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" ENRICHMENT OF SILVER ORES."

A Thesis Submitted to the Faculty of the Graduate School
of the
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by

LOUIS G. RAVICZ.

In partial fulfillment of the requirements for the degree
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ENRICHMENT OF SILVER ORES.¹

INTRODUCTION.

The theory of secondary enrichment was announced in 1900, in three notable papers, published almost contemporaneously by S.F. Emmons², W.H. Weed³ and C.R. Van Hise.⁴ A summary of the process of enrichment of copper deposits by J.F. Kemp⁵ appeared in 1906, and the criteria for the recognition of secondary sulphide enrichment were reviewed by H.L. Ransome⁶ in 1910. An excellent summary by C.F. Tolman⁷ and a comprehensive and detailed treatment of the subject, in which all of the previous work is reviewed and correlated, by W.H. Emmons⁸, were published in 1913. The theory as first proposed was based primarily on observation. In more

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recent years, however, much work toward the solution of the physical and chemical problems involved, has been done in the laboratory. As this paper deals exclusively with the secondary enrichment of silver, only those papers which deal with this subject, wholly or in part need be mentioned here. Among them are contributions by W.H.Weed³, H.C.Cooke⁹, H.N.Stokes,¹⁰ Palmer and Bastin,¹¹ and F.F.Grout.¹²

The factors controlling the solution, transportation and deposition of the metals, are of prime importance. Especially is this so in the case of silver as a small amount of secondary enrichment may make an otherwise valueless deposit, of commercial importance.

1 A thesis presented to the faculty of the University of Minnesota, as part requirement for the degree of Master of Science.

2 Emmons, S.F. "The Secondary Enrichment of Ore Deposits," Trans. Am.Inst.Min.Eng., Vol.30, 1901, pp. 177-217.

- 3 Weed, W.H., "The Enrichment of Gold and Silver Veins,"
Trans. Am.Inst.Min.Eng., Vol.30,1901,pp.424-448.
- 4 Van Hise, C.R., "Some Principles Controlling the De-
position of Ores," Trans. Am.Inst.Min.Eng.,
Vol.30, 1901, pp.27-177.
- 5 Kemp, J.F., "Secondary Enrichment in Ore Deposits of
Copper," Econ.Geol., Vol.1, 1906, pp,11-12.
- 6 Ransome, F.L., "Criteria of Downward Sulphide Enrich-
ment," Econ. Geol., Vol.5, 1910, p.205.
- 7 Tolman, C.F. "Secondary Sulphide Enrichment of Ores,"
Min.and Sci. Press,1913, p.38,141,178.
- 8 Emmons, W.H. "The Enrichment of Sulphide Ores,"
Bull. U.S. Geol. Survey, No.529,1913.
- 9 Cooke, H.C. "Secondary Enrichment of Silver Ores,"
Jour. Geology, Vol.21, 1913, p.1.
- 10 Stokes, H.N. "Experiments on Solution, Transpor-
tation and Deposition of Copper, Silver and
Gold." Econ.Geol., Vol.1, 1906,p.649.
- 11 Palmer, C., and Bastin, E.S. "Precipitants of Gold
and Silver," Econ. Geol.Vol.8,1913,p.140.
- 12 Grout, F.F. "Alkaline Extracts of Metallic Sul-
phides," Econ. Geol., Vol.8, 1913, p.417.

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MINE WATERS.

A study of the behavior of mine waters is essential, in an interpretation of these chemical processes. Mine waters of sulphide ore bodies generally show that the metals are in solution as the sulphates. In many of the waters of silver deposits, however, considerable amounts of carbon dioxide and carbonates are present, and the metals especially silver may also be in solution in this form. The waters of the upper zone are acid sulphate waters, but the acidity gradually decreases, as the waters descend, and they become neutral and even alkaline. In his examination of fifty mine waters, recalculated by the Chase Palmer method, Hodge¹ found that twenty-two were acid, fourteen were neutral and fourteen alkaline; also that salts of the heavy metals occur in relatively large amounts in acid waters, in smaller amounts in neutral, and are practically absent in alkaline waters. Traces of gold and silver are found in the Central Tunnel and C and C

waters of the Comstock lode. Both contain ferric iron. One of these waters is acid; the other is neutral. Ferric sulphate is abundant in the upper zones of ore deposits, where with dilute sulphuric acid, formed from the oxidation of pyrite, exerts a potent solvent effect on the sulphides present. At depth, ferric sulphate after continued contact with the sulphides, during its descent is reduced to ferrous sulphate. Two interesting series, showing the relative activity of minerals in decreasing acidity and in reducing iron in ferric sulphate solution have recently been determined by G. S. Nishihara²

1 Hodge E.T., "The Composition of Waters in Mines of Sulphide Ores." Econ.Geol., Vol.10, 1915.

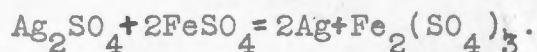
2 Nishihara, G.S., "Rate of Reduction of Acidity by Ore and Gangue Minerals." Econ.Geol., Vol.9, 1914, p.743.

PREVIOUS EXPERIMENTAL WORK.

