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CHALCOCITE ENRICHMENT.¹

ARTHUR C. SPENCER.

PRELIMINARY STATEMENT.

Since 1900, when Emmons,² Weed,³ and Van Hise⁴ presented papers dealing with the downward enrichment of sulphide ores,⁵ the subject has received, perhaps, more attention from working students of ore deposits than any other single phase in the chemistry of ore genesis. Especially with respect to the enrichment of cupriferous materials by secondary deposition the problem has been worked out to the extent that the chemical reactions involved may be indicated in a general way at least; besides which we have a fairly good understanding of the geological conditions which favor or oppose the operation of recognized processes on a scale

¹ From a forthcoming report on the geology and ore deposits of the Ely district, Nevada. Published by permission of the Director of the U. S. Geol. Survey.

² Emmons, S. F., "The Secondary Enrichment of Ore Deposits," *Trans. Am. Inst. Min. Eng.*, February meeting, 1900, Vol. 30, pp. 177-217, 1901.

³ Weed, W. H., "Enrichment of Gold and Silver Veins," *Trans. Am. Inst. Min. Eng.*, February meeting, 1900, Vol. 30, pp. 424-448, 1901; "Enrichment of Metallic Veins by Later Metallic Sulphides," *Bull. Geol. Soc. Am.*, Vol. 11, pp. 179-206, 1900.

⁴ Van Hise, C. R., "Some Principles Controlling the Deposition of Ores," *Trans. Am. Inst. Min. Eng.*, Vol. 30, pp. 27-127, 1901.

⁵ For the bibliography of this subject the reader is referred to the following papers: Tolman, C. F., "Secondary Sulphide Enrichment of Ores," *Min. Sci. Press*, Vol. 106, pp. 180-181, 1913; Emmons, W. H., "The Enrichment of Sulphide Ores," *Bull. U. S. Geol. Survey*, Bull. 529, 1913.

large enough to produce the segregation of copper minerals in bodies of commercial value. The climatic conditions under which the largest or richest bodies of secondary ores have accumulated have not been adequately discussed, so that a full analysis of this portion of the subject remains to be made.

The processes of chalcocite enrichment and the conditions that control the deposition of chalcocite from oxidized copper-bearing solutions are here considered with special reference to the disseminated ores of the Ely district, Nevada, which, as mined, carry from 20 to 60 pounds of copper per ton. The principal ore bodies have been formed by the enrichment of portions of great masses of uniformly pyritized and sericitized monzonite porphyry which carry not more than half of one per cent. of copper as primary chalcopyrite. In form and occurrence the ore bodies are blankets that lie beneath an overburden or capping of fully weathered and oxidized material and grade downward into primarily mineralized rock which has not been enriched. The depth of the capping ranges from a few feet to 250 feet or more and the thickness of the material carrying the secondary chalcocite varies from a few feet up to a maximum of about 400 feet. The ores contain from 5 to perhaps 10 per cent. of metallic sulphides, of which usually somewhat more than half is pyrite. Both chalcopyrite and pyrite have been partly replaced by chalcocite, but the coatings of this secondary mineral are commonly much deeper on the chalcopyrite than on the pyrite, much of which has not been coated at all. The principal nonmetallic minerals—quartz, orthoclase, sericite, and brown mica—are the same as those of the pyritized rock from which the ores have been derived. All these minerals persist in the weathered capping, though usually the brown mica has been bleached and a little kaolin formed, mainly through the decomposition of the orthoclase.

The chemistry of downward chalcocite enrichment may be treated by following in imagination the various incidents of the journey made by rainwater which, falling on the surface, soaks into the ground and penetrates an existing ore body. Rainwater

carries in solution the various gases of the air, including oxygen and carbon dioxide. In arid and semi-arid regions it contains also noteworthy amounts of common salt, which may be regarded as of wind-blown origin. As these waters pass into the soil and into the porous weathered capping that lies above the ore mass they come into contact with orthoclase and mica and with oxidic compounds of iron and copper (including limonite and its congeners), basic sulphates carrying iron or copper, and basic carbonates of copper. Metallic copper and red oxide cuprite are also fairly common in the overburden. The silicate minerals in the capping tend to make the water alkaline,¹ but as they are only slightly attacked this tendency is likewise slight. Of the metallic minerals in the capping, those containing sulphate decompose, being somewhat soluble, the final result being to produce and to leave in place insoluble limonite and copper carbonates and to furnish small amounts of iron and potash sulphates to the solution. Thus far the dissolved oxygen does not enter largely into reaction because most of the minerals of the capping are already fully oxidized. The only exceptions to be noted are cuprite and native copper. Also, the carbonic dioxide has been by no means exhausted.

Everywhere the capping colored characteristically red by ferric iron compounds gives place by a short transition to gray or bluish ore. Above this horizon the waters are able to accomplish little in addition to what had been done in advance by similar waters. Just beneath the capping the solution encounters material rich in sulphide minerals, that are subject to ready oxidation. Here then chemical action between the oxygenated waters and the sulphide minerals ensues, a series of reactions being initiated of which series the culminating reactions involve the deposition of chalcocite. At first the waters contain free sulphuric acid furnished by the decomposition of pyrite, but gradually the acid becomes neutralized by bases furnished by the gangue minerals, and at sufficient depth the solutions become alkaline. If considered

¹ Cameron, F. K., and Bell, J. M., Bull. No. 30, Bureau of Soils, U. S. Dept. of Agriculture, p. 12 et seq., 1905; Clark, F. W., "The Data of Geochemistry," Bull. 491, U. S. Geol. Survey, pp. 454-459, 1911.

with respect to the minerals decomposed the reactions that occur beneath the capping present a succession of oxidations, whereas if considered with respect to the active solution, the changes are of course as consistently in the direction of reduction. The reactions may be considered in three groups, assignable in a general way to higher, intermediate, and lower positions in the body of sulphide-containing material. In the upper part of a sulphide ore body, where atmospheric oxygen is the oxidizing agent; somewhat lower down, where free oxygen has been exhausted ferric sulphate becomes active; and after the oxygen made available by this carrier has been utilized cupric sulphate furnishes oxygen. The action of cupric sulphate on pyrite and chalcopyrite results in the deposition of chalcocite and the consequent enrichment of material carrying the primary sulphides. The formation of secondary chalcocite probably involves a series of transitions or stages, as pyrite—chalcopyrite—bornite—covellite—chalcocite.

The following discussion is incomplete in that the chemistry of the copper minerals that are characteristic of the capping is not considered. Though oxidation in the portion of an ore body that lies just beneath the capping results in the compounding of cupriferous solutions the fact must not be neglected that here also are formed the relatively stable basic carbonates and sulphates, and the even more stable minerals cuprite and metallic copper.

EXPERIMENTAL DATA ON CHALCOCITE DEPOSITION.

Winchell¹ and Tolman, and also Read² obtained coatings of chalcocite by treating pyrite with slightly acid cupric sulphate solution in the presence of SO₂. In experimental work conducted at a temperature of about 200° C. Stokes³ induced the formation of cuprous and cupric sulphides by treating pyrite with

¹ Winchell, H. V., *Bull. Geol. Soc. Am.*, Vol. 14, pp. 269-276, 1903.

