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Supergene Enrichment of Silver Ores with Special Reference to those from Neihart, Montana.

Thomas Walker Page

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SUPERGENE ENRICHMENT OF SILVER ORES
WITH
SPECIAL REFERENCE TO THOSE FROM NEIHART, MONTANA

by
Thomas W. Page

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

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
June, 1934

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INTRODUCTION

General Statement

This paper will set forth the results of a study undertaken as a Baccalaureate thesis problem in Geological Engineering at Montana School of Mines. The problem is divisible into two parts: the development of a technique in the microscopic investigation of ore minerals, and the application of this technique to the study of ores from Neihart.

In the development of a technique it was necessary to learn the fundamentals of ore microscopy as applied to the various minerals of silver, which included the use of reflected polarized light, etch reactions, microchemical analysis, and sight recognition of minerals (1). In addition it was necessary to become familiar with the accepted criteria of sequence, replacement, and other textural phenomena (2, 3, 4).

It was found that the silver minerals are a particularly complex subject since they closely resemble one another and frequently occur as earthy aggregates or as small grains. Specimens of rich silver ores and pure minerals were secured from the museum and stock room and attempts were made to develop new criteria for their recognition. Certain sources of difficulty were found, among which was the fact that few of the minerals corresponded to the descriptions on the card. One specimen in particular, described as proustite, was found to be geocronite. Microchemical methods

were, in general, unsuccessful because of the insolubility of silver compounds. Use of chromic acid solution which was developed by the Department of Ore Dressing gave inconsistent results, although it is believed that the use of such etching solutions holds much promise.

Neihart

Neihart, in the Little Belt Mountains, is credited with a production, in gold, silver, lead, and copper, of over \$2,000,000 during the period 1881-1893. The lodes are fissure fillings and replacements along sheeted zones in pre-Cambrian gneiss. They are related to intrusions of diorite, syenite (?), and granite porphyry which are probably of post-Cretaceous age.

In common with many other camps in western United States, Neihart has become a shadow of its former self because of the exhaustion of the shallow, rich ores. Whether these rich ores should be attributed to downward enrichment or to hypogene deposition is an open question, but a solution of this question should be of some moment. In the first case, it would not be unreasonable to expect a considerable quantity of low-grade, primary ore at greater depths; in the second case, complete exhaustion, from a mining standpoint, would be a reasonable postulate. This study of Neihart ores was undertaken to try to determine the extent of silver enrichment in the ores which are now found in the lower workings of the mines.

Results

The results of this study are of benefit chiefly as experience in geological investigations. Very little new material has been added to the existing knowledge of silver minerals and new phenomena of ore deposition were not discovered.

REVIEW OF SUPERGENE ENRICHMENT

Definition

Supergene enrichment is that process by which vein material, unstable under surface conditions, is leached from the upper portions of a deposit by atmospheric agencies and redeposited in an environment generally at lower depths in which it is stable. It frequently results in the formation of ore deposits which are commercially profitable from lean or worthless hypogene ores. The importance of such enrichment can hardly be overrated.

Some Effects of the Process

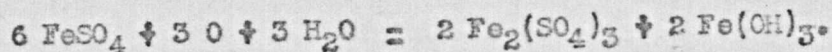
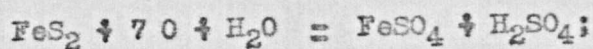
Many of the mining camps which take a fundamental and colorful part in the history of western America owe their importance to the phenomenon of supergene enrichment. The shallow, high-grade ores of Butte, the mighty "Porphyry Copper" ventures, other localities, as well as many a camp which failed to live up to expectations, attest the part played by this agency. But as the old camps become exhausted of their high-grade ores a new aspect of the process confronts the investigator.

Supergene enrichment is obviously a process of concentration. It postulates the existence at depth of large masses of hypogene material, or "protore", from which the concentrated, rich, supergene ores have been derived. Advances in the technique of ore dressing have now made possible the profitable exploitation of many low-grade ores, and it is hoped that application of new processes will result in the revival of many idle mining districts. However, evidence is being accumulated, some of which will be presented hereafter, which indicates that supergene enrichment has played no part in the formation of many bonanzas, that they were rich primary shoots within veins, and that beneath these high-grade deposits no large bodies of low-grade ores may be expected within the limits of

reasonable prospecting. This points to a need for new methods in the search for ore deposits, and application of such methods in areas which lack the obvious signs of mineralization on which depends the popular reputation of the "practical prospector."

Chemistry of Supergene Enrichment (5, 6)

As soon as a sulphide deposit is exposed at the surface it is immediately attacked by atmospheric agencies. Combination with oxygen produces sulphates and sulphuric acid, which, as they are formed, assist in the process of oxidation and solution. Solutions thus formed percolate downward until they reach the permanent ground-water level where, due to changed conditions, the metals so borne are reprecipitated as secondary sulphides. The most important reagents in the process of leaching and transportation are, with water, sulphuric acid and ferric sulphate. Both of these compounds can be formed by the oxidation of pyrite according to the type reactions:



Metallic sulphides, with few exceptions, are soluble to some extent in sulphuric acid, but the dissolving power of the acid is remarkably increased when some oxidizing agent is present. Ferric sulphate is such an agent, making the acid liberated by the oxidation of pyrite much more effective than it would be if the sulphate were absent. Other materials have similar effect, manganese being noteworthy in this connection.

Precipitation of metallic sulphides from supergene solutions may be effected in several ways. The absence of free oxygen below the water level causes precipitation, as does a reduction in the amount of ferric sulphate present. Sulphuric acid liberates hydrogen sulphide when it reacts with certain metallic sulphides, and this, in turn, precipitates many metals from solutions of their salts.

