

SYNTHESIS OF CHALCOCITE AND ITS GENESIS AT BUTTE  
MONTANA

BY HORACE V. WINCHELL

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## COPPER PRODUCTION OF BUTTE

Since 1880 the mines of Butte, Montana, have produced approximately 1,250,000 tons of fine copper. They are now yielding about 200,000,000 pounds per annum, and have attained a maximum depth of 2,200 feet.

Notwithstanding the statements of some writers on ore deposits,\* the copper ore of this mining camp is not chalcopyrite, nor is this mineral at all common here. Indeed, it is about as rare as covellite, and a good specimen of either is difficult to procure.

## PRINCIPAL ORE MINERAL

Chalcocite is the principal copper mineral, although bornite and enargite are common; and it is probable that more than 75 per cent of the total output of Butte copper has come from the smelting of the mineral chalcocite or copper glance. It is found in all the mines and on all levels from the highest unoxidized level to the bottom workings. It occurs in small crystalline specks, in black powder, and in massive

\* Ed. Fuchs et L. De Launay: *Traité des Gîtes Minéraux et Métallifères*, vol. ii, pp. 263, 265.

• Eissler: *Hydro-Metallurgy of Copper*, p. 29.

veins, sometimes many feet in thickness and of most remarkable vertical and lateral extent.

#### PARAGENESIS OF CHALCOCITE IN BUTTE

A study of the veins and ores and the paragenesis of the various minerals furnishes convincing proof that the copper glance is one of the latest minerals to be formed in the veins. It occurs crystallized or massive on pyrite, quartz, zinc blende, altered granite, and enargite. It fills fault crevices and fractures either in the veins or the country rock. It is also found in extremely thin films on pyrite, chalcopyrite, covellite, and blende, as well as upon the non-metallic rock and vein minerals.

The lodes themselves are quartzose veins and represent more or less completely replaced country granite. The nature of this granite has been fully described by Mr W. H. Weed.\*

There have been two or more separate periods of fracturing and mineralization in the copper area; but chalcocite is found in the fractures of all ages. It is frequently found cementing vein minerals like pyrite which may have been broken apart by earth movements or internal strains. It is also found in great purity and abundance associated with the clay "gouges" of strike or cross-faults, where there is the best opportunity for the circulation of waters from the surface. As depth increases the percentage of pyrite and enargite increases in comparison with that of chalcocite. While the ores of the camp, as mined, may have averaged 8 per cent or 10 per cent copper for the first thousand feet from the surface, they will not exceed an average of 6 per cent copper for the second thousand feet of vertical extent. It is impossible to arrive at exact figures as to the ratio of chalcocite to total copper; but it is a fact that the percentage of chalcocite is decreasing, and that of enargite increasing, with the depth of the mines.

#### CHEMISTRY OF COPPER SULPHIDE

Coming now to the question of the genesis of this chalcocite, it should be borne in mind that copper glance or chalcocite is cuprous sulphide ( $\text{Cu}_2\text{S}$ ), and that covellite is cupric sulphide ( $\text{CuS}$ ).

It should also be remembered that hydrogen sulphide and soluble sulphides normally precipitate  $\text{CuS}$  (not  $\text{Cu}_2\text{S}$ ) from copper solutions, whether acid or alkaline.† Cupric salts, with an excess of hydrogen sulphide, always yield an appreciable amount of cuprous sulphide;‡

\* Journal of Geology, vol. vii, no. 8, pp. 737-750.

† Douglas and Prescott's Qualitative Analysis, 7th edition, p. 89.

‡ Brauner: C. N., 1896, 74, 99; Compt. rend., 1884, 98, 1492.

and it is known that solutions of cupric salts are reduced to cuprous salts by boiling with sulphurous acid.\* Moreover, sodium thiosulphate added to hot solutions of copper salts gives a black precipitate of cuprous sulphide. † It therefore becomes at once apparent that the precipitating agent in these veins can not have been a soluble sulphide unless there were at the same time a reducing agent strong enough to reduce the cupric sulphate to cuprous sulphate and precipitate cuprous sulphide, and not strong enough to reduce it to native copper.

#### LITERATURE OF COPPER GLANCE

The mineral chalcocite has been formed, both artificially and naturally, in recent times, and is referred to by numerous writers as follows: ‡

Daubrée § found chalcocite crystals accidentally developed on coins and copper instruments which had lain for a long time in damp ground, as at Bourbonnes-les-Bains, Plombières, etcetera.

De Gouvenain || found crystals of copper glance on fragments of copper which had been for some time in the warm spring of Bourbon-l'Archambault.

