

OXIDATION OF A SULFIDE BODY, GLOVE MINE, SANTA CRUZ COUNTY, ARIZONA

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ABSTRACT

The Glove Mine is located on the southern extremity of an isolated synclinal sedimentary block of Paleozoic and Cretaceous sediments on the southern flank of the Santa Rita Mountains in Santa Cruz County about forty miles south of Tucson, Arizona.

Fluids probably associated with a Laramide (?) quartz monzonite intrusive have deposited argentiferous galena, sphalerite, chalcopyrite, pyrite, and quartz along permeable zones caused by fault intersections within a favorable limestone bed of the Pennsylvanian-Permian Naco group. As a result of extensive oxidation, only relics of the primary sulfides exist in the mined portion of the deposit. Cerussite, and lesser amounts of angle-site, wulfenite, smithsonite, and other oxidation products of the primary sulfides have been concentrated in solution caverns.

The ore body can be divided into three general zones on the basis of metal content and mineral assemblage. These zones are (A) the upper oxidized and leached zone, (B) the silver-enriched intermediate zone, and (C) the sulfide zone. The behavior of individual metals and minerals is dependent upon local Eh-pH conditions as well as other environmental factors affecting mineral stability. In response to changes in environment, mineral and metal assemblages vary not only between the zones but within them as well.

INTRODUCTION

THE Glove Mine is a small, oxide, lead-silver-zinc deposit about 40 miles south of Tucson, Arizona. The mine is in the Tyndall Mining District in section 30, T20S, R14E, on the southwestern flank of the Santa Rita Mountains at an elevation of approximately 4,200 feet (Fig. 1).

The original claims of the Glove group were located in 1907. Production commenced in 1911 and has continued intermittently under various operators until the present. The bulk of production took place from 1951 to 1959 under the management of the Sunrise Mining Company, which produced from 20 to 25 tons of lead-silver ore per day. In all, more than 21,000 tons of ore averaging 7.6 ozs silver, 25.5% Pb, 4.1% Zn, and 0.1% Cu per ton and worth slightly more than one million dollars have been produced.

GENERAL GEOLOGY

The Glove Mine is on the southern limb of an isolated synclinal sedimentary block. This block of Paleozoic and Cretaceous sediments may represent a deformed remnant of the southwestern limb of an anticline that was breached by Laramide (?) quartz monzonite intrusives (Harald Drewes, personal communication, 1965) which form the main mass of the Santa Rita

Mountains. In the vicinity of the mine, the southern flank of the syncline is composed of limestones, siltstones, and shales of the Naco group of Pennsylvanian-Permian age (1) which strike N75W-N60W and dip approximately 60° northeast (Fig. 2).

The limestones are intruded by a latite porphyry sill that reaches a maximum observed surface thickness of approximately 30 feet several hundred feet east of the Glove adit portal. This sill is discontinuous, and generally follows bedding trends in the limestone north of the Glove fault.

The Glove fault separates sediments of the Naco group on the north from the quartz monzonite to the south. This fault clearly follows an intrusive con-

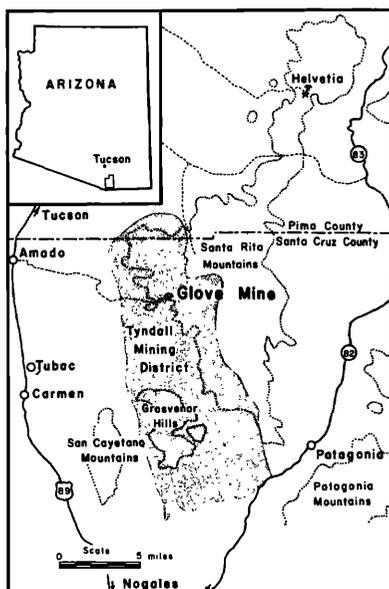


FIG. 1. Index map.

tact, which is roughly concordant with the bedding of the limestone as to strike, but discordant as to dip. The intrusive nature of this contact is most vividly illustrated in the area between the main adit and the 40-foot shaft. Here, the quartz monzonite has sliced into the sediments, partitioning the limestone into thin aligned septa. The contact is nearly vertical, generally dipping steeply to the north.

