a CAMECA SX50 electron microprobe at the University of Arizona by Ken Domanick. Several different beam conditions and beam sizes were tried in order to determine the conditions providing the best analyses. Based on these results, the majority of the analyses were performed using a 15 kV accelerating voltage, either a 20 or 40 nA beam current, focused electron beam, and 20 s peak counting time. Fluid inclusion data from four sites were analyzed to confirm salinities established by an earlier study. X – ray fluorescence analysis was used to determine barium concentration too elevated to be detected using acid digestion. Geochemical analysis, conducted by ALS of Reno, using aqua regia four acid digestion and ICP analysis was conducted on all samples.

Chapter 2 ~ *Regional Geology and Structural Setting*

North – central Arizona is well known for detachment fault related mineral deposits; such deposits exhibit unique mineralogical assemblages. Wide spread regional

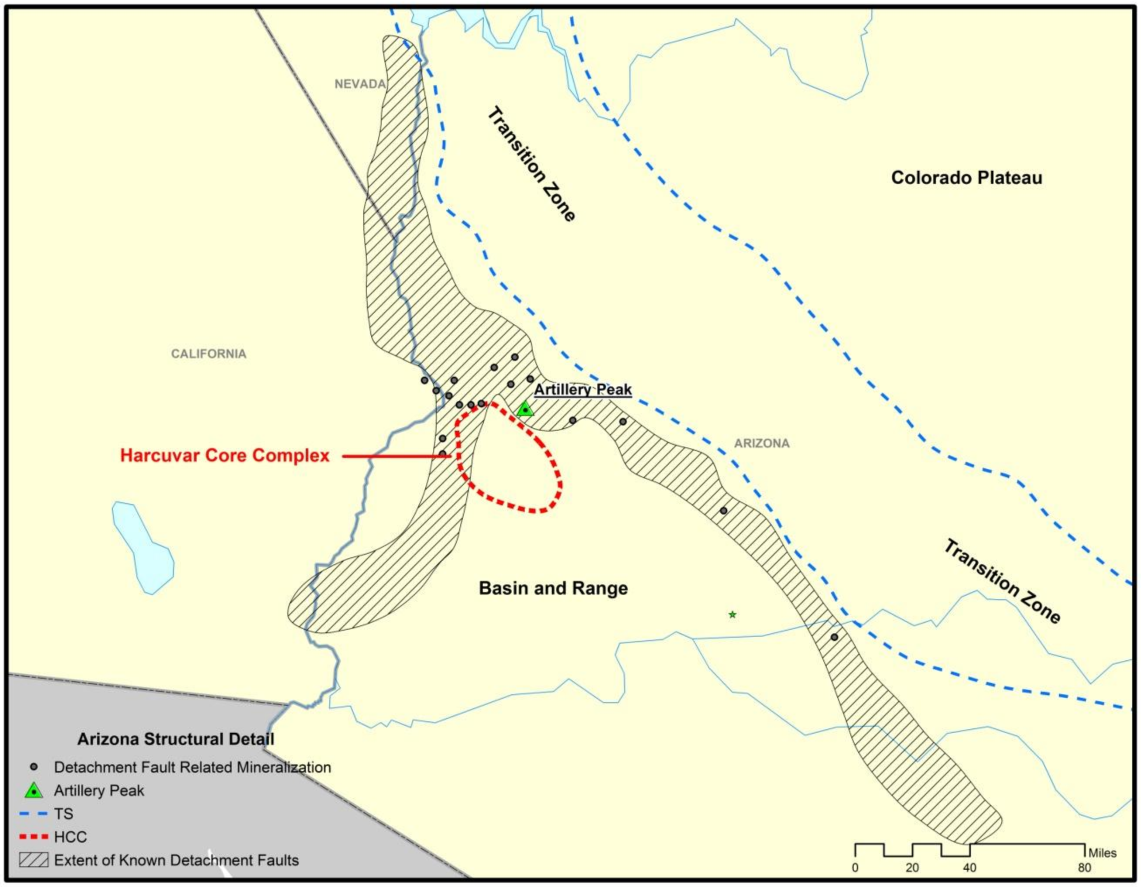


Figure 1 – Regional structural setting near Artillery Peak

detachment faults splaying from the Harcuvar metamorphic core complex exhibit definitive influence on mineral deposition and have recently be categorized as detachment – fault – related mineralization (Long, 2004). The dominant feature in the regional geologic setting is the Buckskin – Rawhide detachment fault, a large low angle normal fault, dipping northeasterly (See Fig 1 and 2). This detachment fault is associated with several precious and base metal deposits which have been a source of limited production. Exposures of Proterozoic mylonitic granitic gneiss are exhumed along the

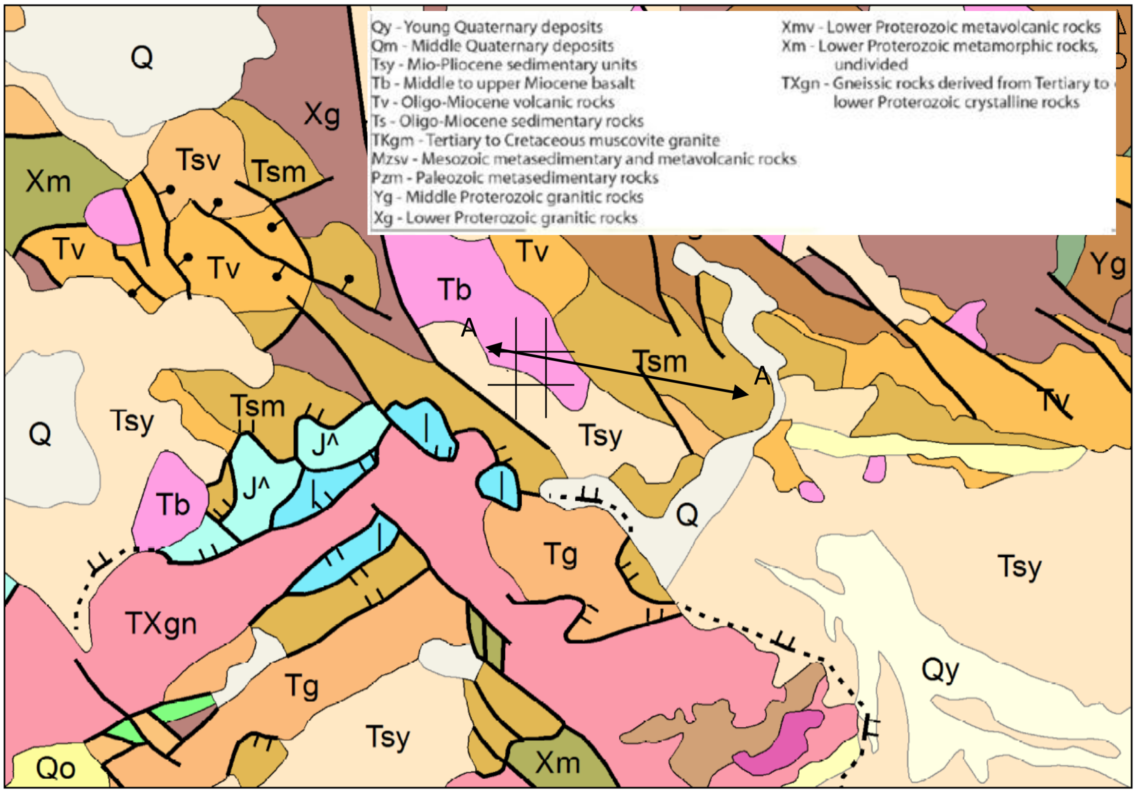


Figure 2 – A-A prime demarks cross section see fig. 3, note detachment fault on the contact of intrusive rocks and Tertiary sedimentary and volcanic rocks

detachment fault exposure west of the study area. Unconformable volcanic and sedimentary rocks from the late Oligocene to late Miocene are perched and gently tilted upon the predominantly Proterozoic package. A small early Tertiary granitic intrusion is a local addition to the basement near the study and helps establish early timing for mid – Miocene basin sedimentation and tectonic activity. Continued activity of the detachment fault has yielded the present day fault block structural profile marked by several steeply dipping north east local faults and basalt capped up thrown blocks (See Fig. 3).

Chapter 3 ~ *Local Geology*

Geology of the Artillery Peak manganese district consists primarily of volcanic and sedimentary units ranging in age from 8 – 25 Ma. Gneissic basement rock is overlain by the Artillery Formation. The lower Artillery Formation consists of a 200m interval of sandstone, overlain by 50m of basalt. The upper Formation consists of the Artillery Peak mega – breccias and conglomerates which are interpreted to be part of catastrophic debris flow taking place before 20 Ma. The entire Formation is cross cut by the Santa Maria intrusion. K/Ar dating of biotite from this intrusion gives a date of 20 Ma. The intrusion is unconformable to the Chapin Formation which sits atop the Artillery and consists of roughly 200 – 250m of "redbrick" sandstone with intervals of unconsolidated sand and gravel. The Sandtrap conglomerate is conformable to the Chapin Formation, but is horizontally crosscut locally by basalt flows, the Cobwebb and Manganese Mesa basalt, 13.3 and 9.5 Ma, respectively (Spencer, 1989). Much of the Sandtrap conglomerate has

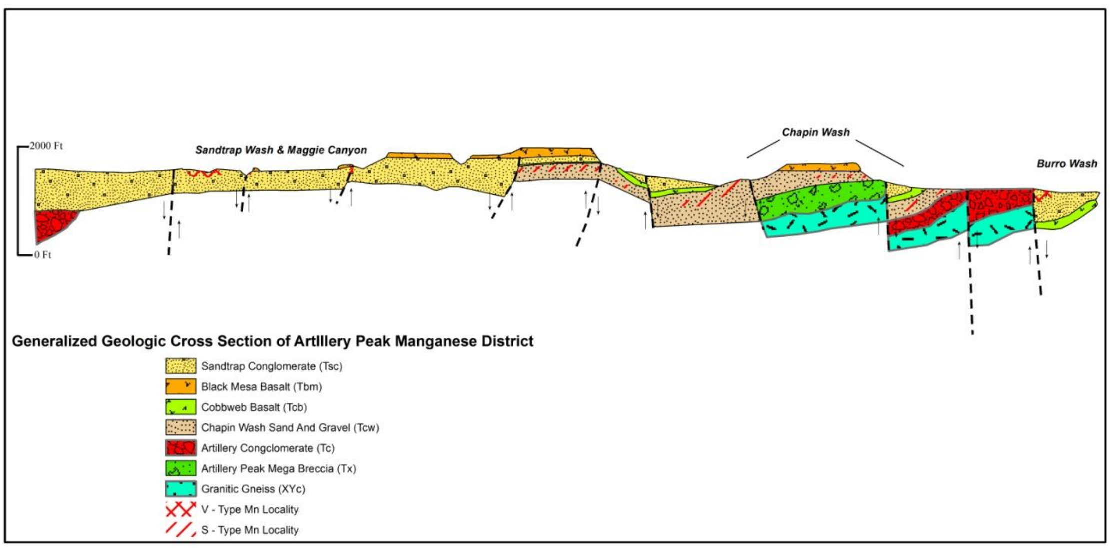


Figure 3 - Section A – A prime, adapted from Lasky and Webber (1949) based on drill logs and study site mapping.

been eroded away leaving basalt capped up – thrown fault blocks. Tectonic evolution of the district primarily occurred during deposition of the Chapin Formation and is marked by a continually increased steeping and thickening of bedded units in the direction of detachment fault dip (Spencer, 1989).

Mapping Area Units ~

Quaternary Alluvium fills narrow shallow canyons throughout the western basin. Material in washes and arroyos may include unconsolidated manganiferous sand and iron rich sands, well rounded – poorly sorted components of the underlying conglomerate, basalt units, and basement material, estimated maximum thickness is no more than 15 m.

Black Mesa Basalts, (aka Manganese Mesa Basalt), are present as float at topographic highs across the western basin and can be found on the margin of the Rudy fault in the eastern section of the mapping area. Manganese Mesa basalt is most evident as the cap stone of up – thrown fault blocks present on to the east of the mapping area. Local hematitic and chloritic alteration is present where obvious pillow structures mark small flow events. Elongated vesicules are infilled with chalcedony. Columnar and blocky structures are common of cap basalt exposures on the up – thrown fault block known as Maggie Mesa which tilts westerly 2 – 3°. Approximate thickness of cap basalt is no greater than 30 m. Exposures in the basin are less than 10m in height and commonly appear as unconsolidated piles of rubble.

The Sandtrap Conglomerate is the dominant lithology within the map area. Sub units of this formation include large grain (cobble) loosely consolidated clast – supported conglomerates, unconsolidated gravel, clay and sand beds, and cemented layered sand beds. This formation is the principal host of manganese vein, fissure, and breccia type rock. Alteration of this unit is best exhibited by deep red to pink coloration associated with calcic and silicic cementation generally of bedded sandstone units. Alteration associated with basalt flow contact exhibits similar characteristic.

The Cobbwebb Basalt does not appear in outcrop within the map area but is present between Sandtrap and the underlying Chapin Wash Formation. Mass wasting and commercial waste piles in northwestern Maggie Canyon probably conceal the basalt flow. Drill intersections exhibit an approximate local thickness of 5 – 10m.

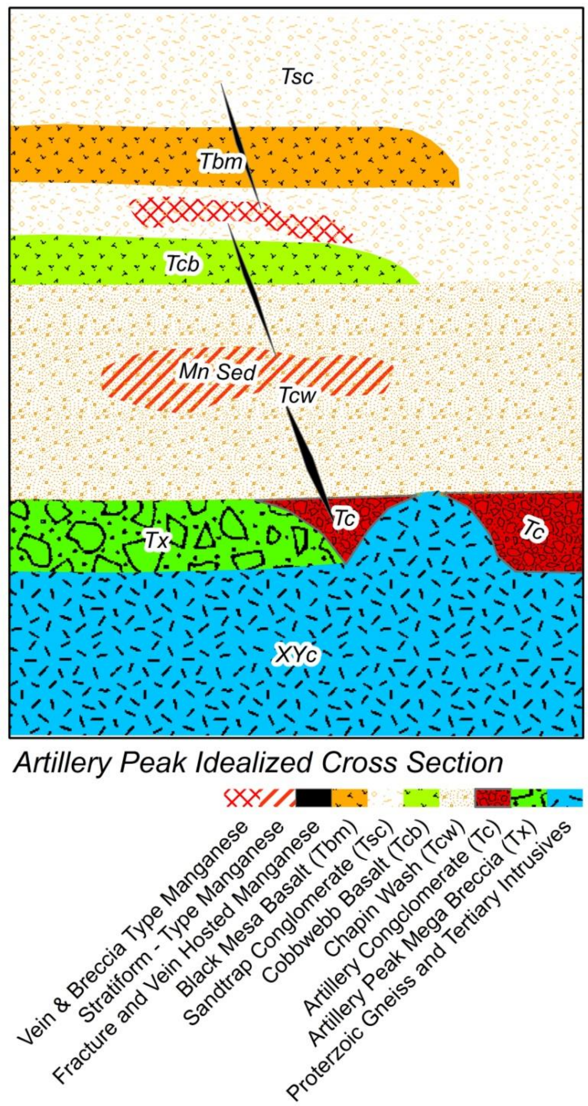


Figure 4 – Composite cross section based on field observations adapted from Spencer, 1991.

The Chapin Wash Formation is represented only in the northwestern most corner of the mapping area and hosts the Maggie Mine which is an altered stratiform manganese deposit and described hereafter in sample site descriptions. This formation contains a variety of strata including marker unit ash and tuff layers which are evident in manganese beds both as detritus and as lithified air fall sequences. Biotite related to early volcanism in formation yields K/Ar dates of 20 Ma and older.

Chapter 4

Manganese Oxide Deposits: Formational Environments and Recent Classifications ~

The primary mineralizing event related to the Artillery Peak distract has been identified as a detachment – fault – related mineral deposit. This model accommodates the structural settings and mineralization associated with the area between Havurcar metamorphic core complex and the minor extensional area known as the Transitional Zone (See Fig 1). Distinguishing characteristics of this model are outlined by recent USGS publications:

- Deposits are controlled by structures formed during detachment faulting. These include the low-angle, detachment-fault system, high-angle faults in the lower-plate just below the detachment fault, and low- to high-angle normal faults in the upper-plate.

- Deposits are commonly brecciated or deformed by movement along or above the detachment fault.

- Chlorite – epidote – calcite alteration occurs along and below the detachment fault. These altered zones locally contain base – metal sulfides and barite.

