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ORGANIC PRECIPITATION OF METALLIC COPPER

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ORGANIC PRECIPITATION OF METALLIC COPPER

By T. S. Lovering

Spongy masses of native copper, found in a bog near Cooke, Mont., are believed to have been precipitated by organic matter. Their occurrence and field relations are such as sharply limit speculations concerning their origin.

FIELD RELATIONS

The bog is 3 miles north of Cooke, on the headwaters of Clarks Fork of the Yellowstone, at an altitude of 9,400 feet. The upper part of Clarks Fork occupies a glacial valley, and the bog is apparently caused by the abrupt change in gradient at the valley head. An area of several acres is covered by spongy wet billowy turf, into which the stream is now cutting.

Instructive sections of the bog may be seen in several prospect trenches, 5 or 6 feet deep, near the Glengarry mine. Most of the material exposed is made up of layers of gravel, sand, and slope wash, but a few thin beds of black muck are found between the coarser sediments. No metallic copper was found in the layers of sand and gravel, but it was abundant in the thin beds of black muck, to which its occurrence is thought to be limited. The muck contains some sand but consists largely of black clayey material full of organic remains. Blackened blades of grass, partly decomposed twigs, and other materials of similar nature are plentiful.

The copper masses range from minute specks to lumps more than an inch in diameter. Most commonly the grains are from a quarter to half an inch across. The masses have an extremely loose and spongy texture and although rather amorphous in appearance are found when examined with a microscope to be entirely crystalline, consisting of a network of spear-shaped crystals.

The surrounding region is well mineralized, and several bodies of pyritic copper ore crop out half a mile above the bog in the saddle separating Scotch Bonnet Mountain from Red Mountain, near the source of Clarks Fork. The recent glaciation has stripped all preexisting gossan from the lodes, and as a result sulphides are now exposed at the surface. The ore consists chiefly of pyrite carrying small amounts of chalcopyrite and gold.

Sulphide ores weather rapidly, and the reactions involved in alteration of this type have been carefully studied by a number of workers.[1] The oxidation of pyrite involves the formation and solution of ferric sulphate, which may then hydrolyze, yielding ferric hydroxide (limonite) and sulphuric acid. The oxidation of chalcopyrite gives cupric sulphate, which remains in solution if the water is slightly acid. The sulphuric acid generated by the hydrolysis of ferric sulphate is ample to acidulate the solution, if it is not neutralized by the country rock. Near the Glengarry mines the country rock is granite or monzonite, which can scarcely have an appreciable neutralizing effect on the water in the stream between the lodes and the copper-bearing bog. These facts explain the occurrence of large quantities of gravel and slope wash above and below the bog, which are thoroughly cemented with limonite and contain no copper compounds, but they do not explain the presence of copper in the swamp.

The field relations indicate that the copper is transported in solution from the lodes to the bog. As cuprous compounds are unstable in surface waters, there is little likelihood that the copper is carried as a cuprous compound. On the other hand, cupric sulphate is formed by the oxidation of chalcopyrite and is stable under the conditions described, and it is highly probable, therefore, that the copper is carried in this form to the swampy area.

As the copper is confined to layers of black muck, the conclusion is inevitable that something in these layers causes the precipitation of metallic copper. The precipitating material differs from the nonprecipitating material in two ways—it contains organic matter, and as plastic clay is present it contains inorganic colloidal substances.

POSSIBLE METHODS OF PRECIPITATION

ADSORPTION

It is well known that colloids have strong adsorptive power, owing to the great surface that they present to a liquid. If metallic copper, therefore, could be precipitated by adsorption, the occurrence of the copper described above would be satisfactorily explained. The term "adsorption" is commonly used to cover the removal of a solute from solution by finely divided solid material. This usage is more popular than scientific, as there are at least three processes which may be involved.

