

## EXPERIMENTS ON THE SOLUTION, TRANSPORTATION AND DEPOSITION OF COPPER, SILVER AND GOLD.

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### INTRODUCTION.

The experiments described in this paper were made some three years ago in the laboratory of the U. S. Geological Survey. Owing to the writer's transfer to the Bureau of Standards and to another field of chemical work, the investigation had to be discontinued. As there seems to be no prospect of resuming it in the immediate future, and as numerous requests for the publication of the preliminary results have been made by geologists to whom they were privately communicated, it seems advisable to give them out in their present incomplete form. The writer can lay no claim to being a geologist and therefore, apart from a few suggestions, he has thought it best to leave to geologists the discussion of any possible bearing on the theory of ore deposition which they may possess. It need only be pointed out, by way of summary, that through the reversal of certain reactions by fall of temperature, solutions carrying ferric or cupric salts, after acting upon certain minerals at a somewhat elevated temperature, may, upon reaching cooler regions, deposit metallic copper, silver or gold, and that by a similar change of temperature, neutral or acid solutions carrying ferrous and cupric salts may yield hematite at one place and metallic copper at another.

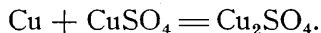
### SOLUTION AND DEPOSITION OF COPPER.

#### SOLUTION OF METALLIC COPPER BY HOT CUPRIC SULPHATE SOLUTION AND ITS REDEPOSITION ON COOLING.

Foerster and Seidel<sup>1</sup> showed that certain deviations from expected results in working with the copper voltameter were to

<sup>1</sup> *Zeit. Anorg. Chem.*, 14, 118 (1897).

be explained by the solvent action of cupric sulphate solution on metallic copper, according to the equation



They further demonstrated that the reaction is reversible. When metallic copper is in contact with cupric sulphate solution there is always a certain amount of cuprous sulphate formed, which is quite considerable even at a moderately elevated temperature. A solution saturated with cuprous sulphate in equilibrium with cupric sulphate readily deposits metallic copper on cooling. Richards, Collins and Heimrod<sup>1</sup> devised an apparatus with continuous circulation of cupric sulphate solution, which was heated in one portion of the circuit containing metallic copper, and cooled in another, where the greater part of the dissolved metal was redeposited. In this way considerable amounts of copper could be recrystallized. Abel<sup>2</sup> developed the theory of the reaction more fully.

The conclusion from these experiments which interests us most is that cuprous sulphate may exist in more concentrated form in conjunction with cupric sulphate at a high, than at a low temperature; that a solution saturated with it will deposit metallic copper on cooling and that therefore a solution in which cupric sulphate has been partly reduced to cuprous sulphate, may, if carried to another and cooler region, deposit metallic copper.

A simple apparatus, with continuous circulation, was devised to illustrate the behavior of hot ascending solutions, in the lower and warmer part of which the reaction between the mineral or metal and the solution was brought about, while in the upper, cooler portion the reaction was reversed, with deposition of metal. A glass tube of about 4 mm. caliber, bent at an angle of about 120° and having limbs of about 12 cm. long, contained the solution and the substance to be acted on, the latter being in the lower, vertical limb. The lower limb was inserted in a narrow gas pipe closed at the bottom and immersed in a bath of Wood's

<sup>1</sup> *Zeit. physikal. Chem.*, 32, 324 (1900).

<sup>2</sup> *Zeit. Anorg. Chem.*, 26, 381 (1901).

fusible alloy. The alloy was contained in a piece of  $2\frac{1}{2}$ " gas pipe, 6" long, closed at top and bottom by caps, the narrow pipe being screwed into the top cap. The object of the narrow pipe was to prevent scattering of the alloy in case of explosion. Four such pipes were inserted into the cap, admitting of three simultaneous experiments, the fourth pipe carrying a thermometer, while in the center of the cap was a hole admitting an ordinary Reichert's temperature regulator, by which the bath could be kept fairly closely at  $200^{\circ}$ , the temperature employed in all the experiments. The upper inclined limb of the tube was water jacketed and cooled by a continuous current of water. The tube was charged by introducing the substance and then nearly filling with the solution, displacing the air by carbon dioxide and sealing off at the upper end. This left a small gas bubble, which was gradually dissolved by the hot solution and liberated on heating in the lower end, where it remained. To prevent this surrounding the substance to be acted on, the latter was carried on a small glass support. Under these conditions the convection was so slow that the lower limb was practically the temperature of the bath, and when the tube was charged with metallic copper and acidified cupric sulphate solution, the metal was rapidly dissolved and deposited in crystals in the upper limb.