² Read, T. T., "Secondary Enrichment of Copper-iron Sulphides," *Trans. Am. Inst. Min. Eng.*, Vol. 37, pp. 297-303, 1906.

³ Stokes, H. N., "On Pyrite and Marcasite," *Bull. U. S. Geol. Survey No. 186*, p. 44, 1900; "Experiments on the Solution, Transportation, and Deposition of Copper, Silver, and Gold," *ECON. GEOL.*, Vol. 1, pp. 644-650, 1906.

cupric sulphate solution slightly acidified with sulphuric acid. The work of Stokes was followed by that of Read already mentioned, and by noteworthy observations by Sullivan. Pulverized pyrite¹ and chalcopyrite shaken in a dilute solution of copper sulphate caused the solution to lose its color. By contact with 20 grams of pyrite during three days 40 cm. of cupric sulphate solution lost .04 grams of copper out of .097 grams originally present.

The experiments of Sullivan are important because they show that pyrite and chalcopyrite can cause the precipitation of copper from sulphate solution at ordinary temperatures without the intervention of a strong reducing agent such as was used by Winchell, and it is sufficiently obvious that the insoluble compound formed must be a sulphide. But the action is ordinarily so reluctant that investigators of the subject have usually failed to get visible coatings on pyrite or chalcopyrite as the result of treatment in the cold with simple solutions of cupric sulphate. However, by subjecting fragments of chalcopyrite to the action of a weak solution of cupric sulphate during three months, Welsh² and Stewart obtained both a tarnish, having the purple tinge of bornite, and "some thin black films."

The writer has found that bornite reacts readily with cupric sulphate and that indigo coatings may be formed on that mineral in a few hours by simply immersing it in a solution of the copper salt. Under prolonged treatment the indigo colors first developed changes to a steely blue which gradually fades until it gives place to the gray color which is so characteristic of chalcocite. Attempts to obtain similar results with chalcopyrite were not successful when cupric sulphate was used alone, but in the presence of ferrous sulphate this mineral soon becomes tarnished and passes through a series of color changes which repeated observation has shown to occur in a definite and predictable order. First

¹ Sullivan, E. C., "Discussion Relating to the Formation of Secondary Copper Sulphides in Criticism of Read's Paper," *Trans. Am. Inst. Min. Eng.*, Vol. 37, p. 894, 1907.

² Welsh, T. W. B., and Stewart, C. A., "Note on the Effect of Calcite Gangue on the Secondary Enrichment of Copper Veins," *ECON. GEOL.*, Vol. 7, pp. 785-787, 1912.

the natural yellow of the mineral darkens slightly, then the surface becomes brownish with a bronzy tone, then pink, light purple, darker purple, indigo, and various shades of steely blue with gradually lessening depth. The final result is a gray coating of metallic luster which turns blue under the Stokes¹ test for chalcocite. Between the blue and gray stages the surface of the mineral becomes yellowish or bronzy, the appearance being as though the film first developed had been dissolved. In various trials the whole transition has required from five to ten days, and in certain trials the final chalcocite stage was not attained at all. The same succession of colors, except the apparent reversion to chalcopyrite, may be obtained by another method which will be described further on. By means of a mixed copper and iron solution spots of blue resembling covellite may be developed on pyrite within a few hours, but so far as observed this mineral does not become uniformly coated, as does chalcopyrite. When the natural acidity of a solution containing cupric sulphate was increased by adding a little sulphuric acid, chalcopyrite remained untarnished at the end of four months, and Winchell states that pyrite fragments immersed in acidified cupric sulphate solution showed no visible alteration at the end of two years.

While both bornite and chalcopyrite have been artificially coated with gray chalcocite films, the gray coatings have been preceded in all successful experiments by indigo-colored films which are regarded as covellite. An unsuccessful attempt was made to form chalcocite directly by treating granulated bornite with a solution containing ferrous sulphate in molecular concentration about four times that of cupric sulphate. In this experiment the ferrous sulphate solution was freshly reduced. The mineral and the liquids employed were freed from air by ebullition under reduced pressure at 60° C. The apparatus was sealed under exhaust and was cooled before the reagents were brought into contact with the mineral. After the lapse of about four days the bornite had assumed a deep indigo color which is taken to indicate

¹ A fragment of chalcocite boiled for a moment with 10 per cent. ferric sulphate solution turns blue. *ECON. GEOL.*, Vol. 1, p. 23, 1903.

the development of covellite. After three weeks had passed the general tone of the granular powder was gray, but some of the grains still had blue surfaces. At the end of three months the material was removed from the apparatus for examination. Under the microscope most of the grains had the appearance of chalcocite but certain surfaces showed the color of covellite. A sample of the original mineral was found to contain a small amount of chalcopyrite and specks of covellite, the latter being present in about the same proportion as in the treated material. It therefore appears that the bornite and chalcopyrite were both coated with chalcocite whereas the original covellite remained unaltered. Like results were attained in a solution that carried equivalent concentrations of copper and iron. In both experiments the concentration of the copper salt was about .02 of the formula weight of cupric sulphate. Natural covellite was treated with solutions of corresponding composition but no change of color had resulted at the end of four months.

The foregoing observations have led to the suggestion that the change of pyrite or chalcopyrite to chalcocite may be considered as an alteration involving a series of steps, or perhaps even a continuous progression through indefinite compounds or mixtures of iron-copper sulphides.¹ Discussion of the suggested change pyrite to chalcopyrite is not offered for lack of adequate basis furnished by experiment or observation. On the other hand, the change chalcopyrite through bornite and covellite to chalcocite may be brought about artificially in various ways, some of which have been already noted, and so far as the writer's experiments have gone it seems to be impossible to change chalcopyrite to chalcocite without traversing the bornite and covellite stages, or to convert bornite into chalcocite except through covellite as an intervening product. Still it seems probable that in nature the covellite stage may not always enter into the series, though the chemical environment which would favor the more direct change to chalcocite can not be stated definitely at present. Experimental results with bornite and cupric sulphate indicate that the change covellite to chalcocite may occur and there is a strong suggestion that the

¹ See table on page 638.

transformation proceeds in such a way that graduated mixtures of CuS and Cu_2S are formed. This suggestion is supported by Graton and Murdock who have noted that natural "chalcocite" is not always gray in color but shows various shades of steely blue such as might result from minute intergrowth of chalcocite and covellite.

Specimens of copper ore described by Graton and Murdock¹ contain the series pyrite, chalcopyrite, bornite, covellite, and chalcocite, the mutual space relations of the several minerals being such that each mineral of higher copper content appears to have been derived from the alteration of the mineral next below it in the series. Graton and Murdock state that all these minerals² have been observed by them as described in different parts of a single polished specimen, under examination by means of the reflecting microscope, but that all the copper-bearing phases were not noted about any single grain of pyrite. Mr. Bastin, of the Geological Survey, has shown the writer a specimen of copper ore from Gilpin County, Colorado, which represents partly altered chalcopyrite. Certain surfaces show chalcocite apparently lying directly on the chalcopyrite. On the other surfaces, and evidently of later origin, are complex films with covellite outside and a substance resembling bornite beneath. In different places may be noted bronzy effects, grading in tone from the normal color of bornite to a purple hue intermediate between bornite and covellite, as though bornite had been plated over with a translucent film of the indigo mineral. Similar color effects are to be obtained, according to Read,³ by treating chalcopyrite with copper sulphate solution in the presence of SO_2 .