1. A dissolved salt may so react with a solid that an exchange of ions takes place, usually referred to as "base exchange." Sullivan[2] tested the adsorptive powers of kaolin, shale, orthoclase, albite, microcline, pyrite, and biotite by treating these minerals with a 1 per

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[1] Emmons, W. H., The enrichment of ore deposits: U. S. Geol. Survey Bull. 625, pp. 106, 452, 1917.

[2] Sullivan, E. C., Chemistry of ore deposition, precipitation of copper by natural silicates: Econ. Geology, vol. 1, pp. 67-75, 1905.

cent solution of $CuSO_4$. He found that in all these tests base exchange occurred and that the amount of copper leaving the solution was in molecular proportion to the amount of base entering the solution, except a small amount of copper—about 10 per cent—which was withdrawn as $CuSO_4$.

2. A solid may take up molecules of a dissolved salt without any apparent chemical reaction, as is illustrated by the adsorption of copper as $CuSO_4$ mentioned above. This process has also been investigated by Correns,[3] who concludes that not more than 0.8 per cent of copper could be held in this way during sedimentation and that a higher metallic content indicates chemical action.

3. From an ionized solution an ion is selectively adsorbed by a solid which does not apparently undergo any molecular rearrangement, although the ion not adsorbed changes the character of the surrounding solution. This process is illustrated by the action of a chemically inert substance such as lampblack on silver nitrate. If a solution of silver nitrate is passed through a tube containing fuller's earth or lampblack, metallic silver soon becomes visible near the top of the tube, and the acidity of the filtrate increases markedly. In studying this process, it is well to remember that the inert lampblack may have previously adsorbed some reducing gas such as H_2 or CH_4, which may be the true cause of precipitation. The writer passed a solution of $CuSO_4$ through very pure lampblack for two weeks and found that only a trace of copper had been taken from the solution. A corresponding amount of sulphate had also been removed, indicating the adsorption of copper sulphate without precipitation of metallic copper.

The difficulty of precipitating metallic copper by "adsorption" from sulphate solutions seems established by the experiments cited above.

BIOCHEMICAL ACTION

The decomposition of the vegetal matter in the black mud is accomplished by low forms of life, which may live long after air has been cut off from them by burial beneath a heavy cover. Bacteria are known to live in the absence of gaseous oxygen and to reduce oxygen compounds of iron,[4] manganese,[5] and sulphur,[6] using the oxygen thus liberated in their life processes. Although solutions of copper salts are known to be strongly toxic to many forms of algae, yeast, molds, and bacteria (1 part of copper in 1,000,000 will kill

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[3] Correns, C. W., *Adsorptionsversuche mit verdünnten Kupfer-und Bleilosungen und ihre Bedeutung für die Erzlagerstättenkunde*: Kolloid-Zeitschr., vol. 34, pp. 341-349, 1924.

[4] Harder, E. C., Iron-depositing bacteria and their geologic relations: U. S. Geol. Survey Prof. Paper 113, 1919.

[5] Thiel, G. A., Manganese precipitation by microorganisms: Econ. Geology, vol. 20, pp. 301-310, 1925.

[6] Zinsser, Hans, A textbook of bacteriology, pp. 67-69, 1922. Löhnis, Felix, and Fred, E. B., Textbook of agricultural bacteriology, p. 136, 1923.

tubercle bacilli),[7] some forms are very resistant. It thus seemed advisable to test the possibility that low forms of life had in some way caused the precipitation of metallic copper in the occurrence under consideration.

Preliminary experiments proved that microorganisms in the copper-carrying mud could live in solutions containing 1 part by weight of copper in 2,500 parts of solution. As a solution of this strength is almost unknown in nature,[8] even in copper mines, solutions of copper sulphate whose copper concentration ranged from $\frac{1}{10000}$ to $\frac{1}{50000}$ were made up. A small amount of bactopeptone was added to each solution, which was then sterilized and inoculated with the black copper-carrying mud. Sterile controls were made up at the same time, and their original clear blue or green color remained unchanged throughout the experiment, indicating that the bactopeptone by itself was inactive. The inoculated solutions, however, clouded in 48 hours, changed color from blue to green, and in the course of a few weeks became dirty gray and heavily charged with flocculent suspended matter.