A review of the work referred to above and

of the literature brings forth the fact, that silver minerals with the exception of the halides, cerargyrite, bromyrite, embolite and iodyrite, and possibly also native silver, may be either of primary or secondary origin. These minerals include, not only the sulphide, but many complex compounds of silver with arsenic and antimony. In the experiments cited, the precipitate was usually the free metal, although Cooke¹ obtained some silver sulphide by the interaction of metallic silver with freshly precipitated sulphur. Palmer and Bastin² by precipitation with metallic sulphides obtained some sulphide but much larger amounts of the free metal. Grout³ following up this line of work confirmed the tests of Palmer and Bastin and determined in addition, that when ferric sulphate is present in the solution, the free metal is not precipitated except by the more active sulphides, whereas the sulphide may be. Rickard⁴ obtained metallic silver by precipitation with carbonaceous matter. Weed⁵ states that native silver is formed in films and crystalline masses by reduct-

ion with ferrous sulphate according to the following reaction:



Native silver is abundant in the deposits at Cobalt, Ont., but is less prominent in the western districts. In the latter, the most important silver mineral is argentite; characteristic also is a long series of complex silver sulphantimonides and sulpharsenides; and it is often difficult to determine whether they are primary or secondary. Among them are proustite, pyrargyrite, miargyrite, stephanite, polybasite, and silver-bearing tetrahedrite (freibergite) and galena.

Silver is soluble in dilute sulphuric acid, but the sulphide is only sparingly attacked by the acid alone. In the presence of ferric sulphate, however, the solubility of the sulphide is greatly increased. Cooke⁶ has shown that a small amount of ferric sulphate is effective and believes the function of the ferric sulphate is to oxidize any hydrogen sulphide that may form and which would retard the further solution of silver sulphide. In ore deposits containing abundant

calcite in the gangue, the transportation of silver as the carbonate is not an impossibility. The normal carbonate is soluble to the extent of .031 gms. per liter⁷ Johnston⁸ states, moreover, that silver carbonate is soluble in water saturated with carbon dioxide at 15 degrees C., to the extent of .846 gms. per liter, or about twenty-seven times the normal saturation. The presence of even a small amount of carbon dioxide in the solution, greatly increases the solubility. It is thought the silver exists in the form of a bicarbonate.

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1 Op. cit. P.25.

2 Loc. cit.

3 Op. cit. p.420.

4 Rickard, T.A., "The Enterprise Mine, Rico, Colorado,"
Trans. Am. Inst. Min.Eng., Vol.26, 1896, p.978.

5 Op. cit. p. 431.

6 Idem. p. 12.

7 Seidell, Solubilities of Inorganic Compounds, 1913,
P.282.

8 Johnston, G.S., Chem.News, 54, 1886, p. 75.

EXPERIMENTAL WORK.

SILVER MINERALS WITH ALKALINE CARBONATES.

A series of experiments were attempted to determine if silver, and its sulphides are soluble in alkaline carbonates, as stated by Van Hise. The minerals tested were argentite, pyrargyrite, proustite, polybasite, hessite, cerargyrite, argentiferous, tetrahedrite and galena, and metallic silver. The tests were made in 150 c.c. glass stoppered bottles. Five grams of the mineral, pulverized to 80 mesh were used in each test. Samples were put up in duplicate. To one set was added, 100 c.c. of a 1 per cent solution of potassium bicarbonate; to the second set, the same amount and strength of normal carbonate. The bottles were thoroughly shaken daily. After a period of three months, 25 c.c. of the solution was taken from each and tested for silver with sodium chloride. In no instance did a precipitate form. A few drops of a strong solution of potassium iodide, which would form the very insoluble silver iodide, was added, but no

precipitate or even an opalescence was noted. The same minerals were then treated with a hot solution of sodium carbonate, and kept at a boiling temperature for several hours, but no silver was dissolved. From the pyrargyrite, a trace of antimony sulphide was leached, and from the proustite, considerable arsenic sulphide.

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1 Van Hise, C.R. "A Treatise on Metamorphism,"
Monograph U.S. Geol. Survey, No.47,1904,p.1099.

EFFECT OF CARBONATES ON SILVER SOLUTIONS.

Since calcium carbonate readily precipitates gold and copper from their solutions, it has been thought by some that calcite in a silver deposit is unfavorable to the formation of deep zones of silver enrichment. But calcite, in solutions of silver bicarbonate and silver sulphate that have concentrations of silver below a certain point has no precipitating effect. To determine this point 10 gms. of calcite pulverized to 200 mesh was treated in a small glass

stoppered bottle with 100 c.c. of silver bicarbonate solution. The silver bicarbonate was made by dissolving the normal carbonate in water containing carbon dioxide and contained .40 gms. of silver per liter. Precipitation of black metallic silver or the oxide began immediately. The bottle was shaken daily. At intervals a small sample of the solution was removed and titrated. In a week's time when the action had ceased there was .1544 gms. of silver per liter in solution. The solution was allowed to remain in contact with the calcite for six weeks longer when another sample was taken and titrated. The silver content was the same. With silver sulphate solution in the presence of excess calcite, in the same manner, .5281 gms. of silver per liter remained in solution. When the amount of the silver was below the values given no precipitation took place. When 100 c.c. of a solution of silver bicarbonate of one-half that concentration was treated with calcite, in three weeks no silver had precipitated.