"The enriched sulphide was dark green in color; during the month it had become successively bronzy, purple, and dark steely blue."

This statement is open to the interpretation that the surface

¹ Graton, L. C., and Murdock, Joseph, "The Sulphide Ores of Copper," *Trans. Am. Inst. Min. Eng.*, Vol. 4, pp. 754-755, 1913.

² Compare relations of bornite as described by R. H. Sales, *ECON. GEOL.*, Vol. 5, p. 682, 1910.

³ Read, T. T., "Secondary Enrichment of Copper-iron Sulphides," *Trans. Am. Inst. Min. Eng.*, Vol. 37, p. 300, 1907.

of the film deposited on the chalcopyrite passed through the stages bornite and covellite and that some chalcocite was formed.

The colors observed by Read and present in the Gilpin County specimen referred to above may be readily obtained by another simple procedure, and the observer can hardly fail to conclude that the colors obtained indicate the formation of the minerals bornite, covellite, and chalcocite. If any member of the series chalcopyrite, bornite, covellite is touched by a piece of iron while it is immersed in a cupric sulphate solution the mineral changes color almost instantly, and in a short time becomes coated with the mineral next above it in the series. The brilliant indigo of covellite changes to the dull gray so characteristic of chalcocite, bornite assumes a blue color unmistakably like that of covellite, and chalcopyrite takes on a bronzy hue resembling that of bornite. Furthermore, within a very short time the bronze plating on chalcopyrite gives place to or is hidden by a film of covellite; then within an hour or so the surface turns to a chalcocite gray, and finally metallic copper is deposited. When pyrite is used in place of a cupriferous sulphide the effect of the iron is sufficient to throw down metallic copper rather quickly, but by scraping away the metal and again placing the mineral in contact with iron in the solution it is possible to obtain deposits of copper sulphides. In this way spots having somewhat the same color as chalcopyrite and others bronzy like bornite may be developed on pyrite along with unmistakable films of covellite and of chalcocite. If copper is used instead of iron the results are essentially the same with chalcopyrite, bornite and covellite. For instance, covellite may be coated with chalcocite by contact with copper in a solution of cupric sulphate. It is obvious that the speed of reaction may be varied by employing different metals as inductors, or by employing minerals to cause electrolytic action. Very pleasing results have been obtained by placing in a solution of cupric sulphate a polished specimen of intergrown chalcopyrite and pyrrhotite. Here a pinkish bronze color resembling that of bornite appeared within a few days but gradually changed to purple, deep purple and finally to indigo-blue. On the most reactive grains the covel-

lite color was fully developed in about eight weeks, but the surface in general became blue only after 12 weeks, and even then certain areas were still bronzy. At the end of four months no gray color had developed to indicate the formation of chalcocite, but the color was a paler blue than that of natural covellite.

It may be suggested that the results described, which were obtained under ordinary temperatures, may actually epitomize the course of reaction between the primary sulphides and copper salts held in oxidized solutions penetrating from the surface. Even if the means employed to produce the results in a short time are not comparable with those involved in natural processes, perhaps the conditions under which the experiments were made may be considered to be less unnatural than those prevailing in mineral syntheses effected under high temperatures.

Since in nature coatings of covellite and of chalcocite are found on grains of pyrite without observable films of other members of the series between the primary and the secondary mineral, the contention might be made that intermediate products have not been involved in the change, and that the suggested step process is therefore disproved. This conclusion does not necessarily follow, because intermediate phases may exist in films too thin to be observed, or if formed may have disappeared through conversion into some mineral standing higher in the series. However, this may be, it would seem that the true course of the chemical action between pyrite and chalcopyrite on the one side and cupric sulphate on the other can be determined by sufficiently detailed investigations in extension of the experiments made by Sullivan which are referred to on page 625. In future work the effects of ferrous and ferric sulphates and of sulphuric acid in known concentrations should be determined.

SOURCE OF OXYGEN.

Before taking up the threefold series of reactions leading to chalcocite deposition, it is of interest to inquire whether the oxygen dissolved in rainwater could alone have effected the oxidation of

the mass of material which has contributed the secondary copper now contained in any given ore body. This query may be answered in the negative. The ore body at Copper Flat, assumed to average 1.5 per cent. copper, carries as much added or secondary copper as could be furnished by the complete leaching of 400 feet of primary material containing one half of one per cent. copper: but with about 100 feet of existing cap rock still containing at least one half per cent. copper in oxidic minerals, the total depth of material which has been oxidized to produce the present mass of chalcocite ore can not have been less than 500 feet. It is assumed that all of this 500 feet of material passed through the chalcocite stage, so that a goodly part of the copper has been several times dissolved and redeposited. This being true, the amount of oxygen required would be the same as the amount necessary to oxidize 500 feet of ore such as now exists. By considering the amount of oxygen that water can absorb by contact with the air under atmospheric pressure at 7,000 feet elevation, and at the present mean annual temperature of the region, it is found that, even allowing that precipitation in the past has been 25 per cent. greater than at present, and that so much as 60 per cent. of the rainfall could have penetrated to the ore body, the oxygen required to oxidize 500 feet of ore like that now existing would require the contributions of rainfall during a longer period than physicists and geologists are willing to allow for the entire history of the earth.¹ Although all the assumptions made tend to a minimum, the time required, as calculated in this way, is still so inordinately great as to demand a different hypothesis in regard to the manner in which oxygen has been delivered to the place of sulphide decomposition. It is thought therefore that a large part of the oxygen must have been derived from air that circulated through the oxidized capping. The pore space in this material amounts to more than 10 per cent. of the total bulk of the rock and there can be no doubt that when the cellular openings

¹ Becker, G. F., "The Age of the Earth," Smithsonian Misc. Coll., Vol. 56, No. 6, pp. 1-28, 1910. This is the most recent review of various estimates by different methods. Dr. Becker regards 60 million years as the figure most nearly in accord with the data now in hand.

are not water-filled they must be occupied by air. It would seem then, that the greater part of the oxidation must take place during such times as the sulphides are merely moist rather than when they are flooded, because then the water could receive oxygen from the air in contact with it at the same rate at which oxygen is being taken out of solution by the reactions of oxidation. Thus the water would remain saturated under the conditions of partial pressure pertaining to the proportions of various gases contained in the subterranean air. Within a short distance beneath the completely oxidized and porous capping the rock becomes much less pervious, and here the solutions would be present only as capillary films essentially filling the interspaces and therefore leaving no room for air to penetrate. The train of reasoning may be carried one step farther. Even if some air does penetrate the sulphide ore body the circulation would be comparatively sluggish, and since all of the supply must pass by the sulphides in process of oxidation it is apparent that the oxygen might be entirely depleted, so that the gases reaching the ore mass would be merely the inert constituents of the atmosphere plus carbon dioxide.