Rammelsberg ¶ discovered two small cubical crystals in furnace product from Mansfeld containing iron, nickel, cobalt, zinc, and manganese isomorphous with the copper.

Scheerer \*\* found small rhombic crystals, supposed to be chalcocite, in a reverberatory furnace at Freiberg.

Mitscherlich †† obtained octahedral chalcocite artificially by melting a proper mixture of copper and sulphur.

Durocher †† reproduced the rhombic variety by heating in a red-hot tube vapor of copper chloride and sulphuretted hydrogen.

Becquerel §§ obtained copper glance in hexagonal plates by the same method which he employed in the formation of galenite.

Sénarmont ||| obtained only an amorphous precipitate by warming to 200° in a sealed tube a mixture of copper sulphate, bicarbonate of soda, and potassium sulphide.

\* Kohner: Chem. Centralblatt, 1886, 813.

† Vortmann: Monatshefte für Chemie, 1889, 9, 165.

‡ Fouqué and Lévy: Synthèse des Minéraux des Roches, p. 294; M. L. Bourgeois: Reproduction artificielle des minéraux, 1884, p. 38; Meunier: Méthodes de Synthèse en Minéralogie, 1891, pp. 69, 75.

§ Daubrée: Compt. rend., vol. lxxx, 1875, 461.

|| De Gouvenain: Compt. rend., vol. lxxx, 1875, 1297.

¶ Rammelsberg: Metallurgie, p. 224.

\*\* Scheerer: Hütten-Erzeugnisse, p. 366.

†† Mitscherlich: Pogg. Ann., xxviii, 1831, 167.

‡‡ Durocher: Compt. rend., xxxii, 1851, 825.

§§ Becquerel: Compt. rend., xxxii, 1852, 38.

||| Sénarmont: Ann. ph. ch., xxxii, 1851, 129.

Copper heated to 200° in a closed vessel, in presence of a solution of sulphurous acid, according to the method of Geitner, did not yield satisfactory results. Under similar conditions, a solution of copper sulphite yielded crystalline scales differing from chalcocite in composition, perhaps covellite.

Margottet\* obtained crystallized copper glance by the slow passage of hydrogen charged with sulphur vapors over copper at red heat.

Meunier † speaks of the employment of solid precipitants, saying that the reaction in such cases is slow, and favorable for crystallization, and moreover reproduces conditions frequently found in nature. He thus obtained crystals of cuprite, alunite, copper, cotunnite, and matlockite. He is convinced, as the result of many experiments, that the natural sulphides, in the presence of suitable metallic solutions, reduce the metal dissolved to the metallic state; and instances the coating of gold which is deposited on galena when immersed in auric chloride, and of silver when galena is immersed in nitrate of silver. All the sulphides which he has examined produce similar metallic precipitates.

#### CHALCOCITE ON COINS

The usual explanation given for the formation of copper glance on coins in spring waters is that it is due to the reducing action of carbon.

In his "Minéralogie de la France," ‡ for example, A. Lacroix, in describing the copper sulphide minerals found incrusting old bronze coins in the springs of Bourbonnes-les-Bains, § says:

"The chalcocite formed in thermal springs or in fresh water at the expense of Roman coins is explained by the action on the bronze of soluble sulphides, themselves the product of the reduction of sulphates by organic material."

Organic matter is present in the mine waters of Butte, but is not able to reduce all the ferric sulphate to ferrous sulphate, much less have any appreciable effect on the copper salts.

#### ARTIFICIAL FORMATION OF CHALCOCITE

After considering the geological history and physical structure of these ore deposits, the writer came to the conclusion some three years ago that the copper glance was formed by a chemical reaction between copper sulphate in solution in descending waters and the iron pyrites and other primary sulphide minerals lying below. In order to ascertain the truth or falsity of this theory, laboratory experiments were undertaken by the

\* Margottet: *Compt. rend.*, lxxxv, 1877, 1142.

† Meunier, *op. cit.*, 308.

‡ Vol. ii, p. 515.

§ Daubrée: *Annales des Mines*, viii, 439, 1875.

writer and carried on by Messrs S. J. Gormly and C. F. Tolman in the laboratories of the Anaconda Copper Mining company.

The first experiments were conducted with a relatively small amount of cupriferos pyrite and a dilute solution of copper sulphate. The results, as reported, show the formation first of  $\text{SO}_2$  and then of  $\text{H}_2\text{SO}_4$ ; the solution of both copper and iron and the precipitation of the iron as ferric hydrate, and the formation of copper sulphide.

Analyses of the mine waters showed no ferrous salt in the strong "copper water," but disclosed the presence of quantities of cuprous salts, in acid solution.