Therefore, since only traces of the metals are found in mine waters, calcite cannot cause precipitation of the silver in such dilute solutions.

Neither does siderite in the gangue necessarily suppress the development of deep zones of silver enrichment. True, the action of acid on siderite is to liberate ferrous sulphate, which would ordinarily precipitate silver as the metal. As the descending solutions carry ferric sulphate in addition to acid, some substance to reduce this must be present, as in its presence, the silver will not be precipitated. Furthermore, in a mixture of equal parts of ferrous and ferric sulphate considerable silver will be held in solution so that a mineral water will have to be thoroughly reduced before all of the silver will precipitate. A bottle in which was placed pulverized siderite and to which was added ferric sulphate, dilute sulphuric acid and some silver sulphate has now stood for a month without precipitation of silver. On the addition of tetrahedrite to a portion of the solution,

the ferric sulphate was rapidly reduced and the silver precipitated.

Rhodochrosite is inert as regards the precipitation of silver. Manganous sulphate, formed by the action of acids on the mineral is not a reducing agent and would, therefore, have no effect comparable to ferrous sulphate.

Since mine waters in the deeper zone become alkaline, it is pertinent to determine the action of alkalis on silver-bearing solutions. Accordingly, dilute silver bicarbonate and sulphate solutions were treated with strong alkaline carbonate. White precipitates formed immediately in both solutions. The precipitates were filtered off and the solutions titrated for the silver content. In the bicarbonate solution, .019 gms. of silver per liter still remained; in the sulphate solution .1 gm. Both solutions were strongly alkaline to methyl orange, and contained an excess of alkaline carbonate. In dilute solutions of silver bicarbonate and sulphate, a considerable amount

of the alkaline carbonate must be added before precipitation takes place. The exact reactions are not known as the state in which the silver salt exists may be either bicarbonate, the normal carbonate, or both.

As a group, the carbonates rapidly neutralize the acidity of the solutions and as a result there would be an alkaline zone at moderate depth. The point must not be overlooked that carbon dioxide is liberated in the process and that even a small amount of carbon dioxide in the solutions greatly increases the solubility of the silver carbonate. The alkaline zone is in itself not unfavorable to the development of deep zones of enrichment. What, then, precipitates the silver? The various reagents that may be operative will be discussed below.

EFFECT OF ALKALINE SULPHIDE.

The sulphosalts of silver are unstable in the presence of hot alkaline sulphide. They are readily leached of their arsenic and antimony sulphide

by this hot alkaline solution. When pyrargyrite was treated with a hot, one-half per cent solution of sodium sulphide, the finely pulverized red powder turned black. This black residue was filtered, carefully washed and on testing, sulphur and silver were obtained, but no antimony. On acidifying the filtrate, a red amorphous precipitate of antimony trisulphide was obtained. Proustite acted similar to pyrargyrite and readily yielded its arsenic to the alkaline sulphide. Polybasite also acted in a similar manner, but for the removal of all the antimony, a short period of boiling was necessary. Silver-free tetrahedrite and arsenopyrite were treated with the hot alkaline sulphide, but no antimony or arsenic was leached from these minerals by the one-half per cent solution. With a strong solution, about three per cent, and boiling for a considerable period some antimony sulphide was leached from tetrahedrite.

Many ore deposits have doubtless formed

formed through precipitation by hot ascending waters, probably charged with alkaline sulphide, chloride and carbonate solutions of the metals. If these waters, containing alkalie sulphides, rising up through fissures and openings in the rocks, precipitate their metallic content by a decrease of temperature and pressure only, silver sulphide will probably have been deposited before the solutions have cooled to 100 degrees C., because the sulphide of silver is not attacked by alkaline solutions and is therefore stable at that temperature; but the sulphides of arsenic and antimony will not precipitate until cooler surroundings are reached because they can be readily dissolved by such solutions at lower temperatures. Under the conditions postulated, that is, precipitation of the metals from alkaline sulphide solutions by decrease in temperature and pressure only, the sulphosalts of silver could not be primary minerals. But alkaline sulphide solutions of stibnite and orpiment are stable at room temperatures in airtight containers. Only when acidified or exposed to

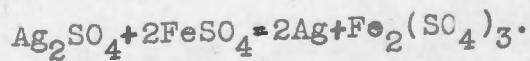
the atmosphere, do the sulphides of arsenic and antimony separate out. Indeed, the home of stibnite is in deposits formed near the surface, although it is not exclusively confined to such occurrences. However, if precipitation takes place by the mingling of hot ascending alkaline sulphide and carbonate waters with downward percolating acid or oxygenated waters, then, simultaneous precipitation of the component sulphides may result in the formation of complex silver minerals. As acid conditions do not penetrate to great depths below the surface, deposits in which the sulphosalts of silver are primary are those formed at shallow depth, and in these, the sulphosalts might occur intergrown with stibnite and other primary minerals characteristic of such deposits. In ore deposits known to have formed at intermediate or greater depth, beyond the active influence of superficial acidic waters, it is probable that these minerals are secondary; and we may classify them with kaolin, alunite, marcasite,

wurtzite and possibly other minerals which may be primary in deposits formed at shallow depth but are generally secondary when found in veins of the intermediate or deep zone.