Minor showings of lead-copper mineralization crop out in the area of the Glove workings. Mineralization is in the limestone, generally associated with the quartz monzonite or latite porphyry contacts, although some lead and copper showings do occur in the limestone some distance from these contacts.

All mineralized outcrops are essentially the same. The limestone is marbled, but is only locally iron-stained. Lead minerals occur as small stringers and blebs in minor fracture zones. Cerussite, commonly with galena

cores, is by far the most common lead mineral, although in particularly tight ground, tarnished galena is present. Evidence of copper mineralization is not readily apparent, but small splotches of copper "bloom" are sometimes noticeable. Sphalerite or other zinc minerals were not noted on the surface.

Description of Rock Types

Quartz Monzonite.—The quartz monzonite in the mine area has been described by Anthony (1) as the "fine quartz monzonite" to distinguish it from a "coarse quartz monzonite," which occurs as isolated masses within it and as

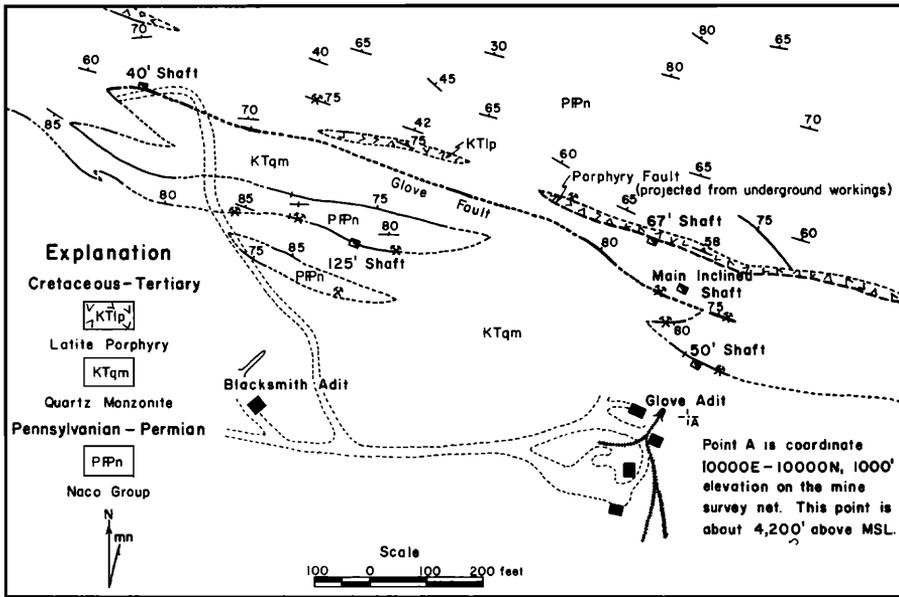


FIG. 2. Generalized geology of the Glove Mine area.

a large intrusive mass to the northeast. The quartz monzonite in the mine area varies from fine- to medium-grain. It generally weathers to a light orange-brown shade due to a fine coating of limonite. Anthony (1) from thin section analysis quantitatively estimated the mineral constituents of the quartz monzonite to be (in percent): quartz, 50; micropertthite, 30; andesine-oligoclase ($Ab_{68}-An_{32}$), 17; limonite, 2; and unknown silicate mineral, 1. Primary mafic silicate minerals are absent in all but one of the sections studied. This section contains about 25 percent hornblende which probably represents a local accumulation along the contact.

Latite Porphyry.—The latite porphyry weathers greenish to greenish-gray and contains abundant phenocrysts of chalky white plagioclase. In unaltered areas underground, it has a more uniform green appearance. The majority of the phenocrysts are plagioclase, although minor orthoclase and rare quartz phenocrysts are also present. Primary quartz constitutes approximately 3

percent of the groundmass. The remainder is largely orthoclase. There are no primary mafic silicate minerals. Opaque minerals constitute about 2 percent of the rock.

Naco Group.—The limestone sequence in which the Glove Mine is located has been identified as a portion of the Naco limestone, and included in the Naco group of Bryant (2). It consists of alternating limestone and siltstone with minor interbedded shale units. The limestones weather white, pink, gray, and brown. The siltstones and cherty layers generally weather to a shade of greenish brown or black. Underground, the limestone beds are generally white, although they may be pink, gray, or various shades of brown depending upon the type and degree of alteration. The siltstone units underground are generally some shade of green, gray-green, or more rarely gray.

