UPWARD SECONDARY SULPHIDE ENRICHMENT¹ AND CHALCOCITE FORMATION AT BUTTE, MONTANA.

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Though first hinted at by Gonzalo y Tarín² in his monograph on Huelva, in 1888, and by Fuchs and de Launay,³ in 1893, the development of the idea of secondary sulphide enrichment is the result almost entirely of the observations of American geologists and constitutes perhaps the most important American contribution to the theory of ore-deposits.

The pioneer papers of S. F. Emmons,⁴ Weed,⁵ and Van Hise⁶ appeared almost simultaneously in the same year (1900). Ransome's⁷ valuable paper on "Criteria of Downward Sulphide Enrichment" was followed by interesting discussions by Foote, Gregory, Keyes, Louis, Sales, Wells, and A. N. Winchell in volume five of ECONOMIC GEOLOGY. An excellent short summary of secondary sulphide enrichment (with bibliography) by Tolman⁸ appeared early in 1913, and recently a comprehensive summary of the whole subject by W. H. Emmons⁹ has been published by the United States Geological Survey.

¹ The objection to the use of the term has been pointed out to the writer by Prof. C. F. Tolman and Prof. W. H. Emmons. Prof. Emmons suggests *deep-seated metasomatic development of chalcocite*, but for the sake of argument the term as given is retained.

² Reference cited by Becker in Emmons' volume on Ore Deposits, p. xxxix.

³ "Traité des Gîtes Minéraux et Metallifères," Vol. 2, pp. 230-234.

⁴ "The Secondary Enrichment of Ore-Deposits," *Trans. Am. Inst. Min. Eng.*, Vol. 30, pp. 177-217.

⁵ "Enrichment of Mineral Veins by Later Metallic Sulphides," *Bull. Geol. Soc. Am.*, Vol. 11, pp. 179-206.

⁶ "Some Principles Controlling the Deposition of Ores," *Trans. Am. Inst. Min. Eng.*, Vol. 30, pp. 27-177.

⁷ *ECON. GEOL.*, Vol. 5, pp. 205-220, 1910.

⁸ *Mining and Scientific Press*, Vol. 106, pp. 38, 141, 178, 1913.

⁹ "The Enrichment of Sulphide Ores," *Bull. 529, U. S. Geol. Surv.*, 1913.

As usually defined, secondary sulphide enrichment refers to the enrichment of sulphide minerals by descending, cold, acid (or possibly neutral) waters. It is usually explained by the action of soluble sulphates of the oxidized zone upon the unaltered sulphides below.¹

In a recent study of a disseminated copper ore from a mine in Plumas County, California, the name and location of which must be withheld for the present, the writer came to the conclusion that one of the ore-minerals, chalcocite, which appears as rims around the bornite, was formed by ascending, rather than by descending, solutions.

The ore-minerals in this Plumas County mine include magnetite, hematite, bornite, chalcopyrite, and chalcocite. They

FIG. 67. ($\times 25$ times.) Norite-diorite from Plumas County, California.
O = Ore minerals; hy = hypersthene; pl = plagioclase; bi = biotite.

are disseminated through a norite-diorite (consisting of plagioclase (AbAn), hypersthene, diopside, hornblende, biotite, and chlorite with accessory apatite, titanite, interstitial quartz, analcite, and epidote) in such a way as to indicate that they have been formed at the end of the magmatic period by pneumatolytic²

¹ Grout (ECON. GEOL., Vol. 8, pp. 407-433, 1913) has recently advanced the view that the sulphides of the secondary enrichment zone may be formed by the interaction of soluble sulphates from above with alkaline solutions from below.

² I use this word in a general sense, not in its original restricted sense.

agents which have deposited their metallic contents by a partial replacement of the silicate minerals. Fig. 67 is a drawing of a thin section showing the relation of the ore-minerals (mostly hematite and magnetite in this case) to the hypersthene, biotite and plagioclase. The replacement of the silicates by ore-minerals is unmistakable (see especially biotite at the left-center of the drawing). This is a magmatic sulphide ore but it may be classed under the "Gîtes de immédiat départ" of de Launay,¹ for which there is no suitable English equivalent. The silicate minerals in these Plumas County ore-bearing rocks are (for the most part) perfectly fresh. The replacement of the feldspars and other silicates has not been accompanied by silicification, or kaolinization, or by sericitization to any great extent². What little hydrothermal alteration there is, is almost certainly independent of the ore-deposition, though there are evidences that hornblende was formed from diopside and chlorite from biotite by pneumatolysis. It is in no sense comparable to the disseminated mineralization of the so-called porphyry coppers of Bingham and Ely.