OXIDATION BY FREE OXYGEN.

Beneath the capping the sulphides first encountered by waters that carry dissolved oxygen are pyrite and chalcopyrite. Just at the top of any porphyry ore body grains of these minerals persist after the removal of chalcocite coatings which they carried at a time when the bottom of the capping was slightly higher than at present. Here too is to be found some pyrite which never carried more than the slightest coating of chalcocite.

The sulphides named are of course readily decomposed by the oxygen-bearing solution. The partial oxidation of pyrite with ferrous sulphate as a product has been indicated by Gottschalk and Buehler¹ by means of the two equations:

¹ Gottschalk, V. H., and Buehler, H. A., "Oxidation of Sulphides," *ECON. GEOL.*, Vol. 7, p. 16, 1912.

The complete oxidation of pyrite may be considered as taking place in some such manner as is outlined by the foregoing equations and the following series,¹ in which equation (3) is derived from (1) and (2).

For chalcopyrite, equations essentially analogous to (1) and (3) are:

Part of the ferric sulphate formed at the upper surface of the body where free oxygen is present decomposes to form basic iron sulphates and hydrated iron oxide, another part may be supposed to pass downward in solution and to attack pyrite, chalcopyrite, and chalcocite. The formation of iron hydroxide may be represented in various ways, for example as follows:

The equations which have been given indicate that the decomposition of pyrite yields sulphuric acid, and ferric sulphate. Under natural conditions, solutions carrying these substances come into contact with chalcocite only a short distance below the point where pyrite and chalcopyrite are first encountered. Here, if any free oxygen remains, chalcocite is decomposed with the formation of cupric sulphate:

¹ Compare Stokes, H. N., "On Pyrite and Marcasite," Bull. No. 186, U. S. Geol. Survey, pp. 15 and 19, 1901; Lindgren, W., "Copper Deposits of Clifton-Morenci District," Prof. Paper U. S. Geol. Survey No. 43, p. 179, 1905. This author gives an extended bibliography relating to pyrite oxidation. Allen, E. T., "Sulphides of Iron and their Genesis," *Min. Sci. Press*, Vol. 103, pp. 413-414, 1911; Gottschalk, V. H., and Buehler, H. A., "Oxidation of Sulphides," *ECON. GEOL.*, Vol. 7, p. 16, 1912; Tolman, C. F., "Secondary Sulphide Enrichment of Ores," *Min. Sci. Press*, Vol. 42, p. 40, 1913.

The reaction indicated by this equation may be considered as using up the last of the free oxygen which can reach a body of enriched porphyry ore under ordinary conditions. At points immediately below those where the free oxygen has been entirely consumed, ferric sulphate and cupric sulphate are present. Both these compounds are capable of oxidizing the sulphides, but the former is more readily reduced than the latter, and it may be supposed to undergo almost complete reduction to ferrous sulphate before the latter can come into play as an oxidizing agent.

OXIDATION BY FERRIC SULPHATE.

Where chalcocite and the other sulphides occur together, and especially where, as in the Ely ore bodies, the chalcocite is in actual contact with pyrite or chalcopyrite in the form of coatings, it is the first mineral to be attacked by ferric sulphate and it acts as a temporary protection against the decomposition of these minerals. The latter point has been proved experimentally by Gottschalk and Buehler¹ and fully confirmed by Wells.²

According to Vogt³ the action of ferric sulphate on chalcocite, which would come into play below the shell of nearly complete oxidation is as follows:

But if the sulphur set free reacts with more ferric sulphate, SO_2 might be formed and with still more ferric sulphate sulphuric acid will result, and eventually we may arrive at the equation suggested by Weed,⁴ which may be deduced from equations (5), (7), and (8):

¹ Gottschalk, V. H., and Buehler, H. A., *ECON. GEOL.*, Vol. 7, p. 31, 1912.

² Wells, R. C., "Electrical Potentials between Conducting Minerals and Solutions," *Jour. Wash. Acad. Sci.*, Vol. 2, pp. 514-516, 1912.

³ Vogt, J. H. L., "Problems in the Geology of Ore Deposits," *Trans. Am. Inst. Min. Eng.*, Vol. 31, p. 166, 1902.

⁴ Weed, W. H., "Enrichment of Gold and Silver Veins," *Trans. Am. Inst. Min. Eng.*, Vol. 30, p. 429, 1901.

Equation (5a) may be regarded also as summarizing a series of oxidation steps such as the following:

The same reagent, ferric sulphate, may be considered as acting on pyrite in a manner represented more or less adequately by the following group of equations where equation (9) is derived by means of equations (6) to (8).

It is to be noted that equation (9) is comparable with equation (1). For chalcopyrite an expression similar to (9) is:

In the study of places in the ore pits where the decompositions indicated above are in progress the observer must remark the short space that intervenes between capping fully oxidized and the subjacent ore wherein to casual observation chalcocite shows no sign of having been attacked. In so far as the decomposing power of the downward moving waters depends upon the presence of free oxygen that power appears in general to be almost spent within a shell of material scarcely more than three feet thick, though a certain amount of impoverishment may be going on to a considerably greater depth through the action of ferric sulphate upon chalcocite (see equations (5) and (5a)). It should be noted, of course, that the under surface of the oxidized capping is very irregular: as a natural result of fractures in the ore mass. A cross section of the surface between the capping and the ore resembles the exaggerated profile comparing mountain heights which is to be found in our older school geographies.

PARTIAL RESUMÉ.

The foregoing discussion should make clear the following points. First, that waters from the surface penetrating a body of porphyry ore will continue to decompose strongly the metallic sulphides present so long as they contain or can acquire free oxygen, or so long as they contain ferric sulphate. Second, that where chalcocite, pyrite, and chalcopyrite are all present the chalcocite will be largely and perhaps fully decomposed before the other minerals are attacked. Third, that the decomposition of chalcocite, pyrite, and chalcopyrite effects the reduction of ferric salts contained in the solution. Fourth, that the decomposition of pyrite, chalcopyrite, and chalcocite each tends to produce sulphuric acid. Fifth, that the decomposition of chalcocite and of chalcopyrite furnish cupric sulphate to the solution. Briefly then, when oxygen-bearing waters reach the upper part of the mass of sulphide-bearing rock the consumption of the dissolved oxygen begins at once, and before the waters can progress downward for any considerable distance all of this free oxygen is used up in decomposing the sulphides. Also within a short distance, ferric sulphate is largely reduced to ferrous sulphate. So long as free oxygen is present the decomposition of chalcocite will progress until no sulphuric acid remains uncombined. It should be added that cuprous and ferric irons are always present in small concentration¹ in any solution containing cupric and ferrous sulphates.

OXIDATION BY CUPRIC SULPHATE.