The experiments repeatedly showed that  $\text{SO}_2$  is formed by the action of pyrite and chalcopyrite upon  $\text{CuSO}_4$ , and that the  $\text{SO}_2$  reduces some of the copper ions of the  $\text{CuSO}_4$  to the cuprous form. According to theoretical chemistry, a relatively insoluble compound may be precipitated by very small amounts of a salt containing one of the ions of the insoluble compound, if a large amount of the salt containing the other ion is present. To test this, a solution of copper sulphate was treated with the sulphides of arsenic, lead, copper, iron, zinc, and with pyrite; and in each case copper sulphide was precipitated, proving that these sulphides may precipitate copper sulphides from a solution of a copper salt. It is probable also that the more insoluble the precipitating sulphide, the more concentrated must be the solution of copper sulphate.

To produce a solution containing cuprous ions, the above-mentioned sulphides were treated with a solution of copper sulphate ( $\text{CuSO}_4$ ) and  $\text{SO}_2$ , and precipitates were formed in each instance. An analysis of the precipitate formed by copper sulphide showed a precipitation of 12 per cent of the weight of the original  $\text{CuS}$  as  $\text{Cu}_2\text{S}$ , indicating the formation of chalcocite under these conditions.

It was not ascertained whether the iron salts will reduce enough copper to form  $\text{Cu}_2\text{S}$  in presence of pyrite or other sulphides, or whether the  $\text{SO}_2$  formed by solution of the pyrite and other sulphides is the active agent.

Knowing full well that it might be urged that the formation of a precipitate of a certain chemical composition is quite a different matter from the production of a mineral having the same composition, the experiment now about to be briefly described was undertaken and carried to completion with exceedingly gratifying and satisfactory results.

In a slightly acid solution containing sulphurous anhydride ( $\text{SO}_2$ ) was digested pyrite ( $\text{FeS}_2$ ) at ordinary temperature and pressure for three months. The pyrite taken was ordinary "jig concentrates," about one-fourth of an inch in diameter, from the Parrot concentrator at Butte, and of the following composition:

SO <sub>2</sub> .....	8.30
CaO.....	Trace
MnO.....	None
Fe.....	41.20
Cu.....	1.50
Zn.....	0.20
S.....	48.70
	<hr/>
	99.90

Dividing these results by the molecular weights, the molecular constitution is represented as follows:

Fe.....	0.736
Cu. ...	0.024
Zn.....	0.003
S.....	1.522

After standing for three months in an ordinarily well lighted room, inclosed in a sealed jar to exclude the atmosphere, the formerly yellow grains of pyrite were completely plated with a solid coating of a dark blue-black mineral, and so closely resemble grains of solid chalcocite that they can only be distinguished from the latter by breaking them open, while in another jar which stood alongside, similarly sealed and exposed to light and ordinary temperature, containing pyrite and copper sulphate solution (but no SO<sub>2</sub>), the grains of pyrite were just as bright and yellow as before they were immersed. Indeed, there has been no visible alteration on the surface of grains which have now been thus immersed in copper sulphate without SO<sub>2</sub> for two years, while in an adjacent jar containing SO<sub>2</sub> there has been formed what appears to be, and undoubtedly is, a fine coating of chalcocite.

From the first jar there were taken some of the larger grains for analyses, with results as follows:

SiO <sub>2</sub> .....	9.60
CaO.....	....
MnO.....	....
Fe.....	40.10
Cu.....	3.60
Zn.....	....
S.....	46.30
	<hr/>
	99.60

CaO, MnO, and Zn not determined.

The molecular constitution is now Fe, 0.716; Cu, 0.057, and S, 1.448. There are .016 equivalents of sulphur left over (after calculating the iron as FeS<sub>2</sub>) to unite with the copper. The exact theoretical amount to form Cu<sub>2</sub>S is .014, and the surplus sulphur may be combined with zinc,

lime, or manganese. That the mineral coating thus formed on the jig-concentrates is clearly chalcocite can not be doubted from a mere inspection of the samples and comparison with ore from the mines.

#### CHEMISTRY OF OXIDATION OF PYRITE

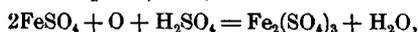
The chemical changes involved in the oxidation of pyrite have been discussed by S. H. Emmons\* and by Penrose,† and more recently by Van Hise, Weed, Emmons, and others, and the equations given indicate the formation of sulphur and sulphurous anhydride as a product of such oxidation.