The organic scum that formed in the solution of $\frac{1}{10000}$ strength had a pronounced copper color. On examination under the microscope it proved to consist of innumerable rodlike bacteria (bacilli) and countless minute spear-shaped flakes having a metallic luster and the characteristic color of copper. As cuprous oxide somewhat resembles metallic copper, some of the cupriferous matter was heated in dilute H_2SO_4 and filtered, and the filtrate was tested for traces of copper. Negative results were obtained, indicating that no cuprous oxide had been present; the scum when warmed with dilute nitric acid and tested in a similar way gave positive results, clearly confirming the ocular evidence that the copper-colored flakes were metallic copper. The liquid in the flask was filtered from the suspended matter. Careful tests with ammonia, hydrogen sulphide, ferrocyanide, and potassium xanthate failed to show even a trace of copper in this filtrate. The material remaining on the filter paper was ignited and subjected to the same tests as the filtrate and invariably gave strong positive reactions.

Although the reduction of cupric sulphate to metallic copper by organic material had been thus proved, the mechanism of the process was not apparent. Two means of reduction are believed to be possible: (1) The waste products resulting from the metabolism of the bacteria might reduce the copper compound to metallic copper; (2) the copper compound might be consumed by the organisms and broken down by their metabolism, and metallic copper thus precipitated.

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[7] Linden, V., The inhibitory effect of copper salts on pathogenic bacteria (abstract from Centralbl. Bakteriologie, Parasitenkunde u. Infectionskrankheiten, Abt. 1, pp. 85, 136–166, 1920): Chem. Abstracts, vol. 15, p. 3144, 1921.

[8] Emmons, W. H., op. cit., p. 97.

To test these two possibilities fresh solutions were made up, and the amount of bactopeptone added to them was carefully controlled. As the composition of bactopeptone is extremely variable, the amount needed to unite with the copper could not be calculated. It was found that slow addition of this peptone to the nearly colorless dilute solutions of cupric sulphate produced a greenish-blue color, which deepened with addition of more peptone until a point was reached beyond which no further change was produced. As the depth of color was proportional to the concentration of copper it was inferred that the color was produced by the union of the copper and organic material. Cupric sulphate solutions with a concentration of $\frac{1}{10000}$ were prepared, some containing insufficient bactopeptone to satisfy the copper, some just enough to satisfy the copper, and others an excess of bactopeptone. In the solutions of the first group growth was so strongly inhibited that at the end of seven weeks they had changed only to the extent of becoming opalescent. Penicillium (a mold) grew vigorously for a time in one flask but apparently had no effect on the copper compound. Careful examination revealed the presence of some highly motile rods at the end of seven weeks, suggesting that although lack of food inhibited their growth the copper did not have a toxic effect. As bactopeptone consists of a number of organic substances, it is quite probable that some of these substances do not combine with the copper, and as life persisted but precipitation did not take place it is inferred that the bacteria used material not combined with copper for their food.

In the second experiment, in which sufficient peptone was added to satisfy the copper, results were obtained somewhat similar to those just described. The cultures clouded slowly, and a light-colored sediment gradually accumulated in the bottom of the flasks. This sediment was tested for copper, but none was found.

The solutions to which an excess of organic material was added soon changed in appearance, and a flocculent light-colored sediment was formed containing coppery-colored films that proved to contain copper.

As no copper was thrown down in the first two experiments, it appears that the bacteria can not utilize the copper compound for food. The formation of copper-carrying sediment in the third experiment suggests that the copper is precipitated as a result of reaction with the waste products of bacterial metabolism and that the copper compound is not to be considered a direct source of energy that the organism utilizes in its life processes.