PRECIPITATION OF SILVER MINERALS

METALLIC SILVER.

Ferrous sulphate acting on a solution of silver sulphate or silver carbonate, readily precipitates metallic silver which comes down as a cloud of silvery flakes, in the sulphate solution, and as a finely divided black precipitate in the carbonate solution. The action, however, is not complete; a considerable amount of silver remains in solution, due undoubtedly to the presence of ferric sulphate which is formed in the process. The reactions may be written as follows:



These reactions take place in very dilute solutions;

a solution of ferrous sulphate, containing 10 parts per million readily precipitated silver from a .1 per cent sulphate solution. The action was not complete. When the sulphides, chalcopyrite and pyrrhotite were added to portions of the solution, the silver was entirely precipitated, slowly with chalcopyrite and quite rapidly with pyrrhotite.

This condition is analagous to that in nature where ferric sulphate is reduced to the ferrous state, as the solutions descend, by reaction with the primary sulphides present. Moreover, as conditions in depth are favorable for the formation of ferrous sulphate at the expense of the ferric¹, all the silver will eventually be precipitated, either as the metal by ferrous sulphate or as argentite by the sulphides present, or possibly as a mixture of the two. Such a condition seems to have existed at Creede, Colo., where in depth are found, mixtures of native silver and secondary argentite. Native silver has a wide

range for it occurs in the oxidized zone, derived from argentite and the sulphosalts by weathering and oxidation, and it is found deposited with calcite and barite at a depth of a thousand feet below the surface, and hundreds of feet below the water level as at Aspen, Colorado.

 1 Hodge, E.T. loc. cit.

ARGENTITE.

Argentite and the sulphosalts, not native silver, are the commonest and most important secondary silver minerals, although in a number of their occurrences they are primary. Argentite may possibly be formed at shallow depths by the action of hydrogen sulphide and some metallic sulphides on the silver-bearing solutions. Wells¹ has shown, the action of dilute sulphuric acid on pyrrhotite, galena and sphalerite liberates hydrogen sulphide, which will precipitate silver sulphide from highly dilute solutions.

It is somewhat doubtful, however, whether the dilute acid solutions as found in nature will be effective in liberating hydrogen sulphide from all of the sulphides. For instance, sphalerite and galena, as will be discussed later, are weak or inactive in their precipitation of silver from dilute acid sulphate solutions. On the contrary pyrrhotite is quite active. At slightly greater depths, metallic sulphides, or alkaline sulphides formed by alkalies reacting with metallic sulphides, may precipitate silver sulphide. The action of ferrous sulphate, and some sulphides in the absence of ferric sulphate, is to precipitate silver as the metal, but under certain conditions, this metallic silver may be changed to a sulphide or sulphosalt.

When a strip of silver was suspended in a solution of alkaline sulphide, a tarnish of black silver sulphide formed on the metal. In less than a month's time, the silver was coated with a black finely crystalline aggregate which had penetrated half

way through the strip. In some places, the strip was entirely eaten away. In a similar manner when a strip of silver was suspended in a solution of sodium sulphantimonite, made by dissolving stibnite in alkaline sulphide, a red tarnish coated the silver, and in the same length of time, it was also covered with a finely crystalline surface. Some of this material was carefully removed and its streak tested. It gave a ruby-red streak, closely resembling that of pyrargyrite.

Whether some of the argentite and pyrargyrite are formed in nature in this way is not known although it is possible. Pseudomorphs of cerargyrite, ruby silver, argentite and stephanite after native silver are mentioned by Dana². For this replacement, the conditions necessary must be alkaline solutions acting on the sulphides and then coming in contact with native silver. To test this theory further, crushed pyrite and pyrrhotite were placed in separate

bottles, to which was added 100 c.c. of a 1 per cent solution of alkaline carbonate. A strip of silver was then suspended in the liquid. In six weeks a black tarnish had appeared on each, faint in the case of pyrite, quite deep with pyrrhotite.

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1 Wells, R.C. quoted by W.H.Emmons. Bull.U.S. Geol. Survey No.529, P.59.

2 Dana, System of Mineralogy, 6th ed., p. 20.

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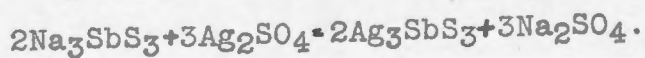
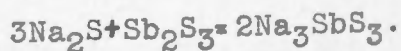
FORMATION OF THE DOUBLE SALTS.

