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A Study and Application of the Process of Supergene Enrichment of Silver Ores.

Arthur C. Verling

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A STUDY AND APPLICATION
of the
PROCESS OF SUPERGENE ENRICHMENT OF SILVER ORES

by

Arthur C. Verling

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

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BUTTE, MONTANA
June, 1936
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MONTANA SCHOOL OF MINES
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a. Looking west—showing physiography.

b. Looking northeast—Butte in the background.

c. Looking east over the Ardsley district.
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Introduction

In many deposits of silver ores the grade of the ore decreases considerably a few hundred feet below the surface, and it is believed that in many cases the better ores owe their richness in part to the process of sulphide enrichment. It is recognized, however, that many rich silver ores are hypogene deposits that have been affected very little, if any, by processes of enrichment. Since the hazards of estimating the continuity and quality of ore deposits beyond visible openings may be lessened by an understanding of the principles of economic geology, a knowledge of the processes of supergene enrichment is essential for intelligent exploitation. Especially is this so in the case with silver ores, as a small amount of enrichment may make an otherwise valueless deposit, of commercial importance. The possibility of encountering a zone of enrichment may have a fundamental bearing upon the appraisal of an extension estimated to lie beyond a certain sampled face in a superficially developed mine. Another point which is of equally great importance, for upon it rests the life of the mine, lies in the ability to foretell to what depths the enrichment zones are likely to persist.
This Bachelor's thesis in Geological Engineering at Montana School of Mines was undertaken from this practical or economic point of view rather than from the purely scientific standpoint. It is the writer's opinion that the accuracy of the application of laboratory investigations to geologic problems must be verified by field observations; otherwise, regardless of how correct the experimental work, it cannot be claimed to solve the problem attacked. The effective employment of the concept of supergene enrichment in practice requires statement of evidence in fairly exact terms, mapping distribution of critical features, and determination of ground where combinations of controlling conditions exist.

In the limited time in which an undergraduate thesis must be done it is rarely possible to get a thesis problem in enrichment which combines field and laboratory study. In December, 1935, an opportunity arose to inspect the Anna Mine, which is about three miles southwest of Butte. Subsequently, Professor P. A. Schafer of the Montana School of Mines became engineer in charge at the Anna Mine, thus making possible the desired field and laboratory study.

The writer acknowledges his indebtedness to Dr. E. S. Perry, head of the Geology Department at Montana School of Mines, for his valuable help and advice; to Professor P. A. Schafer and officials of the Anna Mine, who kindly extended facilities for securing specimens, studying the geology in the mine, and for making available maps and assay returns. For these courtesies, the writer expresses his sincere thanks.
Chemistry of Supergene Enrichment

If, after the formation of a mineral deposit, it is subjected to a new environment, new minerals will tend to be formed. When exposed to weathering at or near the surface, they tend to break down and form soluble salts and minerals that are stable under surface conditions. Many of the metals form soluble sulphates which are carried downward in solution to depths where air is excluded, favoring redeposition. In this way the metals in a low grade or almost valueless deposit are continually being concentrated by supergene enrichment in certain portions of the ore bodies, particularly those just below the oxidizing environment.

Oxidation of the sulphide ores in the outcrop of a deposit forms sulphates and sulphuric acid, if iron sulphides are present, as they almost universally are. In the presence of sulphuric acid and ferric sulphate, silver is dissolved and carried downward by ground water circulation as metallic sulphates. Cooke established the following equation where $\text{CFe}^+$' equals concentration of ferric ion, $\text{CFe}^{2+}$ equals concentration of ferrous ion, and $\text{CAg}^+$ equals concentration of silver ion in solution:

$$\frac{\text{CFe}^+}{\text{CFe}^{2+} \times \text{CAg}^+} = 163$$

From this equation it is evident that the increase of ferric iron in the solution will greatly increase the solution of silver, and that the increase in ferrous iron will favor its precipitation. In the vadose oxidizing zone ferric sulphate
is plentiful and solution predominates, but below the water level, oxygen is sealed out, and ferrous sulphate accumulates, thus favoring precipitation.