A most important action in precipitation is that of certain metallic sulphides on solutions of the salts of other metals. When salt solutions are in contact with sulphides an exchange reaction occurs wherein the metal in solution replaces the metal of the sulphide. This reaction depends on the relative solubilities of the sulphides of the metals involved. Schurmann's series, so called, shows the effect of several metals on each other; Hg, Ag, Cu, Bi, Cd, Pb, Zn, Ni, Co, Fe, Mn. Any metal in solution will replace any metal lower in the series, the farther apart the two metals in the series the more nearly complete the reaction.

The above outlines the fundamentals of the chemistry of supergene enrichment, but it should be remembered that the process is made highly complicated by the vast variety and variability of natural conditions. Experiments are frequently at variance with facts as seen in the field, natural environments are difficult to reproduce, and only generalizations of the broadest sort can be deduced from the sharply limited work possible in a laboratory.

"Zoning" Due to Oxidation and Enrichment

A deposit which has been subjected to oxidation and enrichment differs vertically in its content and texture so that it may be divided into definite zones. The topmost zone, that of oxidation, is essentially one of solution. It exhibits a loose, cellular texture and leached material which may bear no resemblance to the texture of the original ore. Its mineral content is largely hydrated oxides of iron, oxy-salts of other metals, and insoluble materials such as gangue minerals, kaolin, or, possibly, silver chloride or metallic gold. Enrichment, especially of gold, may occur by the removal of unwanted constituents, leaving the less soluble metal.

The zone of oxidation gives place gradually to the next lower zone, that of the secondary sulphides. This is essentially a zone of deposition. Its texture may be loose and finely granular, as in the "sooty" chalcocite of Butte and the United Verde Extension, or as compact as that of the original ore. Replacement of the primary sulphides by the supergene minerals is a prominent feature, the replacement giving rise to a reticulated, veined, irregular texture wherein the outline of original crystals may be completely destroyed. The upper boundary of the zone of supergene enrichment, since it is determined by penetration of ground-water, has a tendency to correspond roughly with the topography of the surface. With gain in depth the zone of secondary enrichment gives way to that of the hypogene ore.

CHEMISTRY OF SILVER ENRICHMENT

Silver Minerals

Silver occurs in a rather large number of minerals most of which are rare. Emmons (6) gives the following abridged list, and a more extensive catalogue may be found in Clarke's Data of Geochemistry (7).

Native silver		(Common)
Cerargyrite	AgCl	(Common)
Bromyrite	AgBr	(Rare)
Embolite	Ag(Cl,Br)	(Rare)
Iodyrite	AgI	(Rare)
Argentite	Ag ₂ S	(Common)
Pyrargyrite	3Ag ₂ S:Sb ₂ S ₃	(Common)
Proustite	3Ag ₂ S:As ₂ S ₃	(Rare)
Stephenite	5Ag ₂ S:Sb ₂ S ₃	(Common)
Polybasite	9Ag ₂ S:Sb ₂ S ₃	(Common)

Pearcite	$9Ag_2S:As_2S_3$	(Rare)
Tetrahedrite	$4 Cu_2S:Sb_2S_3$	Silver bearing (Common)
Tennantite	$4Cu_2S:As_2S_3$	Silver bearing (Rare)
Tellurides		

The silver-rich variety of tetrahedrite is known as freibergite.

Native silver, in most of its occurrences, is a secondary mineral, but it is not uncommon in ores which are definitely hypogene. A notable locality for hypogene, possibly high-temperature native silver is at Cobalt, Ontario in conjunction with cobalt-nickel ores (9).

The silver halides are undoubtedly supergene in all their occurrences. They are most typically developed in the oxidized zones of deposits in arid regions.

The sulpho-salt minerals of silver, in which the metal is combined with arsenic or antimony and sulphur, are both hypogene and supergene. They appear most often as late minerals deposited on the earlier sulphides either in well-formed crystals or as "sooty" masses or streaks. Microscopic criteria for their origin are not definite because of the marked resemblance between late hypogene and supergene replacements. They are most abundant near the bottom of the enriched zone and they are sufficiently soluble in sulphuric acid, so they occupy, as it were, a critical position in silver mineral paragenesis. Another interesting and little understood fact is the rarity of the silver-arsenic compounds compared with the silver-antimony compounds.

Argentite, or silver sulphide, is the source of most of the silver in ores. It, also, may be hypogene or supergene; Bastin (10), in a study of ores from the Comstock Lode, and Emons (11), in a description of the same ores, found argentite both at shallow depths and as much as 3,000 feet deep.

The silver contained in freibergite seems to be definitely hypogene. In this mineral it may be held in solid solution, because the highest possible magnifications show homogeneity of polished surfaces of the mineral. The silver which occurs in silver-rich galena is also hypogene. Unlike tetrahedrite galena can hold in solid solution only a small amount of silver, so in all specimens which are rich in silver the metal occurs in minute spots of its compounds in the galena.

F. N. Guild (12) presents a sequence of hypogene and supergene minerals commonly associated in silver ores. It is as follows:

<u>Hypogene</u>	<u>Supergene</u>
Arsenopyrite	Chalcopyrite
Pyrite	Bornite
Sphalerite	Chalcocite, with stromeyerite
Chalcopyrite	Argentite and sulpho-salt minerals
Tetrahedrite	of silver
Chalcopyrite	Covellite
Bornite-chalcocite intergrowths	Native silver
Galena (sometimes with argentite spots)	Oxidized ore minerals, malachite, azurite, cerussite, anglesite,
Sulpho-salt minerals of silver	cerargyrite
Native silver, formed on the early sulphides	

He states that the most useful method of studying the silver minerals is by working out the relationships of the more abundant copper and lead minerals with which they are associated. This, however, may not always be possible. Any of the later minerals may apparently replace any of the earlier minerals. Also, certain members of the series, notably

chalcopyrite, appear in several places in the sequence, and the distinction between the early and later generation of these minerals may be exceedingly difficult to make. Furthermore, additional confusion arises from the marked similarity between the last of the hypogene sequence and the supergene sequence and the generally imperfect suite offered by any particular locality.