The formation of double sulphides constitutes a closely related problem. By precipitation, in a solution of silver nitrate with potassium sulphantimonite, K_3SbS_3 , I. Pouget¹ obtained the amorphous compound Ag_3SbS_3 , equivalent in composition to pyrargyrite. The recent work of Grout² indicates that these salts are probably the result of intermingling solutions of the metals in an alkaline environment. On treating a sodium carbonate extract of stibnite with

a sulphuric acid solution of silver containing more than enough silver to unite with the antimony present, he obtained a compound, the analysis of which indicated approximately the composition of stephanite $(Ag_2S)_5.Sb_2S_3$. The resulting solution was slightly acid.

Some further work along these lines was undertaken. A solution of sodium sulphantimonite was made by boiling an excess of stibnite with sodium sulphide. To this solution, which was considerably diluted before using, was added neutral silver sulphate, in such amount that the resulting solution would contain an excess of antimony sulphide. A reddish brown solution immediately resulted which contained a colloidal precipitate. As such colloidal precipitates result from reactions between two chemical compounds in the absence of electrolytes, the precipitate was readily coagulated when sodium sulphate was added, and settled as a reddish brown gelatinous mass. The resulting solution, contained no silver, gave an alkaline reaction with methyl

orange and on acidifying, a precipitate of antimony sulphide was obtained, indicating antimony to have been in excess. The precipitate was analyzed and gave the following composition, Ag 58.8 per cent, Sb 24.3 per cent, S 16.7 per cent, which closely approaches the composition of pyrargyrite. In a similar manner, by the use of an alkaline sulphide extract of orpiment, a compound approaching proustite in composition was obtained. The same compounds resulted when the carbonate solution was used in place of silver sulphate. The probable reactions involved are:



When the above conditions were varied by having the silver in excess of the amount needed to combine with the antimony present, the resulting compound was variable in composition. The average silver content of several attempts was 71.6 per cent.

Due to the fact that arsenic sulphide is soluble in alkaline carbonate, whereas antimony sulphide is relatively insoluble, the presence of carbonates in mine waters may tend to delay the formation of secondary arsenical sulpho-minerals. A mixture of sodium sulphantimonite and sodium sulpharsenite containing equal parts of antimony and arsenic sulphide was made by mixing alkaline sulphide extracts of stibnite and orpiment. To this solution was added alkaline carbonate and also a solution of silver sulphate in such proportion that either the antimony or arsenic sulphide was in excess of the amount needed to precipitate all the silver. The resulting precipitate contained abundant antimony and only a trace of arsenic. Furthermore; as stated above, when pyrargyrite and proustite were treated with hot alkaline carbonate, only a trace of antimony sulphide was leached from pyrargyrite whereas, considerable arsenic sulphide was dissolved from proustite. These be-

haviors may explain the relative abundance in nature of the antimonial minerals, pyrargyrite, polybasite and tetrahedrite as compared with the corresponding arsenical minerals proustite, pearceite and tennantite, which are rare¹.

For the formation of the sulphosalts in the manner outlined above the following conditions appear to be necessary. Arsenic or antimony must be present in solution derived from the arsenides or antimonides by the action of alkaline solutions. This is possible, for according to Grout³, dilute alkaline carbonate solutions vigorously attack metallic sulphides. Furthermore, traces of arsenic and antimony are found in several neutral and alkaline mine waters. This solution could take place only in an alkaline environment, as acids liberate antimony and arsenic sulphide from alkaline solutions. If now a solution of silver meets this alkaline solution of antimony sulphide, a compound results whose composition depends on

the relative amounts of silver and antimony present. At the top of the alkaline zone, the silver is likely to be in excess, which would result in the formation of polybasite and stephanite. Above these, in the neutral zone, secondary argentite is the more probable. At slightly greater depth in the alkaline zone, conditions will be more favorable for the formation of alkaline solutions of arsenic and antimony sulphides and the precipitate with silver will be proustite and pyrargyrite. If, however, in this alkaline zone, antimonial minerals only sparingly occur, polybasite and stephanite, those minerals with the higher silver content will form. If no minerals of arsenic and antimony are present, only argentite can form. A hypothesis of mingling solutions, and an alkaline zone at moderate depth is not an impossibility and might be considered in the formation of secondary minerals at low temperatures. Alkaline mine waters are not rare below the zone of oxidation. In fact, some of the waters recal-

culated by Hodge⁴ as alkaline were collected within 400 feet of the surface. Deep waters of acid reaction are rare.

The occurrence in nature of these sulphosalts, strongly suggests a genesis by the above method. In the Granite-Bimetallic mine at Phillipsburg, Mont., according to Emmons and Calkins⁵ pyrrargyrite lines vugs or occurs in small veinlets that cut across the banding of the ore. At Tonopah, Nevada, according to Spurr⁶ it coats crevices that cut the primary ore. On the occurrence of pyrrargyrite at Lake City, Colo., Irving and Bancroft say⁷

"Ruby silver occurred, so far as could be learned, in all of the mines at the plane of demarcation between sulphides and oxides and, in generally decreasing quantity, to several hundred feet below this level. Along cracks and fissures it occurred in isolated masses to great depths - for instance, at 1,200 feet in the Golden Fleece and at 1,300 feet in the Ilma. These deep occurrences are, however, uncommon and merely indicate the presence of some easy line of access for downward-moving solutions. Ruby silver has probably resulted from the solutions of silver and antimony obtained by the decomposition of the tetrahedrite and possibly to some extent also from the

argentiferous galena. The chemistry of both the solution and reprecipitation of the antimonial and arsenical sulphur compounds has not yet been worked out in sufficient detail to permit a statement of the probable steps of the process, but the geological facts show that it has occurred. The proofs of the secondary character of the ruby silver are:

1. Its restriction in quantity to the upper levels of the mines.
2. Its invariable occurrence as the latest deposited mineral in the veins, either in cracks or crevices in shattered primary ore or as crystals in cavities.
3. Its occurrence only in isolated bunches in deeper workings, where its origin is probably due to the presence of water channels that permit the downward percolation of water from above.
4. Its complete absence from the great mass of deep-seated ore."