- There is massive potassium feldspar replacement of upper-plate rocks. This alteration appears to generally precede ore formation and is not always spatially associated with mineralization.

- Weak sericite-silica alteration of wall rock is locally present around barite-fluorite veins.

- Most mineralization consists of iron and copper oxides, principally specular to earthy hematite and chrysocolla. Common gangue minerals are chalcedonic to amethystine quartz, ferrous to manganiferous calcite, barite, fluorite and manganese oxides. Distal barite-fluorite veins consist of variable proportions of barite, fluorite, and manganese oxides. Common gangue minerals are quartz and manganiferous calcite.

- Fluid inclusions have moderate homogenization temperatures (150 to 350 °C) and salinities (10 to 23 equivalent weight percent NaCl), compatible with precipitation from connate brines. Fluid inclusions from barite-fluorite veins have lower homogenization temperatures (90 to 200 °C) and are somewhat less saline (6 to 20 equivalent weight percent NaCl), compatible with precipitation from variably cooled and diluted connate brines.

- Host rocks are enriched in Cu, Pb, Zn, Au, Ag, and Ba and are depleted in Mn, Sr, Ni, and Rb. Elements characteristic of epithermal environments, such as As, Sb, Hg, and Tl, occur in very low, background-level concentrations (Long, 2004).

The Artillery Peak Manganese deposit is tightly constrained within this regime of distinguishing features for the model type. However, aspects of vein – type mineralogy lack strong affinity to this model especially regarding salinity and specific mineralogy.

The classification of manganese oxide mineralogy has been a source of confusion for many past authors due to the high degree of similarity of optical and physical characteristic within the mineral group. Several mineral types used within the last 50 years are either obsolete or synonymous with a more popular name. Seminal authors of Artillery Peak Manganese literature, Lasky and Webber, established general descriptions of manganese oxide deposits as either sedimentary rock hosted stratiform – type manganese or hydrothermal vein – type manganese. Several authors have evaluated their observations of the vein type manganese including Mouat (1962), Hewitt (1960), and

Spencer (1991). Mouat's work expanded on the specific mineralogy of vein – type manganese in altered or cemented intervals of stratiform deposits and concluded that recrystallization and modification of primary minerals in veins had occurred in various episodes. Hewitt, who wrote several articles on the district, attempted to establish modal characteristics at the site and identified minerals which are currently considered strictly supergene in nature. More recently authors focusing on deposits abroad, Roy (1968, 1992) and Nicholson (1992), have attempted to establish modal classifications based on genesis. These summaries rely on geochemical and mineralogical associations to establish deposit classification. Work by Nicholson (1992) elaborates on genesis by using two main groups: (1) terrestrial manganese deposits, (2) supergene and hydrothermal systems. Supergene and hydrothermal (hypogene vein system) manganese oxides are subdivided further into terrestrial and marine deposits. Terrestrial deposits include those generated from bogs and enriched and altered organic soils, precipitated directly from fresh water, and forming from weathering effects from previously mineralized sequences. Hydrothermal deposits in terrestrial settings include hot springs and vein occurrences. A separate category known as "Duhbites" defines mineralization forming syngenetically or coincident as a byproduct of a proximal ore body. Classifications by Roy (1992) focus on mineralogy and environmental settings. Roy evaluated hundreds of manganese deposits globally and used interpretations of formational environments to assigned specific primary and gangue mineralogy to specific settings. Presently, these classifications and their sub categories are not strictly synonymous or in agreement with observations or terminology used in current and past literature regarding Artillery Peak. However, past determinations used along with a newer classification are helpful in establishing the probable origin of the manganese oxides in the study area.

Past production in the Artillery Peak district has focused on two depositional modes of manganese oxides; breccias and fissure hosted manganese known generally as vein – type, and stratiform – type deposits consisting of lacustrine sediments ranging from clays to coarse sand grains. Current goals for commercial development are focused on stratiform – type deposits.

Three local basins define the extent of known manganese deposits within the district. The central basin, known as the Chapin Wash, contains by far the most tonnage of known manganese in the district. Basins west and east of the Chapin have experienced

Figure 5 - McGregor Pit face exhibits bedded stratiform manganese consisting of clay to sand size particles with common dense recrystallized lenses.

limited erosion by comparison and have preserved much of the Sandtrap Conglomerate and less of the two younger basalts. The central basin or Chapin Wash, exhibits many exposures of stratiform – type manganese at the surface largely within unconsolidated silts of the Chapin Formation. Basins west and east host abundant vein, fissure, and breccia – hosted manganese which locally cross – cut the youngest basalt cap. Examples of vein – type manganese can be found crosscutting all Miocene units in the district.

Chapter 5

Stratiform –Type Manganese ~

Resource development of stratiform type manganese has revealed the presence of approximately 15 billion pounds of manganese oxides in the Artillery Peak district (Tribe, 2010). The most likely fluid conduit for such a volume of manganese is the Buckskin – Rawhide detachment fault which is exposed just west of the district. The detachment fault is marked by gently dipping mylonitic granitic gneiss. Massive iron oxide and minor copper oxide occur along the fault. Due to chemical and physical affinities, iron and manganese oxide deposits are commonly formed in association with low temperature aqueous fluids. Increases in pH due to interaction with carbonate host rocks can induce iron

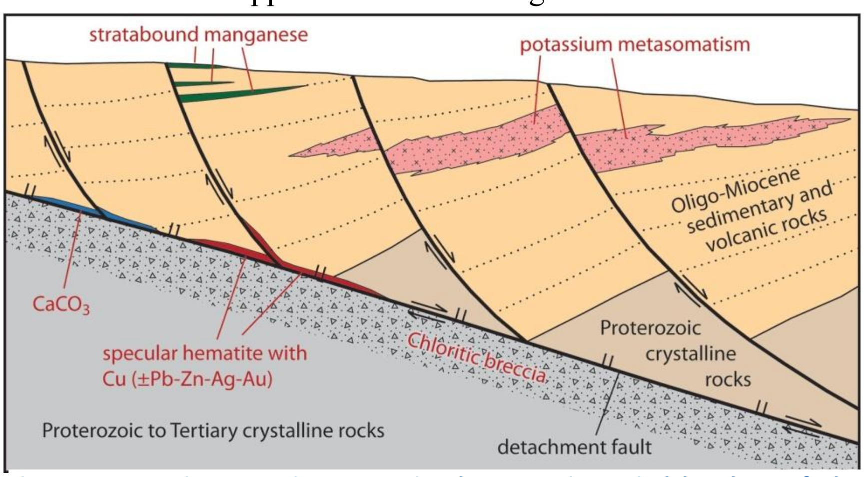


Figure 6 – AZGS Diagrammatic Cross Section demonstrating typical detachment fault related mineralization profile.

deposition and retain manganese in solution until neutralization occurs in near surface environments (Roddy, 1988). Spencer and Welty theorized that hydrothermal fluids associated with multiple base metals deposits along the Buckskin – Rawhide detachment fault retained manganese due to increasingly acidic fluid. Neutralization of these fluids when reacting with ground water and resulting in subsequent deposition is consistent of typical manganese high oxide depositional conditions (Spencer and Welty, 1989) (See Fig. 6).

Manganese may have been deposited directly into unconsolidated sediments or as near surface veins. The setting for such deposition is unknown and subsequent large scale erosion is implied by consistency and volume of present day bedded and pod like manganese deposit which show clear synsedimentary characteristics. This suggests transport to the paleobasin through erosional processes and deposition into a shallow lake or ephemeral playa deposit. Several large stratiform manganese oxide pods are present within valleys and washes which mimic the NW – SE structural setting. The Chapin Wash contains beds ranging from 100 to 1000 m in length (See Fig. 8a). Bed extent may range from several meters up to a kilometer. Beds are commonly interlayered with deep red clay, volcanic ash and other non – manganiferous alluvial sediments. Manganiferous clays to

Figure 7 - White volcanic ash interbedded with manganese at Black Mesa

coarse sands range in thickness, but are generally no greater than 20 m. Petrographic analysis shows that manganese is present as a matrix among grains of many mineralogical origins including a high degree of volcanic glass and lesser felsic components. A discontinuous string of manganese beds is present over 5 km down the Chapin Wash, terminating at Alamo Lake. Neighboring Maggie and Burro Washes to the west and east also contain large stratiform manganese deposits at greater depth.

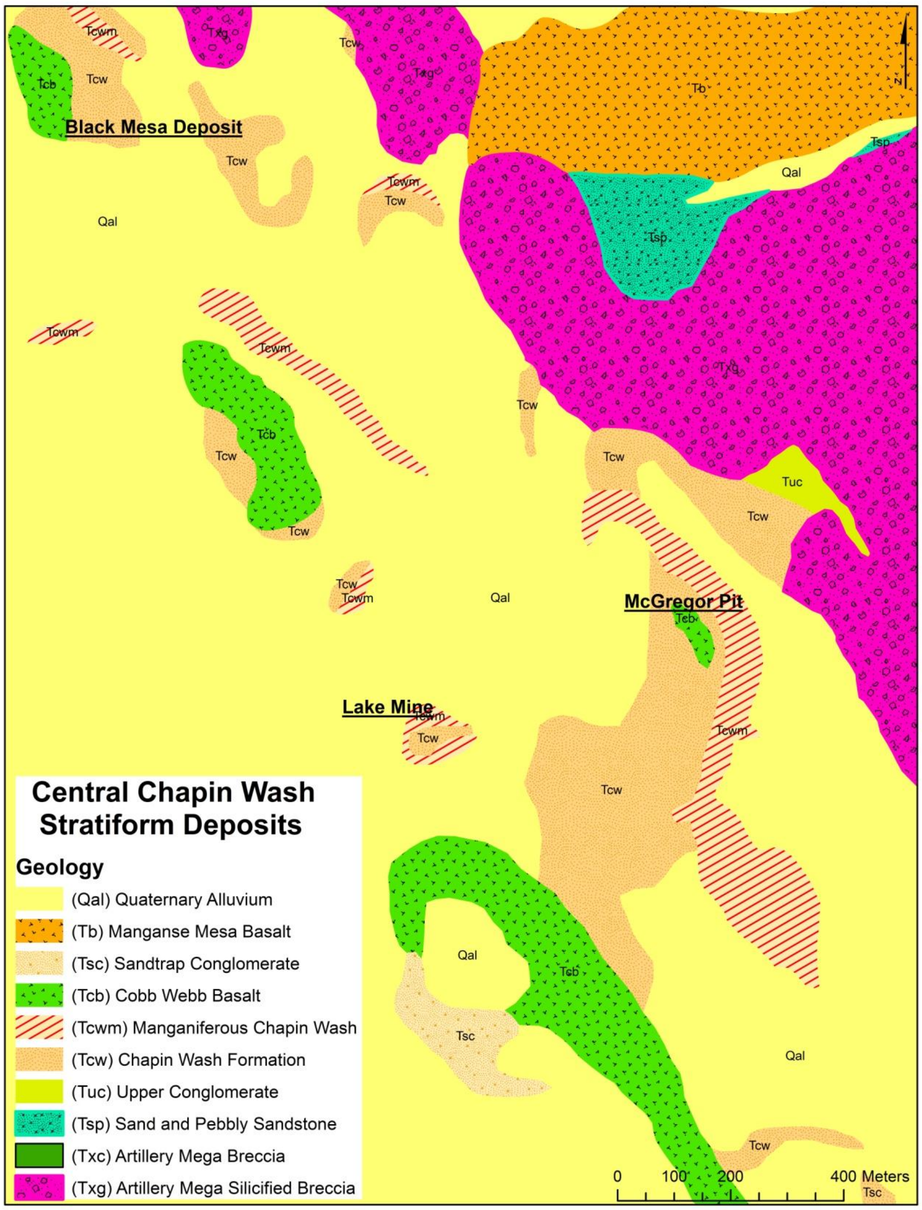


Figure 8a – Surface geology adapted from AZGS mapping program (1989). Stratiform – Type manganese is present in Tcwm unit.

Mineralogy of Stratiform – Type Manganese ~

Recrystallization within these manganese pods is common and several minerals have been identified by optical methods and XRD analysis. Bulk sample geochemistry and XRD analysis of open pit localities generated a formula of $K_{22}Ba_{20}Sr_7Al_2Fe_{26}Mn_{318}O_{557}$ (Tribe, 2010). This assemblage of elements constitutes all of the most common cations likely to form with manganese and oxygen, commercially known as wad. Geochemistry from stratiform deposits at Artillery Peak shows elevated barium, strontium, and zinc. In several cases bedded units show elevated lead and potassium values. Stratiform units exhibit rare intersections of hard apparently recrystallized intervals which are either deep indigo blue, interpreted as psilomelane - romanechite, or dark metallic silver. XRD analysis from sites in south Chapin Wash identified several higher oxides in concretionary rims including potassium bearing cryptomelane, ramsdellite, and pryrolusite (Mouat, 1962).The majority of production of any of the stratiform type deposits has come from the Maggie canyon area. Textures and mineralogy identified optically show that this unit experienced a certain level of alteration via late stage calcic and silicic events. The deposit typically carries higher grades of manganese up to 12 - 14% compared with 4 – 8% in most other bedded units. Cryptomelane and pyrolusite are abundant within dense apparently cemented intervals. Other minor oxides exist as apparent replacements of pryrolusite or rare ramsdellite. Presence of these minerals is normal only if supergene processes occur or if late stage fluids interaction occur (Roy, 1992). Late stage fluid reworking is plausible given the positioning of several local faults crosscutting the deposit as well as late basalt events which contact the stratiform manganese. Geochemical data from drilling shows elevated strontium values associated with higher grades of manganese. Elevated amounts of lead, barium, and potassium are also common.

Characteristics and Sample Localities of Stratiform – Type Manganese ~

Samples collected from stratiform deposits in the central and eastern fault block are not included in the map area. One sample was collected from a bedded manganese outcrop southwest of the map area. Drill results from more than 200 diamond and reverse circulation holes show average grades between 3 – 4% Mn. Locations in the central basin include open cuts on stratiform beds and

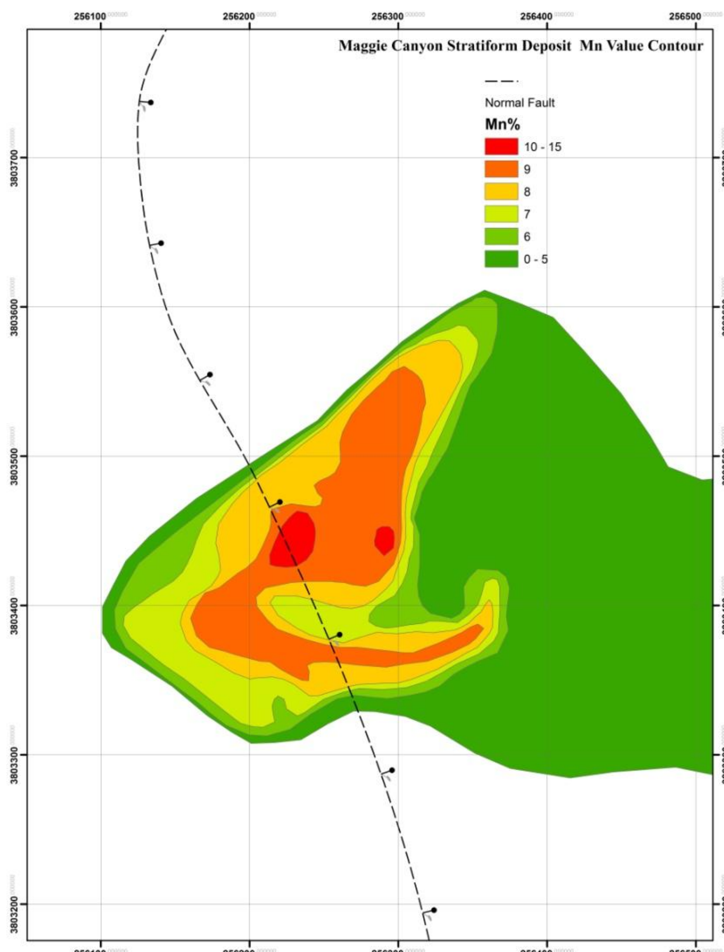


Figure 8b – Stratiform unit at Maggie Mine crosscut by normal fault, note enrichment associated with fault contact.

beds exposed within the Chapin Wash. Additional samples were collected from the Maggie Mine where clear alteration along fault contacts suggest upward fluid movement (See Fig 8).