At this point in the attack on the problem the writer was fortunate enough to obtain the aid of Mr. Mansfield Clark and Mr. Barnett Cohen, of the chemical division of the Hygienic Laboratory, Washington, D. C. The credit for the bacteriologic work described below is entirely theirs. Mr. Cohen isolated four kinds of bacilli from a culture in which copper was being actively precipitated. They were all Grahm negative types; one was a chromatogen and another strongly resembled *Bacillus coli* in general habits of growth. Pure cultures of the four varieties were prepared. It was then discovered that each of these forms had the power to reduce bactopeptone solutions containing copper. This observation proves that the reducing ability is not limited to one species of bacteria, which might well be true if a peculiar type of metabolism were involved in which a copper compound were digested with subsequent precipitation of copper.

Pure cultures of *Bacillus coli* and *Bacillus proteus*, both present in all swamps, were used to inoculate bactopeptone solutions carrying copper in concentrations ranging from $\frac{1}{10000}$ to $\frac{8}{10000}$. These bacteria were actually stimulated by a copper concentration of $\frac{1}{10000}$ and could withstand $\frac{1}{1500}$, although in this concentration growth was very slow. At an optimum temperature of 30° C. both bacteria produced heavy dark-colored sediment within 48 hours. Some of this precipitate was filtered and washed and was boiled with dilute sulphuric acid. The resulting solution failed to give any test for copper, proving that no cuprous oxide had been formed. The precipitate remaining unaltered in the sulphuric acid was decomposed by warming gently with dilute nitric acid, and the presence of copper was proved by two independent tests. Characteristic spearlike flakes of metallic copper were observed in the bacterial sediment when it was examined under the microscope.

Mr. Clark has found that the reduction potential of *Bacillus coli* cultures is greater than that of the hydrogen electrode; thus the ability of such an organism to create a reducing environment capable of precipitating metallic copper from its salts need not be surprising.

A survey of the literature covering the precipitation of metallic copper by organic compounds[9] reveals little that is helpful in understanding the mechanism of bacterial precipitation. Fortunately the metabolism of *Bacillus coli* and many other bacteria has been exhaustively studied, and the principal compounds produced by their attack on proteins, sugars, and similar foods are known. It has been found that proteins are decomposed successively into proteoses and peptones, amines, amino acids, simple organic bases and acids, and under certain conditions simple gases such as methane, carbon dioxide, hydrogen, and hydrogen sulphide. Ketonic acids and ketonic aldehydes are produced through fermentation of amino acids in the presence of sugars. Complex sugars or polysaccharoses are first reduced to simple sugars and may be further decomposed to give alcohol, carbon dioxide, and water. Compounds of the above-named

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[9] Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry, vol. 3, pp. 11-12, Longmans, 1923. See also Abegg, R., and Auerback, F., Handbuch der anorganischen Chemie, Abt. 1 B and 2, pp. 656-657, Hirzel, 1908.

kinds are well represented in vegetal remains,[10] and the search for a strong reducing agent was confined to organic compounds known to exist in plants or their bacterial decomposition products.

Sugars are known to be strongly reductive, and they easily reduce cupric sulphate to cuprous oxide in the alkaline solutions of many organic compounds, as in Fehling's test. Maillard[11] has succeeded in synthesizing humic compounds through the interaction of various sugars with amino acids. He gives convincing evidence that a strongly reducing condensation compound is first formed, which takes oxygen from the air and then yields humin. Sugars and amino acids may be present in both fresh and decaying vegetal matter and are known to be bacterial waste products formed in the metabolism of polysaccharoses and proteins. Humins are widely associated with vegetal material in swamp deposits, and the reason seems adequately explained by Maillard's synthesis.

The writer modified the Maillard procedure in the following manner: Two parts (molecular) of an aqueous amino-acid solution (such as glycocoll) were added to four parts of a sugar solution (levulose or xylose); the liquid was then covered with petrolatum to exclude air, and one part of cupric sulphate was added to it. As the reaction proceeds slowly in the cold, temperatures of 60° to 70° C. were maintained. The solution changed from deep blue through dark green to black, and metallic copper was slowly precipitated. The time required for the reaction varied with temperature, reagents, and the hydrogen ion concentration (pH), ranging from a few minutes to 48 hours. Precipitation did not occur in moderately alkaline or acid solutions but took place readily in faintly alkaline, neutral, and faintly acid solutions. The copper precipitated was identified by both chemical and physical tests. In the presence of sugar, air being excluded, other reagents, not amino acids, such as gallic acid, phloroglucin, and tannic acid, were found to precipitate copper with varying degrees of speed and completeness. A faintly alkaline solution was found to give the best results. It was also discovered that simple ketones such as acetone can be substituted for sugar.