Silver is precipitated at or below the water level in several ways—by reduction of the system containing ferric sulphate, by neutralization of the sulphuric acid, or by contact with certain minerals that precipitate the native metal. Ferrous sulphate precipitates silver from sulphate solutions to give native silver and ferric sulphate. Hydrogen sulphide and alkaline sulphides precipitate silver as sulphide from acid solutions. Below the zone of oxidation, silver is readily precipitated as argentite on account of the low solubility of the sulphide. Acid reacting upon sphalerite, galena, or other sulphides produces hydrogen sulphide which precipitates from a silver sulphate solution native silver, argentite, and stromeyerite. If arsenic or antimony are present, a long list of minerals including pyrargyrite, proustite, stephanite, polybasite, and others may be precipitated. These minerals may be either secondary or primary, but Emmons says(2), "data now available indicate that they are nearly everywhere secondary minerals."

Although oxidation tends to reduce the various ores to a chemically simple and nearly uniform aggregation, the oxidized ore shows significant textures that furnish a clue to what is below. The gossan of an ore high in iron sulphide is likely
to be especially cellular and porous. Along with this material, masses of quartz, slightly stained with iron oxide are common, but, if there is no cellular material, the body is less likely to change to iron sulphide with depth and enrichment is not probable.

**Criteria for Recognition of Supergene Enrichment**

The criteria for the recognition of supergene sulphide deposits have been discussed in several papers. They involve practically all available data relating to the geology and physiography of the region in addition to the observed characteristics of the ore deposits. In the study of a deposit certain general criteria may be applied. Among these are: the vertical distribution of the richer portions of the vein with respect to the present surface and to the level of the ground water; mineralogy of the richer and poorer portions of the deposits and the character and vertical distribution of the component minerals; and paragenesis, or the structural relations shown by the earlier ore and that which has been introduced subsequently.

**Relation to Water Table**

The terms "water table" and "level of ground water" are generally used to describe the upper limit of the zone in which the openings in rocks are filled with water. This upper limit of the zone of saturation is an irregular surface which follows in general the topography of the country and is
modified by the physical character of the rock. Obviously
in regions of varied seasons the water table oscillates with
wet and dry periods. The level of ground water generally stands
at about a hundred feet below the surface. In moist, hilly
countries, its depth varies from a few feet to several
hundred feet, and in arid regions it may extend to much greater
depths.

The ground water level indicates the top of the secondary
sulphide zone at the time that zone was formed. If the water
level is comparatively high or if the rock is much fractured,
there is probably but little precipitation of secondary sulphides
above the water level. The reasons for this are; the rapid
descent of the solutions through the shallow or fractured zone
above the water table, and the sulphides of the more valuable
metals are dissolved readily in an oxidizing environment, but
are not precipitated in such an environment. Protection of the
sulphides below the water level from the oxygen of the air re-
tards or prevents solution. The reducing action in the zone
below the water level drives gold and particularly silver from
solution thus forming a zone of concentration or supergene
enrichment. This zone of secondary ores extends downward to
various distances below the water table. The vertical extent of
the zone differs widely in different districts.

Permeability

Permeability is essential for concentration by redeposi-
tion for it facilitates the downward migration of metal
bearing solutions. If the primary deposits are not permeable,
the solutions that pass downward through the oxidized zones will
move laterally along the vein between the contact of the oxidized and sulphide ores to ultimately escape into the wall rock or reissue as springs. Unless a reducing environment is encountered, the metals will not be redepotted. Rocks that have been shattered by strong movements since the primary ore was deposited are most favorable for deep and extensive enrichment because of their control on ground water circulation.

Fracturing or shattering of the primary ore, resulting in a large number of small openings, is more favorable to enrichment than a few large openings, for a larger surfaced primary ore is exposed to solution. The general association of profitable ore with fissured, broken, permeable ground is well recognized in practical operations and is not to be overlooked in the consideration of supergene enrichment.

**Mineralogy**

The presence of certain minerals in an ore deposit is not a conclusive criteria of enrichment as most of the minerals characteristic of the enrichment zone are precipitated from both cold descending and hot ascending solutions, while the genesis of many others is uncertain. Thus, in the useful lists prepared by Lindgren and by W. H. Emmons, there are very few minerals, outside of those characteristic of the zone of oxidation, that so far as is known are rigidly limited to any one division of the whole vertical range of formation exhibited by the minerals associated in ore deposits. Though not conclusive, the presence of one or more of the silver
minerals argentile, native silver, proustite, pyargyrite, stephanite, polybasite or other complex sulpho-salts is highly suggestive of silver enrichment. The distinctly supergene silver minerals comprise native silver, argentite, cerargyrite, embolite, bromyrite, and iodyrite.

The mineralogy of a deposit is important in that some minerals retard the process of enrichment and cause shallow zones of rich ore, while other minerals exert little or no affect and the zone is then apt to be more extensive and contain lower grade ore.