North – central Chapin Wash ~

Several open pit exposures are present in the north central portion of the Chapin Wash including the McGregor Pit, Lake Mine, and Black Mesa (See Fig. 8a).These exposures are located along a series of local normal faults which in some cases exhibit as much as 15m of up thrown footwall (See Fig 9 and 10). Channel samples and core logging from these sequences show coarse to fine sand – mud sized grains in beds ranging in thickness from millimeter laminations to meter thick sand beds. Thin ash beds can be found at depth at these localities with some preserved sanidine. Beds shift in color and

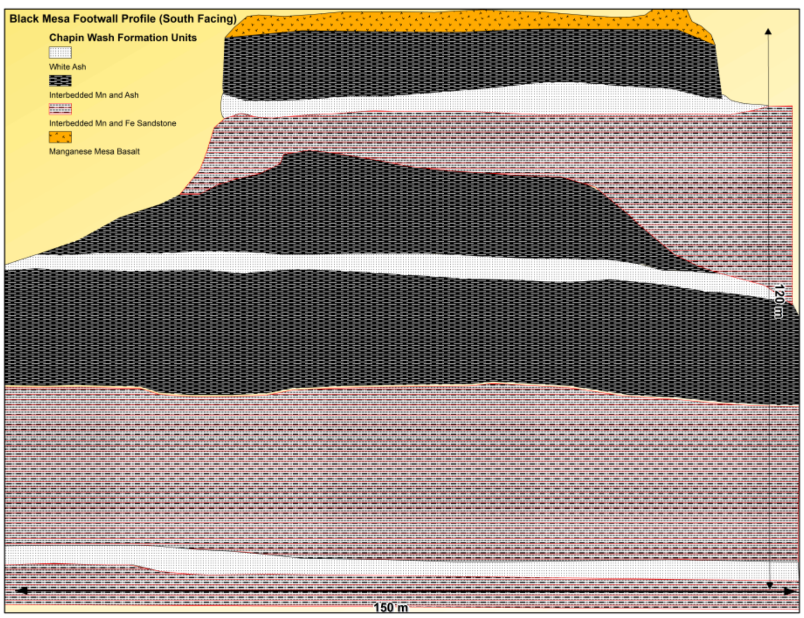


Figure 9 – Black Mesa – Interbedded manganese and ash texture visible in fig. 14

consistency being either jet black, manganiferous or being deep red, ferrous and rarely arkosic. Manganese recrystallization is especially evident in these beds because fresh faces or drill core will appear indigo blue to black. XRD analysis of recrystalized intervals confirms the presence of pyrolusite and associated calcite. Calcic alteration is pervasive in Mn – bearing intervals in this sequence and exhibit elevated Ca, up to 7% with apparently associated anomalous Ba and Al, greater than 1% and 5%, respectively. Mn values within altered intervals exhibit grades up to 20%.

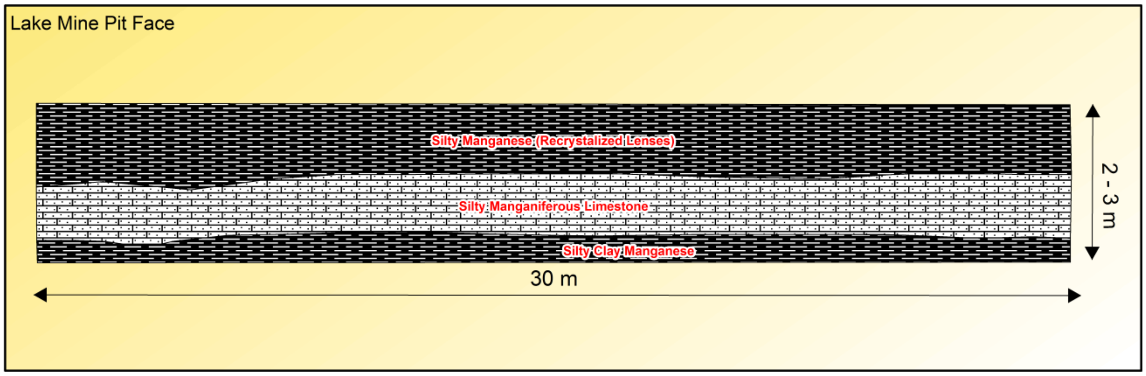


Figure 10 – Lake Mine – Typical interbedding present in carbonate cemented bedded manganese deposits of the Chapin Wash

South Chapin Wash ~

Outcrops of stratiform beds are not well exposed in the south part of the basin including Plancha Mountain, Loves Flat, and Lower Chapin wash. Several adits have been driven into foot wall exposures along the local normal faults in this area. Near surface beds are at most 5m thick and exhibit a smaller variation in grain size. Geochemical analysis confirms high elevated base metal content and XRD confirms the presence of the lead manganate, coronadite. Mineralogy identified by SEM included components of the

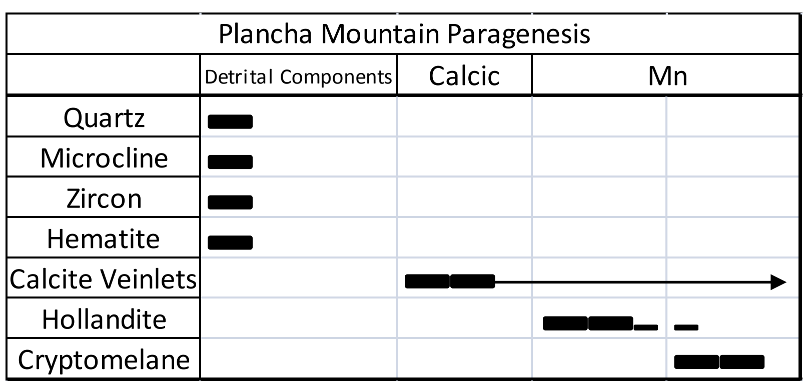


Figure 11 – Calcic flooding cements detrital components and is present in cross cutting veinlets over later manganese oxides.

sandstone clasts and hollandite as matrix with later cryptomelane as a fibrous rind. Later calcite veinlets are also present.

Maggie Mine ~

Two adits and an extensive tunnel were driven into the northwestern flank of Maggie Mesa in order to access the continuous bed of stratiform manganese beneath the basalt – capped rock. Bed thickness ranges from 5 – 15m; grades in the Maggie Mine are generally higher than average, 8 – 12% Mn. Geochemical analysis of rock chip specimens from this outcrop exhibit elevated Pb and Zn, 1.4 and 1.2% respectively. Observations of the Maggie deposits outcrop show distinct alteration zoning which is reflected in the drill results where calcic and silicic cementation is associated with higher grades of Mn. Pervasive calcite veining and alteration are present in outcrop where previous mapping programs identified a normal fault, presumably with very little displacement. As described, above petrographic analysis identified the presence of cryptomelane and pyrolusite (Fig. 13) that was confirmed via XRD analysis. SEM analysis indentified radiating botroidal masses of fibrous hollandite. Variations in internal reflectance with radiating masses indicate compositional differences in Zn, Ba, and Sr.

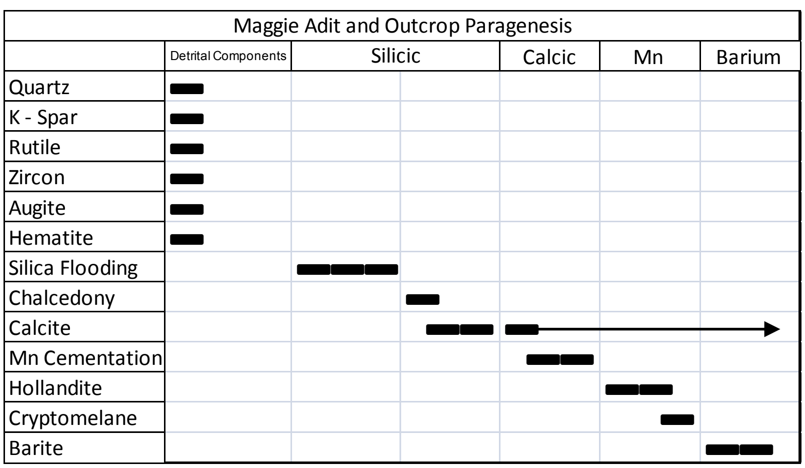


Figure 12 – Primary silica flooding is overridden by continued calcic flooding occurring with manganese emplacement. Late stage barite is developed over Mn

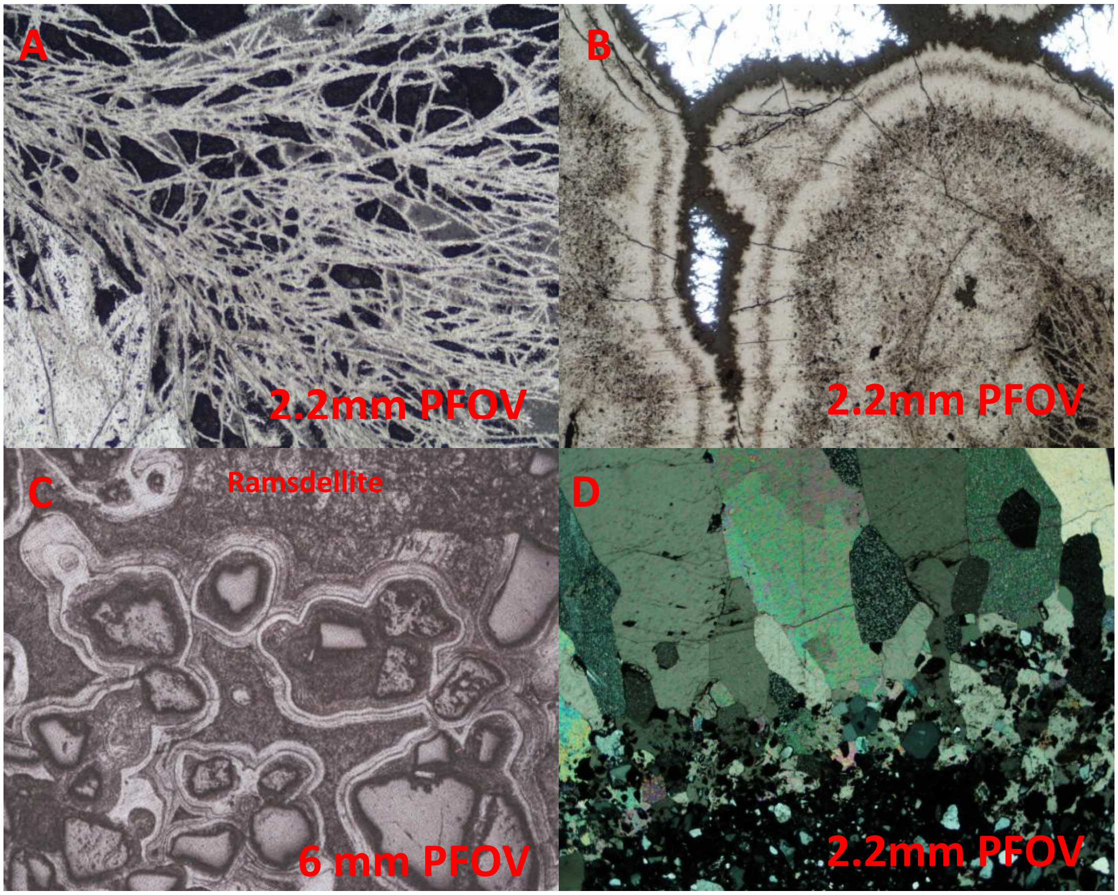


Figure 13 –The Maggie Mine - (A). Cryptomelane infilling factures of ramsdellite. (B). Concretionary rims of pryrolusite, the darker, granular mineral, with cryptomelane. (C). Acicular ramsdellite grains overridden by later cryptomelane and pyrolusite (Mouat, 1962). (D). Massive late stage calcite mingled with wad or manganiferous sediments lacking texture.

Rawhide Wash~

Samples collected from outside the map area show that smaller manganese stratiform beds exist west of Maggie and Sandtrap Wash. Deposits southwest of the map area were previously identified by mapping programs conducted by the Arizona Geological Survey. A bedded unit of manganiferous sandstone exhibiting calcic cementation is exposed within an arroyo near the exhumed margin of the Buckskin – Rawhide detachment fault. Petrographic analysis of this unit shows that sand particles are largely volcanic glass shards, quartz and plagioclase with late calcite and manganese cementation (Fig. 14). The outcrop strikes NW – SE and dips gently 15°northeast. Manganese is present within red brick arkosic sandstone presumably of Sandtrap Formation. Paragenesis for this sample is unclear; however, detrital components within calcic – and manganese – rich matrix suggest at least one pulse of calcic fluid after deposition. The presence of manganese primarily as the matrix and a lack of interbedding of Mn – rich zones but rather undulating fronts suggest Mn either entered the sediment with the calcic fluid or as an earlier fluid stage.

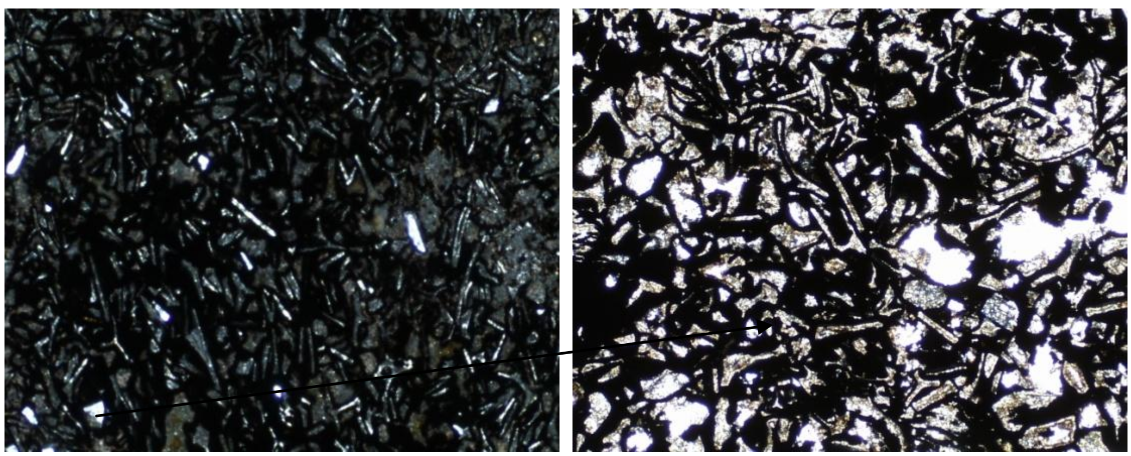


Figure 14 – The Rawhide Wash - Typical stratiform manganese exhibits detrital textures with abundant quartz and calcite in a manganese matrix and volcanic glass shards (4.4mm FOV). (Figure A transmitted light, Figure B normal

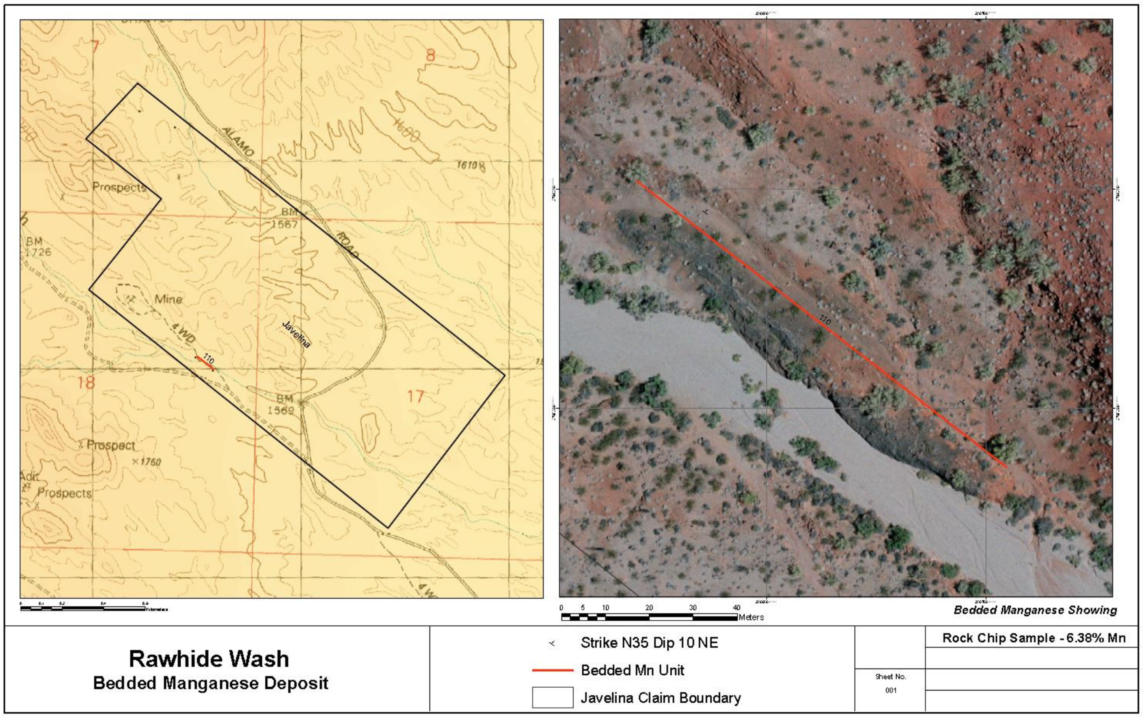


Figure 15 – Map detail prepared for American Manganese Inc. outlining claim boundary and scale of deposit

Chapter 6 ~ *Vein - Type Manganese Deposits*

There are over 30 vein-type manganese deposits in the Artillery Peak district all of which are associated with local faults. Further classification of vein – type manganese may be expanded to include breccia and dense fissure deposits. Veins, manganese – rich breccias, and dense fissure deposits are most abundant in the western basin, the Sandtrap Wash, but can be found throughout the stratagraphic column from early – mid Tertiary Artillery mega – breccia which appear to have silicic and manganiferous cementation, and also within the youngest Manganese Mesa basalt. Vein – type manganese cross cutting the latest basalt is at least younger, approximately 9.5 Ma. Experimental Th/U Helium dating techniques may soon yield dates for vein deposits but will not be included in this discussion. Grades within so called vein type deposits exceed 40% Mn. Some commercial production did focus on exploitation of vein type deposits and many vein localities have open pits and old workings. Despite exhibiting much higher grades, these deposits contain relatively small tonnage compared with stratiform beds and pods and are not densely spaced making extraction unattractive. Areas in the basin show a spatial relationship between stratiform and vein type manganese both stratigraphically above and below beds. The latest work examining depositional modes argues for the development of fissures within local parallel faults resulting in the emplacement of manganese veins through a volcanogenic source associated with younger basal flow events. However, several North American Miocene manganese deposits exhibit vertical migration of stratiform manganese into local faults and fractures due to the movement hydrothermal fluids at a wide range of temperatures (Friedberg, 1983; Roy, 1992).