Although there is no invariable rule respecting the relations of these secondary silver minerals, we may expect in some places to find them occurring in overlapping horizons with argentite above, followed in regular downward order by polybasite, stephanite and pyrargyrite and proustite. At the Granite-Bimetallic mine, the deeper secondary ores contain very little argentite or native metal, the richer minerals being

almost exclusively the dark and light ruby silver.

At Georgetown according to Spurr, Garrey and Ball:⁸

"Below the zone where soft secondary sulphides occur and irregularly overlapping the lower portion of this zone the rich ores contain polybasite, argentiferous tetrahedrite, and ruby silver, better crystallized and more massive than the pulverulent sulphides but also subsequent in origin to the massive galena-blende ore. These richer ores diminish in quantity as depth increases, though gradually and irregularly, so that the lower portion of the veins contains relatively less silver and lead. The best ore in most veins has been found in the uppermost 500 feet, although good ore extends locally down to 700 or 800 feet, and in the Colorado Central and to a minor extent in other veins down to a thousand feet or more."

At the Banner mine, near Silver City, Idaho, rich pockets of argentite ore in a gangue of pyrite, kaolin, quartz and calcite were mined at shallow depth. Below these, the principle ore minerals were pyrargyrite and proustite with little or no argentite.

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1 Pouget, I. Compt. Rend., Vol.124,1897,p.1518.

2 Op. cit. p.425.

3 Idem. p.429.

4 Loc. cit.

5 Emmons, W.H., and Calkins, F.C., "Geology and Ore Deposits of the Phillipsburg quadrangle, Montana." Prof. Paper U.S. Geol. Survey, No. 78, 1913, p. 204.

6 Spurr, J.E., Geology of the Tonopah mining district, Nevada: Prof. Paper U.S. Geol. Survey No. 42, 1905.

7 Irving, J.D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: Bull. U.S. Geol. Survey No. 478, 1911, p. 63.

8 Spurr, J.E., Garrey, G.H., and Ball, S.H., "Economic Geology of the Georgetown quadrangle," Prof. Paper U.S. Geol. Survey, No. 63, 1908, p. 144.

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ACTION OF METALLIC SULPHIDES.

The recent experiments by Palmer and Bastin¹ have a bearing here. By treating several minerals with silver sulphate in a neutral solution, they obtained a precipitate of metallic silver; in some instances a mixture of the sulphide and the metal. They have grouped their results in the following manner:

Very strong, - chalcocite, niccolite.

Strong, - covellite, enargite, bornite, tennantite, tetrahedrite, alabandite, and possibly

cobaltite.

Moderate, - smalltite, marcasite, pyrrhotite, chalcopyrite, arsenopyrite.

Weak or inactive, - cinnabar, stibnite, pyrite, galena, millerite, sphalerite, jamesonite, orpiment, realgar. Mr. F. F. Grout² has determined a series in which acid is present in the solution and which is approximately the same. In several experiments with silver carbonate in the presence of a few of the above minerals, similar action was noted. Tetrahedrite and chalcocite rapidly precipitated silver from the solution, whereas, pyrite was practically inactive.

In the above experiments, the precipitate as mentioned was the free metal. According to Grout,³ however, the presence of ferric sulphate inhibits the formation of the free metal, and the silver is then precipitated as sulphide by an exchange of metals in the mineral. This conclusion is supported by the fact

that in most cases, the metal of the mineral used as a precipitant was found in solution. In one of the experiments performed with the carbonate of silver solution in the presence of chalcopyrite, all of the silver was precipitated. On the addition of ferric sulphate, some silver was redissolved. Some of the sulphides, however, notably chalcocite, are so active that they precipitate free silver from its solutions even though ferric sulphate is present.

As shown above, calcite, rhodochrosite and the carbonates, with the exception of siderite have no direct precipitating effect on the dilute solutions of silver; indirectly they rapidly neutralize acidity, resulting in neutral or alkaline conditions at moderate depth. Nephelite, leucite and possibly the zeolites, if found in ore or wall rock, would have the same general effect, though not so pronounced. In such surroundings the silver may be precipitated as the native metal by organic matter or by ferrous sulphate in the absence of ferric sulphate; as the sulphide, by alkaline sul-

phide, or the metallic sulphides, or as the sulphosalts by alkaline extracts of arsenical and antimonial minerals. The presence of siderite in the gangue may aid in suppressing deep zones of enrichment. It rapidly neutralizes acid and with acid liberates ferrous sulphate. It does not, however, reduce the ferric sulphate present, and in its presence the silver will not be precipitated from dilute solutions by siderite alone. If in addition, sulphides are present, precipitation will take place. In a paper on the Caledonia mine of the Coeur d'Alene, Earl V. Shannon⁴ noted the occurrence of native silver in sideritic ore. The sulphides present are chalcopyrite, galena and tetrahedrite, the latter is nearly everywhere present in the ore.