To start the process, pyrite or some other iron sulphide must be present in the ore, for by its oxidation, ferric sulphate, and sulphuric acid, the potent solvents of the sulphides are derived. With iron sulphide scarce or absent, native silver will be expected in the gossan, and there will be little or no enrichment; with iron sulphide abundant, there will be little native silver in the gossan and greater enrichment.

With the active silver precipitating minerals, as determined by the experiments of Palmer and Bastin (1), alabandite, chalcocite, tetrahedrite, pyrrhotite, niccolite, smaltite, covellite, tennantite, and siderite, shallow zones of enrichment are to be expected. Among the common sulphides which may be associated with the silver minerals and which exert a slower precipitating effect may be mentioned chalcopyrite, sphalerite, galena, stibnite, and pyrite.
**Paragenesis**

Since the deposition of supergene minerals follows the deposition of hypogene minerals it is important that the age relations of all of the minerals of a deposit be established when that is practicable. The zone of sulphide enrichment nearly always contains considerable primary ore, and very often the secondary ore is merely the primary ore containing in its fractures small seams of rich secondary minerals. A microscopic study of the paragenesis of the sulphides, made upon a representative suite of polished surfaces of ore from the oxidized-sulphide transition zone, is indispensable in determining the hypogene or supergene nature of the silver minerals. Although the study of mineral paragenesis does not result in the direct discovery of new orebodies, it is of value in a general study of an ore deposit in that it gives a clue to the complex processes of ore deposition and to the character of the original ore solutions.

**Assays**

Obviously a deposit cannot be enriched by constituents not originally present in at least a small quantity in the primary ore. As enrichment usually produces a gradation from rich ore to lean ore, it is possible by a series of assays to determine the vertical extent of the enriched ore. This comparison of assays of supposedly enriched ore and the primary ore is an important consideration of the problem. If a change of tenor is observed and can be correlated to certain mineral group-
ings, or to topography, ground water level, or zone of oxidation, it is almost certain proof of enrichment. This correlation is essential to distinguish between a vertical gradation due to enrichment and a vertical gradation due to physical and chemical conditions controlling original deposition.

Summary of Criteria of Supergene Silver Enrichment

Because many silver deposits owe their workable grade to supergene processes, it is important to note the features by which the results of the supergene processes may be recognized. As secondary ores are superficial, they will play out in depth, so that the problems of enrichment are vital to intelligent exploitation. The migration of metals depends upon the ore and gangue and many other factors, but the general principals may be applied to the investigation of all deposits. These are summarized briefly here.

Supergene enriched ores are those which are formed by precipitation of certain metals from descending solutions and are recognized by certain characteristic features: Enriched deposits are usually porous and open textured, particularly in the oxidized zone. They commonly show a characteristic zonal arrangement, a leached zone at and near the surface grading into a zone of higher grade sulphides and this into a zone of primary ore. The secondary zones are related to the topography and to the water level which existed at the time they were formed. A porous leached outcrop stained with iron suggests the presence of secondary ones below. The vertical extent of a secondary sulphide zone shows a definite relation
to the permeability of the primary ores and to their mineral composition. Few sulphide minerals are exclusively primary or secondary, yet some are essentially one or the other, and may be indicative of the genesis of the deposit. The texture of an ore and its paragenesis is important and will frequently indicate its origin. A gradation of rich to lean ores as shown by assays together with a correlation to the topography or water level is conclusive evidence of supergene enrichment. By determination of the distribution of these factors, as far as is practicable, it is possible to distinguish supergene enrichment and to indicate ground favorable for enriched ore.
THE ANNA MINE

The Anna Mine comprises one claim, the Anna, in the Ardsley or southwest Butte district about three miles from the School of Mines. The claim is in the upper portion of a waterless gully which dissects the plateau-like foothills south of Silver Bow Creek.

Numerous small mines and many prospect pits are located in the vicinity. Some of these have produced very rich gold and silver ore from the near-surface workings, but none are now being worked except the Anna and the Butte Isle which was opened recently. The fact that most of the mines, several of which have much larger ore bodies than the Anna, are not operating with the present favorable metal prices, suggests that enrichment is the controlling factor in determining the life of a mine in this district.