Mineralogy of Vein - Type Manganese~

Optical and XRD analysis identified several abundant manganese oxides in the Artillery Peak deposits. Cryptomelane is pervasive as a late stage replacement product and most commonly occurs in voids or fractures on the margin of pyrolusite and hollandite (Mouat, 1962). Cryptomelane appears as acicular crystals or as needlelike fibrous rinds. Needles up to 1 – 2mm in length and are locally identifiable in with the naked eye. Hollandite, barium manganese oxide, exhibits strong pleochroic properties and commonly appears as dense tabular euhedra. Rare acicular grains of hollandite have been noted in previous studies. A sample collected from the Priceless open pit mine analyzed by XRD identified coronadite, lead manganate (Hewett, 1971). Recent geochemical analysis of a nearby vein locality confirmed anomalous lead values.

Psilomelane - romanechite was identified by X-ray spectrographic analysis and X-ray powder pattern identification (Mouat,1962). Psilomelane from veins in the central fault block is associated with zinc and barium. Psilomelane was also observed in thin section and is easily recognizable by its indigo blue pleochroic character. Minor ramsdellite is present apparently replacing primary psilomelane and hollandite. Geochemical analysis shows elevated arsenic, barium, calcium, iron, potassium, strontium, zinc, and lead in the majority of rock chip samples collected during mapping.

Characteristics and Localities Vein - Type ~

Thirty – eight samples were collected from vein localities throughout the district. Paragenetic relationships are distinct because manganese veins cross cut various geologic formations throughout the study sites. Photomicrographs from 5 open pit samples within the Sandtrap Wash and Maggie canyon demonstrate the variation in sequencing.

Alamo Queen and RD Block Veins ~

The Alamo Queen open pit mine lies in a down dropped portion of the Manganese Mesa basalt, and is distinctly vessiculated with strong chloritic and hematitic alteration; neither characteristic is typical of that unit at large. This open pit is located on the south extension of the Rudy fault. Local large scale pillow features are also unique to this site. Psilomelane, hollandite, and cryptomelane are present within spaces between pillows, which range from 0.5 – 2m in diameter. Vesicules are in – filled with chalcedony, opal, and calcite.

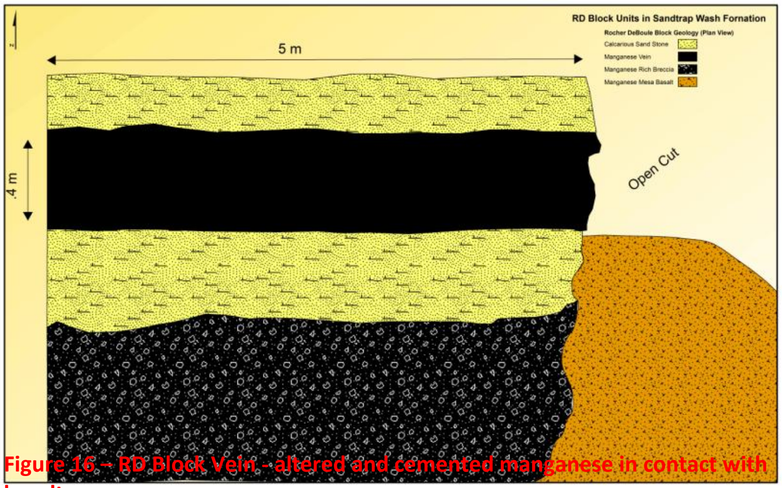


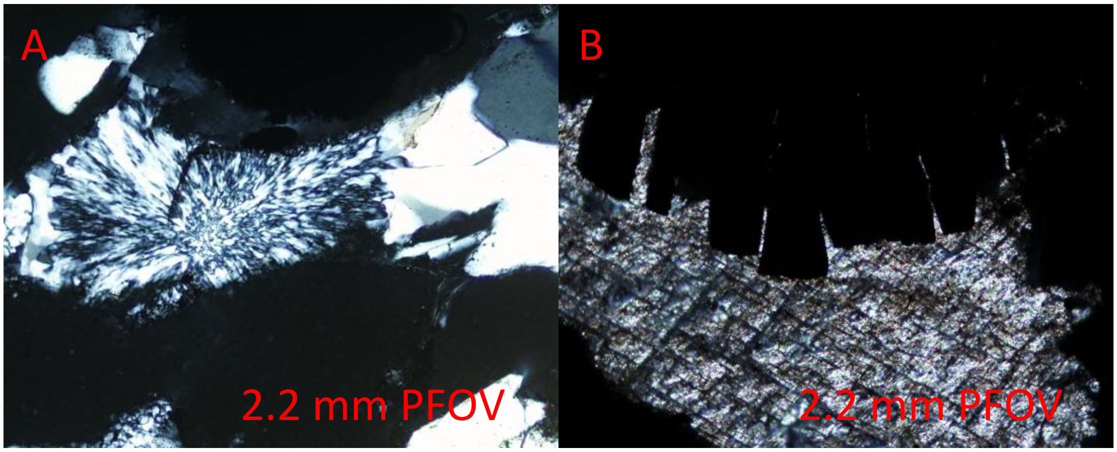
Figure 16 – RD Block Vein - altered and cemented manganese in contact with basalt.

Samples from this location and nearby RD Block vein systems contain the highest manganese values; up to 40% Mn. Calcium and aluminum values are also elevated in this setting up to 4.1 and 4.3%, respectively. Coarse crystalline calcite and minor quartz veinlets are visible along the margins of pillow basalts in association with manganese oxides. Petrographic analysis from these localities indentify hollandite and romanchite – psilomelane. SEM analysis of the RD Block vein system show a suite of high manganse oxides. Large crystals of ramsdellite/pyrolusite are incorporated in a calcic matrix with lesser potassium felspar, quartz, biotite, and hematite.

Figure 17 – Quartz and hydrous silica development occur with and give way to later calcic flooding.

Alamo Queen Paragenesis					
	Primary Minerals	Pottasic	Caclic	Silicic	Mn
K - Spar	▬▬				
Plagioclase	▬▬				
Quartz	▬▬				
Hematite	▬▬				
Biotite	▬▬	▬			
K rich glass		▬▬			
Calcite Veins			▬▬▬	▬▬▬	▬▬▬
Euhedral Calcite			▬▬▬		
Chacdony/Opal				▬	▬▬▬
Pyrolusite					▬
Cryptomelane					▬
Hollandite					
Ramsdellite					▬

Alteration rims on ramsdellite are altered to hollandite. Veinlets of hollandite cross cut the sample. Contact of potassium feldspar/quartz on ramsdellite exhibit alteration of ramsdellite to Pb – rich hollandite or coronadite.



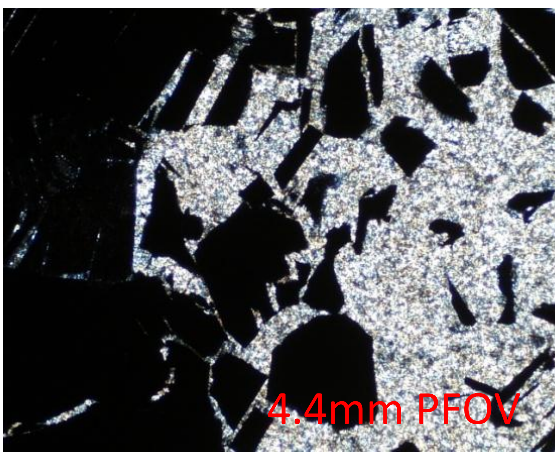


Figure 18 - (A) Hollandite altered to cryptomelane over chalcedony. (B) Hollandite precipitated over hollandite. (C) Blocky pyrolusite – ramsdellite in later calcite.

Figure 19 – Vessiculated Manganese Mesa basalt exhibiting pillow structure with manganese oxide and calcite infilling. Sample location for above photo

Figure 20 – (Top). Manganese and calcite in fractured basalt, and opal – chalcedony infilling vesicules, Webb Vein (bottom). Carbonate cemented manganiferous poorly sorted sediments, Rudy Vein.

Webb and Rudy Veins ~

The Webb and Rudy vein systems are exposed by open cuts and shallow adits along the north extension of the Rudy fault on the footwall. These deposits are also in contact with the Manganese Mesa basalt. The Webb vein system is deposited within fractures of Manganese Mesa basalt and extends along a fault for 200m. Individual veins are 0.25 – 1m wide and may extend 10 – 15m in depth. Manganese mineralization is associated with coarse calcite – minor quartz veins and contain about 8% Mn. Optical analysis indicates that the manganese minerals in this case appear to be paragenetically later than calcic or silicic phases. Delicate cryptomelane needles show high relief and override euhedral quartz and calcite. The Rudy vein system, deposited in the Sandtrap conglomerate, extends along fault strike 150m and is 2m in width at most. The vein has been excavated in a

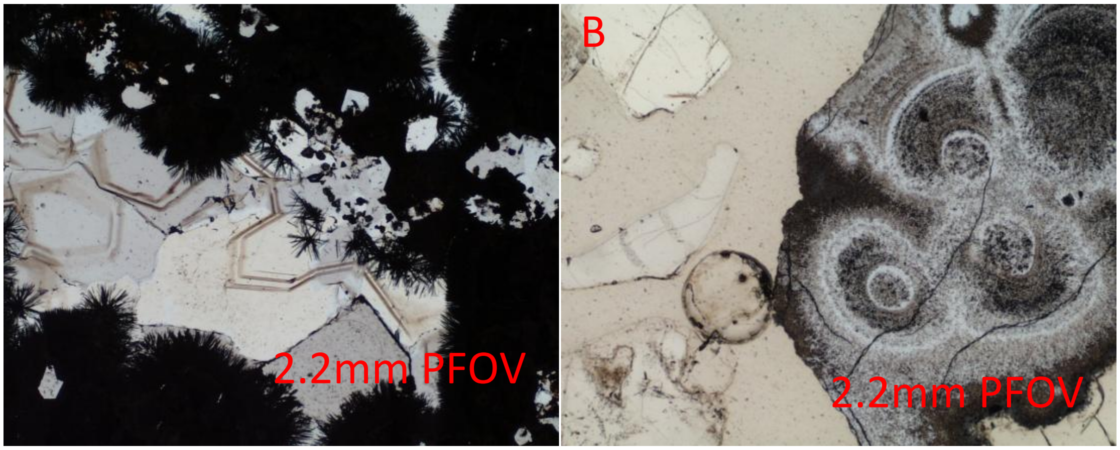


Figure 21 – (A) Euhedral quartz overridden by secondary quartz phase exhibiting explosion textures overprinted by cryptomelane. (B) Manganese oxide of calcite.

deep narrow trench ramping down from the surface to a depth of 25m. Mineralization includes manganese oxide associated with calcite and dense calcite – cemented manganiferous sediment at depth which contains about 19% Mn. XRD analysis identified ramsdellite, MnO_2. SEM analysis from the Webb Vein identified silicic and calcic phases associated with a variety of manganese minerals. Most notable was the presence of large ramsdellite crystals with hollandite alteration rims. A Zn – rich manganese oxide with hydrous platy textures ranging to highly hydrated fibrous textures is observed associated to coronadite and Pb – rich hollandite alteration of ramsdellite. A Ca – Zn – As rich hydroxide mineral appears both

Figure 22 – Calcic flooding and veining occurring through silicic and Mn phases.

Webb Vein Paragenesis			
	Primary Mineralogy	Silicic	Mn
Quartz	▬▬▬		
Quartz Explosion Texture		▬▬	
Calcite	▬ ———	———	———→
Ramsdellite			▬
Pyrolusite			▬
Hataerolite			▬
Coronadite			▬
(Pb,Zn,As) Hydroxides		▬	▬
Mn - Silicates		▬	▬▬
Cryptomelane			▬

interstitial to quartz and as euhedral crystals. This mineral is rimmed by a Pb – V – rich alteration rind. Analysis also identified Mn – silicates as cryptocrystalline groundmass.

North Maggie Wash Open Pit Veins ~

Historical workings present in North Maggie Wash expose near surfaand breccia deposits which appear to be formed along faults. An open cut in the left, downstream, wall of Maggie Wash hosts a dense manganese vein along a 15 – 20° dipping NNE apparent structure. Much of the near surface manganese has been extracted and vein width appears to pinch from 150 to 20 cm as it continues along dip. The vein extends 10 – 12m laterally. Manganese veinlets with calcic fronts pervade fractures above and below the primary vein. Petrographic analysis of multiple thin sections identified altered plagioclase and lesser microcline bounded by later euhedral calcite. Chalcedony and opal follow calcic flooding and form in voids, overriding earlier calcite crystals. XRD analysis of manganese rock chip samples identified pyrolusite, psilomelane – romanechite and ramsdellite. Paragenetic sequencing in thin sections suggests primary quartz with later euhedral quartz and lithic fragments. Manganese mineralization may

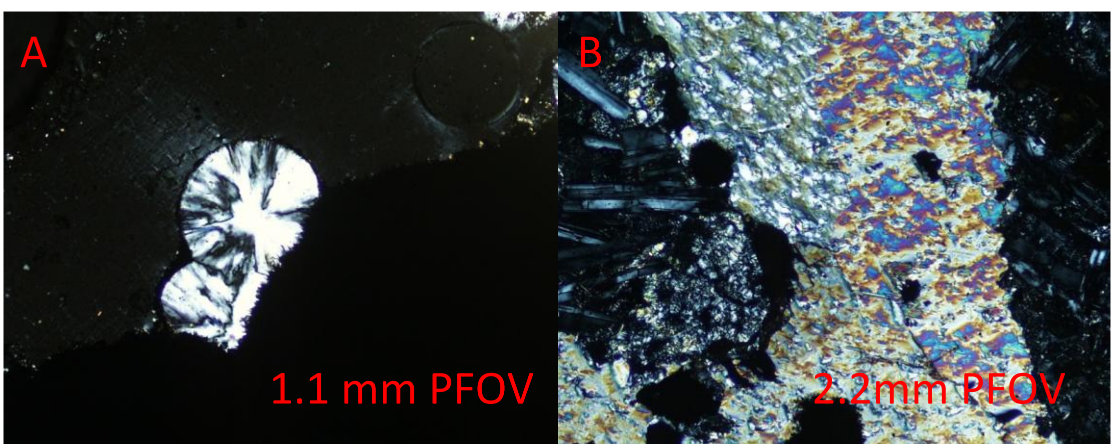


Figure 23 – (A) Calcite with chalcedony infill and overriding hollandite with cryptomelane rims. (B) Calcite interstitial to K– spar and Fe oxides components of alkalic basalt. Hydrous quartz is visible overriding basalt.

have coincided with calcic flooding and appears as banded texture with manganese in outcrop. SEM analysis suggests manganese mineralization is limited to hollandite altering to minor cryptomelane on botryoidal masses.