In the presence then, of the above listed "active" sulphides, shallow zones of enrichment are to be expected; in their absence, deeper zones. It is noteworthy that the sulphides active in the precipitation of silver from its solutions, are those which readily neutralize acidity and reduce iron in ferric sulphate

solution as determined by G.S.Nishihara⁵. As a general rule, silver sulphide enrichment under favorable conditions is rarely found to be effective more than 1,000 feet below the surface on account of the rapid rate at which silver is precipitated from its solutions by so many substances. On the contrary, many of the Mexican bonanzas extended to greater depth, in several instances at Pachuca and Real Del Monte⁶ to 1,650 feet; but to what extent they are the result of secondary enrichment processes is not known.

1 Op. cit. p. 153

2 Op. cit. p. 417

3 Idem. p. 420

4 Shannon, Earl V., "Secondary Enrichment in the Cal-
edonia Mine," *Econ.Geol.*, Vol.8, 1913, p.565.

5 Op. cit. p. 745 and 749

6 Halse, Edward, "Deep Mining in Mexico,"
Trans. Inst.Min. and Met., Vol.3, 1895, p.420.

SUMMARY.

Silver is not dissolved from silver minerals by alkaline carbonates at room temperatures. Metallic silver is also insoluble. Hot solutions of alkaline carbonate do not dissolve silver from argentite or pyrargyrite. From pyrargyrite a trace of antimony sulphide is dissolved, from proustite considerable arsenic sulphide.

Below a certain point in the saturation of silver bicarbonate and silver sulphate, in the presence of an excess of calcite, no silver is precipitated. In solutions containing respectively, less silver than these certain values, silver is not precipitated by calcite. Siderite, though liberating ferrous sulphate with acid, does not reduce the ferric sulphate present, and in the absence of sulphides will have no tendency to precipitate silver and halt the downward enrichment of the metal. Rhodocrosite is inert. Alkalies, such as sodium

carbonate, do not entirely remove the silver from solutions of silver bicarbonate and sulphate. In either case, a considerable quantity of silver remains in solution, which is only precipitated when sulphides are added.

A hot dilute solution of alkaline sulphide readily leaches the antimony sulphide from pyrargyrite, leaving a fine black powder of silver sulphide. The action on polybasite is similar, but not so rapid. Arsenopyrite and tetrahedrite are not so affected by the dilute alkaline sulphide. Due to this behavior, and our present knowledge of the genesis of ore deposits, we may suppose that the sulphosalts of silver may be primary in deposits formed at shallow depth, and secondary in deposits formed at depth.

Ferrous sulphate in a solution as dilute as 10 parts per million, readily precipitates metallic silver from its solutions. Due to the formation of ferric sulphate in the process, however, the precip-

itation is not complete, but readily becomes so in the presence of metallic sulphides.

Argentite may be formed by the action of hydrogen sulphide, metallic sulphides in the presence of ferric sulphate, or alkaline extracts of metallic sulphides, on the silver bearing solutions.

Metallic silver in a solution of alkaline sulphide takes on rapidly a black tarnish, while silver in a solution of sodium sulphantimonite takes on a red tarnish, suggesting in each case the formation of argentite and pyrargyrite respectively.

When an alkaline sulphide extract of stibnite was added to a solution of silver sulphate, in such proportions that the antimony was in excess, and the resulting mixture alkaline, an amorphous compound was obtained, which corresponded in composition to pyrargyrite. In a similar manner, by using an extract of orpiment, a compound approaching proustite was the result. By varying the proportions of the two solutions

in such a manner that after mixing the silver was in excess and the solution slightly acid, a compound resulted which was intermediate in composition between polybasite and stephanite.

Metallic sulphides, in the absence of ferric sulphate, precipitate from silver bearing solutions some sulphide, but an abundance of free metal. In its presence the silver is precipitated as the sulphide, by an exchange of metals, in the mineral. A few very active sulphides precipitate the free metal even in the presence of ferric sulphate, but only after the ferric sulphate is thoroughly reduced.

APPLICATION TO ORE DEPOSITS.

The principle value of the theory of secondary sulphide enrichment is its utilization in the exploration of ore deposits. The processes are influenced by many factors. Among them are temperature, rainfall, altitude and relief. For the recognition of the process, one is recommended to a review

by F. L. Ransome¹. Another point which is of equally great importance lies in the ability to foretell to what depths the secondarily enriched zones are likely to persist. In other words, some minerals retard the process and cause shallow zones of bonanza ore, while other minerals exert little or no effect, and the zone is then apt to be more extensive and contain lower grade ore.