The limestone beds are mostly pure, although they may contain small amounts of silt-sized quartz. The siltstone beds are composed chiefly of quartz, with small amounts of calcite and clay minerals. Chlorite also is present in varying amounts, and was observed in almost all of the sections studied.

Alteration

Contact-metamorphic effects produced by emplacement of the quartz monzonite and latite porphyry are in general relatively minor. Near the contacts, the limestone has been silicified and metamorphosed to a white to pinkish marble, and chlorite is common in the siltstone and cherty layers. At increasing distance from the contacts, these effects diminish and the marbles and chloritized siltstones grade into limestones and siltstones that are typical of the Naco group.

No continuous tactite zone has been developed, and only two minor areas of silication containing epidote and garnet were noted. Iron staining is common, but not strong, along the contact. The single exception noted is a small kidney of specular hematite just to the east of the 50-foot shaft.

In the vicinity of sulfide mineralization, the marbleized limestone is commonly intensely silicified. Silicification generally takes the form of replacement by cryptocrystalline silica such as chalcedony, although it commonly occurs as euhedral quartz containing calcite inclusions and relict structures. Secondary quartz in vugs and as vein filling is also common.

The extent to which the limestone is altered to dolomite, if at all, is unknown. Some replacement of the limestone by siderite and rhodochrosite, however, was observed.

The quartz fragments of the siltstone beds may be extensively veined by calcite, which was probably released during the silicification and marbleization of the limestone. Some of this calcite, however, may represent mobilized calcite present in minor amounts in the siltstone as a cementing material.

Most of the siltstones are moderately chloritized, which gives them a greenish color underground. The chloritization of the siltstones probably occurred as a reaction of minor amounts of clay minerals inherent in the rock, with possible magnesium and calcium introduction, in response to the increased

energy conditions accompanying metamorphism and emplacement of the ore minerals.

The quartz monzonite is unaltered except near the limestone contact where it appears to be slightly silicified. Besides introduced silica, microscopic examination shows the plagioclase and orthoclase feldspars to be partially altered to sericite and kaolinite. The plagioclase feldspars also are altered to calcite. Secondary muscovite, which appears to be the same age as the sericite, is also present but not abundant, and may represent more intense local alteration. Chlorite is common in some specimens as shreds replacing the feldspars or surrounding disseminated pyrite. Limonite is almost universally present as stringers between mineral grains, and as fracture fillings. These alteration effects decrease with distance from the contact.

At the surface, the latite porphyry appears megascopically to be only slightly altered. However, in thin section, the phenocrysts of plagioclase, as well as the groundmass material with its high orthoclase content, are highly altered to sericite, kaolinite, and smaller amounts of calcite, muscovite, and chlorite. Secondary silica derived from the alteration of the feldspars as well as introduced silica is present. This pattern of alteration continues down with uniform intensity at least to the 300-level of the mine, which is the lowest depth at which the sill has been intersected.

GEOLOGY OF THE ORE DEPOSIT

The metamorphosed limestone beds in the underground workings are cut by a series of faults that have approximately the same attitude as the bedding. These faults are, for the most part, tight, and show no evidence of extensive movement. Solution by ground water aided by acids from the oxidation of the sulfides, especially in the zones of brecciation developed at fault intersections, has produced cavernous pipes which trend approximately S60E and plunge roughly 30° southeast.

Three major faults are associated with the ore body. The Porphyry fault is probably the master fault of the mine area. It lies along the footwall side of the latite porphyry sill, and follows the same N60-75W, 60N attitude as the sill (Fig. 3). The Main fault "horsetails" off the Porphyry fault at approximately the 180-level, and assumes a more northwesterly strike, although its dip remains fairly constant at 60° northeast (Fig. 4). The South fault also "horsetails" off the Porphyry fault in the vicinity of the 180-level. At its intersection with the Main fault, (Fig. 4) the South fault has an attitude of approximately N60E, 45-60S.

Minor faults that "horsetail" off these major faults are not common in the upper levels, but become more abundant with depth. Below the 180-level, they are important as sites for ore deposition.