Shannon Breccia Hosted Manganese Deposit ~

The Shannon deposit is located in the westernmost portion of the map area, along an inferred shear zone. This structure is defined by a breccia zone approximately 500m in length along an east – west trend. Recent road cuts expose short exposures of fault breccia with later calcic and manganiferous infill. Highly angular heterolithic clasts occur with a matrix support of black and white banded calcite among dense pyrolusite and psilomelane – romanechite crystals. Euhedral calcite crystals 1 – 2cm in length are present in voids, capping dense manganese accumulations. XRD analysis detected ramsdellite and cryptomelane with lesser coronadite. Analysis of powdered rock chip samples show a high degree of calcite associated with manganese oxides at this locality.

McGregor Vent and Breccia Hosted Manganese ~

Closely associated stratiform and vein – type deposits are present near the McGregor open pit. Silicified fault breccias exposed on the footwall of a normal fault 200m east of the pit show well defined manganiferous and ferrous zones. These silicified breccias exhibit only surficial manganese

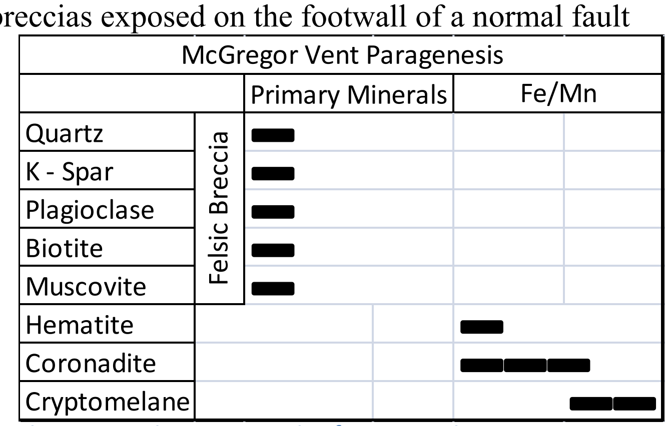


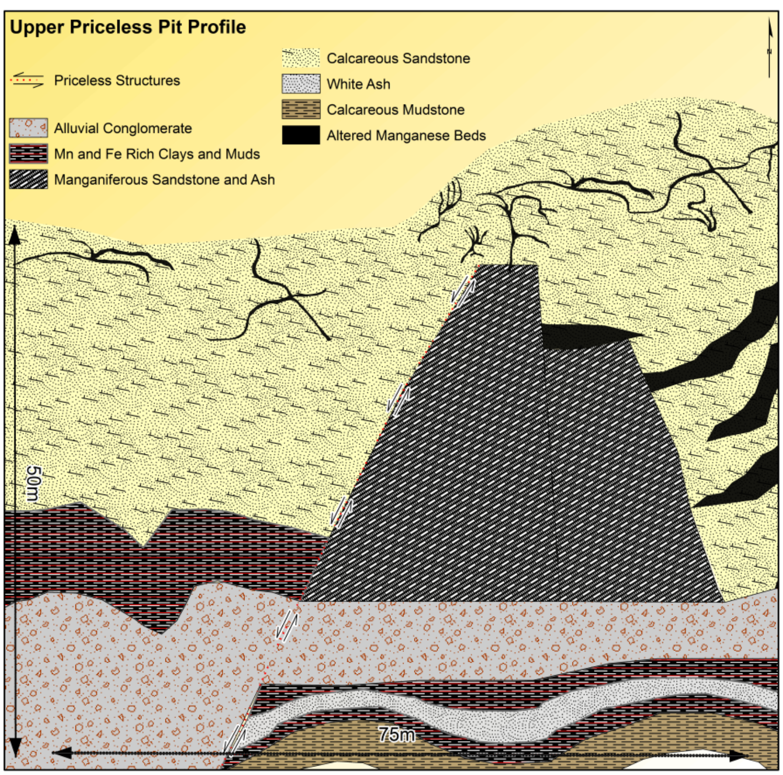
Figure 24 – Primary Fe reaction fronts on vein – type Mn.

and iron staining and do not contain significant grades of Mn consistent with other breccias. The fault is marked by the presence of granitic material from the underlying Artillery Peak megabreccia exhumed on the footwall. Dense silicified manganese is present 50m from the fault, west of the breccia. Discontinuous fissures are oriented parallel to the fault and may be 1 – 2m in width and 2 – 4m in length. XRD and petrographic analysis of fissure deposition identified abundant quartz and cryptomelane. SEM analysis identified Pb – rich hollandite or coronadite as cemented matrix for felsic clasts.

Priceless Pit Veins and Stock ~

Manganese showings in the eastern basin are bound in altered units of the Sandtrap conglomerate and the Chapin Wash Formation. Manganese veins are present in red brick arkosic sandstones, calcareous mudstone, and unconsolidated manganiferous silts – sands. Outcrops of the Cobbwebb basalt are spatially associated with veining. The Priceless pit was excavated in two

Figure 25 – Upper Priceless Pit bisected by normal faulting



levels to a depth of 30m and is no greater than 100m by 50m. Exposures in the lower pit show barite veins, 1 – 2cm, associated with manganese mineralization. A local normal fault bisects the pit and exhibits limited displacement (See Fig. 26 and 29) The Priceless pit exhibits a range of unusual mineral and geochemical associations. XRF analysis detected barium values of 15% in manganese veining. Geochemical analysis showed elevated Zn, Sr, Pb, Al, Fe, and K associated with veining and enriched sediments. Fe concentration exceeded 10%. K values ranged from 3 – 5%. Optical identification of cryptomelane was confirmed by XRD analysis. XRD analysis also identified coronadite confirming results from Mouat's 1962 study. SEM analysis identified hematite cementation of felsic clasts. Manganese mineralization appears to be associated with a late reaction rim of hydrous Fe – oxide. Botryoidal manganese shows chemical variations exhibited by banding in internal reflectance when view in reflected light. Darker strontium – rich bands may indicate the development of rare strontiomelane ($SrMn_6Mn_2O_{16}$) from hollandite.

Priceless Pit Paragenesis			
	Primary Minerals		Fe/Mn
Quartz	Arkosic Sandstone	▬	
K - Spar		▬	
Calcite		▬	
Hematite		▬	
Ilmenite		▬	
Hydrous Fe			▬
Hollandite			▬▬
Cryptomelane			▬

Figure 26 – Hydrous Fe occurs as a reaction front with the initial emplacement of manganese.

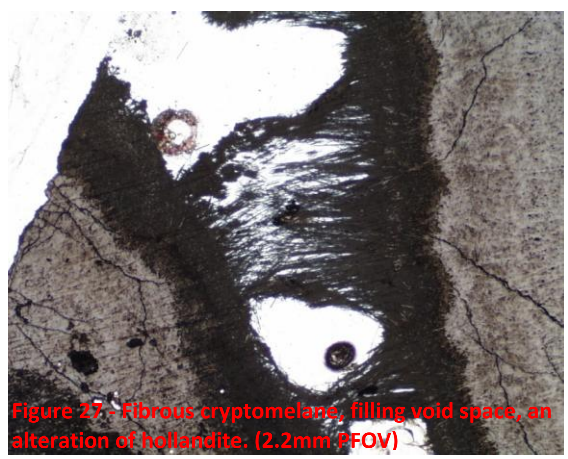


Figure 27 - Fibrous cryptomelane, filling void space, an alteration of hollandite. (2.2mm PFOV)

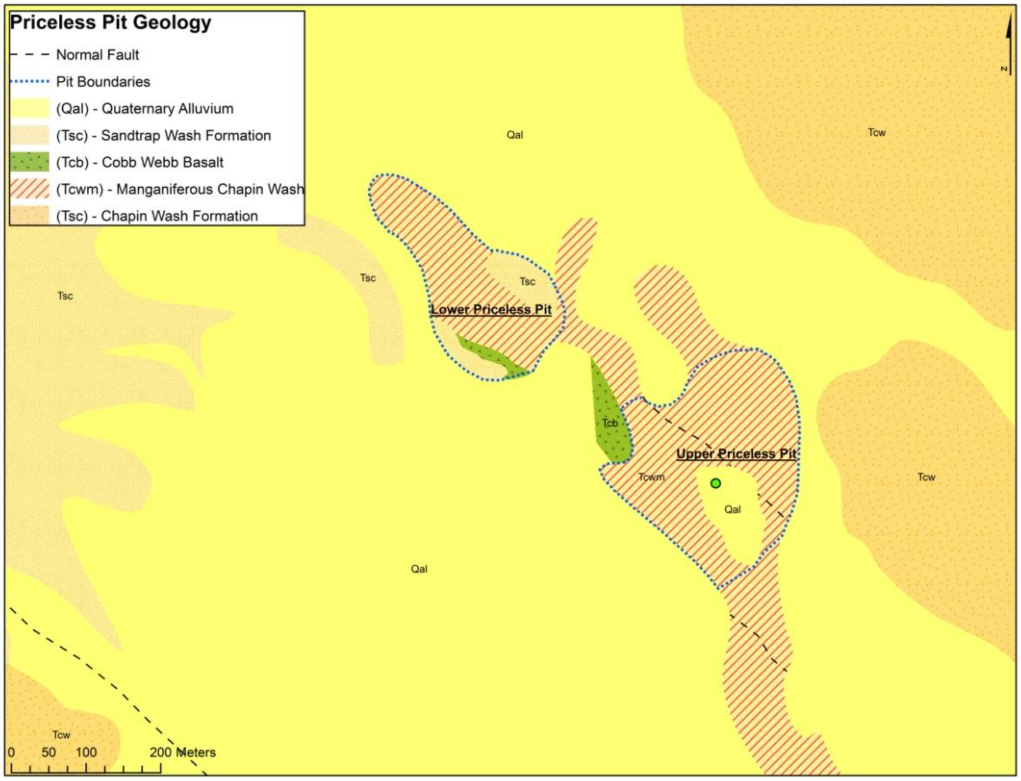


Figure 28 – Upper and Lower Priceless Pit on trend with local normal faults

Figure 29 - Upper Priceless Pit exhibiting calcic and manganiferous cementation. Note local normal fault

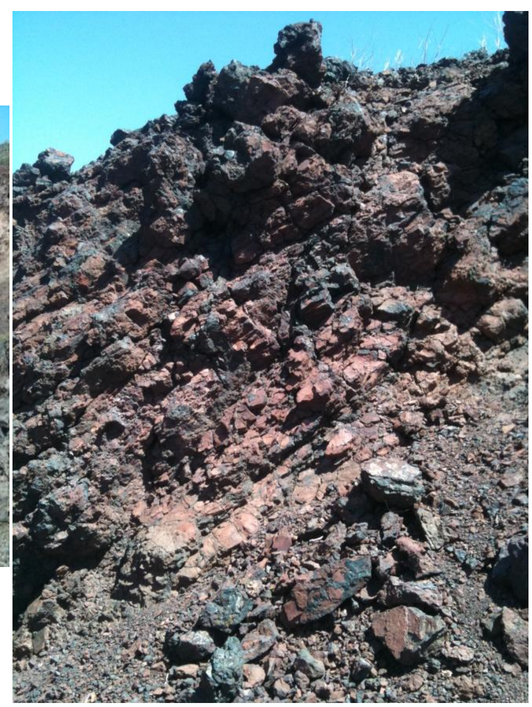
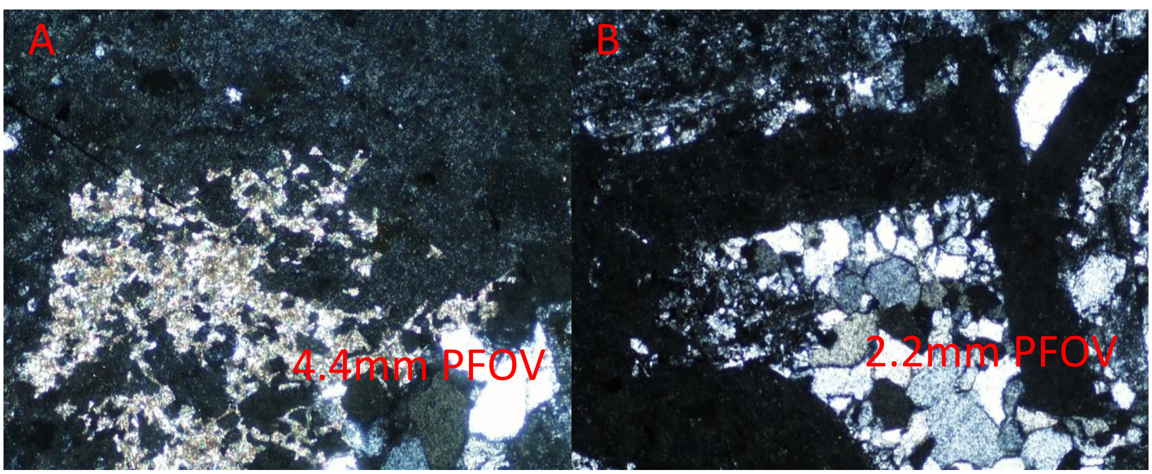


Figure 30 - Pervasive manganese veining in calcareous sandstone cap rock.

Burro Wash ~

Manganese rich sediments and veins are present in silicified outcrops throughout the north western portion of the Burrow Wash drainage. Small scale bedded and vein deposits are spatially related and exhibit barite veins 5 – 7cm thick. Barite veining is related to crystalline manganese mineralization. Nearby bedded sequences show interbedded ash units. Geochemistry from these sites shows elevated barium and strontium. This locality exhibits relatively high Ag concentrations, by comparison, at 75 ppm. Paragenetic sequencing shows that silicic flooding occurs later followed by progressive calcite crystal development. Manganese mineralization appears to coincide with early barite emplacement.

Figure 32 – (A) Tabular barite phenocrysts 2 – 4mm long overridden by quartz and later calcite. (2) A second phase of barite (fully terminated) with interstitial quartz.



Vein – Type Fluid Inclusions ~

Several vein deposits elsewhere in the district exhibit fluorite, calcite, black calcite, quartz chalcedony, and barite. Fluid inclusion data from these sites show a range of minimum formation temperatures from 165° – 225°. Select freezing analysis data shows final melting near 0°. Salinities calculated during earlier studies are between 0 – 3% wt. NaCl equivalent. These low salinities are not consistent with fluid inclusion salinities from the mineralization related to the Buckskin – Rawhide detachment fault which range from 20 – 35% NaCl (Spencer, 1991).

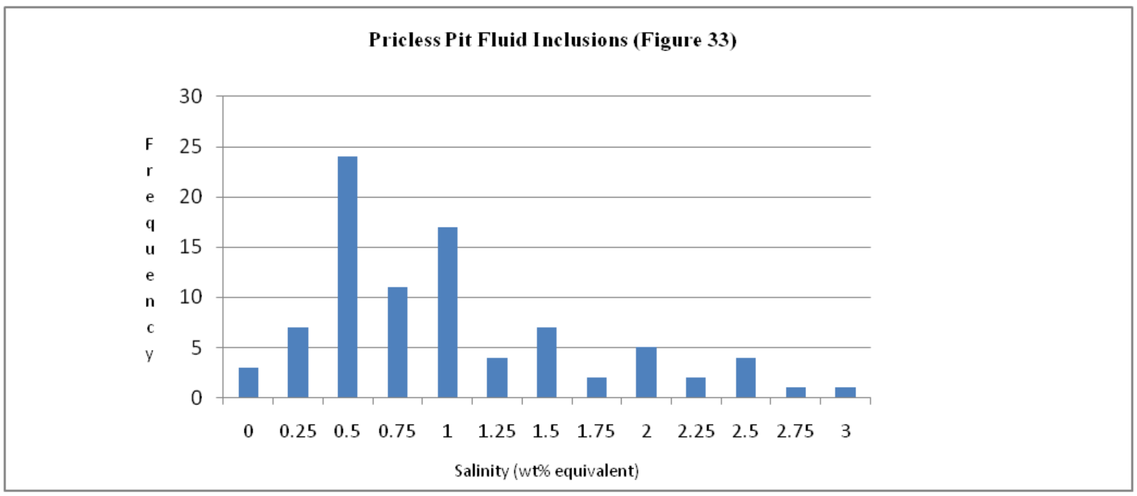


Figure 33 – Fluid inclusion data from Spencer (1989).