Geology

The country rock of the region is quartz-monzonite which is cut by large and small dikes, and irregular masses of aplite. The best vein structures are in granite. The brittle character of the aplite seems to have caused the vein to split into numerous stringers which were less favorable for mineralization. The eastern half of the Anna claim is underlain by granite and the western half, by aplite. West of the claim the contrast in the character of the vein as it cuts through the two kinds of rock is well illustrated. In the
granite the vein is strong and well defined, being about ten
feet wide and four hundred feet long. Going eastward it passes
into a large body of aplite which extends into the Anna claim.
In this aplite the vein is broken up and dissipated in small
stringers. This situation is strikingly brought out by the
distribution of the prospecting pits along the outcrops. (Plate 1)

Two veins which are somewhat cut up by faulting are ex-
posed on the 150 foot level, and are uncovered at the surface by
trenches. The veins are very small, commonly 2 inches and
occasionally 14 inches in width, the average being about 5 inches.
Although small in width, the veins are rather persistent, the
No. 3 vein being followed for nearly 300 feet without showing a
tendency to die out. The strikes of the veins are northwest,
southeast and east-west, probably corresponding to the east-west
Anaconda set at Butte. The dip is invariably to the south from
40° to 80°, but is generally at about 70°.

Several small ore shoots were developed by a widening of
the vein to 3-14 inches. Increase in the richness of the ore
accompanies widening, although the bulk of the vein filling
becomes quartz. Close examination of the ore shoots reveals a
suggestion of widening due to irregularities or curvatures in
the vein fissure. Steep places are wider than flat places.
Bends to the right cause a widening, to the left, a pinching.
These facts define the relative movement of the walls of the
vein fissure when the fracture was formed. The hanging wall
moved down and westward, relative to the footwall.

The tenor of the ore varies remarkably from almost nothing
ANNA MINE
SURFACE MAP
Mapped by P.A. Schafer
ANNA MINE
SURFACE MAP

Drawn by P.A. Schafer
to several hundred dollars per ton. The ore is of the siliceous type consisting chiefly of quartz, considerable pyrite, small amounts of galena and sphalerite, and supergene argentite, native silver, and native gold. A mineral of the appearance of pyrargyrite was observed in small amounts by use of the microscope.

Mining has exposed numerous small faults and several larger ones. There is one which appears to have produced considerable offset. The position of this fault is such that the Anna vein, as exposed on the surface, is not cut by any of the mine workings. (Plate 2) A crosscut driven south from No. 2 drift came upon a fault about normal to it, and failed to pick up the supposed Anna vein. Beyond this fault is another which is about in line with the cross cut. This fault should cut the No. 3 vein just beyond the present face. A fault, probably a split from the larger one, cuts the vein 35 feet back from the face. The ore is slightly fractured and contains slickensides, both of which are indicative of post-mineral movement along the vein.

The Anna Mine is developed at a depth of 150 feet, with most of the ore proving to be primary. The ground water level stands at about 80 feet below the surface as was indicated by the depth to water in the shaft. Stoping above the level has not, as yet, reached the water table. Assay returns show the 150 foot level to be practically the bottom of the enrichment zone. Returns from the east stope above the level increased
with height, while those from the winze level, which is 50 feet lower, decreased three fold. In the last 100 feet of the No. 3 vein considerable enrichment has penetrated to the level and extends to an undetermined depth below. This zone, though very slightly oxidized, is clearly defined by iron oxide stains on the rock. The deep enrichment is undoubtedly due to the increased circulation caused by the cross cutting faults. It is interesting to note that in the fall of 1935, sixteen miners were discharged because of their apprehension over the large flow of water in this zone. (Plate 3)

Mineral Relationships and Paragenesis

A study of the paragenesis of the ores from the Anna Mine was made with a metallographic microscope upon a suite of 23 polished sections. The purpose was to establish the hypogene or supergene nature of the silver minerals and to get an estimate of the relative amounts of the source mineral of silver in the primary ore.

The ores show a distinct succession of the primary minerals, all deposited, however, during a single general sequence. The succession began with the deposition of quartz which continued until almost the end. Pyrite in considerable amounts was the first sulphide deposited. In some places the quartz and pyrite was slightly fractured before the later sulphides were introduced, but along most parts of the fissures the sulphides were deposited without much interruption around and with the later quartz. Next came minor amounts of galena
Long section showing relation of secondary sulphide zone to faults.
and, contemporaneously, sphalerite and small amounts of associated chalcopyrite. Minute amounts of silver minerals appear as a replacement of the galena. Supergene enrichment followed later with the deposition of argentite, native silver, and native gold in the cracks and openings in the fractured ore. (Plate 4)

Quartz—The age relationship of quartz is well established in the Anna ores. In narrow parts of the vein, that is 2 inches wide, quartz crystals line the walls, showing it to be the first mineral to have been deposited. In the wider parts of the veins quartz with small amounts of sulphides completely fills the fissures. In places, quartz and sulphides show mutual boundary structures, while commonly the sulphides are cut by veinlets and hexagonal crystals of quartz.