A fault zone along the hanging wall side of the sill produced a small ore pipe above the adit level (Fig. 3), but exploration on the 210-level failed to pick up the possible downward projection of this pipe.

A period of minor post-mineralization adjustment is evidenced by curving

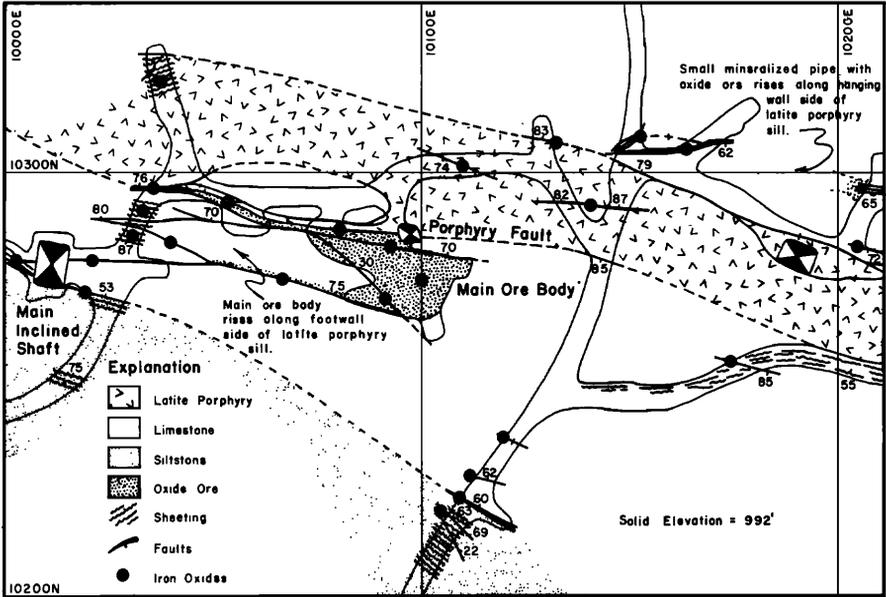


FIG. 3. Generalized geology of the Glove Mine—adit level.

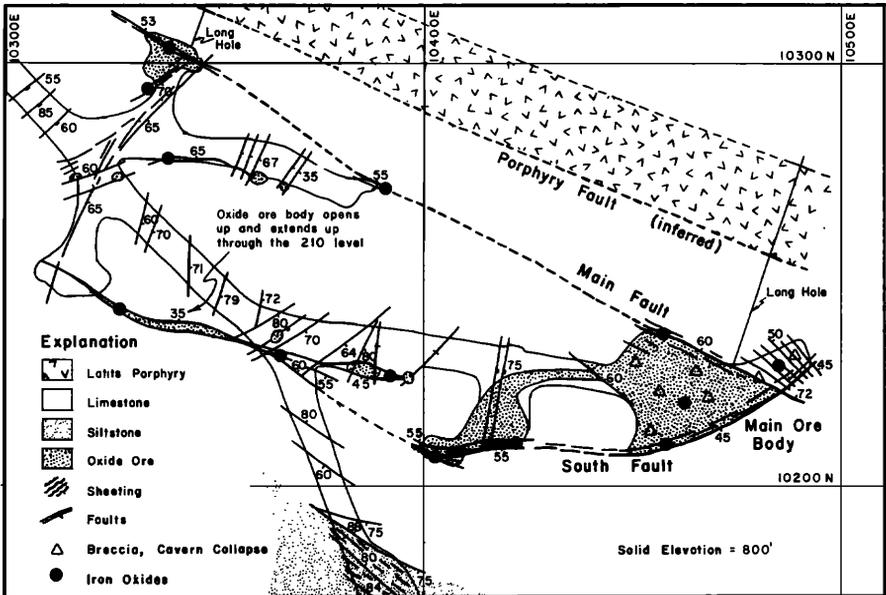


FIG. 4. Generalized geology of the Glove Mine—240 level.

cleavage faces in the galena. However, no evidence of any post-ore offsets was noted.