Chapter 7 ~ *Related Deposits and Settings*

San Francisco Manganese, Jalisco, Mexico ~

The San Francisco manganese deposit is located 13km northeast of Autlan, Mexico. The principal orebody consists of interbedded layers of manganese oxides and iron oxides which have been completely encased in tuffaceous material. Interpretations of the depositional environment suggest a shallow lacustrine environment indicated by the presence of freshwater gastropods and the lack of a significant carbonate assemblage normally associated with restricted basin. Further evidence of this setting is exhibited by the presence of ripple marks and other macrofossils within ore – body. Sources for iron – rich sediments and primary braunite mineralization are proposed to be volcanogenic in nature. However, manganese deposition and zoning is attributed to elevated potassium content in depositional waters and later diagenetic recrystallization. Interlayered manganese and iron oxides are, for the most part, structurally unchanged.

The manganese ore – body is hosted within the medial portion of the San Francisco Formation. The lower San Francisco Formation is gray, green, brown and purple, fine – grained to conglomeratic tuff and contains rounded to angular crystals and lithic fragments. Crystal fragments are dominantly potassium feldspar. Difference in sorting and rounding throughout the formation reflect volcanic evolution in the province. Large angular breccias are indicative of chaotic rock avalanche such as lahars; ubiquitous tuffaceous units are indicative of sustained ash – fall events. A local ignimbrite contains charred wood fragments. Proximal sequences show rounding and grain size patterns suggestive of a fluvial environment. The gradual thinning of the formation to the east – northeast and an overall decreasing in that grain size distally suggest that clastic constituents were supplied from the west southwest. The tuffaceous host several magmatic intrusive bodies such as; dikes, sills, plugs and flows of trachyte, porphyry, and fine – grained andesite. These intrusions are observed cross cutting the manganese zone in places, but show no noticeable effect on the manganese deposit. The manganese is bound within a grayish – green tuff and is underlain by a 2m lens of red fissle tuff exhibiting ripple marks. The manganese deposit consists of a series of lenticular beds interfingered with tuff units present on the rim of the tuffacious host. Manganese is interlayered with limey, tuffaceous shale in the upper part of the orebody. Braunite, (Mn_2O_3) the primary manganese oxide present, is interlayered with hematite. Calcite and cryptocrystalline silica are pervasive throughout the ore zone. Barite is also present interstitially and within fractures and small lenses upward in the sequence. Layers of braunite and hematite are finely bedded with sharp contact layers several centimeters thick. In spite of fine bedding persisting throughout the paleobasin, the sequence as a

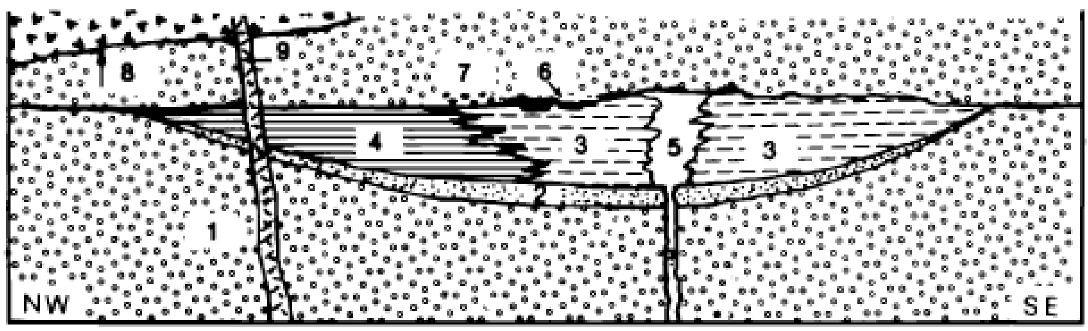


Figure 34 – Diagrammatic sketch of the San Francisco manganese deposit and the surrounding rocks. (1). Underlying Tuff; (2). Shale Lens; (3). Manganese Oxides; (4). Iron Oxides; (5). Travertine Plug; (6). Conglomerate; (7). Overlying Tuff; (8) Trachyte; (9) Andesite Porphyry Dike (Zantop, 1971)

whole is marked by a sharp Mn – Fe grade boundary with the southeast basin being more manganese – rich and the northwest being iron – rich. Gradation appears to be inconsistent with primary emplacement and may suggest late fluid influence.

Presence of steel – gray coarsely – crystalline pyrolusite with acicular radiating blades may represent recrystallized MnO_2 similar to ramsdellite polymorph development at stratiform units at Artillery Peak. The interpretation for the origin of the Mn – Fe rich ores constrained in the Autlan basin is as yet unsettled. However, clear hydrothermal influences played a role in deposition or at least enrichment of the ore zone. The close association of cryptocrystalline silica and travertine indicate a hot spring source. Zantop (1978) argues for a syngenetic relationship between volcanically – derived material and a continued hydrothermal supply with later diagenetic recrystaliztion. The development of ore grade manganese oxide banding of oxides is a matter of Eh – pH variation during deposition. An increase in pH would induce iron precipitation. North – south zoning is an indication of source proximity and potassium content in depositional waters. The diagenesis of potassium – rich glass may have aided in Mn scavenging and concentration.

Lucifer Manganese Deposit, La Paz, Baja California Sur, Mexico ~

Stratiform manganese deposits present in Mexico's Southern Baja peninsula and are also mid – Tertiary. As with the Artillery Peak vein – type manganese, both are thought to be a product of low temperature aqueous fluids which weather out and erode to become stratiform – type manganese. Two types of alteration are significant to mineralization at this locality; destruction of mafic silicates minerals from proximal volcanic assemblages and argillization of glassy groundmass material associated with depletion and remobilization of manganese. Hydrothermal fluids transported via fractures related to extensional deformation associated with basin formation in the Gulf of California are considered the origin of vein – type manganese in this setting. Mineralized fractures and hydrothermal alteration are present stratigraphically below the deposits (Friedberg, 1983). Though terrestrial in nature, this type of manganese deposit is probably more analogous with present day spreading centers considering manganese mineralogy and associated rock composition.

Like the Autlan deposit, the Lucifer manganese beds are hosted in a series of volcanic tuffaceous beds known as the Boleo Formation. Four distinct units make up the formation, which are essentially interbedded tuffs and conglomerates of volcanic composition. A tuffaceous sequence approximately 15m from the base of the unit contains the maximum thickness of manganese oxide. Tuffs in this sequence are well stratified and poorly indurated. The Comondu Volcanic Formation contacts this sequence on the south west margin. Manganese – rich sediments had previously overlain the volcanic and base layer conglomerate packages indicated by the presence of dense manganese – rich fracture fill stratigraphically above and in between the interpreted source and the present orebody (Fig. 35).

Paleotopography has controlled the overall shape and expanse of the deposit in its current form. Like the Artillery Peak manganese, downward fracture filling has served as a means of consolidation. Another similarity shared by Lucifer and both aforementioned deposits is the presence of chaotic breccias and boulders with manganiferous matrix material. Mineralogy of manganese ore is predominantly pyrolusite. Isostuctural manganese oxide varieties such as; hollandite, cryptomelane, ramsdellite, and coronadite also occur (Freiberg, 1983). Smectite is commonly associated with these ore minerals. Hematite and goethite are locally abundant. Two forms of alteration are present in areas that experienced downward or lateral migration of hydrothermal manganese – bearing fluids; (1) destruction of mafic silicates in host rocks and (2) argillization of rock in contact with pyrolusite. Augite and orthopyroxene are altered to iddingsite and chlorophaeite which may indicate the depletion of manganese from host rocks. Rocks of the Comondu volcanics in contact with manganese oxide exhibit argillization; vesicules and fractures in altered rocks are filled with smectite and other less common clays as well as minor amounts of adularia. Friedberg's (1983) argument concerning origin of the deposit is dependent on an active hydrothermal source such as hot springs. Soft sediment deformation and interfingering tuff and Mn units are further support of a syngenetic emplacement of an aqueous ore solution in a shallow marine environment.

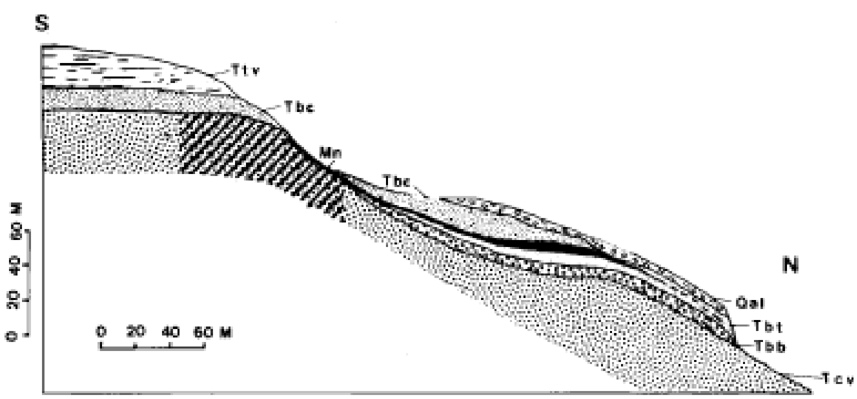


Figure 35 – Diagrammatic cross section of the Lucifer deposit. Shaded region represents the hypothetical extent of pervasive manganese mineralization and hydrothermal alteration of Comondu Volcanics. (Tbc – Tuffaceous Conglomerates, Tbt – Boleo Tuff, Tbb – Basal Conglomerate, Tvc – Comondu Volcanics) (Freidberg, 1983)

Vein – Type Manganese Oxide of the Southwest U.S. ~

D. Hewett (1966) is credited for much of the seminal work regarding the modes of manganese oxide deposition. His paper entitled "Veins of Hypogene Manganese Oxide Minerals in the Southwestern United States" identifies the vital characteristics alteration, depositional environment/mode, relative age, and mineralogy of vein and fissure types.

Like Roy (1992) and later authors, he evaluated approximately 200 vein – type manganese deposits in the Southwestern United States and Northern Mexico (Fig. 36). His focus was distinguishing common features based on age and interpreted depositional environments of vein – type deposits. He developed the following characteristic of manganese vein deposits in the Southwestern U.S.; components interstitial to vein fluorite and barite, potassium feldspar (adularia) replacement in wall rock, common in middle to late – Tertiary local basins. Affinities amongst host – rock alteration and basic assemblages consistent throughout vein deposits of the Southwest include: agglomerates, intermediate volcanic rocks, and volcanic tuffs. Dominant alteration type in wall rock is potassic or related and occasionally silicic. Adularia is commonly assoiciated with vien localities in Southern California, New Mexico and Colorado. Structural features of vein type manganese in tertiary host rock tend to lie in fractures in homoclinal blocks; fault blocks of tertiary origin generally dip no greater than 10°. Vein systems usually have near parallel orientations and exhibit steep dips with mineralized intervals no greater than 600ft below the present surface. Downward termination of mineralization is almost certain from deposit to deposit. Dominant minerals present include psilomelane – romanechite, hollandite, cryptomelane, and coronadite. Hewett and Fleischer (1959) identified 11 common manganese oxide minerals at vein localities. These minerals are indicative of several modes of deposition, but are generally separated into two groups. Mineralogy for vein systems of which host rocks contain low manganese content are as follows; psilomelane, hollandite, cryptomelane, coronadite, pryrolusite, and ramsdellite. Tertiary vein systems with low grade host rocks are abundant in Southern California, Arizona, Southern Nevada, and New Mexico. These are generally the product of predominantly volcanic hosts. Vein – type deposits with host rocks having elevated manganese content include; hausmannite, pyrochroite, and jacobsite. A second group of oxides originates from manganese deficient host rocks, specifically rhyolite and gneiss; manganese minerals in this group include braunite and bixbyite which are associated with ophiolites, clearly non – terrestrial in origin. Non – metallic minerals are included in Hewett's (1959) rendering of vein – type characteristics. Varieties of white and black calcite are commonly associated with manganese veining, these exhibiting layer crystals terminated by flat rhombs, also common as void filling druse or frosting textures, common in Arizona and New Mexico. Trace metal aspects of vein – type manganese include elevated levels of strontium and thallium.

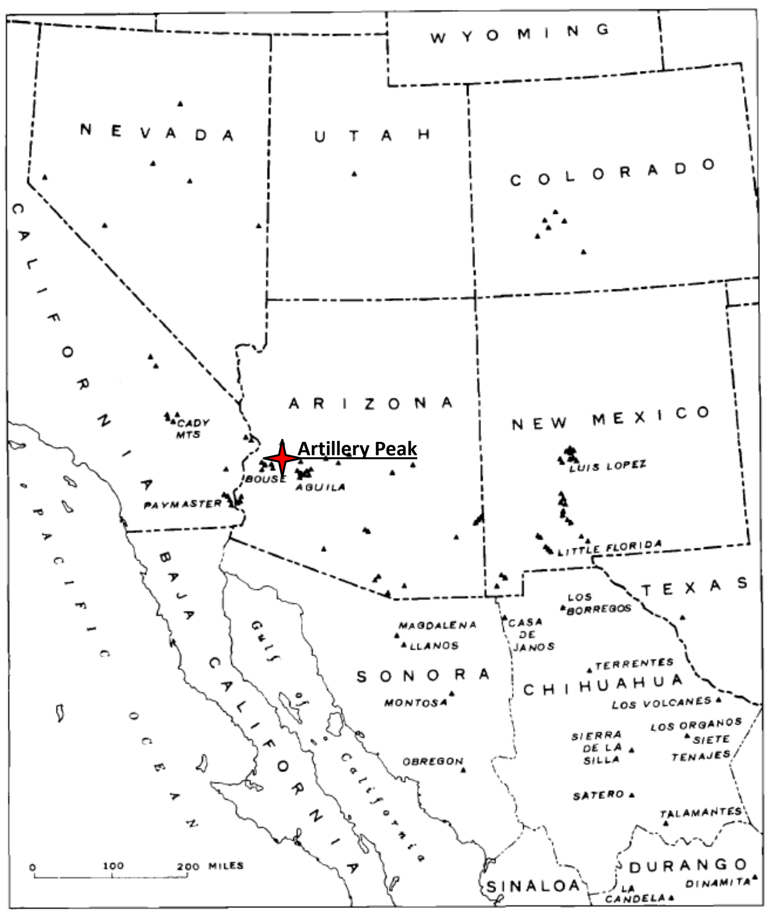


Figure 36 - Distribution of manganese oxide mineral deposits in Southwestern US and Mexico (Hewitt, 1959).

Chapter 8 ~ *Discussion*

Field observations establish that vein – type manganese is not obviously volcanogenic and is not the source of stratiform manganese in a broad scale as proposed by a recent commercial technical report (Tribe, 2010). Vein – type systems are present in the youngest basalt and cross cut all other formations stratigraphically below, excluding the gneissic basement. Detailed sequencing of veins has not yet been established, however, characteristics including; crosscutting relationships, volumetric scale, lack of vertical extent, and paragenetically late development of manganese minerals in vein – type systems lead to the conclusion that onset of veining was short lived. Proximity of many vein – type deposits to both young altered alkalic basalts and stratiform – type deposits may suggest contact metamorphism as a mobilization mechanism. Recent drilling of two vein – type localities indicates stratiform deposits 45 – 60m directly below veins. Composition and timing of the basalt flows are consistent with requirements necessary for manganese mobilization. Petrographic analysis of basalts in contact with manganese exhibit a high degree of potassium feldspar and hydrous Fe. Alkalic basalt is typical near extensional zones like that of central Arizona and especially in detachment fault settings (Roddy, 1988). Other late – Miocene alkalic basalt flows have been documented by the USGS in west central Arizona where flows are known to trend southwest from Bagdad to Phoenix on the margin of the Zone of Transition and the Basin and Range. Late basalts show intense alteration in manganese bearing zones but elevated potassium metasomatism has been documented throughout the district, and is not constrained by mineralization (Spencer, 1989). Mineralogy of vein – type manganese systems is significant because it demonstrates formational conditions within a wide range of temperatures and environments. Based on Roy's (1968) classification the genetic types of manganese mineral veins at Artillery Peak should be considered either supergene or metamorphic in nature. Pyrolusite, psilomelane – romanechite, cryptomelane, and coronadite most commonly form under supergene conditions or due to metamorphic

Distribution of Manganese Minerals in Deposits of Different Genetic Type

Mineral Sub Group	Minerals	Formational Settings			
		Hypogene	Sedimentary Recrystalization	Metamorphic	"Supergene"
Higher Oxides	Pyrolusite	Upper System			
	Cryptomelane	Upper System			
	Psilmomelane - Romanichite	Upper System			
	Coronadite				
	Trodorkite		Deep Sea Nodules		
Hydroxides	Manganite				
	Pyrochorite				
Lower Oxides	Hollandite				
	Braunite				
Silicate	Bementite				
	Rhodonite			Silicate Deposit only	
Carbonate	Rhodochrosite	Lower Zone		Carbonate Deposit only	
Sulfides	Alabandite	Lower Zone			

Very Commom
Common
Present
Rare
Very Rare

Figure 37 – Supriya Roy's classification of genesis based on mineralogy (1968).

influences (Roy, 1991). These minerals can be formed as weathering products of common hypogene vein systems minerals such as; braunite, rhodonite, and bixbyite but these minerals do not occur on any level in the district (Hewitt, 59).