Pyrite—The deposition of pyrite began after that of the initial quartz and appears to have continued throughout the sequence. In the narrow parts of the veins the pyrite fills the fissures between the lining of quartz crystals. These crystals are somewhat corroded by the pyrite, but still retain their comb-like appearance. In the wider portions of the veins, the pyrite is disseminated in relatively small amounts along with sphalerite and galena. In almost every specimen that showed galena, pyrite would be found replacing it, a small amount of which would remain as a core completely surrounded by pyrite. The larger masses of pyrite and quartz
are fractured, veined, and cemented by later sulphides. Although no gold was observed in the microscopic examination of the finely fractured pyrite, it is believed that this pyrite is, at least in part, the host for the gold. This opinion is substantiated by the high gold content, as determined by assays, of a shoot of massive pyrite in the No. 2 vein near the cross-cut.

Galena—Galena is always associated with sphalerite which predominates. The universal association of galena and sphalerite would suggest that the two minerals are of contemporaneous deposition, but detailed investigation reveals that galena is usually earlier than sphalerite as evidenced by embayments in sphalerite bounded galena. Its most common occurrence is as a filling in the fractured pyrite and quartz, and as small sparsely disseminated masses within the quartz. Etch tests failed to show the presence of inclusions of silver minerals in the galena, and it was too disseminated to isolate for a silver assay.

Sphalerite—Sphalerite is more abundant than the galena. It appears to have started deposition just after that of galena and to have been then deposited contemporaneously. The sphalerite usually replaces pyrite or galena, but it does not cement the fractured pyrite and quartz as does galena. Deep in the oxidized zone it is stained by pyrite and tends to crumpled into individual crystals.

Chalcopyrite—Chalcopyrite is characteristically present in the sphalerite as tiny blebs and rows of minute specks, commonly believed to be the result of the process of
exsolution. It is occasionally found surrounding galena in a field of sphalerite, apparently being attracted to or induced to be deposited as a replacement of the galena rather than by being dropped by exsolution.

Pyrargyrite—This mineral occurs very sparingly as a replacement along the borders of galena and was the only silver mineral found in the primary ore. It was identified by etch tests but could not be positively determined by microchemical tests because of its minuteness.

Argentite—Distinctly supergene argentite occurs in the ores of the aforementioned enriched zone. The secondary nature is apparent from its deposition as thin megascopic plates along the fractures in quartz. (Plate 5) Numerous specimens were found and in each the argentite was associated with quartz only.

Native silver—This one of the most important minerals in the deposit. It occurs in the enriched zone as masses of nodular grains hung together in a dendritic-like pattern, as leaf-like forms, as small rosettes, as thin plates, and as wires and hooks. (a, b, c, d-Plate 5). Most of the masses had a diameter of about one-eighth inch, except where plated, these being as much as an inch in length. In nearly every specimen the silver was associated with or deposited around a grain of sphalerite.

Native gold—Delicate masses of wire gold and individual hooks were commonly found associated with the native silver. (e, Plate 5) The gold appears to be replacing the
Plate 5

a. Hook of native silver on edge of sphalerite. X 16.

b. Native silver deposited on edge of sphalerite. X 16.

d. Plate of silver on quartz—showing porosity of secondary ore. X4.

e. Hooks of native gold replacing silver. X 16.

f. Secondary argentite deposited along fissure in quartz. X 4.
silver as the hooks grow out around the edges of the silver with finer ones on the surface.

CONCLUSIONS

Field and laboratory study has shown that supergene enrichment is mainly responsible for the workability of the rich silver shoots at the Anna Mine. The application of the field criteria of supergene enrichment gave conclusive evidence of enrichment, and showed the control of faulting on the depth to which enrichment extended. The laboratory study showed the rich ores to be due principally to their content of supergene silver minerals, while the primary ore contained only minute amounts of hypogene pyrargyrite. It was recognized that enrichment was confined to ground in which all of the following controlling conditions were combined: depth within a few hundred feet of the surface, enough primary silver mineral to supply silver-bearing supergene solutions, certain zones of fractures by which downward movement of solutions is facilitated, resulting in concentration, and presence of minerals such as galena, sphalerite, and pyrite, which induce precipitation.
REFERENCES