The real agency of this  $\text{SO}_2$  and its probable role as an active reducing agent, capable, for example, of reducing cupric sulphate to cuprous sulphate preparatory to its deposition as cuprous sulphide, seems to have been overlooked. The equations given by Emmons are as follows:

- “ 1.  $\text{FeS}_2 + \text{O}_3 + \text{H}_2\text{O} = \text{FeS} + \text{H}_2\text{SO}_4$ .
2.  $\text{FeS} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2\text{S}$ .
3.  $\text{FeS}_2 + \text{O} + 2\text{H}_2\text{S} = \text{FeS} + 2\text{H}_2\text{O} + 3\text{S}$ .
4.  $\text{S} + \text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ .

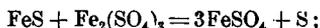
That is to say, the oxygen of the atmosphere and the moisture of the ground and air convert part of the sulphur into sulphuric acid and leave a residue of iron monosulphide, which is then attacked by the sulphuric acid with formation of ferrous sulphate and evolution of sulphuretted hydrogen. This latter reacts with the sulphurous anhydride formed (together with sulphuric acid) by the oxidation of the sulphur in the marcasite, and produces water and free sulphur, the latter of which is in its turn oxidized and produces a further quantity of sulphuric acid, and so on. Hence, as the result of the first attack on the ores we should expect to find ferrous sulphate, sulphuretted hydrogen, free sulphur, and sulphuric acid.

Now, a solution of ferrous sulphate eagerly absorbs atmospheric oxygen and sulphuric acid to form ferric sulphate, thus,



and therefore, although I have spoken of ferrous sulphate and free sulphuric acid as amongst the first results of the gossan-forming action, they are rapidly converted into a solution of ferric sulphate; and it is in this latter form that they are usually found in mine-waters and the like. In some cases, however, where local circumstances impede peroxidation, ferrous sulphate remains in considerable quantity, as, for example, in the manufacture of copper by exposing large heaps of pyrite to the action of the atmosphere and moisture.

Let us next consider what will be the action of the ferric sulphate upon the remaining ferrous sulphide. This is shown by the following equation:

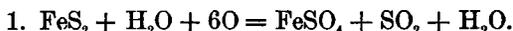


or, in other words, one molecule of ferric sulphate will abstract one molecule of iron from ferrous sulphide, forming 3 molecules of ferrous sulphate and setting free the sulphur.”

\* Engineering and Mining Journal, Dec. 17, 1892, p. 582.

† Journal of Geology, 1894, pp. 288-317.

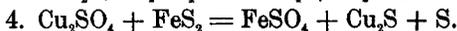
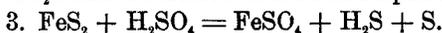
The essential part of these operations may be expressed in a condensed form as follows:



The  $\text{SO}_2$  perhaps aided by the ferrous sulphate, reduces a portion of the copper, as follows:



The acid solution would perhaps form  $\text{H}_2\text{S}$  by attacking the pyrite; and  $\text{CuS}$  would be formed, except for the presence of the  $\text{SO}_2$ , which holds the copper in the form of cuprous sulphate and makes the precipitate cuprous sulphide; or, if  $\text{H}_2\text{S}$  be not formed by the acid present, and if the  $\text{Cu}_2\text{S}$  is more insoluble than  $\text{FeS}_2$ , there would be a precipitation of  $\text{Cu}_2\text{S}$  and a solution of iron as sulphate.



In nature, the oxidation of pyrite sometimes leaves residual sulphur, but usually the sulphur is oxidized and again taken into solution.

#### CHALCOCITE A SECONDARY MINERAL AND PRIMARY ORE

It will be observed that the solutions here employed are all acid solutions and contain no alkaline carbonates. This corresponds with the conditions existing in the Butte mines now and for a long period since the flows of ascending waters ceased and the work of oxidation and erosion began. It seems probable that the waters which have thus deposited chalcocite as a secondary mineral have in most cases been acid waters, and that their movement has been downward. It does not necessarily follow, however, that chalcocite can not be formed in any other way; in fact it is quite possible that ascending alkaline solutions containing copper might deposit chalcocite as a primary ore. In that event we should almost certainly find hematite formed as an associated mineral. Indeed this oxide of iron has been reported from some mines under conditions precluding the supposition of origin through the action of descending waters. No hematite, however, is found in the lower levels of Butte mines, nor have alkaline carbonates been found in considerable quantity.

At many points in the Butte mines are found ores precisely similar in appearance to those thus produced synthetically. Frequently these ores, at first supposed to be pure chalcocite, on analysis prove to be low grade, and on breaking disclose an interior of solid pyrite and a mere surface film of copper glance. So far as I am aware, this is the first account of the synthesis of chalcocite in the wet way, and the first time it has been experimentally demonstrated that important sulphide ore deposits are enriched far below the surface of the ground water by reaction between oxidized solutions from and above the original sulphides.