The progress of the surface derived waters has been followed to the point where they contain no free oxygen and only a minor amount of ferric sulphate, but where they carry ferrous sulphate, cupric sulphate, and sulphuric acid. Thus far on its downward journey it may be assumed that the cupric sulphate has been pro-

¹ Stokes, H. N., "Experiments on the Solution, Transportation, and Deposition of Copper, Silver, and Gold," *ECON. GEOL.*, Vol. 1, pp. 644-650, 1906; Wells, R. C., "Discussion on Secondary Enrichment," *ECON. GEOL.*, Vol. 5, pp. 481-482, 1910.

tected from reduction because at ordinary temperatures and in acid solution it is less readily reduced than ferric sulphate.¹

Beyond the place where the ferric sulphate concentration in the solution has been reduced to a certain minimum, cupric sulphate comes into play as an oxidizing agent. The sulphides with which the solution comes into contact are chalcocite, chalcopyrite, and pyrite. At ordinary temperatures in the absence of oxygen, dilute sulphuric acid does not decompose chalcocite, and Wells² has shown that chalcopyrite and pyrite are probably not attacked under the same conditions. It is to be noted, however, that at high temperatures cupric sulphate reacts with chalcocite³ to form covellite and cuprous sulphate, and on cooling the latter decomposes, a product of its decomposition being metallic copper. On the other hand it would appear that cupric sulphate does attack chalcopyrite and pyrite at ordinary temperatures, so that iron passes into solution as ferrous sulphate, sulphuric acid is formed, and a copper sulphide is deposited. The last part of this statement is supported by the fact that covellite and chalcocite are common products in nature where copper sulphate solutions from the upper zone of oxidation have encountered pyrite and chalcopyrite. Although very little quantitative laboratory work has been done in connection with this subject, the work of Stokes⁴ has furnished two equations which aim to represent the changes pyrite to covellite and pyrite to chalcocite in molecular proportions.

The Stokes equation for chalcocite formed by replacement of pyrite through the action of cupric sulphate may be built up empirically by the method which has been used in the derivation of equations (3) and (9) (see pp. 633 and 635). Thus:

¹ Stokes, H. N., *ECON. GEOL.*, Vol. 1, p. 646, 1906.

² Record of experiments given by E. H. Emmons, *Bull. U. S. Geol. Survey* No. 529.

³ Stokes, H. N., *loc. cit.*, p. 648.

⁴ Stokes, H. N., "Experiments on the Action of Various Solutions on Pyrite and Marcasite," *ECON. GEOL.*, Vol. 2, pp. 15-23, 1906.

⁵ Vogt, J. H. L., "Problems in the Geology of Ore Deposits," *Trans. Am. Inst. Min. Eng.*, Vol. 31, p. 166, 1902.

In a similar manner the following equation indicating the replacement of pyrite by covellite may be deduced:

As thus derived each of the Stokes equations appears to summarize a succession of oxidation effects. It is probable that the complete reactions involve several steps, including the temporary formation of chalcopyrite and perhaps the progressive formation of several mineral species intermediate in composition between chalcopyrite and chalcocite. The minerals of what may be called the pyrite-chalcocite series are given in the following table in which the order is that of increasing copper content.

PYRITE-CHALCOCITE SERIES.

Mineral.	Formula.	Constitution According to Hintze.
Pyrite.....	FeS_2	
Chalcopyrrhotite	CuFe_4S_5	$(\text{FeS}_2)_2(\text{Fe, Cu}'')$
Barracanite	CuFe_2S_4	$(\text{FeS}_2)_2\text{Cu}''$
Cubanite	CuFe_2S_3	$\text{FeS}_2(\text{FeCu}')$
Chalcopyrite	CuFeS_2	$\text{Cu}_2\text{SFe}_2\text{S}_3$
Barnhardtite	$\text{Cu}_4\text{Fe}_2\text{S}_5$	$2\text{Cu}_2\text{SFe}_2\text{S}_3$
Bornite ³ (1)	Cu_3FeS_3	$3\text{Cu}_2\text{SFe}_2\text{S}_3$
Bornite (2)	Cu_5FeS_4	$5\text{Cu}_2\text{SFe}_2\text{S}_3$
Bornite (3)	Cu_6FeS_5	$9\text{Cu}_2\text{SFe}_2\text{S}_3$
Covellite	CuS	CuS
Chalcocite	Cu_2S	Cu_2S

No discussion of the minerals standing between pyrite and

¹ As intermediate between this equation and the one foregoing the following reaction should be considered: $4\text{H}_2\text{O} + 6\text{CuSO}_4 + \text{S} = 3\text{Cu}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4$. See Stokes, *op. cit.*, p. 44.

² Stokes, *op. cit.*, p. 22.

³ Hintze, "Handbuch der Mineralogie," gives the three formulas here presented in his discussion of bornite. The second formula ~~is~~ the one adopted by B. J. Harrington, *Am. Jour. Sci.*, 4th ser., Vol. 16, p. 151, 1903.

chalcopyrite in the table is here attempted, but it may be suggested that the other iron-bearing members of the series are formed successively as stages in the production of covellite or chalcocite through the action of cupric sulphate upon pyrite or chalcopyrite. The basis for this suggestion is given in a foregoing section. Here the contemplated change pyrite to chalcopyrite, though not yet adequately verified by experimental work, may be indicated by an equation which is readily deduced by the method employed in arriving at equation (10):

Next for the changes chalcopyrite to chalcocite and to covellite we may have summary equations analogous to (10) and (11) thus:

Equation (13) and analogous expressions, which may be deduced to indicate the same final products where barnhardtite or any member of the bornite group is taken as the mineral undergoing replacement, are all reducible to a single expression in which the active part of the mineral molecule is considered to be solely the iron sulphide which it contains. Equation (13) may be written thus:

As the expression suggests that $5\text{Cu}_2\text{S}$ has undergone no change we have by subtraction:

Finally by algebraically combining equations (10) and (11) or equations (13) and (14) so as to eliminate FeS_2 from the first

or CuFeS_2 from the second pair, an expression is found for the conversion of covellite into chalcocite, or the reverse:

Presented in this essentially empirical way the chemistry of the secondary copper sulphides centers about the three reactions represented by equations (12), (15), and (16), and these reactions are therefore regarded as particularly worthy of investigation by quantitative work in the chemical laboratory.

ALTERATION OF COVELLITE TO CHALCOCITE.

The supposed change covellite to chalcocite under the action of cupric sulphate (equation 16) has not been established by experiments in which essentially pure natural covellite was used, but as already stated the transition ensues where bornite which has been coated with covellite is further treated with cupric sulphate solution, and the change in color from indigo to gray takes place more quickly in a solution already containing ferrous sulphate in addition to cupric sulphate. The experiment described on page 625 was devised with the expectation that chalcocite would be directly formed without the intervening covellite stage. This expectation was based upon the known reversible reaction between ferrous and cupric sulphates which produces cuprous and ferric ions in the solution:

While chalcocite was not directly formed, the observed hastening of the final chalcocite stage strongly suggests that the relative concentrations of cupric and ferrous salts in the downward moving solution may be one of the principal factors in determining whether covellite or chalcocite is to be the end stage in the sulphide enrichment of copper ores. In this experiment the

¹ Stokes, H. N., "On Pyrite and Marcasite," Bull. U. S. Geol. Survey No. 186, pp. 44-45, 1901. This reversible reaction was studied by Stokes, who says: "It is doubtless to the reduction of the cupric sulphate by sulphur and by ferrous sulphate that the formation of chalcocite from pyrite is to be ascribed."

color change from covellite-blue to chalcocite-gray occurs by gradation through steely-blue. The possible import of this succession of colors which is observed also when natural covellite is touched by iron or copper while immersed in a cupric sulphate solution has been discussed on page 627.