Solution of Silver (13)

Hypogene silver minerals are decomposed by sulphuric acid, the decomposition product being silver sulphate. The solubility of silver sulphate is 5.5 grams per liter of water. The decomposition is remarkably hastened by the addition of a trace of ferric sulphate, which serves a double purpose in that it removes hydrogen sulphide and assists in the oxidation of silver compounds.

Both sulphuric acid and ferric sulphate are derived from pyrite, so enrichment would not be expected in deposits in which pyrite is absent. Such deposits, however, are extremely rare.

Silver may also be dissolved and transported as the carbonate, but little data is available on its behavior as such in dilute solutions. The solubility of silver carbonate is of the order of 0.032 grams per liter of water. It is known, however, that silver is transported far in deposits which contain much carbonate.

Precipitation of Silver

Silver compounds may be precipitated from dilute silver sulphate solutions in several ways. Native silver is precipitated from solution when the amount of free sulphuric acid present is reduced by reaction with sulphides. It is also deposited when the ferric sulphate present is reduced to ferrous sulphate. According to Cooke (14) metallic silver thus formed is relatively stable in the presence of ground-waters; ferric

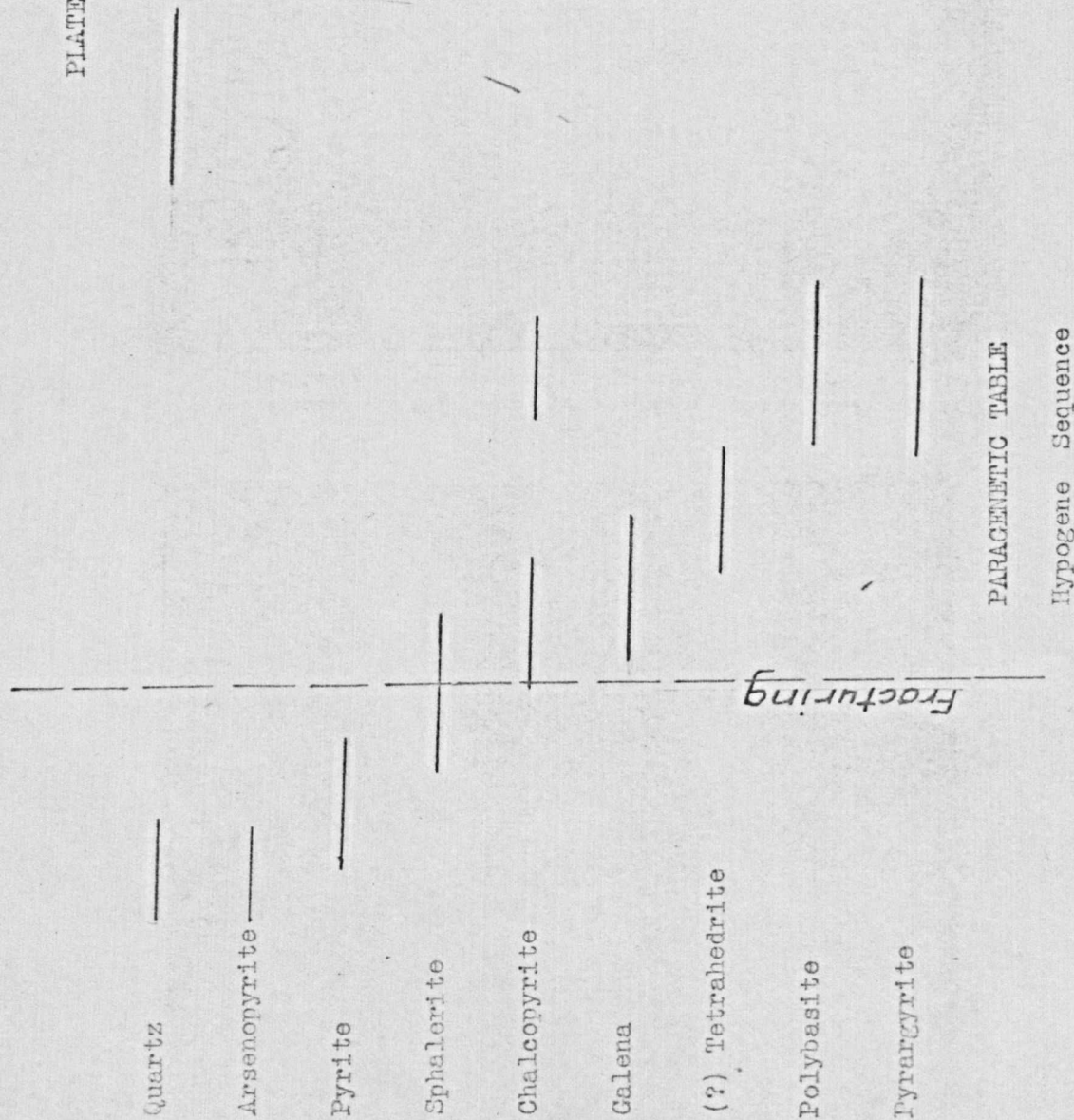
sulphate in the solutions to which it is exposed cannot attack it so long as there is sufficient silver sulphate in the solutions to maintain equilibrium. The native silver thus formed, in common with secondary sulphides, is, however, a transitional product. Changes in the elevation of the ground-water level, due to erosion or other causes, change the environment of the precipitated minerals; and they may be continually redissolved and reprecipitated. This accentuates the necessity for field evidence in problems connected with supergene enrichment.