Ore Bodies

The main-stope complex, which has been mined from the surface to the 360-level, is in the form of a series of coalescing pipes that are irregular in plan and section (Fig. 5). These pipes developed along zones of permeability formed by faults and fault intersections within the favorable limestone. Ore

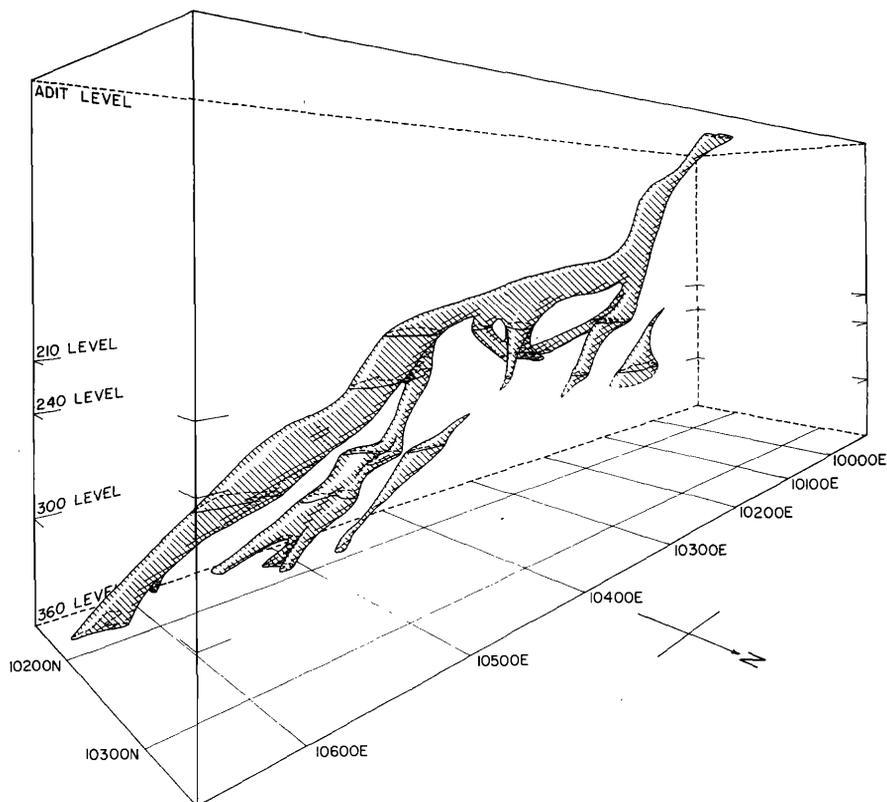


FIG. 5. Generalized view of the Glove ore body.

fluids ascending along these permeable zones replaced the limestone forming stringers and bands of massive sulfide and some minor sulfide disseminations.

Later, acids from oxidation of the sulfides further leached the limestone, forming a complicated system of caverns controlled largely by the original permeable zones and the sulfide pipes. As the caverns enlarged, they were filled with the oxidation products of the sulfide minerals, along with quantities of wad, calcite, gypsum, and minor silica. Boulders of limestone and marble that collapsed from the backs during the leaching of the cavern are scattered

throughout this cavern fill, and other limestone boulders and partitions represent remnants of undissolved country rock.

Most of the present oxide-filled pipes apparently were sites of primary mineralization. However, many of the smaller and shorter pipes appear to be post-mineral caverns leached in barren limestone and subsequently filled with the oxidation products derived from neighboring sulfide zones.

The leaching of the limestone and the downward migration of the metals has enriched the ore body considerably within the zone of oxidation increasing a possible primary lead-zinc grade of perhaps 20 percent to as much as 40 percent or more in certain areas.

Ore Controls

The lead-zinc-silver mineralization at the Glove Mine is primarily limestone replacement although some fissure-filling occurs. Although the mineralization is post-intrusion, the ore-bearing fluids are probably associated with the emplacement of the quartz monzonite and the latite porphyry sill. Sulfide deposition appears to have been controlled by permeable zones of brecciation and fissuring caused by faults and fault intersections within a favorable limestone bed. The control is mainly physical and related to the permeability of the rock, but is also chemical in that a "favorable" limestone was replaced. Smaller faults that converge upward into the larger fault zones probably channeled the mineralizing fluids into the main ore zones.