In addition to the experiments with bornite, the attempt was made to change covellite to chalcocite by treating it with a mixture of cupric and ferrous sulphate. In each of three experiments one gram of powdered covellite was treated in sealed tubes with about 55 cm.³ of solution from which all air had been exhausted. In one experiment the strength of the solution with respect to copper was about .02 F.,¹ and with respect to iron .17 F.; in another experiment copper .02 F.; iron .017 F.; while in the third experiment no cupric sulphate was used, ferrous sulphate being present in about .09 F. concentration. At the end of three months the mineral showed no notable change in color in any of the tubes. Chalcocite similarly treated with ferrous sulphate solution also remained apparently unchanged.

If the reaction contemplated by equation (16) when read from left to right could be established, the result would be of noteworthy importance in the theory of chalcocite deposition.

Inspection of this expression indicates that in a solution already containing sulphuric acid in any considerable concentration, covellite, rather than chalcocite, would be the stable mineral. In other words, a solution of relatively high acidity would tend to the formation and persistence of covellite while decreasing acidity would favor deposition of chalcocite. Thus, theoretically considered, it follows also that where silicate or carbonate minerals are present to take up free sulphuric acid, chalcocite would be the more stable of the two sulphides, a conclusion which is in harmony with the very considerable aggregate loss of bases during the alteration of pyrite porphyry through chalcocite ore to the leached and fully oxidized capping, and also with the observed alkaline reaction of the Brooks mine water.

¹ Here the symbol F. is used to indicate formula weight.

VOLUME RELATIONS IN CHALCOCITE DEPOSITION.

The replacement of pyrite by chalcocite, if considered as taking place according to equation (10), would involve a material increase in volume, whereas the corresponding replacement of chalcopyrite by chalcocite according to equation (13) would occur with a slight decrease in volume. Definite figures can not, of course, be given to represent these theoretical changes in volume but if the limits are calculated¹ the figures for pyrite to chalcocite show expansion ranging between 54 and 75 per cent., while those for chalcopyrite to chalcocite show contraction ranging from 6 to 15 per cent. From this it would appear that the replacement of chalcopyrite by chalcocite would take place more readily than the replacement of pyrite by chalcocite if cupric sulphate is the only reagent in the solution to be considered. That chalcopyrite is actually more susceptible than pyrite to replacement by chalcocite is strikingly illustrated by relations to be noted in specimens of porphyry ore from the Ely mines. Detailed examination of polished surfaces and of thin slices shows that as a rule most of the secondary chalcocite has formed on chalcopyrite. In certain specimens containing no visible chalcopyrite the pyrite has been deeply changed to chalcocite, but where both of the primary sulphides are present and where the chalcopyrite grains are deeply coated with chalcocite, the neighboring grains of pyrite are either covered by very thin films or have not been coated at all. Similar relations of sensitiveness to chemical attack are exhibited under the following experimental conditions: If fragments of chalcopyrite and of pyrite are touched simultaneously by pieces of iron while immersed in a solution of cupric sulphate, a very noteworthy effect is immediately apparent on the surface of the chalcopyrite but the pyrite at first seems to be inert. It is possible by this procedure to form on chalcopyrite a brilliant blue coating, presumably covellite, and to withdraw the iron pieces while the pyrite is still bright and fresh.

From the volume relations which have been indicated and the

¹ In these calculations the figures used for specific weight are: pyrite, 4.83-5.2; chalcopyrite, 4.1-4.2; chalcocite, 5.5-5.8.

observed scanty replacement of pyrite by chalcocite in the porphyry ores, the writer is inclined to the belief that in general the replacement of pyrite by chalcocite does not take place unless the active solution contains, in addition to cupric sulphate, some other substance capable of attacking either the pyrite or the chalcocite. Many observations indicate that metasomatic replacement of one mineral by another usually takes place in such a way that the new mineral occupies the same space as the old mineral. This relation has been convincingly set forth by Lindgren,¹ and by Bastin.² With reference to secondary chalcocite, Ransome³ makes the following statement:

"In the Miami-Inspiration ore bodies of the Globe district, many of the specks of chalcocite are solidly embedded in the silicified schist and in veinlets of quartz, so that they have the appearance of being products of the earliest period of mineralization. Yet the evidence here is conclusive that these specks of chalcocite have resulted from the alteration of pyrite and chalcopyrite, and probably in most cases exactly fill the space once occupied by the present mineral. All stages may be seen from pyrite thinly coated with chalcocite to solid chalcocite."

If the relation of equal volume holds as it is believed to hold in the replacement of pyrite by chalcocite it is obvious that not all the changes involved are summarized by the Stokes equation. In replacement by equal volume the product contains less chalcocite than would correspond molecularly with the pyrite that has been destroyed, and it seems that the removal of the excess material must be accounted for as a result of the attack of some reagent other than cupric sulphate. It is possible that chalcocite replacement of pyrite is promoted by the presence of a minor concentration of ferric sulphate in the active solution. It is difficult to obtain a visible deposit of copper sulphide on pyrite or chalcopyrite by treatment with a solution of cupric sulphate

¹ Lindgren, W., "The Nature of Replacement," *ECON. GEOL.*, Vol. 7, pp. 521-535, 1912.

² Bastin, E. S., "Metasomatism in Sulphide Enrichment," *ECON. GEOL.*, Vol. 8, pp. 51-63, 1913.

³ Ransome, F. L., "Criteria of Downward Sulphide Enrichment," *ECON. GEOL.*, Vol. 5, p. 218, 1910.

alone, yet blue coatings may be readily formed on either mineral if ferrous sulphate is added. This fact may have a direct bearing on the problem under consideration. The reaction is accelerated by heating, but it takes place within a few hours at ordinary temperature. During the progress of the reaction insoluble iron compounds are precipitated and after sulphide deposition has taken place the solution responds to the test for ferric iron with potassium sulphocyanide. As already noted (p. 640) ferric sulphate is formed by the interaction of ferrous and cupric sulphates in solution, so that obviously secondary covellite and chalcocite are both formed in the presence of at least minute concentrations of ferric sulphate.

COMPOSITION OF MINE WATER.

Chemical analyses of samples of water from the Ruth and Brooks porphyry mines are given in the subjoined table:

Composition of Waters from Porphyry Mines.