Despite the ease of reduction of metallic silver from solutions of silver sulphate, it is a rare mineral in most camps. As depth is gained by the transporting solutions the conditions for its fixation become more favorable from a chemical point, but it is, nevertheless, found most abundantly in the zone of oxidation.

Argentite, silver sulphide, is the most common silver mineral. It is produced from silver sulphate solutions by several different reactions. Hydrogen sulphide and alkaline sulphides precipitate it directly. Sulphur and native silver produced by the reduction of ferric sulphate can react to produce argentite. Because of its low solubility it is found most abundantly just below the zone of oxidation.

The silver sulpho-salts are formed in and below the argentite zone under conditions that are not clear. Cooke (14) found that stibnite, realgar, and orpiment abstract silver from solutions of its salts, Grout (15) and Ravicz (16) obtained amorphous silver-arsenic compounds and silver-antimony compounds by reactions between dilute acid solutions of silver sulphate and alkaline solutions of antimony and arsenic sulphides. The exact compositions of these compounds were indefinite, although they seemed to be in accord with the natural minerals. An important point is that the compositions of the products seemed to be markedly changed by

PLATE 1.



PARAGENETIC TABLE

Hypogene Sequence

slight changes in the acidity or alkalinity or concentrations of the reacting solutions.

An interesting and unexplained point in connection with the sulpho-salt minerals is the abundance of silver-antimony compounds compared with the rarity of silver-arsenic compounds. With the exception of enargite, $3\text{Cu}_2\text{S}:\text{As}_2\text{S}_3$, which is itself an uncommon mineral, and its homologue, famatinite, $3\text{Cu}_2\text{S}:\text{Sb}_2\text{S}_3$, which is decidedly uncommon in its occurrence, the same statement is applicable to the sulpho-salts of copper and lead. Most, if not all, of these compounds are regarded as hypogene, but an analogy between silver and copper and lead may not be permissible. It is possible that hypogene arsenic is simply not available, although Emons states that it is as common an element as antimony. Arsenic compounds are more soluble in both acid and alkaline solutions than antimony, so they would tend to be transported farther in both hypogene and supergene solutions. But in supergene zones of deposition they would have to be found somewhere, which they are not, and in hypogene deposits they might not be deposited except sparingly as rare compounds, which seems to be the case. Ravicz found that hot, dilute, alkaline sulphide solutions readily leach antimony sulphide from pyrargyrite to leave argentite, but that tetrahedrite and arsenopyrite are not so affected. This led him to believe that silver sulpho-salts are secondary in deep deposits, primary in shallow. In the opinion of the writer the relative abundance of silver-antimony compounds is evidence of the general hypogene character of the silver sulpho-salts, particularly since the corresponding minerals of copper and lead are regarded as hypogene.

A most important method of precipitation of metals from solution is by replacement of earlier sulphides, as referred to on page 6. The position of silver in Schurmann's series would indicate that this is one

of the chief methods by which it would be removed from supergene solutions. It is undoubtedly a weighty factor in the chemistry of silver enrichment, but it is of interest to note that Grout (15) found that galena and sphalerite, two of the most abundant minerals in silver deposits, have a very weak effect.

In several localities bonanza silver ores consisting of silver halides have been found. They occur as shallow deposits in arid regions, and their environment points to the conclusion that they are entirely secondary. The halogen salts of silver are very insoluble in acids, and silver as sulfate, reacting with a halogen, will be immediately precipitated. Some difficulty is found in explaining the origin of the chlorine, bromine, or iodine necessary for the formation of silver halides, but the general opinion seems to be that they are contained in surface waters, or blown from the sea. This is not altogether satisfactory, but accurate data is not available. Minerals containing these elements are very insoluble under atmospheric conditions, and they occur always in the zone of oxidation. Hot springs sometimes contain halogens. The deposits of silver halides are always epithermal, or shallow, and little is known about the behavior of otherwise well-known compounds under the complex conditions prevailing in hydrothermal solutions. It seems, therefore, that the wholly supergene nature of these minerals is not entirely substantiated.

Summary of Supergene Enrichment of Silver

Silver in the oxidized zones of sulphide deposits is dissolved by sulphuric acid and ferric sulphate generated by the oxidation of pyrite. As a dilute sulphate solution in ground-waters it is transported downward in the vein in which it occurs, and, as depth is gained, it is

redeposited as the native metal, as a sulphide, as a replacement of earlier sulphides, and, possibly, as a sulpho-salt. The actual extent or magnitude of this enrichment is not yet determined. Certainly it does not occur on any such scale as that proven for copper. In many mines rich silver ores have been mined down to moderate depths (1,000 feet more or less), only to suddenly play out along fairly concordant lines. Emmons (17) quite justly points out that although many large bonanzas of silver, such as the Comstock and Tonopah, are recognized as of hypogene origin, the relationship of rich ore to the present surface, as at Philipsburg, Montana; Creede, Bonanza, and Red Mountain, Colorado; is too definite and general to be ignored. In one respect, however, the last word, if true, is had by McLaughlin and Sales (18). They state that supergene enrichment of silver has not been responsible for the formation of additional rich ore on hypogene ore which was not originally rich enough in silver to be mined.