FIG. 68. ($\times 25$.) Primary chalcocite (cc), bornite (bo), and chalcopyrite (cp) in feldspar (f). q=quartz. Plumas County, California.

A complete description of this interesting ore-deposit will be presented in a future paper. For the present I will simply present the evidence which points to upward secondary sulphide enrichment. Fig. 68 (from a granodiorite or quartz-monzonite

¹ "Gîtes Minéraux et Metallifères," Vol. I, p. I, 1913.

² In the only slide of the suite which contains tourmaline the feldspars are in part sericitized and in part perfectly fresh.

variant of the main rock-type) shows chalcocite¹ which, together with bornite and chalcopyrite, have partly replaced a feldspar crystal, for the two portions of the feldspar, *f* and *f'*, are in optical continuity.

The secondary chalcocite is found in five different specimens as rims around bornite principally. In Fig. 69 primary bornite and chalcopyrite have replaced biotite and the secondary chalcocite occurs around the bornite and to a slight extent around the chalcopyrite. In this specimen the biotite and plagioclase are perfectly fresh. The only possible mineral which may be called

FIG. 69. ($\times 25$.) Primary chalcopyrite (*cp*) and bornite (*bo*) and secondary chalcocite (*cc*) with biotite (*bi*) and plagioclase (*pl*). Plumas County, California.

an alteration product is a little chlorite and it is probably a pneumatolytic mineral.

Another specimen consists of plagioclase, quartz, chlorite, tourmaline with primary magnetite, primary bornite and secondary rims of chalcocite around the bornite. The evidence of pneumatolysis is clear in this case. The chlorite has probably been formed from biotite, though there are no remnants of biotite left. The plagioclase is in part fresh and in part sericitized. There is evidence that this is oxidized ore.

In another specimen, consisting of perfectly fresh plagioclase, hornblende and biotite with magnetite and hematite, there was found a piece of compact chalcocite with a core of bornite. This

¹ This was first thought to be original chalcocite but a study of the polished section seems to show that it may be secondary.

specimen came from a soft seam, but there was no evidence of oxidation.

Narrow one-inch pegmatite veins consisting of plagioclase (albite) quartz, titanite, apatite, epidote, chlorite and calcite contain chalcopryrite and a little bornite as primary constituents. Fig. 70 is a sketch of bornite with secondary rims of chalcocite from one of these pegmatites. The constriction in the lower part of the right-hand sketch of Fig. 70, the embayment of chalcocite in the upper part of the left-hand sketch, and the isolation of bornite in spots is conclusive evidence that the chalcocite was formed, in part at least, at the expense of the bornite and not simply as a deposition around the bornite.

FIG. 70. ($\times 25$.) Secondary veins of chalcocite (cc) around bornite (bo) in pegmatite. Plumas County, California.

In still another specimen, with a high copper content, chalcocite occurs as rims around bornite. In this case the positive identification of the chalcocite is based upon a chemical analysis of selected rock chips made by Mr. G. W. Jordan, chemistry student at Stanford University. His results are as follows:

	Mol. Ratios.
Cu = 43.95	0.691
Fe = 5.12	0.109
S = 14.15	0.472

A mixture of fifteen parts of chalcocite (Cu_2S) and eight parts of bornite (Cu_5FeS_4) is necessary to account for the high copper to sulphur ratio indicated by the analysis. As chalcopryrite is absent in the slide and as a nitric acid solution was taken,

the analysis, on recalculation, proves that the chalcocite contains iron (about 6 per cent.).

There are three possible methods of formation of the chalcocite rims.

1. Simple deposition (primary enrichment).
2. Descending secondary sulphide enrichment.
3. Ascending secondary sulphide enrichment.

As the chalcocite is formed at the expense of the bornite (see Fig. 70) the first method of formation may be dismissed.