The zone of brecciation at the intersection of the Main and South faults is the locus of ore deposition in the main stope area from the 180- to the 360-level. However, in the lower levels, the South fault appears to have exerted an increasing amount of control over ore deposition. Below the 240-level, the latite porphyry sill seems to have had no effect upon sulfide deposition. However, above the 240- and 180-levels where the Main and South faults are captured by the Porphyry fault, the sill appears to have acted as an impermeable deflecting barrier that channeled the ascending fluids along the Porphyry fault on its footwall side. This prevented, to a large extent, the spreading of the mineralizing fluids into the limestones to the north, and explains why only one small mineralized pipe exists on the hangingwall side of the sill. Above the 180-level, the Porphyry fault is the dominant control of ore deposition.

Host rock alteration may represent a more subtle form of control. The favorable limestone bed is relatively pure carbonate, and the underlying siltstone is largely quartz. The limestone associated with the ore pipes appears to have been slightly silicified, whereas areas of more intense silicification seem to have been bypassed as sites of sulfide deposition. It thus appears that pure or only moderately silicified limestone were favorable to ore deposition, whereas the siltstone and the intensely silicified limestone were unfavorable.

Sulfide Mineralization

Hypogene metallization is quite simple. It consists of minor amounts of pyrite and chalcopyrite associated with galena and sphalerite.

OXIDATION OF PRIMARY SULFIDES

The oxide portion of the Glove Mine is wholly above the water table. During periods of high seasonal rainfall, surface runoff is captured by open fractures and cavernous zones in the limestone, which provide for entry and downward percolation of ground water. The oxidizing environment of the lead-zinc sulfides has been, then, one of alternating periods of moistness and dryness, with perhaps some intervals of flooding. Water in this oxidizing environment is constantly receiving atmospheric oxygen as the dissolved oxygen is being consumed by the oxidation of the sulfides.

In the oxide portion of the ore body in areas of unrestricted ground water and atmospheric movement, as in the caverns of the main ore body, solutions would tend to have a high pH because of their frequent if not constant contact with the limestones. However, in stagnant backwash areas of restricted circulation, the oxidation products of the sulfides can effectively insulate the ground water solutions from extensive contact with the limestones, and thereby permit lower pH conditions. Therefore, it appears that in the oxide zone above the water table, the pH of the vadose water solutions is partially a function of circulation.

The ore body can be divided into three general zones on the basis of metal content and mineral assemblage. These zones are: (A) the upper oxidized and leached zone, (B) the silver enriched intermediate zone, and (C) the sulfide zone.

The upper oxidized and leached zone (A) roughly extends from the surface to the 300-level. Along with abundant iron oxides, wad, and gypsum, this zone contains remnants of all sulfide minerals, cerussite, anglesite, and wulfenite. Cerussite is the dominant lead mineral. Zinc values are present in the order of 5 percent or less. Silver values are also low, and average less than 5 ounces per ton. The Ag:Pb ratio varies between 0.2 and 0.3. The Zn:Pb ratio is low and is nearly constant at 0.1.

The intermediate zone (B) extends from the 300- to about the 360-level. It has a ragged interface with the underlying sulfide zone (C). In addition to all the minerals common to zone (A), the intermediate zone contains abundant encrustations of "dry bone" smithsonite. Cerussite remains the dominant lead mineral. Wulfenite becomes much less abundant and smaller in crystal size. Average zinc values rise to 13 percent, and the zone is enriched in silver, which averages approximately 13 ounces per ton. The Ag:Pb ratio is high, varying between 0.4 and 0.7, and the Zn:Pb ratio increases with depth until a ratio of 0.6 is reached.

The sulfide zone (C) extends below the 360-level and contains approximately equal amounts of galena and sphalerite, and smaller amounts of pyrite. Chalcopyrite is present as minor disseminations and as exsolution blebs in the sphalerite. Minor amounts of supergene covellite commonly replace the hypogene sulfides. Silver values are intermediate between zones (A) and (B) and average about 8 ounces per ton. The Ag:Pb ratio is constant at 0.4 and the Zn:Pb ratio reaches 1:1.

The behavior of the individual metals present in the mine is dependent

upon the local environment and varies not only between the zones but within them as well. This is illustrated graphically in Figure 6. Galena exists in all three zones. It is least abundant in the upper oxide and leached zone and increases in abundance downward until it represents approximately 50 percent of the metal sulfides in the sulfide zone. In the upper portions of the mine, it exists in areas of tight ground where the effects of oxidation have not reached and as remnant cores in lead carbonate and sulfate aggregates.