ORES OF THE NEIHART DISTRICT

Previous Work

Weed, in his description of the geology of the Little Belt Mountains (19), devotes a short section to the Neihart district. Bastin (20) used and described one of Weed's specimens in a study of enrichment of ores. Hurst (21) also made a limited study of Neihart ores.

Mineralogy

The Neihart ores contain a rather wide variety of minerals. The list includes, in the order of their abundance, pyrite, sphalerite, galena, chalcopyrite, and varying amounts of arsenopyrite, tetrahedrite, silver minerals, and gold. Gangue minerals are quartz, barite, and carbonates.

Relationships and Paragenesis

A feature of the minerals in the Neihart ores is their close correspondence to the sequence quoted above from Guild (p. 8). No definite variations were noted. In the opinion of the writer the best method of attacking a description of the various minerals encountered is to take them up individually in the belief that such a division of the subject will lead to a unified whole from which certain broad conclusions can be justly drawn.

Quartz.--Quartz occurs in at least two generations; the first as a replacement of wall rocks and as vein filling, the second as a comb-like lining of vugs deposited on the earlier sulphides. The first generation is of the milky variety. It shows, in general, more or less fracturing and brecciation, the fractures being filled and the quartz being to some extent replaced by the sulphides deposited later. The second generation occurs as clear, well-formed crystals varying in size from fine, needle-like forms to individuals one-half centimeter long.

The clear crystalline nature of this later quartz, which seems to be the last mineral deposited, indicates a hypogene origin for the mineral. It would be expected that supergene quartz would be of the chalcedonic variety, certainly not the glassy, individual crystals lining vugs and druses which are found. It seems reasonable, therefore, to conclude that minerals deposited earlier than this quartz are hypogene. One other possibility, under this assumption, presents itself. There could have been a renewal of hypogene activity after a period of supergene deposition. No evidence for this was found.

Arsenopyrite.--Arsenopyrite occurs sparingly as small, rhombic crystals which are apparently contemporaneous with the early quartz in which they always occur.

Pyrite.--Pyrite occurs as a filling of interstices in the earlier quartz, in which case it is sometimes molded around quartz grains, and it occurs as well-formed crystals which replace the quartz in which they occur. The pyrite, like the quartz, shows more or less fracturing. Later sulphides have been deposited as filling in the fractures and have, to varying degrees, replaced the pyrite.

This fracturing of the pyrite seems to have been a factor in the deposition of the later, valuable sulphides. On the basis of the above, no valuable mineralization would be expected in a segment of a quartz-pyrite vein which failed to show such structure.

Sphalerite.--The period of deposition of this mineral appears in some cases to have begun before the pyrite period ended. In other specimens it is decidedly later than the pyrite, the latter being its most common occurrence. It fills fractures and replaces the pyrite in most cases, in others it is molded around sharp pyrite boundaries without affecting them. The sphalerite in these ores varies from a clear, resinous variety with good, reddish internal reflection to the dark, iron-rich variety known as marmatite. There seems to be no difference in the paragenesis of the two, and both may be seen in the same specimen.

Chalcopyrite.--This, the most prominent copper mineral observed, with the exception of a little azurite in some of the highly oxidized specimens, occurs as small inclusions in sphalerite. It may also be seen as small masses and lenticular bodies in galena and pyrargyrite and tetrahedrite, but whether these occurrences are replacement remnants, replacements of the enclosing mineral, or the result of exsolution, was not definitely determined. Two generations, however, are recognized. That in sphalerite probably represents exsolution, and it is essentially contemporaneous with that mineral. The other may be a second hypogene

generation. Although the chalcopyrite inclusions in sphalerite are occasionally untouched by metasomatism which removes the sphalerite, they are generally replaced along with their matrix. The blebs of the second generation are generally larger than the spots which appear in sphalerite.

Tetrahedrite.--This mineral is not common, and where seen it occurred as small bodies the identification of which was uncertain. In one of the specimens a mineral thought to be tetrahedrite was later than galena, which is at variance with its ordinary position, as given by Guild, and earlier than pyrargyrite, but this mineral may have been argentite. Ores rich in silver contain no more tetrahedrite than those which are lean, so the possibility of freibergite as a hypogene source of silver may be discounted.

Galena.--Galena was deposited during the last of the period of sphalerite deposition and later. Its most common occurrence is as a replacement of sphalerite. Pyrite in contact with galena sometimes shows "bitten into" boundaries, but whether this represents replacement of pyrite by galena or replacement of sphalerite which had replaced the pyrite is not clear. There seemed to be a tendency for galena to replace sphalerite which was in contact with pyrite more readily than it replaced independent sphalerite masses. Thin veinlets of galena in pyrite were often observed which, under high magnification, showed very small remnants of sphalerite or chalcopyrite.

It was expected that the galena of some of the rich silver specimens would show small inclusions of silver minerals when etched, but this phenomenon was not noted. In most of the rich silver ores the silver minerals could be seen as definite masses of varying size.

Argentite.--Where seen, this mineral occurred as small bodies of uncertain relationships. It appears to be later than galena, but a definite position in the sequence could not be assigned to it. The bulk of the silver in these ores is not in argentite.

Polybasite.--This mineral occurs as crystalline coatings on all minerals with the exception of the latest quartz. It is seen largely as well-developed crystals of tabular habit on the walls of vugs and druses. This mode of occurrence may indicate a hypogene origin for the mineral, a conclusion also reached by both Weed and Hurst. Hurst also regards polybasite as the source of all the other silver minerals in these ores. Weed describes a specimen from Neihart, his description being quoted by Hurst, consisting of a spongy mass of polybasite from the oxidized zone left behind as the galena on which it was deposited was removed by pyrite oxidation products. But the reaction product of galena and sulphuric acid is the very insoluble lead sulphate, anglesite, and it seems unlikely that so strong an attack on galena would leave polybasite unscathed. So the derivation of all other silver minerals from polybasite does not seem reasonable, particularly since the evidence cited is directly opposed to the dissolving and transportation of polybasite at all.