Whatever its source, the chalcocite is a secondary¹ mineral. The question remains as to whether the formation of the secondary chalcocite was caused by downward-moving, cold, oxidizing, acid solutions or by upward-moving, hot (or warm), non-oxidizing, alkaline solutions.

Aside from the microscopic evidence presented, the geological evidence kindly supplied me by Mr. H. W. Turner, of San Francisco, points to the formation of chalcocite by ascending solutions of some kind. According to Mr. Turner there are no strong persistent fissures or crushed zones. The only fissures in the norite-diorite which have any evident connection with mineralization are the narrow pegmatites mentioned above. Most of the fractures observed are post-mineral. Joint-seams are numerous but, as far as examined, they do not contain sulphides. Near the surface the fractures and joint planes contain chrysocolla. No effects of dynamic or contact metamorphism are apparent.

Of the five specimens containing secondary chalcocite, three have no possible connection with oxidation. Of the other two, one (Fig. 69) contains perfectly fresh biotite and plagioclase. This specimen occurs just below a seam along which there was, according to Mr. Turner, some oxidation by surface waters. The presence of oxidation near this seam is probably a coincidence, for the specimen with tourmaline shows much more alteration (sericitization) and it occurs without any possible connection with oxidizing surface waters. In the case of the chalcocite in the pegmatite (Fig. 70) there seems to be no possible con-

¹ I use *secondary* in a mineralogical sense.

nection with oxidation. The calcite, chlorite, and epidote which occur in the pegmatites are not alteration products, though they are the last minerals to be formed (probably at comparatively low temperatures from solutions).

Both the geological evidence and microscopic evidence, especially the freshness of the silicate minerals, the absence of silicification and kaolinization, and the absence of porosity, are opposed to the idea of downward sulphide enrichment by sulphate waters. There remains to be considered secondary sulphide enrichment by ascending solutions which were probably alkaline. Copper sulphide is somewhat soluble in ammonium sulphide. The compound $(\text{NH}_4)_2\text{S}_5 \cdot 2\text{CuS}$ or $(\text{NH}_4)_2\text{Cu}_2\text{S}_4$ is known, as are also $\text{Na}_2\text{S} \cdot 2\text{CuS} \cdot \text{Cu}_2\text{S}$ and $\text{K}_2\text{S} \cdot 2\text{CuS} \cdot 3\text{Cu}_2\text{S}$.¹ The possibility of copper acting as an acid-forming element is shown by the above compounds as well as by double salts such as $\text{CuF}_2 \cdot 2\text{KF}$ and $\text{CuCl}_2 \cdot \text{KCl}$. A potassium cuprate is said to have been prepared by Fremy. It is possible to write various equations which furnish Cu_2S (chalcocite) by the action of alkaline sulpho-salts upon Cu_5FeS_4 (bornite) but in the absence of experimental proof it is hardly advisable.

The primary ores of the Plumas County norite-diorite were probably formed by gases or pneumatolytic vapors which deposited their metallic contents by replacing the silicate minerals. The secondary chalcocite found as rims around the bornite were probably deposited at a lower temperature at a somewhat later stage by gaseo-aqueous or hydrothermal solutions. The joint-seams referred to perhaps facilitated the passage of these solutions. Later there was slight oxidation by surface waters along the seams but the secondary chalcocite was evidently formed by solutions from below rather than by the surface waters from above.

According to the logical use of the term, secondary sulphide enrichment does not necessarily mean downward enrichment though it is usually so defined. As sulphides (and sulpho-salts) are involved and the chalcocite is secondary and as there is en-

¹ Moissan, "Traité de Chémie Minérale," Vol. 5.

richment the term *upward secondary sulphide enrichment* may be used. It is somewhat cumbersome but I know of no better term. It is perhaps well to contrast it with downward secondary sulphide enrichment.

The idea of upward secondary sulphide enrichment I gained not from any theoretical or *a priori* considerations but from the study of thin sections of the Plumas County ores to which reference has been made.

Several months after I reached the conclusion that the chalcocite in the Plumas County ores was formed by ascending solutions I ran across the following statement made by Weed¹ in an article entitled "Ore Deposition and Vein Enrichment by Ascending Hot Waters."