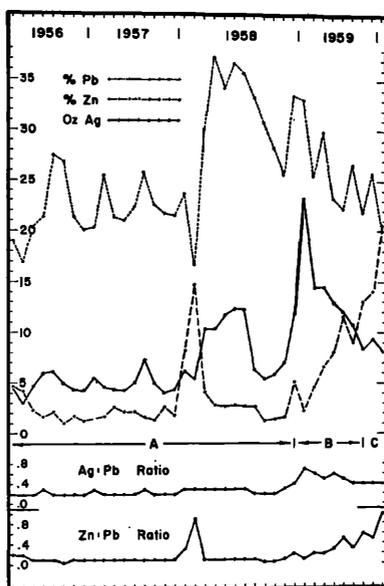


FIG. 6. Ore grade and metal ratios 1956 through 1960.

The plots on the graph represent the average monthly ore grade and the metal ratios (calculated to the nearest 0.1) as computed from smelter returns. Shipments to the smelter were not made in every month of the period presented, so each year is not necessarily represented by 12 figures. During period "A" the upper oxidized and leached zone was mined. Silver and zinc values are low; the Ag:Pb ratio ranges between 0.2 and 0.3; and the Zn:Pb ratio is low. The zinc anomalies represent the mining of large amounts of smithsonite on the 300-level. During period "B" the silver-enriched intermediate zone was mined. Silver values are high, zinc values increase, the Ag:Pb ratio is high, and the Zn:Pb ratio increases. During period "C" substantial amounts were mined from the sulfide zone. Silver values decrease, zinc values increase, the Ag:Pb ratio is intermediate, and the Zn:Pb ratio reaches 1:1.

Galena alters directly to cerussite or anglesite. In the oxide zone, in areas in which the ground water has a high CO_2 content and unrestricted movement (conditions favorable for high pH), galena alters directly to cerussite. These conditions are typical of the caverns of the main ore complex and explain the predominance of cerussite in these areas. Cerussite is the main ore mineral and has been mined as massive bodies, encrustations, and "sand car-

bonate" associated with other oxide products of the cavern fill from the surface to the top of the sulfide zone on the 360-level.

The environments of stability of anglesite and cerussite are quite different. In the presence of CO_2 and the carbonate ion, anglesite is stable in an acid environment whereas cerussite is stable in mildly acidic to basic conditions (4). Anglesite is not as common as cerussite. This is as would be expected because circulating acid water would be quickly neutralized by contact with the limestone host rock producing an environment in which cerussite is the stable mineral. However, in stagnant areas of limited circulation away from the main zones of ground water circulation, oxidation of the sulfides could produce a low pH environment and would provide a sulfate ion source. Anglesite is found in such environments at the Glove, and as such exists throughout the extent of the oxide zone from the surface to the 360-level.

The lead oxides plattnerite (PbO_2), massicot (PbO), and minium (Pb_3O_4) were not noted and if present, are probably quite rare.

Wulfenite (PbMoO_4) is common, and exists as fine crystals throughout the entire oxide body and as spectacular crystalline aggregates along the backs and sides of numerous caverns above the 300-level. In one stope, between the 180- and 210-levels, it was the principal lead ore.

Molybdenite was not noted in polished section in or around any of the sulfide minerals. Examination of polished sections under vertical and oblique illumination failed to reveal any galena altering directly to wulfenite. If molybdenum were present in the galena, direct alteration to wulfenite would be expected as wulfenite is the stable oxidized lead mineral in the presence of the molybdate ion (4). Cerussite will be stable and form only after all the molybdate ions have been combined. In the absence of a molybdate ion source, wulfenite becomes unstable and is removed in solution to be reprecipitated later by the presence of a large lead ion concentration or by evaporation of the solution.

Sphalerite was not recognized above the 300-level, but at that level became fairly abundant. Smithsonite was also first recognized at this level, although zinc values of 5 percent had been encountered in mining from the surface. Zinc above the 300-level is finely disseminated throughout the oxide zone, and its mineral form is not known. The absence of zinc values equal to those of lead in the upper oxide zone is probably due to the greater solubility of the zinc minerals, and their migration and later precipitation on the lower levels.