Manganese is highly mobile in acidic organic soils of the temperate and subarctic zones, but especially Ni laterites formed in tropical conditions are well known for producing economic concentrations via remobilization (Roy, 1997). Influences of pH, organic matter, lime, and phosphate on heavy metal availability in soils are understood principally in terms of their influence on the chemistries of hydrous oxides of Mn and Fe (Post, 1999).The late – Miocene environment in central Arizona may have been conducive in accommodating mobilization especially in developing hydrous metals. Widespread development of vegetation during the late – Miocene implies that availability of fresh water and associated phosphate, organic material and metal rich soils are good assumptions in regard to the depositional setting in central Arizona. The presence of hydrous manganese minerals and alkalic pillow basalt demonstrate that at least two vein – type deposits were emplaced into a lacustrine settings. Given these factors it seems likely that lacustrine or near surface waters would be high pH during vein – type deposition. Spencer's (1989, 1991) interpretation of manganese vein – type origin elaborates on the fluid environment during the time of deposition.

> "The red – brick sandstone that hosts the manganese deposit in most of the Artillery Mountains is strongly altered by potassium metasomatism. K – metasomatism is thought to occur under low – temperature conditions in the presence of saline alkaline water under lakes or playas and occurred over large areas in west – central Arizona during the Miocene. In some areas, K – metasomatism has completely converted rocks to an assemblage of potassium feldspar, quartz, and hematite. Because K – metasomatism can chemically modify large volumes of rock and apparently removes manganese, it seems feasible that chemical and hydrological conditions associated with this type of alteration could liberate, transport, and reconcentrate manganese. The vein deposits are several million years younger than the stratiform deposits; thus, the two are not obviously related. The spatial association of the two deposit, however, suggests that the manganese in the vein deposits was derived from the stratiform deposits. This movement of the manganese could be due to the hydrothermal circulation associated with basaltic magmatism or to ground water movement unrelated to magmatism (Spencer, 1991)

Cryptomelane can be the product of weathering in sedimentary environments usually as the modification of pyrolusite or other higher temperature oxides (Roy, 1991). In true vein settings cryptomelane is precipitated under slightly oxidizing conditions from low temperature alkaline solutions in the percolation zone and may indicate fluctuations in the water table. Pyrolusite is known to be modified to hollandite at 550°C indicating a late stage heating event potentially associated with mobilization (Roy, 1992). Heating may be related to the latest basalt flow or alkaline fluids present in the basin as a result of flow events.

Manganese oxides have strong sorption capacity for cationic species in depositional fluids and rock hosts. Sorption capacity is reflected in the chemistry of the oxides and varies depending on the fluid environment, fresh water, seawater, or hydrothermal fluids (Nicholson, 1992). Characteristics of geochemical and mineralogical enrichment can be separated into statistically significant groups. Diagnostic plots help classify manganese oxides into genetic type within certain sub groups; supergene hydrothermal, supergene marine and terrestrial, supergene dubhite, and sedex. Duhbites are defined as manganese oxides derived from weathering of a mineralized sequence (Nicholson, 1992). The discussion is limited to hydrothermal or supergene plots to evaluate veins at the study site. Hydrothermal deposits characteristically show enrichments of As – Ba – Cu – Li – Mo – Pb – Sb – Sr – V – Zn and Mn – As in association (Nicholson, 1992). There is no statistically significant relationship between As and Mn in any of the geochemical data collected from Artillery Peak. All vein – type systems lack Cu – Li – Mo – Sb (Appendix D). Terrestrial supergene manganese deposits show uniquely high barium content and show a relationship between Ba and Mn.

Elevated Ba and associated Mn is an established trend at Artillery Peak within both manganese types. Dubhites characteristically show high levels of Zn and Pb and show a Pb – Mn base metal association, again, a recognizable trend at some Artillery Peak vein – type deposits. A diagnostic plot evaluating Co + Ni (wt%) v. As + Cu + Mo + Pb + V + Zn (wt%) places Artillery Peak vein samples as being fresh water supergene in origin.

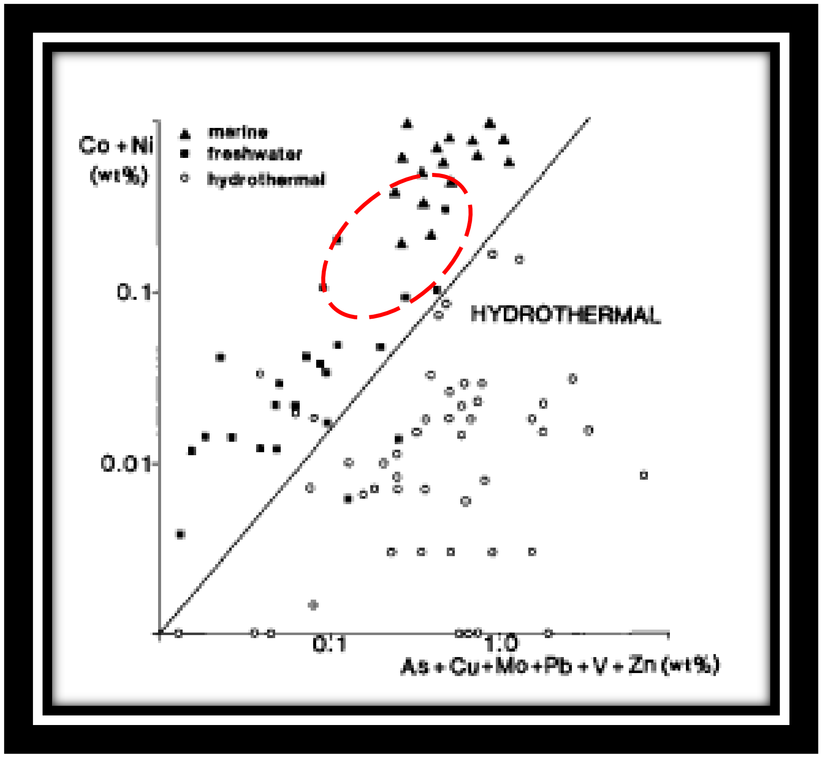


Figure 38 – Nicholson's (1992) base metal ratio diagnostic plot showing geochemistry from Artillery Peak vein – type localities exhibiting base metal assemblage ratios indicating supergene or metamorphic origins with fresh and sailine water influence (shown in red elipse).

Fluid inclusion data from associated veins illustrate very low salinities not consistent with hydrothermal vein salinities in the area, but minimum temperatures do not reflect a high temperature event capable of creating manganese oxide modification. These factors suggest that young manganese veining events are not strictly hydrothermal if at all. Several mineralizing fluid events have clearly affected vein mineralogy and distribution.

Observations made during this study suggest past models for both stratiform and vein deposits must be revaluated. Lasky and Webber (1949) and many authors have suggested that stratiform manganese deposits were a product of protracted erosional events acting upon some massive hot spring deposits. However, the presence of manganese as a matrix, specifically at the South Alamo locality where undulating Mn – rich fronts suggest late manganese fluid cementation of sands and argues for hydrothermal introduction. The bulk of stratiform deposits in Chapin Wash do exhibit obvious detrital characteristics with lacustrine depositional aspects such as ripple marks, transgression and regression grain size patterns, and soft – sediment deformation. However, thin sections from these localities still place manganese as a matrix commonly associated with late calcite. The irregular morphology and sorting of deposits in the central basing may also suggest an alternative mode. The greatest tonnage of manganese by far exists in unconsolidated sand pods which are a likely host for rising hydrothermal fluids, especially if porous sand pods contained meteoric water with a low enough pH to accommodate Mn precipitation. Spencer's (1991) evaluation of the Artillery Peak district proposed that stratiform units may be a product of manganese deposition via a chemical process so near the surface that they became reworked into local sedimentary process and progression. The presence of continuous Mn – rich clays interbedded with other non – manganiferous impermeable sediments demonstrates that at least some manganese arrived in the basin due to erosional influences. Lasky and Webber (1949) noted manganese – rich mud flakes in bedded deposits served as further reinforcement of a syngenetic origin. Further evaluation of detrital manganese is necessary to establish detailed timing of deposition. Pure hydrothermal manganese has poor crystallinity and is extremely fissile; detrital grains of Mn are cryptocrystalline. The presence of matrix manganese may simply be a product of detrital manganese mineral behavior during diagenetic recrystallization. If stratiform manganese is the product of hydrothermal emplacement then the assumed age of 13.5 ma is also in question. However, the absence

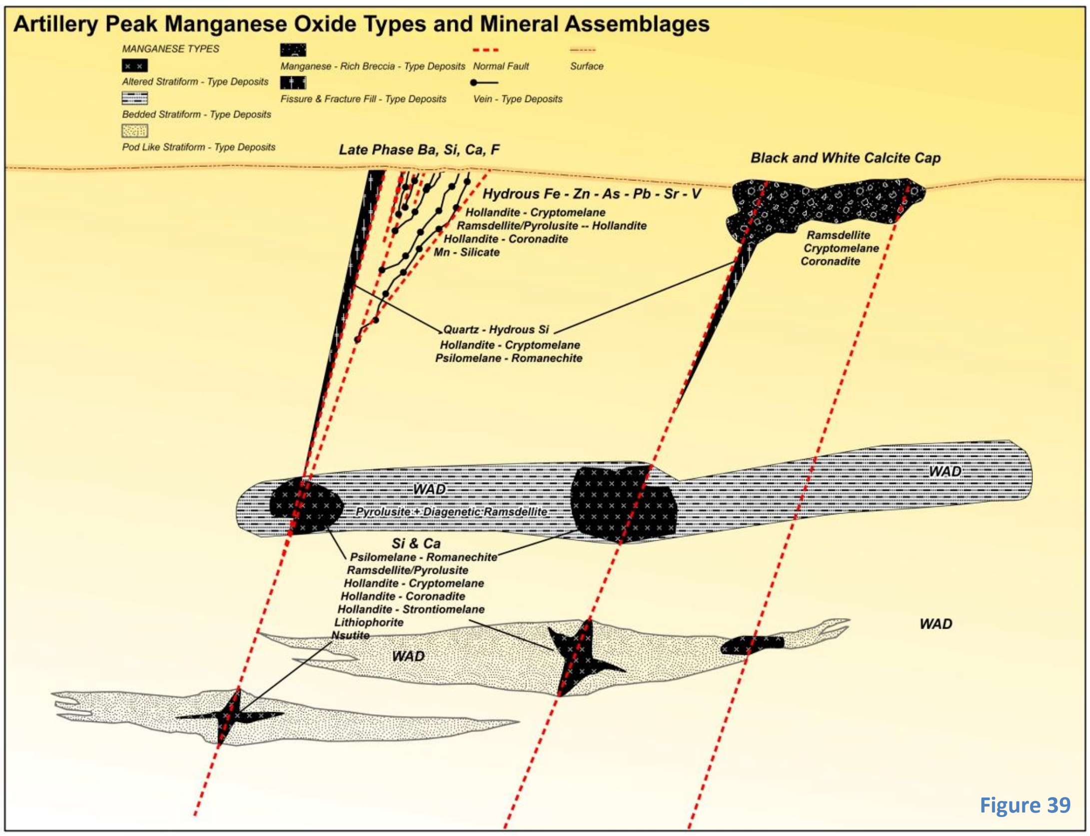


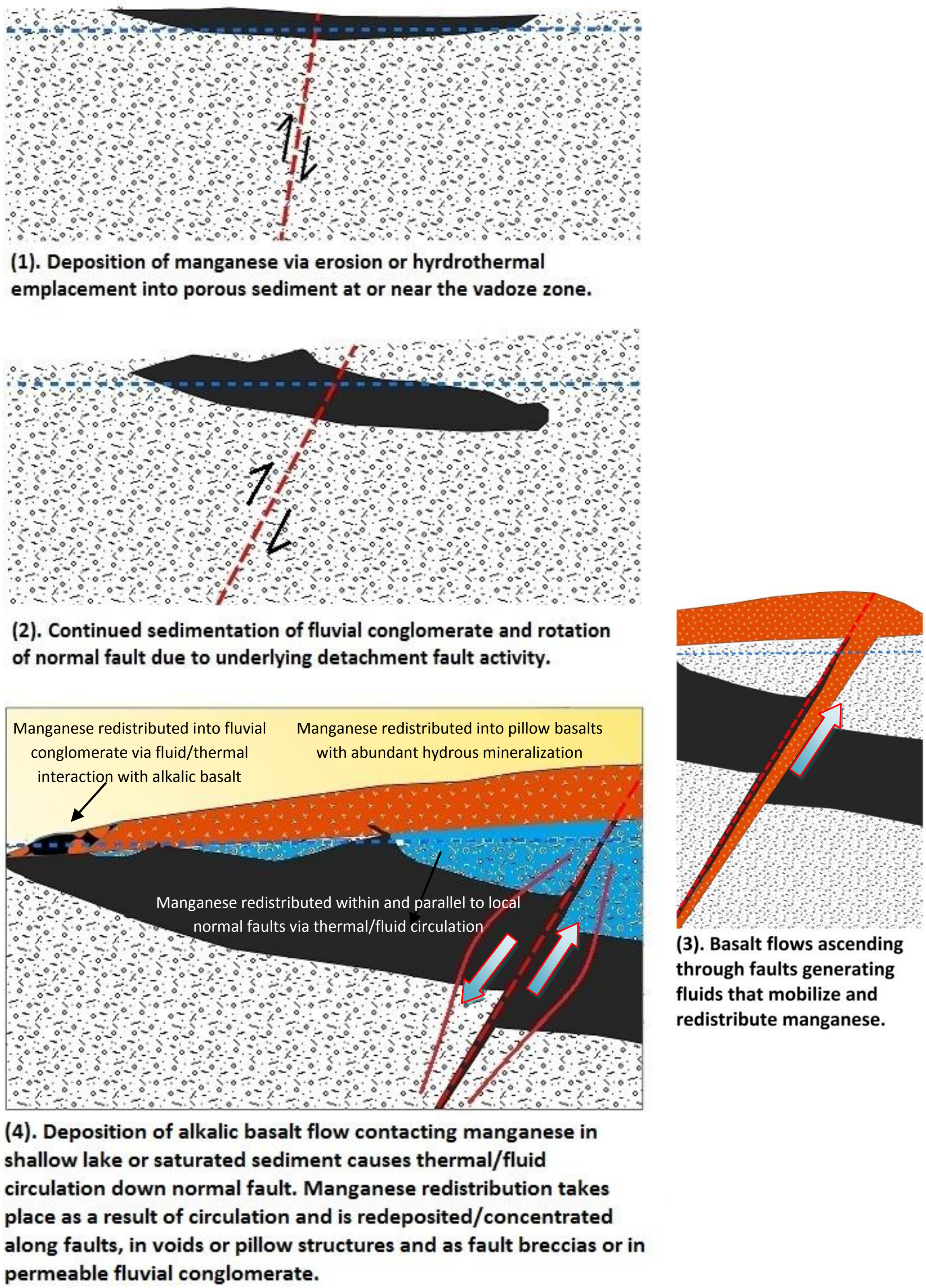
Figure 39

of stratiform - type manganese in younger strata and apparent zones of local remobilization within large bedded and pod – like deposits suggests that vein – type mineralization is derived from hydrothermal remobilization of the stratiform – type manganese deposits. Figure 39 summarizes the stratagraphic, structural, and mineralogical variations observed and documented in the Artillery Peak area. Both bedded and pod – like stratiform deposits have experience mineralogical changes due to later fluid introduction along faults cutting them. These same faults may have acted as conduits for the original manganiferous fluids responsible for the stratiform manganese bodies. The later fluids added Ba – Si – F – Ca to vein deposits (See Fig. 39)