Pyrargyrite.--Pyrargyrite, like polybasite, was deposited during the last phases of mineralization. It also, occurs as crystals on the walls of vugs and druses, but it is also to be seen replacing galena. The later quartz is sometimes seen as crystalline coatings of pyrargyrite. These features indicate a hypogene origin for this silver mineral also, since, if it were supergene, it would be expected to coat the later quartz.

Bastin examined some of Weed's specimens from Neihart, and he describes pyrargyrite mixed with polybasite, into which it grades. He regards the pyrargyrite as undoubted alteration product of polybasite, and the polybasite as a replacement product of galena. The chemistry of the derivation of polybasite from galena is rather vague, but if the silver sulphide involved be derived from the galena, some source must be determined for the antimony, and a hypogene source seems most reasonable. In connection with the alteration of polybasite to pyrargyrite, however, the experiments of Ravicz (p. 11) do not indicate that such an alteration is hypogene, since leaching by hot, alkaline solutions would be expected to increase, rather than decrease, the silver content of the minerals involved. Bastin also describes in the same paper a specimen in which polybasite and pyrargyrite replace galena along very small cleavages and along the boundaries of crystals of galena and quartz. His argument is to the effect that galena has caused the precipitation of the silver minerals from supergene solutions. Opposed to this conclusion is the work of Grout (p. 12), who found that the precipitating powers of galena on dilute, cold solutions of silver sulphate are very low.

Native silver.--Metallic silver is sparingly found as small specks or wires in certain specimens of earthy, highly oxidized ores. It was not found in conjunction with any of the sulphide specimens.

CONCLUSIONS

The relationships of the silver minerals in these ores to their accompanying minerals, their mode of occurrence, and the predominance of sulpho-salt compounds lead to the conclusion that the bulk of the silver present is hypogene. Enrichment has occurred, as is indicated by the native silver in some ores from the zone of oxidation, but apparently it

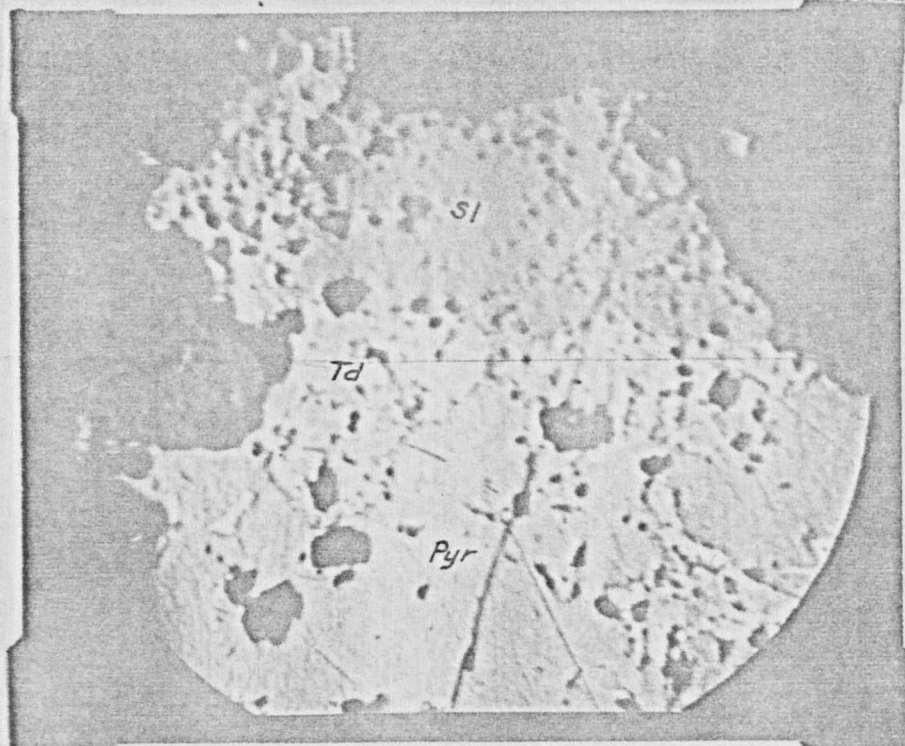
has not been an important factor in the production of the rich ores available for examination. Lacking field evidence, no more definite statement as to the extent of enrichment can be made. Microscopic evidence and examination of hand specimens certainly do not indicate that it has taken place to any great extent.

The silver minerals appear to have been deposited during the latest stages of hypogene mineralization under moderate conditions of temperature and pressure. Evidence for this conclusion rests on their paragenetic position and a lack of characteristics which would definitely prove that important enrichment has occurred.