"The enrichment of mineral-veins as the result of the migration of material from an upper oxidized or disintegrated part of a vein to a lower level, where it is redeposited, is now, I believe, quite generally accepted as one explanation of the occurrence of bonanzas in gold- and silver-veins, as well as that of bodies of high-grade ores in cupriferous deposits. Vogt has called attention to the fact that there are numerous examples of such rich shoots which are 'of exclusively primary character and dependent upon the laws which governed the original ore-deposition.' To this I would add that there are also other examples which are neither of primary origin nor due to descending waters, but result from a reopening of the veins and their penetration by ascending heated waters whose metallic contents are deposited by reaction with the primary pyrite (and possibly other minerals), forming 'secondary' enrichments."

Weed attributes the bonanza silver ores of Neihart, Montana, and the enargite of Butte, Montana, to secondary enrichment by ascending solutions but says nothing about chalcocite.

This paper by Weed has evidently been overlooked, even by Weed himself, for in his recent report of Butte² there is no mention of even the possibility of upward secondary enrichment.

The formation of chalcocite at Butte is one of the most interesting and widely discussed questions in the literature of ore-deposits, for the Butte mines are unique because of the great

¹ *Trans. Am. Inst. Min. Eng.*, Vol. 33, p. 747, 1902.

² Prof. Paper, U. S. Geol. Surv., No. 74, 1912.

depths at which large masses of chalcocite-bearing ores are found.

Until recently chalcocite has been generally looked upon as a product of descending sulphide enrichment. The discovery of graphic intergrowths of chalcocite and bornite in the Virgilina district of North Carolina and Virginia by Laney,¹ in 1911, amounted practically to proof of the primary origin of chalcocite. Graton and Murdoch,² from a careful microscopic study, come to the conclusion that chalcocite is often primary.

As to the Butte chalcocite S. F. Emmons,³ H. V. Winchell,⁴ Kirk,⁵ and Weed,⁶ all express the opinion that it is largely of secondary origin.

Sales⁷ was the first to assign a primary origin to the deep-seated chalcocite at Butte. Graton and Murdoch⁸ come to the same conclusion by a microscopic study of the ores.

Two of the more recent complete papers which take almost diametrically opposite views as to the origin of the Butte chalcocite are those of Kirk⁹ and Sales.¹⁰ The controversy concerns the gray massive or solid chalcocite mixed with bornite and enargite from the deeper levels.

All will probably admit that the "sooty" chalcocite, which occurs just below the oxidized zone, is formed by descending waters while the occurrence of large, distinct crystals¹¹ of chalcocite in the deepest levels may be taken as evidence of their primary origin by ascending solutions.

Kirk's¹² arguments in favor of the secondary origin of chalco-

¹ ECON. GEOL., Vol. 6, pp. 399-411.

² *Bull. Am. Inst. Min. Eng.*, No. 77, pp. 741-797, May, 1913.

³ *Loc. cit.*, 1900.

⁴ *Bull. Geol. Soc. Am.*, Vol. 14, pp. 269-276, 1903.

⁵ ECON. GEOL., Vol. 7, pp. 35-82, 1912.

⁶ Prof. Paper 74, U. S. Geol. Surv., 1912.

⁷ ECON. GEOL., Vol. 5, p. 681, 1910.

⁸ *Loc. cit.*, p. 768.

⁹ ECON. GEOL., Vol. 7, pp. 35-82, 1912.

¹⁰ *Bull. Trans. Am. Inst. Min. Eng.*, No. 80, pp. 1523-1626, August, 1913.

¹¹ I have seen pseudo-hexagonal chalcocite crystals of tabular habit from Butte which measure up to one inch in size.