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

If the halogens are present in the mine waters, they will precipitate the minerals cerargyrite, embolite, bromyrite and iodyrite. These minerals appear to be stable in the presence of sulphuric acid and

ferric sulphate and consequently remain in the upper portions of ore deposits, giving a considerable enrichment at or near the surface. Deposits of this type are best developed in arid regions and occur in the Great Basin region of the west.

In deposits containing the "active" minerals, alabandite, chalcocite, tetrahedrite, pyrrhotite, miccolite, smalltite, covellite, tennantite, and siderite with sulphides, 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.

Examples in which the above discussed processes have influenced the deposition of secondary silver minerals are numerous, and only a few need be cited here. At Cobalt, Ontario, the principle sulphides include smalltite, cobaltite, chloanthite, niccolite, and bismuth sulphide with some arsenopyrite and tetra-

hedrite. Pyrite is rare. The ore minerals are native metal, argentite, proustite, pyrargyrite and dyscrasite. The gangue includes quartz and calcite. Extending downward 200 to 300 feet below the surface are rich silver minerals, largely in veinlets in earlier sulphides. The change from rich to low grade ore is very abrupt both in depth and along the strike. Van Hise² and Emmons³ have attributed these richer silver ores to processes of sulphide enrichment, but Miller⁴ believes that this feature of the genesis has been over-emphasized. The precipitation of the silver could have been accomplished by the niccolite, smalltite and cobaltite in the ore.

At Wood River, Idaho, according to Lindgren⁵, the ore consists of galena, zinc blende, and tetrahedrite, with but little pyrite and chalcopyrite; the gangue is siderite, or intermediate calcium, iron and magnesium carbonates, with a little quartz. Among the ore minerals, tetrahedrite is the principal carrier of

silver. The ore shoots are markedly irregular. A marked deterioration may often be observed in depth; the large bodies of rich silver ore are found comparatively near the surface. The upper, oxidized parts of the veins are enriched by secondary silver chloride, native silver and pyrargyrite. In the tetrahedrite-rhodocrosite veins at Lake City,⁶ Colorado, the ores contain mainly galena, pyrite and tetrahedrite, the last rich in silver, with some pyrite in a gangue of quartz, barite and rhodocrosite. The precipitation of native silver in sideritic-sulphide ores at the Caledonia mine in the Coeur d'Alene has been mentioned. The ores of the same mine according to O.H.Hershey⁷ contain tetrahedrite, some of which is said to assay as high as 3,000 ounces of silver per ton. In these districts tetrahedrite was undoubtedly the active precipitant of the silver, although at the Caledonia mine, siderite may have influenced.

In deposits in which chalcocite is the chief ore mineral, a concentration of silver is usually found

at the top of the chalcocite zone.⁸ Abundant pyrrhotite would also halt the downward migration of silver very effectively, but there are few important pyrrhotitic deposits that carry much silver. The primary ore, at Ducktown, Tenn., carries only a few cents to the ton, but some of the ores of the secondary chalcocite zone carried more than .5 per cent of silver. Pyrrhotite is present in the primary ore.

Among the deposits in which the processes of secondary sulphide enrichment have been effective, and have consequently resulted in deeper zones of enrichment, may be mentioned the Granite-Bimetallic at Phillipsburg, Mont., and deposits at Georgetown, Creede and Aspen, Colo. At the Granite-Bimetallic mine⁹ the primary ore, consists of quartz and rhodocrosite with pyrite, arsenopyrite, galena and tetrahedrite, at several places abundant zinc blende in the primary ore, below the richer sulphides. No pyrrhotite was noted. Rich ore with secondary cer-

argyrite, native silver and ruby silver in cracks across the older sulphides appeared in considerable amount 200 to 400 feet below the surface and extended to depths of 800 or 900 feet. At the Comstock Lode,¹⁰ some of the great bonanzas extended to a depth of 2,000 feet, but to what extent they are secondarily enriched is not known. The ore consists of quartz with some calcite, in places banded with pyrite, galena, chalcopyrite, zinc blende, and finely distributed rich silver minerals, mainly, argentite, stephanite and polybasite. The occurrence at Georgetown where good ore extended locally down to 700 or 800 feet, and in the Colorado Central and to a minor extent in other veins down to 1,000 feet, has already been cited.

At Aspen, Colo. Spurr¹¹ differentiates the deposits into three classes -- (1) barite veins, (2) silver sulphides, sulphantimonites and sulpharsenites, (3) galena and zinc blende veins. The barite veins

are generally barren. After their development rich sulphides, such as argentite, polybasite and tetrahedrite were deposited. A remarkable shoot of polybasite ore yielding many million dollars was mined in the Molly Gibson mine, at a depth of a few hundred feet below the surface. At Aspen, native silver has a wide range and is abundant in fissures and vugs of limestone and shale 900 to 1,000 feet below the surface and is distinctly later than the primary lean galena - zinc blende ores.

In conclusion, the writer wishes to thank Dr. W.H.Emmons and Professor F.F.Grout for their many helpful suggestions and indispensable aid during the progress of the work and the preparation of this report.

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 - 6 Loc. cit.
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