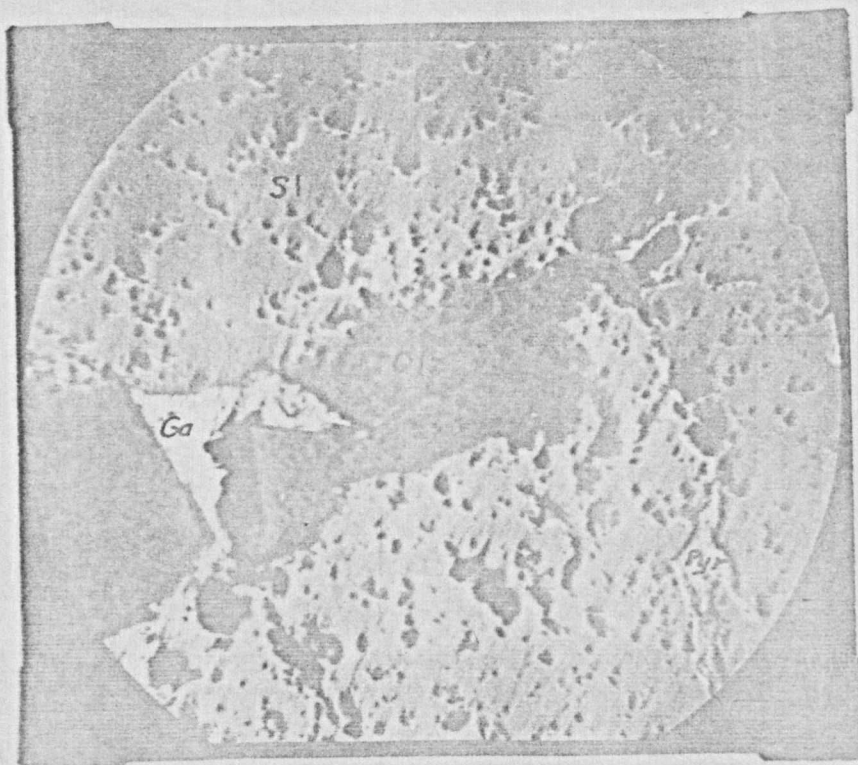
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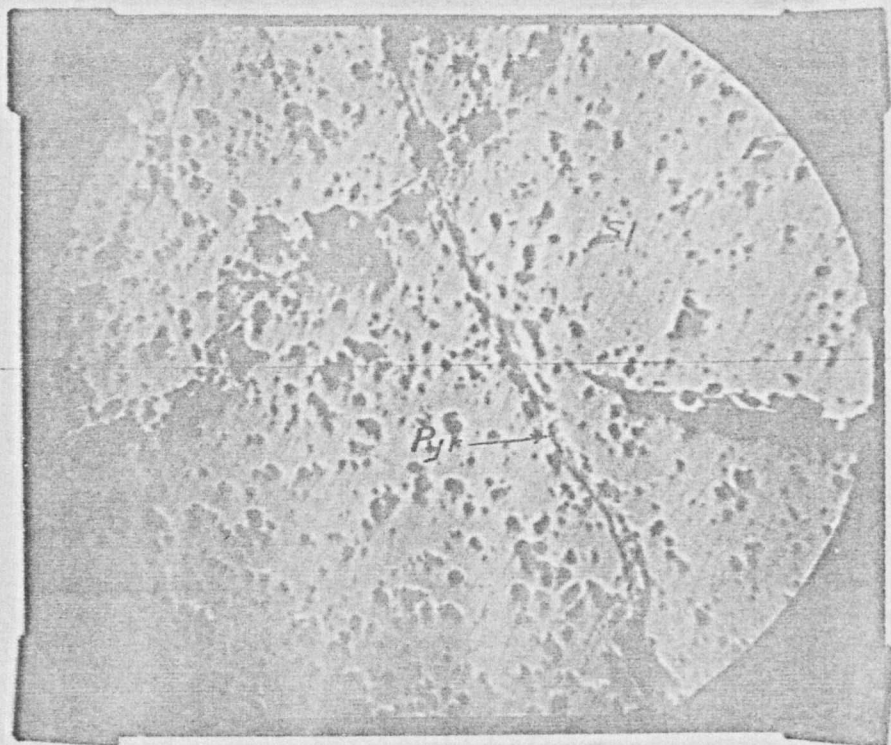
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A. Pyrargyrite replacing tetrahedrite which is replacing sphalerite.
(Qtz, quartz; Sl, sphalerite; Td, tetrahedrite; Pyr, pyrargyrite.)
x 420

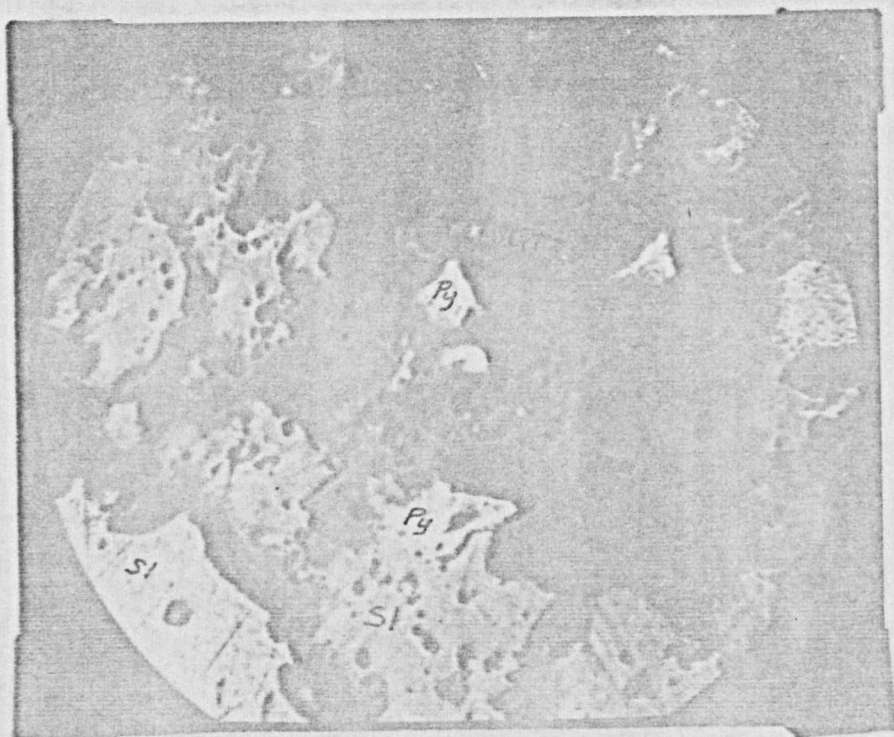


B. Later quartz replacing sphalerite and galena along a fissure previously filled with pyrargyrite. (Sl, sphalerite; Qtz, quartz; Ga, galena; Pyr, pyrargyrite.) x420.