In an oxidizing aqueous solution smithsonite is the least soluble of the supergene zinc minerals, and hence the most stable mineral in the pH range 6.2 to 8.1 (4). This suggests that smithsonite might also be the zinc mineral disseminated throughout the upper oxide zone. However, in the absence of a plentiful supply of ground water in a dry environment, the carbon dioxide concentration may be so low that hydrozincite ($2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$) would be more stable than smithsonite (4). In this event, a portion of the zinc values above the 300-level could quite well be present as hydrozincite.

Below the 300-level, in the intermediate oxide zone, zinc values increase to the order of 15 to 20 percent as veins and encrustations of "dry bone" smithsonite and as sphalerite remnants associated with galena. At the top

of the sulfide zone, near the 360-level, sphalerite and galena occur in approximately equal amounts in stringers and grains scattered throughout the calcite of the ore zone. Minor chalcopyrite, covellite, and pyrite are associated with the sphalerite and galena as inclusions, replacements and separate grains.

Silver values are approximately covariant with lead values (Fig. 6). The relative concentration of silver is highest in anglesite, intermediate in galena, and lowest in cerussite. In the upper levels of the mine, silver values have averaged approximately 4.5 ounces per ton. The amount of silver slowly increases with depth, and the greatest concentration of silver is just above the 360-level. This high silver zone occurs as an irregular blanket just above the ragged interface between the sulfide and intermediate oxide zones. In this zone, silver values have been as high as 27 ounces per ton, with 13 ounces per ton as a fair approximation of the average. The silver content drops to approximately 8 ounces per ton in the sulfide zone.

Silver in the form of primary argentite nor any of the secondary silver minerals were recognized in polished section. Primary silver probably exists as ions "admitted" into the galena crystal structure. Evidently there is insufficient material, such as a chloride ion sources, to immediately fix the silver ions released by the oxidation of galena. Silver ions apparently enter into solution and are washed down to the zone of increased sulfide content at and slightly above the top of the sulfide zone. Upon contact with the sulfides, they probably precipitate to form secondary argentite or react with the oxides to form such minerals as argentiferous plumbojarosite and argentojarosite. Continued leaching and downward migration of the silver from the upper oxidized zone would thus tend to form the irregular blanket of increased silver values that is found in the intermediate zone just above the top of the sulfide zone.

PARAGENETIC SEQUENCE

Hydrothermal mineralization began after the intrusion of the quartz monzonite and the latite porphyry, and the fracturing of the limestones. Quartz and possibly pyrite were introduced first, followed by sphalerite, chalcopyrite, and galena. Subsequent oxidation of the primary minerals resulted in the breakdown of sulfides and the formation of covellite and the variety of oxide minerals found in the mine.

The general paragenetic sequence as developed from geologic relations and polished section study is given in Figure 7. The list of supergene minerals is by no means complete; the mineral assemblage is complex and varied, and is complicated by mechanical mixing. Many of the minerals are exceedingly fine-grained, and cannot be identified by general megascopic or optical techniques.

It is recognized that a supergene paragenetic sequence has little meaning unless related to a particular Eh-pH environment (3). In many instances, such an environment alone has little meaning, as, for example, the amount of dissolved carbon dioxide may bear a controlling relationship to mineral stability. The minerals are in constant interaction with one another, and mineral suites vary with changes in environment. Different mineral suites

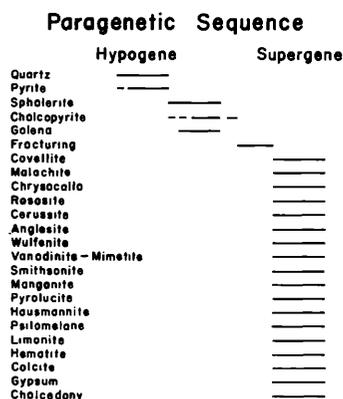


FIG. 7. Paragenetic sequence.

are stable at different levels of the mine. One mineral may form and remain stable at one location, but be highly unstable in an adjacent environment. Therefore, the supergene minerals are placed on the diagram as being contemporaneous, as indeed they are.

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DENVER, COLORADO,
Dec. 27, 1965

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