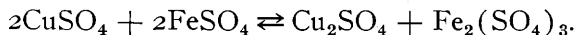
#### FERROUS SULPHATE AND CUPRIC SULPHATE.

That ferrous compounds are agents in reducing copper from its salts has long been suspected by geologists.<sup>1</sup> H. C. Biddle<sup>2</sup> has shown experimentally that metallic copper may be formed when an alkaline carbonate in excess acts on a solution of cupric and ferrous sulphates. Up to the time of my experiments, however, the reduction of cupric salts to metallic copper by ferrous salts in neutral or acid solution had not been effected. In fact, it was very well known that such solutions do not deposit copper or give other sign of the reduction of the cupric compound. I

<sup>1</sup> Pumpelly, *Am. Journ. Sci.* (3), 2, 188, 243, 374 (1871). Geol. Survey of Michigan, Vol. I., pt. 2, p. 19 (1873). R. D. Irving, U. S. Geol. Survey, monograph V., p. 419 (1881-3).

<sup>2</sup> *Am. Chem. Journ.*, 26, 377 (1901); *Journ. Geology*, 9, 430 (1901).

have shown elsewhere<sup>1</sup> that when these sulphates are heated together in solution at 200° there is a deposition of ferric oxide with cuprous oxide and possibly metallic copper. The reaction between the sulphate may be expressed by the reversible equation



Ferric sulphate undergoes partial hydrolysis to ferric hydrate and sulphuric acid, especially at higher temperatures, at which also the ferric hydrate may be deposited as hematite, while cuprous sulphate, if sufficiently concentrated, deposits metallic copper on cooling as shown above. We should therefore expect a deposition of hematite in the hotter, and of metallic copper in the cooler region. This was clearly verified with the apparatus just described. The tube was filled with a solution containing in 40 c.c., 2 grams crystallized ferrous sulphate free from ferric salt and 1.8 grams crystallized cupric sulphate, these being the proportions required by the above equation. After heating the lower limb for an hour at 200°, a crystalline deposit of copper was observed in the upper limb, while after 20 hours there was an abundant crystallization of copper in the upper limb, and the lower limb was lined with a black crust, showing a blood red color by transmitted light. This was seen under the microscope to consist of granules which were blood red by transmitted light, and which gave a red powder, being thus sufficiently characterized as hematite. No other substances were deposited. The reaction can obviously continue until the hematite is in equilibrium with the liberated sulphuric acid at the temperature employed.

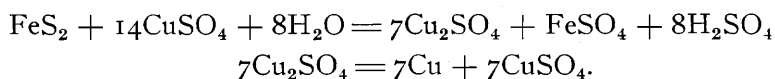
#### PYRITE AND CUPRIC SULPHATE.

I have shown elsewhere<sup>2</sup> that pyrite, heated with a solution of cupric sulphate, gives rise to sulphides of copper, ferrous and ferric salts, and in the case of cupric chloride, to cuprous chloride also. We should expect under the conditions of the previous experiment to get a deposit of metallic copper in the upper limb and of hematite in the lower limb. Powdered pyrite was heated

<sup>1</sup> U. S. Geol. Survey Bulletin 186, p. 44.

<sup>2</sup> U. S. Geol. Survey Bulletin 186, p. 42, 44.

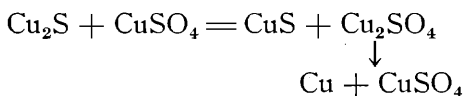
with a slightly acidified 10 per cent. cupric sulphate solution for 18 hours at 200°. Crystalline copper was deposited, as expected, in the upper limb, while the contents of the lower limb were much darker in color and in part had the color of bornite. Hematite was not looked for, but may have been present. The cuprous sulphate which gave rise to the deposition of copper may have come not only from the reducing action of the ferrous salt, but also of the pyrite upon the cupric sulphate, as shown by the experiment with cupric chloride just referred to, and as expressed by the equations



That there is a partial oxidation of the sulphur of the pyrite to sulphuric acid cannot be doubted.