Bacteria commonly produce H_2S by the reduction of sulphates, but as metallic copper was precipitated in the bog deposit and no CuS could be detected it is quite evident that this gas had not formed. In the experiments just described, compounds commonly excreted by bacteria precipitated metallic copper but did not reduce the sulphate to a sulphide. This fact further corroborates the conclusion that bacteria did not directly reduce the copper sulphate.

A precipitated solution containing copper, sugar, and amino acid was dialyzed, and some of the resulting clear liquor was tested for

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[10] Onslow, M. W., Practical plant biochemistry, Cambridge Univ. Press, 1920.

[11] Maillard, L. C., Synthèse des matières humiques par action des acides amines sur les sucres réducteurs: Annales chimie et phys., vol. 5, pp. 258 et seq., 1916; Identité des matières humiques synthésés avec les matières humiques naturelles: Idem, vol. 7, p. 113, 1917.

sulphate. The presence of sulphate was indicated by a heavy precipitate of $BaSO_4$ when a solution of $BaCl_2$ was added. The acidity of the dialyzed solution was found to be decidedly higher than it had been before the precipitation of the copper. The clear liquor was concentrated on the steam bath to a thick sirup that smelled strongly of caramelizing sugar, indicating the action of free acid on the excess sugar present. From this work the writer concludes that free sulphuric acid is formed during the reduction of the copper and tentatively suggests the following type of reaction:

$$Cu^{++}SO_4^{--} + 2H^+(OH)^- + R' + R \rightleftarrows Cu^0 + H_2^+SO_4^{--} + R''(OH)_2^- + R'''$$

where R, R′, R″, and R‴ are organic compounds.

The mechanism of the reaction will be further investigated by E. Theodore Erickson, of the United States Geological Survey. The writer wishes to acknowledge the help of Mr. Erickson, who brought the Maillard reaction to his attention and gave many helpful suggestions during the investigation.

Waksman and Lomanitz[12] have shown that mixed cultures produce much smaller amounts of amino acids than pure cultures, although easily perceptible amounts are generally present. This is due to the fact that soil contains bacteria that live on the amino acids produced through the metabolism of protein by other forms. As an infinite number of bacterial combinations are possible, experimental work with controlled mixtures was not undertaken. It is well known to bacteriologists that facultative anaerobes—bacteria that can live with air or without it—such as *Proteus vulgaris*, can decompose proteins[13] into amines, amino acids, indol, H_2S, and other compounds, either in the presence or in the absence of air. As amino acids were found under the adverse conditions supplied by mixed aerobic cultures described above, their production in the muck of a swamp seems assured. Sugars and ketones are always present in the early stages of plant decomposition, and ketones are probably formed up to a very late stage in the process. Under these conditions reduction of cupric sulphate or organic copper compounds would take place. It is probable that the precipitation by organic material of gold, silver, copper, vanadinite, and carnotite, mentioned by Clarke,[4] has a similar chemical explanation.

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[12] Waksman, S. A., and Lomanitz, A., Contributions to the chemistry of the decomposition of proteins and amino acids by various groups of microorganisms: Jour. Agr. Research, vol. 30, pp. 263–283, 1925.

[13] Rettger, L. F., Studies on putrefaction: Jour. Biol. Chemistry, vol. 13, p. 344, 1912.

[14] Clarke, F. W., The data of geochemistry, 5th ed.: U. S. Geol. Survey Bull. 770, pp. 660, 664, 672, 724, 727, 1925.