¹² *Loc. cit.*

cite by descending solutions are based principally upon its association with kaolin. As Sales¹ has pointed out, this association does not prove that kaolin and chalcocite have formed from the same kind of solutions. But even if that be granted, the kaolin may have been formed by ascending waters instead of by descending waters. Collins,² Butler,³ Rösler,⁴ and Gregory,⁵ all assign a deep-seated origin to some kaolinite. Rösler goes so far as to say that it is always a pneumatolytic product, but its occurrence in sedimentary rocks is an argument against this extreme view. Kirk⁶ says that casual observers distinguish between primary and secondary chalcocite according as it is in solid or sooty form. As Kirk determined the secondary character of both forms by microscopic examination he lays no stress upon the difference between the two forms. He thinks that solid chalcocite formed when the deposition of chalcocite kept pace with the solution of pyrite and the sooty chalcocite when the solution of pyrite was more rapid than the deposition of chalcocite. This may be true, but Graton and Murdoch⁷ state that the sooty chalcocite represents a stage of incipient decomposition. At any rate these two forms of chalcocite at Butte represent distinct stages of chalcocite deposition.

In a recent, very complete article on the Butte ore-deposits, Sales⁸ presents evidence that the massive chalcocite is largely primary and has been formed by ascending solutions. Mr. Sales' article is probably the most complete one that has yet appeared on the Butte deposits and as he has had unusual opportunities for observation and study his conclusions deserve careful consideration.

His arguments favoring the primary origin of chalcocite are as follows:

¹ *Loc. cit.*, p. 1624.

² *Mineralogical Magazine*, Vol. 7, p. 205.

³ *Ibid.*, Vol. 15, p. 128.

⁴ *Neues Jahrb. f. Min.*, Beil. Bd., Vol. 15, p. 231, 1902.

⁵ *ECON. GEOL.*, Vol. 5, p. 678.

⁶ *Loc. cit.*, p. 73.

⁷ *Loc. cit.*, p. 770.

⁸ *Loc. cit.*

1. Its occurrence in abundance at deep levels.
2. Its intimate association with bornite, pyrite and enargite in a manner indicating their simultaneous deposition.
3. The occurrence of chalcocite is independent of the present surface topography.
4. Chalcocite is due to a relatively old mineralization for there are indications that massive chalcocite existed prior to the Steward fault period.
5. Chalcocite replaces granite at deep levels.
6. Certain ore-shoots are capped by hundreds of feet of barren crushed granite.
7. The occurrence of undoubted primary ores in faults of the Steward system which cut chalcocite ore-bodies in the Blue veins is proof that ascending solutions depositing primary ore continued in action after the formation of the Blue vein chalcocite.
8. The size and richness of the ore-bodies have no apparent relation to the depth of the zone of oxidation.
9. In the Mountain Chief ore-shoot of the Jessie vein an ore consisting of chalcocite, bornite, enargite, and pyrite lies below chalcopyrite ore (see plate V., p. 1557).

All of these arguments, in favor of the formation of primary chalcocite by ascending solutions, are valid. Sales' valuable paper lacks but one thing and that is the microscopic evidence of the primary character of the chalcocite. If we omit the second of the above arguments, which was apparently not based upon microscopic examination, we have proof simply that the chalcocite is formed by ascending solutions. The primary or secondary nature of the chalcocite, then, is in doubt. Simpson¹ made a microscopic study of the Butte ores but as his object was primarily to determine to what the copper content of the low-grade copper-bearing pyrite was due, he naturally avoided the high-grade chalcocite ores. He found, however, that chalcocite was the last mineral formed.

I have made polished sections of all the rich chalcocite ores from Butte that are available. The specimens consist of solid,

¹ ECON. GEOL., Vol. 3, p. 635, 1908.

massive chalcocite, with which are associated either bornite or pyrite. Unfortunately I do not know the levels or mines from which these specimens come.¹

No. 1 is a massive chalcocite in which are embedded irregular pieces and discontinuous stringers of bornite (see Fig. 71). The secondary nature of the chalcocite is apparent.

No. 2 appears nearly homogenous in the hand specimen but the polished section shows large, irregular pieces of bornite embedded in a matrix of solid chalcocite, the chalcocite being in slight excess. There is also a little pyrite present. As the chalcocite surrounds and penetrates the bornite in veinlets it is evidently formed at the expense of the bornite.

No. 3 consists of irregular streaks of bornite and chalcocite. Although the bornite is in excess the chalcocite constitutes its matrix. The invasion of the chalcocite into the bornite is very clear.

FIG. 71.

FIG. 71. ($\times 5$.) Bornite (bo), chalcocite (cc). Butte, Montana.

FIG. 72.