(Parts per million.)		
	I.	II.
Na	35	33
K	11	27.6
Ca	126	105.7
Mg	trace	26.3
Fe''	19	36.4
Fe'''	none	42.0
SO ₄	256	556.0
Cl	8.5	55.4
CO ₂	38 ¹	
HCO ₃	117 ¹	
SiO ₂	28	94.0
Total	638.5	976.4
Reaction	alkaline	not stated

I. Water from Brooks inclined shaft of the Giroux Consolidated Company collected in September, 1910. The preceding summer had been dry and the water stood about 230 feet below

¹ Total CO₂ distributed between CO₂ and HCO₃ in proportions to balance the reacting values of bases and acids. As reported, the analysis shows HCO₃ 156 parts per million.

the surface. A test was made for copper with negative result. Analysis made in the laboratory of the Geological Survey by Dr. Chase Palmer. Ferrous iron was determined immediately after taking the sample to be 22 parts per million so that the iron was all in the ferrous state. For this determination the writer is indebted to Mr. A. J. Sale.

II. Water from Ruth mine. Composition calculated to parts per million of ions, from analysis by Dr. Harry East Miller, recorded by A. C. Lawson.¹

The analysis of the Ruth mine water was originally stated in the following form:

Analysis of Ruth Mine Water Grains per Gallon of 231 Cu. In.

SiO ₂ + insoluble matter	5.50
NaCl	4.88
KCl	.55
K ₂ SO ₄	2.96
FeSO ₄	5.77
Fe ₂ (SO ₄) ₃	8.78
CaSO ₄	20.99
MgSO ₄	7.61
Organic matter and water of sulphates	6.96
Total	64.00

In regard to this analysis Professor Lawson¹ says:

"It is probable that the proportion of ferric sulphate is higher than is actually the case in the mine, owing to the difficulty of preventing oxidation of the ferrous salt. The result is interesting as an indication of the materials which are being leached from the porphyry by the descending meteoric waters. Another sample of the mine water analyzed in the mine laboratory as expeditiously as possible after collection, by Mr. Herbert Ross, gave results from which it would appear that the iron of the mine water is nearly all in the ferrous state."

The form in which the Ruth analysis is stated does not enable classification of the water, but the Brooks analysis indicates the following characteristics:²

¹ Lawson, A. C., "The Copper Deposits of the Robinson Mining District, Nevada," Pub. Bull. Univ. of Cal., Dept. of Geology, Vol. 4, p. 332, 1906.

² Palmer, Chase, "The Geochemical Interpretation of Water Analysis," Bull. U. S. Geol. Survey No. 475, p. 13, 1911.

	Per cent.
Primary salinity	20.6
Secondary salinity	42.8
Primary alkalinity	00.0
Secondary alkalinity	29.0
Sub alkalinity	7.6
	<hr/> 100.0

It should be noted that the mine waters that have been analyzed are in a way the complement of the pyrite porphyry for they contain in solution the bases which are known to have been leached out of the rock during the processes of enrichment and of ore decomposition. The high proportion of lime in both of the mine waters indicates that the mines have received contributions of water through percolation from the limestone masses which adjoin the ore masses, because the porphyry ores are essentially free from lime. The indicated absence of magnesium in the Brooks mine water appears to be anomalous for the analyses of samples indicate that the ore porphyry of the district carries more of this element than it does of lime.

The alkaline reaction of the Brooks mine water bears out the suggestion that has been made on another page that the waters from which chalcocite has been deposited were probably not strongly acid.

CHEMICAL CHARACTER OF SOLUTIONS WHICH DEPOSIT CHALCOCITE.

Among the products of the oxidation of pyrite is sulphuric acid so that the solutions which carry copper from the places of decomposition to those of chalcocite deposition must be distinctly acid when they are first formed, and it is well known that waters collected from the upper levels of mines in pyritic ore bodies usually show an acid reaction. However, carbonate and many silicate gangue minerals are decomposed by acids and when such minerals are long in contact with the descending solutions their bases are taken into combination and the original acidity of the solution gradually disappears. Attention has been recently directed to the fact that the waters in certain copper mines are

less and less acid at lower and lower levels,¹ and are alkaline in some of the deepest workings, and there can be little doubt that this state of affairs is general. A sample of water collected from a point near the top of the water table in one of the Ely porphyry mines was found to be distinctly alkaline (see p. 644). Although these observations have led to the suggestion that a reduction of acidity in descending metalliferous solutions may be important in connection with secondary sulphide deposition² it is not obvious, merely because solutions in a given case have become alkaline as a result of reaction with gangue minerals, that the conclusion must follow that no part of the dissolved copper could have been deposited before the alkaline state had been reached. The opposite contention that acidity may be necessary for the progress of copper sulphide enrichment is suggested by Welsh³ and Stewart who found by experiment that, while chalcopyrite may be coated with films resembling bornite by treatment with cupric sulphate solution, the presence of calcite prevents the reaction. These writers state that,

"The ordinary copper sulphate is acid and the effect of the calcite may be to neutralize this acidity."

The present writer has observed that artificial coatings may be readily formed on chalcopyrite in solutions possessing only the slight acidity due to the presence of cupric and ferrous sulphates, but that when a little sulphuric acid is added the mineral remains untarnished. Also Winchell⁴ states that, while he obtained chalcocite in the presence of SO₂, without this reducing agent pyrite was not visibly attacked by acidified cupric sulphate at the end of two years.

From the foregoing observations it appears likely that under natural conditions chalcocite will not replace primary sulphides

¹ Emmons, W. H., "The Enrichment of Sulphide Ores," Bull. U. S. Geol. Survey No. 529, pp. 60 and 89, 1913.

² Wells, R. C., discussion of a paper by F. L. Ransome, on "The Criteria of Downward Enrichment," ECON. GEOL., Vol. 5, p. 482, 1910; Emmons, W. H., *loc. cit.*, p. 60.

³ Welsh, T. W. B., and Stewart, C. A., "Note on the Effect of Calcite Gangue on the Secondary Enrichment of Copper Veins," ECON. GEOL., Vol. 7, pp. 785-787, 1912.

⁴ *Op. cit.*, p. 274.

when the acidity of the cupriferous solutions exceeds some rather small minimum, but that an alkaline condition is not necessary in order that the reaction may proceed.

CHALCOCITE DEPOSITION IN THE PRESENCE OF CALCITE.

At several places in the Ely district chalcocite has been noted in the form of secondary coatings on pyrite and chalcopyrite disseminated through masses of partly weathered metamorphosed limestone lying beneath a surficial shell of fully oxidized material. Considerable bodies of enriched material in altered limestone masses have been developed in the Old Glory mine where the original matrix of the primary sulphides, though consisting largely of lime silicate minerals, also comprises considerable calcite. In material of this sort the deposition of chalcocite would appear to be uncommon according to D. C. Bard¹ who states, as a result of his observations, that sulphide enrichment is usually lacking where the gangue comprises much calcite. The explanation offered is that copper sulphate reacts with calcite to form copper carbonate, so that only an excess of the copper salt above that required for replacement of calcite can finally appear as covellite or chalcocite.

Welsh and Stewart² treated chalcopyrite in the presence of calcite, and also chalcopyrite mixed with quartz, with moving solutions of cupric sulphate in upright tubes so arranged that the lower part of the column was continually flooded. These writers state that,

"In the calcite chalcopyrite mixture the calcite above the water level was distinctly tinged with green, while none of the chalcopyrite showed any change. In the tube containing quartz and chalcopyrite no change above the water level was noted, but the chalcopyrite for four inches below this level showed clearly the purple tinge of bornite, and upon closer examination some thin black films were found."