#### CHALCOCITE AND COVELLITE WITH CUPRIC SULPHATE.

Experiments with chalcocite and cupric sulphate show that the former is readily decomposed with deposition of metallic copper in the cold region. Covellite, however, was very resistant, no deposit of copper being observed after 2 days' continuous heating at 200–230°, using saturated cupric sulphate solution. The reaction in the case of chalcocite may be thus expressed:



#### SIDERITE AND CUPRIC SULPHATE.

Ten per cent. neutral cupric sulphate solution was heated at 200° with coarsely powdered siderite in the lower limb. Metallic copper was deposited in the upper limb, and also in the lower; there was also a formation of hematite and malachite in the lower limb.

#### HORNBLLENDE AND CUPRIC SULPHATE.

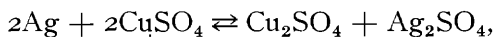
In order to try the action of a ferrous silicate, a powdered hornblende rich in ferrous iron was heated with 10 per cent. cupric sulphate solution containing about 2 per cent. free sulphuric

acid. After heating about 12 hours, considerable metallic copper was deposited in the upper limb, while the lower hot limb contained hematite.

#### SOLUTION AND DEPOSITION OF SILVER BY HOT ASCENDING SOLUTIONS.

##### SILVER AND CUPRIC SULPHATE.

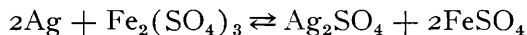
In this experiment silver powder was heated for 15 hours at 200° with a solution containing 5 per cent. crystallized cupric sulphate and 2 per cent. free sulphuric acid. The silver was completely dissolved and deposited in crystallized form in the upper limb. The reaction is obviously:



the reaction reversing at the lower temperature. As no metallic copper was thrown out it is clear that the cuprous sulphate reduces the silver salt before it begins to deposit copper.

##### SILVER AND FERRIC SULPHATE.

It is well known that ferric sulphate solution dissolves silver, the more, the hotter the solution, while on the contrary ferrous sulphate reduces silver salts. This reversible reaction, which is represented by the equation



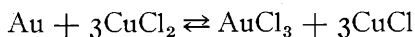
was illustrated by the following experiment. Silver foil was heated in the lower limb of the tube with 7.5 c.c. of a solution of ferric alum containing .75 grams iron per liter, and 2.5 c.c. 30 per cent. sulphuric acid to prevent hydrolysis. A copious deposit of crystals of silver formed in the upper cool limb.

#### SOLUTION AND DEPOSITION OF GOLD BY HOT ASCENDING SOLUTION.

##### GOLD AND CUPRIC SALTS.

Gold leaf was heated at 200° with a solution containing 85 grams crystallized cupric chloride and 133 c.c. 20 per cent. hydrochloric acid in a liter. After 16 hours, the gold was found to

be completely deposited in crystalline form in the upper limb. The reaction is presumably



the cuprous chloride reducing the gold solution as the temperature falls. Cupric sulphate solution was without action. Addition of a chloride to the cupric sulphate would doubtless lead to the above result.

#### GOLD AND FERRIC SALTS.

It is a favorite theory that ferric sulphate is a solvent for gold. While this cannot be absolutely denied, the following experiments show that under the unusually favorable conditions involved in the method employed, no solvent action could be detected, unless a chloride is present at the same time.

#### GOLD AND FERRIC SULPHATE.

Gold leaf was heated with a solution of ferric alum containing 10 grams iron and 15 grams free sulphuric acid per liter. After 52 hours continuous heating at 200° not a trace of gold had been deposited in the upper limb, and the gold leaf was unchanged.

The experiment was then repeated with the addition of .01 gram sodium chloride. After 40 hours heating, a small amount of gold had been deposited in the cold limb. The ferric chloride formed from the sodium chloride is obviously the active agent in this case. This was further confirmed by the following experiment.

#### GOLD AND FERRIC CHLORIDE.

Gold leaf was heated in a mixture of 2 parts 20 per cent. solution of crystallized ferric chloride and 1 part 20 per cent. hydrochloric acid at 200°. The ferric salt was free from nitric acid. After 27 hours, the gold was found to be completely deposited as crystals in the upper limb. The reaction may be expressed by the equation