FIG. 72. ($\times 5$.) Pyrite (py) and chalcocite (cc). Butte, Montana.

No. 4 is a massive chalcocite with conchoidal fracture and fine granular structure somewhat resembling fine-grained galena. Polished sections show small, widely spaced, subhedral crystals of pyrite as illustrated by Fig. 72. The pyrite boundaries are somewhat irregular as if the chalcocite had been formed at its expense. It is probable that bornite was originally present in this specimen and has been entirely replaced by the chalcocite, pyrite perhaps remaining behind because it is resistant.²

¹ Recently I have examined a specimen from the 1600-ft. level of the Leonard mine which shows chalcocite secondary after bornite.

² In specimens from Bingham, Utah, the order or ease in which minerals were attacked by chalcocite is: (1) bornite, (2) chalcopyrite, (3) pyrite.

The granular character of this chalcocite is perhaps indicative of the secondary origin but the lack of it does not necessarily mean that the mineral is of primary origin. In specimen No. 1, for example, the massive chalcocite is certainly secondary but it does not show a fine-grained structure.

The microscopic evidence proves the secondary character of the massive chalcocite. I have also observed chalcocite formed at the expense of bornite in specimens from the Poderosa mine, Collahuasi, Chili, in lignite replacements from the Sierra Oscura Mts., New Mexico, and in veinlets in monzonite-porphry from Bingham, Utah. Chalcocite secondary after bornite was also observed by Graton and Murdoch on specimens from Ajo, Arizona, and by Weed in the Virgilina district of North Carolina and Virginia.

One of Graton and Murdoch's figures (No. 22, the right-hand figure¹) of the Butte ores I would interpret as secondary chalcocite formed from bornite instead of as a sub-graphic intergrowth of bornite and chalcocite. A sharp boundary between two minerals is not incompatible with the formation of one at the expense of the other.

Kirk argues in favor of secondary chalcocite formed by descending solutions, while Sales argues in favor of primary chalcocite formed by ascending solutions. While Weed² comes to the conclusion that most of the chalcocite is the product of descending sulphide enrichment he makes the following significant statement:

"... It is undoubtedly in process of formation by descending waters at the present time but as the great ore-bodies are far below the present level of ground water they can not be produced by the reactions commonly offered in explanation."

The great depth of oxidation and enrichment at Bisbee (down to 1,600 ft.) has been satisfactorily explained by Ransome³ as due to oxidation and enrichment in pre-Cretaceous time. But accord-

¹ *Loc. cit.*

² Prof. Paper, U. S. Geol. Surv., No. 74, p. 76, 1912.

³ Bull. U. S. Geol. Surv. No. 529, p. 182, 1913.

ing to Sales¹ there is no necessity of assuming extremely deep meteoric ground-water circulation to account for the Butte chalcocite. The secondary character of the massive chalcocite is proved by microscopic evidence given by the writer.² But the arguments of Sales against the formation of chalcocite by descending solutions are, in my opinion, unanswerable. *As far as the available evidence goes, do we not have proof of the formation of massive chalcocite at Butte by upward secondary sulphide enrichment?* Only in this way can the conflicting views of competent observers be reconciled.

Then, instead of two periods of chalcocite formation we have three:³

1. Primary chalcocite formed by ascending solutions.
Virgilina District, N. C.-Va.; Butte.
2. Secondary chalcocite formed by ascending solutions.
Butte; Plumas Co., Cal.
3. Secondary chalcocite formed by descending solutions.
Bisbee; Morenci; Butte.

All three of the stages are probably found at Butte. It must be admitted that the addition of a third stage of chalcocite deposition complicates matters, but the evidence points in that direction.

The criteria for upward secondary sulphide enrichment must be of both a geological and a mineralogical nature. Without microscopic evidence it is doubtful whether it can be distinguished from primary enrichment and without geological evidence it is doubtful whether it can be distinguished from downward secondary enrichment.

¹ *Loc. cit.*, p. 1618.

² Kirk (*loc. cit.*) also mentions that he has repeatedly observed solid chalcocite surrounding a nucleus of pyrite.

³ Prof. C. F. Tolman has suggested a fourth possibility, *i. e.*, primary chalcocite formed by descending solutions.