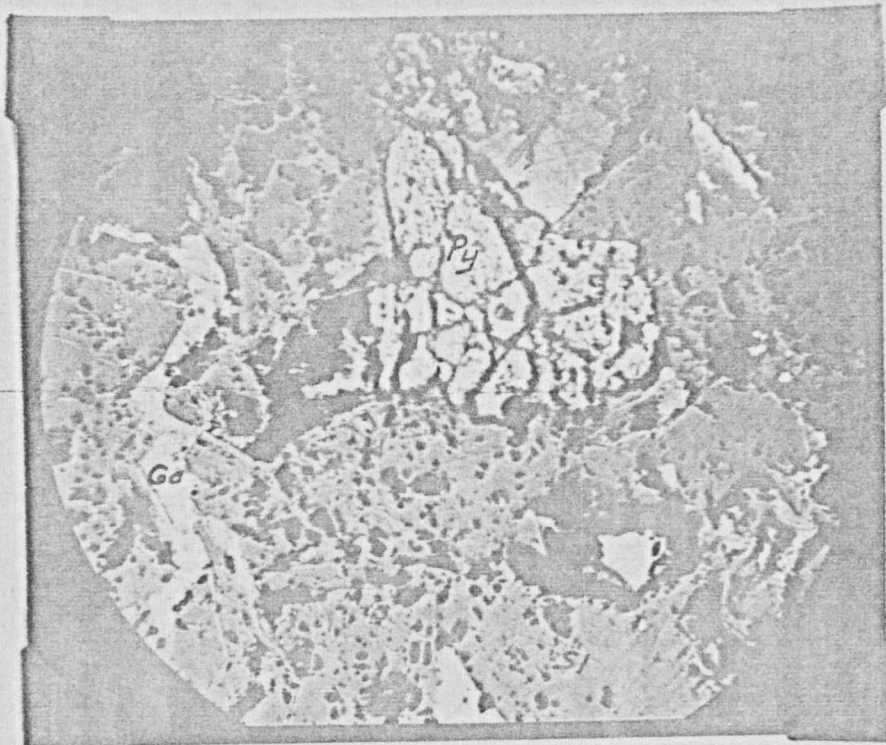
A. Veinlet of pyrrargyrite in sphalerite.
(Sl, sphalerite; Pyr, pyrrargyrite.)

x 420

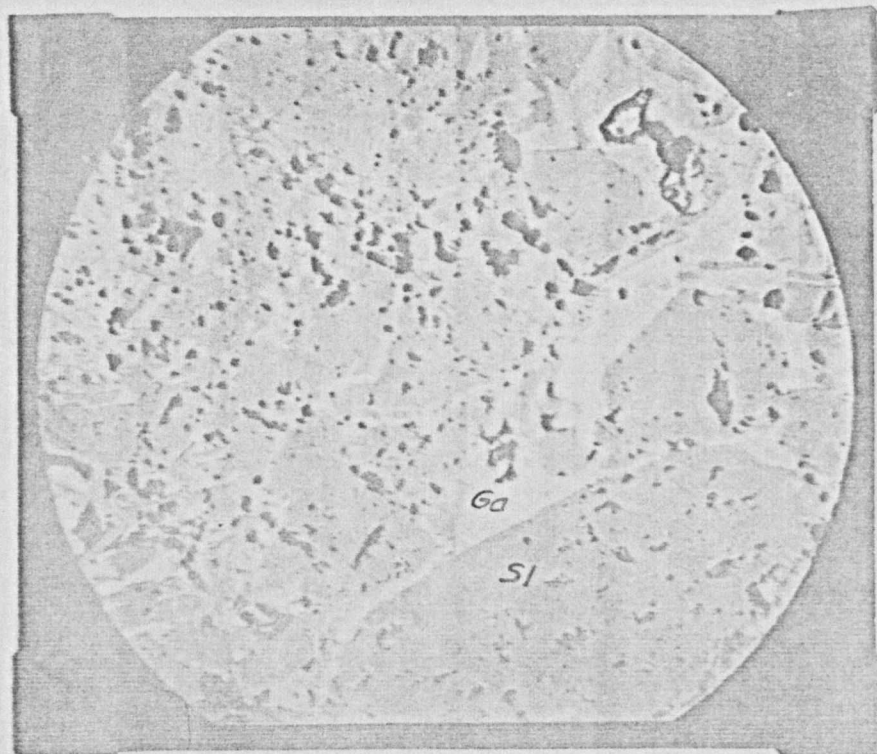


B. Fractures in early quartz filled by pyrite, sphalerite replacing both. (Qtz, quartz; Py, pyrite; Sl, sphalerite.)

x 420



A. Fractured pyrite filled and partially replaced by sphalerite which is veined and replaced by galena. (Py, pyrite; Ga, galena; Sl, sphalerite.) x 420



B. Sphalerite "breccia" cemented by galena. (Ga, galena; Sl, sphalerite.) x 420