Chapter 9 ~ *Conclusions*

The Artillery Peak manganese district may be the product of a range of depositional modes and should not be limited to standing classifications which regard primarily mineralization as being a syngenetic stratiform system with later hydrothermal veining. Interpretations of analytical work, field observations, and comparative mineralogy/geochemistry demonstrate the need for an alternative or coexisting model. Amendments to the stratiform – type manganese description may be expanded to include aspects such as: (1) local deposition of manganese – rich fluids into lake beds or sub – surface permeable sediments at or below the water table and, (2) local redistribution and recrystallization due to Eh – pH shifts in fluid environments. Classification of vein – type manganese should be an affirmation of Spencer's (1991) proposal describing vein – type origins. Aspects of classification elaborating on Spencer's concept may include; (1) manganese vein mineralogy related to metamorphic and supergene processes, (2) spatially associated vein – type and stratiform – type manganese deposits, (3) proximity to fluid conduits and underlying local alkalic basalt flows and or local basalts ascending through local faults and mobilizing stratiform – type manganse into parallel structures, breccias, and other porous medium, and (4) depostion of manganese oxides and hydrous manganese minerals into the vadose zone. (See Fig. 40)

Figure 40 – Theoretical depositional model for vein – type manganese



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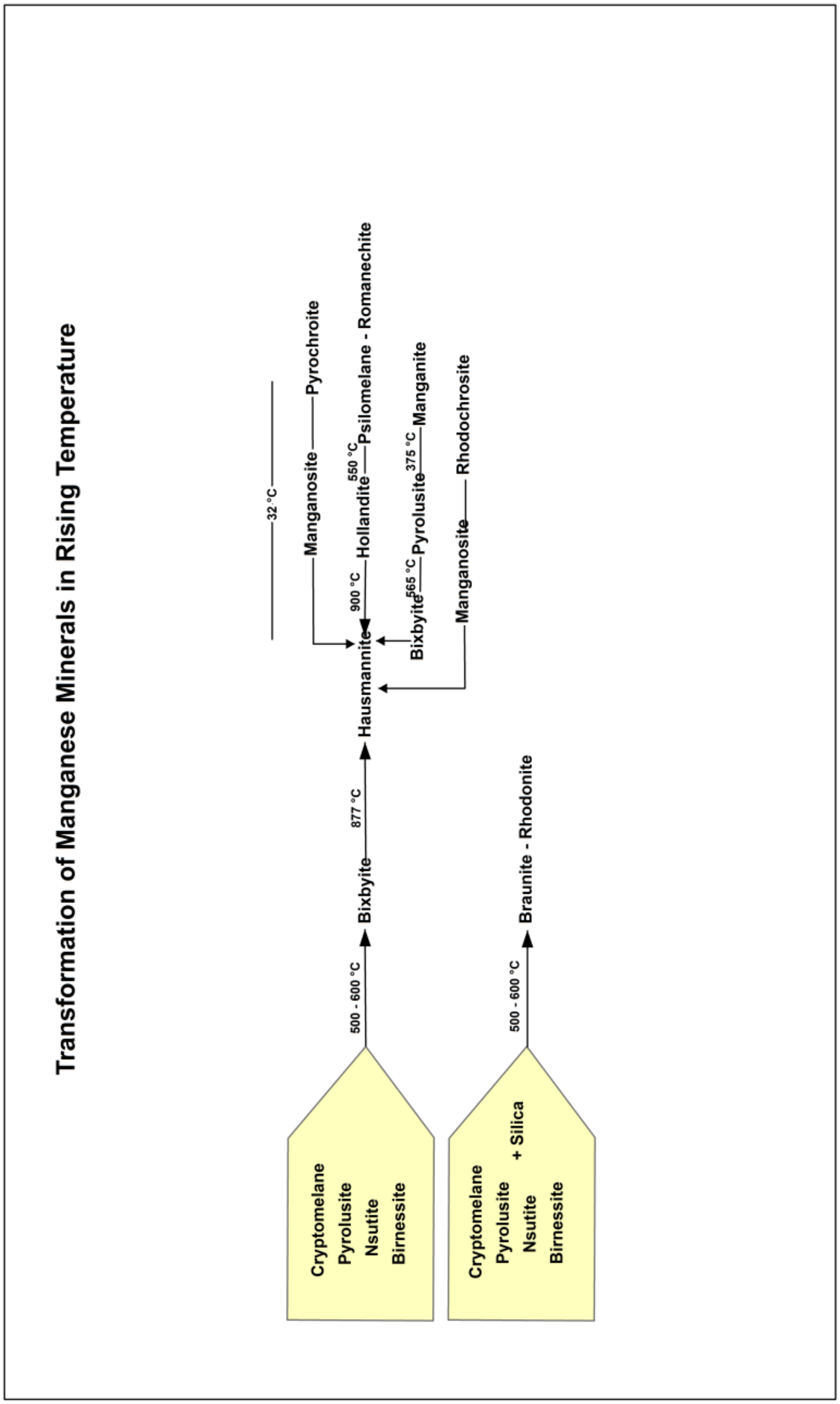
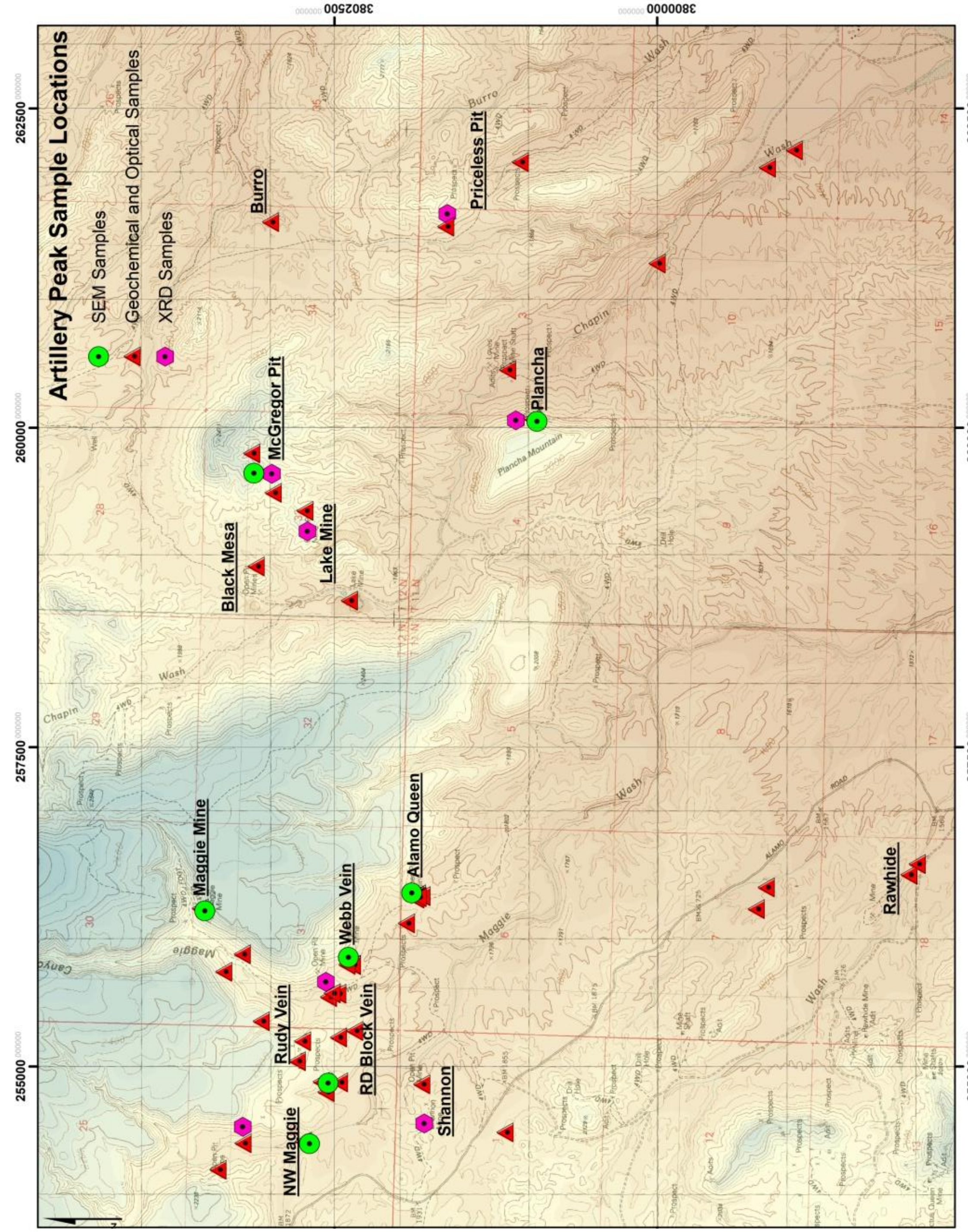
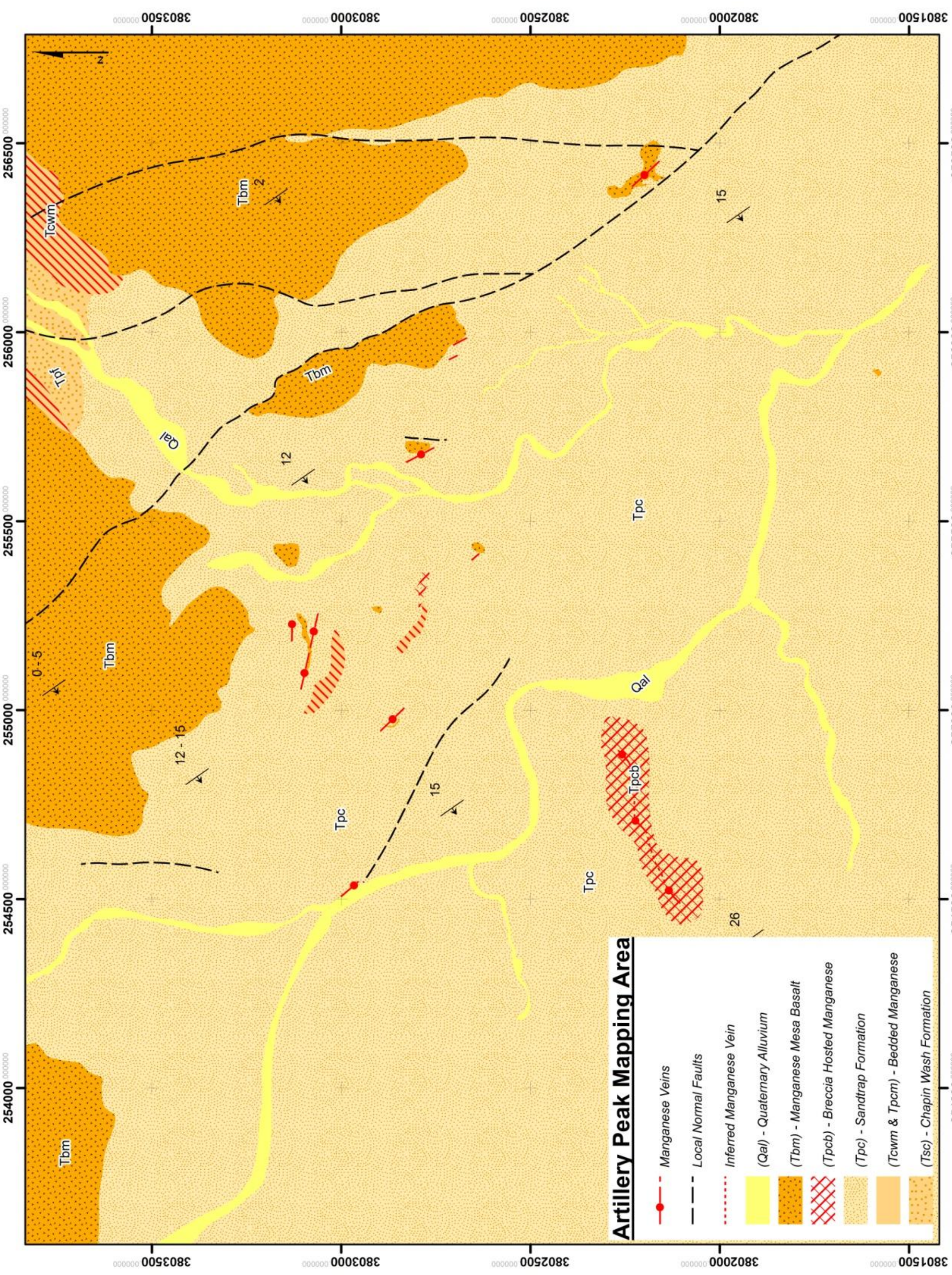
Appendices



Appendix A


Artillery Peak Sample Locations
SEM Samples
Geochemical and Optical Samples
XRD Samples
Burro
Priceless Pit
McGregor Pit
Plancha
Black Mesa
Lake Mine
Maggie Mine
Alamo Queen
Webb Vein
Rudy Vein
RD Block Vein
NW Maggie
Shannon
Rawhide
Plancha Mountain
Chapin
Wash
Maggie
255000
257500
260000
262500
3802500
3800000

Appendix B


Artillery Peak Mapping Area
Manganese Veins
Local Normal Faults
Inferred Manganese Vein
(Qal) - Quaternary Alluvium
(Tbm) - Manganese Mesa Basalt
(Tpcb) - Breccia Hosted Manganese
(Tpc) - Sandtrap Formation
(Tcwm & Tpcm) - Bedded Manganese
(Tsc) - Chapin Wash Formation
N
Tbm
Tcwm
Tpf
Qal
Tpc
Tpcb
3803500
3803000
3802500
3802000
3801500
254000
254500
255000
255500
256000
256500

Appendix C

Appendix D

		Al	As	Ba	Ca	Cu	Fe	K	Mg	Mo	Na	Pb	S	Sr	Ti	Zn	Pb	Zn	Mn
	DESCRIPTION	%	ppm	ppm	%	ppm	%	%	%	ppm	%	ppm	%	ppm	%	ppm	%	%	%
Burro Wash	Lower Priceless	3.61	1420	>10000	2.15	250	1.48	4.96	0.11	101	0.22	4900	0.1	960	0.2	1170			22
	Upper Pricelss Pit	2.44	3100	>10000	1.75	204	10.35	2.89	0.08	309	1.01	961	0.1	4430	0.14	3230			22.4
	Upper Burro Wash	3.96	773	>10000	6.64	92	0.93	3.21	0.12	79	0.98	>10000	0.18	441	0.12	375	2.18		8.81
	Lower Burrow Wash	0.74	166	6940	1.06	238	0.65	0.66	0.02	45	0.04	129	0.05	1955	0.03	320			2.71
Maggie Wash	Maggie Wash	1.33	658	>10000	1.68	76	2.53	1.14	0.06	96	0.55	436	0.05	1875	0.05	487			12.85
	South Alamo	5.04	565	>10000	2.26	115	2.12	5.05	0.16	20	0.38	1450	0.08	813	0.19	362			6.38
	North Maggie Wash Open Cut	2.67	846	>10000	6.36	754	1.75	0.77	0.5	134	0.79	746	0.04	1740	0.16	1190			19.15
	Webb Vein	0.04	2360	>10000	4.31	282	0.16	0.04	0.03	10	0.04	2000	0.17	394	<0.01	>10000		1.295	7.81
	Maggie Mine	0.72	757	>10000	5.49	711	0.51	0.63	0.07	27	0.15	>10000	0.06	1625	0.04	>10000	1.405	1.12	19.05
	Rd Block Veins and Breccia	4.16	655	8340	3.8	143	1.41	3.47	0.21	23	0.79	1425	0.08	275	0.15	1060			13.6
	Alamo Queen	2.83	1750	>10000	4.35	594	1.52	1.29	0.43	238	0.93	128	0.06	3790	0.16	1950			30.9
	Rd Block Massive Vein	0.42	1860	>10000	5.05	2360	0.24	0.37	0.16	178	0.42	4900	0.13	4780	0.01	2420			40.6
Chapin Wash	Lower Chapin Wash	3.59	1030	>10000	3.83	403	1.37	3.01	0.59	229	1.03	5620	0.13	6200	0.17	3750			21.1
	McGregor Breccia	5.89	401	8470	0.67	131	1.48	3.98	0.32	152	1.78	7130	0.03	500	0.15	356			7.18
	Lake Mine	2.79	1670	>10000	4.79	60	0.89	2.7	0.33	112	0.6	97	0.1	3330	0.1	620			21
	Lake Mine	3.42	899	>10000	7.47	32	0.91	3	0.65	75	0.77	57	0.08	2860	0.11	731			11.9
	Manganese Mesa	5.75	477	9320	2.15	30	1.83	3.29	0.59	24	1.18	667	0.02	1555	0.2	702			5.5