In this experiment the solution draining from the calcite-chalcopyrite mixture still contained cupric sulphate, and the authors suggest that secondary sulphide was not precipitated be-

¹ Bard, D. C., "Absence of Secondary Copper-sulphide Enrichment in Calcite Gangue," *ECON. GEOL.*, Vol. 5, pp. 59-61, 1910.

² *Op. cit.*

cause the solution may have been rendered alkaline through reaction with the calcite. Whether the explanation offered is the true one or not, on its face the experiment bears out the suggestion presented by Bard that the presence of calcite is unfavorable for the deposition of secondary copper sulphides. However, the present writer has found that calcite does not precipitate copper from a solution containing both cupric and ferrous sulphates, and, furthermore, that by means of such a solution pyrite and chalcopyrite may be readily coated with secondary sulphide films in the presence of large amounts of calcite.

Because specimens of the chalcocite-bearing ore from the Old Glory mine now contain no calcite, the possibility remains that here the secondary sulphide was not actually deposited in the presence of calcite but only in material from which calcite had previously been removed as the result of solution by sulphuric acid. Observations more detailed than those that have been made would be required to determine whether the last of the original calcite disappeared before or after chalcocite enrichment occurred.

WATER TABLE RELATIONS DURING CHALCOCITE DEPOSITION.

The position of standing water in the porphyry mines of the Ely district varies from time to time. No systematic record of rise and fall is at hand, but in the autumn of 1910 the water in some of the mines was about 30 feet higher than in the autumn of 1909. In general the chalcocite porphyry, though lying mainly above the water table, continues downward below the highest position of standing water, and possibly below the levels to which the water top may sink at the lowest stage. It seems probable, however, that no porphyry containing so much as 0.5 per cent. of secondary copper occurs at lower levels than those where the top of ground water may have stood during the dry epochs of the Quaternary period. Before the first expansion of the Great Basin lakes and in the interval between the two expansions the climate was probably somewhat drier than it has been during the present epoch, and the mean position of standing water may have been for considerable periods from 50 to 100 feet lower than it is now. In the Alpha mine, where the ore bodies are not of the disseminated

type but are rather of the nature of compact segregations, the water table is now fully 200 feet higher than it has been formerly. Here oxidation has penetrated more than 1,200 feet below the surface, while the natural level of standing water is at a depth of about 1,020 feet. On the other hand, during those epochs when the Great Basin lakes were in flood stage, in the porphyry ore masses the water level certainly stood much above its present mean position. Deposits of iron-copper sinter that occur near some of the mines furnish good evidence that the chalcocite ore was once at least submerged to a height so great that part of the products of its oxidation escaped into the surface drainage. This event is correlated on physiographic evidence with the first Quaternary humid epoch, when rather steady streams were undoubtedly flowing in the district, and as the next later humid epoch seems to have been wetter than the first, the ore bodies may have been submerged a second time. If the later flood stage of the groundwater was higher than the earlier, the top of the ore body would have been below water level, a supposition which would adequately account for the lack of sinter deposits in the swales which were eroded during the second humid epoch. Presumably similar alternations of low and high water were characteristic of late Pliocene time when the principal segregation of chalcocite is believed to have occurred.

It would seem that a considerable body of sulphides lying above the water table would offer the best possible conditions for the retention of copper taken into solution by oxidizing surface waters. This suggestion is based in part upon the conception that the speed of reaction between copper solutions and primary sulphides is slow under the most favorable conditions, and presumably extremely slow after grains of pyrite and chalcopyrite have received moderately deep films of chalcocite. A long journey involving contact with a very large number of primary sulphide grains would be more favorable to precipitation of a larger proportion of the dissolved copper than a short journey during which correspondingly few grains would be encountered by any unit volume of solution. A low water table and a high position of the ore top would tend to produce a thick ore body of rather

uniform grade from near its top to somewhere near its bottom. So long as the solutions could be exhausted above standing water, the enriched material would grade imperceptibly into the primary material. On the other hand, if copper were not exhausted above standing water, precipitation should continue within a relatively thin shell of material just below the water table, because the solutions in this situation would necessarily move laterally rather than downward, and their flow or passage would be at a diminished rate, permitting much longer contact with reacting primary sulphides in a limited mass of material. During such times as the groundwater may have stood well up in material previously enriched, the tendency would have been to produce layers of ore carrying more than the average amount of copper. What is possibly the record of a former high stage of groundwater is seen in the local occurrence of particularly rich layers of ore beneath from 20 to 50 feet of medium-grade material lying just under the oxidized capping.

DATES OF CHALCOCITE ENRICHMENT.

In foregoing sections which deal with the chemistry of chalcocite enrichment, the idea has been developed that the porphyry ore bodies of the Ely district are currently subject to wastage in their upper portions, and to accretion of copper in their lower portions. A similar downward transfer of copper has undoubtedly been going on in the past, and it is obvious that the present ore bodies are the successors of similar segregations which formerly existed above the places where the enriched material is now found. The rocks along the metamorphosed zone were undoubtedly charged with pyrite and chalcopyrite for several hundred, and perhaps for several thousand, feet above the present surface, and the earliest formation of disseminated chalcocite ores may be thought of as having occurred when, as a result of erosion, the masses of pyritized rock first came under the action of oxidizing solutions. This conception would carry the operations of chalcocite enrichment a long way back into the past.

It is held that the volcanic rocks, of probable Pliocene age, which now occur from place to place within the district formerly

extended over much wider areas, and probably covered all of the ore belt. But the pyritized rocks had been undergoing erosion for a long time before the period of volcanic extravaſation and there can be no reasonable doubt that the processes of chalcocite enrichment had been going on hand in hand with the gradual lowering of the land surface. However, it is not safe to conclude that ore bodies comparable with those of the present existed at any particular time, and it is not possible to state whether or not thick masses of disseminated chalcocite ore existed when the rhyolite lavas flowed out upon the old land surface.

The processes of weathering and chalcocite deposition must have been in abeyance during a long period devoted to the erosion of the rhyolite, but when the rocks of the metamorphosed zone had been partially stripped these processes again came into play and have since been operative except for such interruptions as resulted when the ore bodies may have been overtopped by groundwater.

On physiographic grounds it seems certain that there has been practically no erosion of the ground above the ore bodies since the beginning of the pre-Bouneville epoch (the first division of Quaternary time) during which great alluvial cones were built up throughout the region about the mouths of lateral canyons that open out into the broad north-south valleys. All of the secondary copper contained in the present ore bodies had therefore been segregated below the now existing surface before the close of the Pliocene, and the fact that thick masses of enriched material exist is due to conditions during the latter part of Pliocene time that were prevailingly favorable for the precipitation and accumulation of copper in the form of chalcocite.

While essentially all of the secondary or added copper now present in the disseminated ore bodies had been brought together before the beginning of Quaternary time, it seems almost necessary to believe that redistribution of the metal has since been going on with the result that the tops of the ore bodies have been gradually falling to lower and lower positions. No basis has been found, however, for determining what portion of the depth of oxidized capping is attributable to Quaternary decomposition.