

NATURAL SOLUTIONS OF CINNABAR, GOLD
AND ASSOCIATED SULPHIDES.

BY GEORGE F. BECKER.

ART. XXIII.—*Natural solutions of Cinnabar, Gold and associated sulphides*; by GEORGE F. BECKER.

IN the course of investigations on the geology of the quicksilver deposits of the Pacific slope I have taken up the question of the state of combination in which quicksilver is dissolved in natural waters. Pyrite or marcasite almost invariably accompanies cinnabar, gold is known to be associated with cinnabar in a considerable number of cases, copper sulphides or sulphosalts are also not infrequent in quicksilver mines, and sulphides of arsenic and antimony are known to occur in a similar association. Zinblende too has been found with cinnabar. The solubility of these substances has been incidentally examined. In performing the experiments I had the assistance of Dr. W. H. Melville, who also made all the quantitative analyses involved. The results obtained seem interesting enough to justify their publication, in an abbreviated form, in advance of the monograph of which they will form a part. They also possess some value from a purely chemical point of view, and may interest readers of this Journal who are not geologists.

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The waters of Steamboat Springs are now depositing gold, probably in the metallic state; sulphides of arsenic, antimony and mercury; sulphides or sulpho-salts of silver, lead, copper and zinc; iron oxide and possibly also iron sulphides; manganese, nickel and cobalt compounds, with a variety of earthy minerals. The sulphides which are most abundant in the deposits are found in solution in the water itself, while the remaining metallic compounds occur in deposits from springs now active, or which have been active within a few years. These springs are thus actually adding to the ore deposit of the locality, which has been worked for quicksilver in former years and would again be exploited were the price of this metal to return to the figure at which it stood a few years since. At Sulphur Bank also there is reason to suppose that ore deposition is still in progress, though the opportunities for determining this point are greatly inferior to those presented at Steamboat Springs. The waters of the two localities are closely analogous. Both contain sodium carbonate, sodium chloride, sulphur in one or more forms and borax as principal constituents, and both are extremely hot, those at Steamboat Springs in some cases reaching the boiling point. In attempting to determine in what forms the ores enumerated can be held in solution in such waters, it is manifestly expedient to begin by studying the simplest possible solutions of the sulphides and particularly of cinnabar.*

Solubility of HgS in mixtures of Na²S and NaOH.—A series of experiments were made in my laboratory with a view of testing

* *Previous investigation.*—The solubility of mercuric sulphide in alkaline compounds containing sulphur has long been recognized by experimental and industrial chemists. This fact is the foundation of the methods of preparation of vermilion in the wet way, first described by G. S. C. Kirchoff in 1799 (Scheerer's Allgem. Journ. der Chem., vol. ii, p. 290). In 1829, C. Brunner (Pogg. Ann., vol. xv, p. 593) discovered the double soluble salt $\text{HgS}, \text{K}_2\text{S}, + 5\text{H}_2\text{O}$. Later Dr. Rheinhardt Weber (Pogg. Ann., 1856, vol. xcvi, p. 76), reexamined the properties and formation of this salt, which he found could exist only in the presence of free caustic alkali. In opposition to Prof. Stein, Dr. Weber is extremely positive in his statements that mercuric sulphide is entirely insoluble either in the simple sulphides of sodium and potassium, or in the sulphhydrates of these metals, excepting in the presence of free hydrates. Dr. Weber's solvent was not, as he evidently supposes, a mixture of hydrate and sulphhydrate but of simple sulphide and sulphhydrate.

In 1864, Mr. C. T. Barfoed (Journ. für prakt. Chemie, 1864, vol. xciii, p. 230) investigated the behavior of mercuric sulphide to sodium sulphides. He, like Dr. Weber, found the metallic sulphide wholly insoluble in the sulphhydrate, but soluble in the simple sulphide, and in mixtures of the latter either with the sulphhydrate or with the hydrate. He insists that the necessary and sufficient condition for the solubility of mercuric sulphide is the presence of sodic monosulphide.

The assertion is frequently made in chemical writings (for example Graham-Otto, 5th Ed., part 3, vol. ii, p. 1119) in spite of the result obtained by Weber and by Barfoed that mercuric sulphide is soluble in sodic sulphhydrate. In 1876, Mr. M. C. Méhu (Russian Journ. of Pharm., reported in *Jahresbericht der Chemie*, 1876, p. 282), examined the soluble crystalline mercury-sodium salt corresponding to Brun-

the relative effect of the quantity of sodium sulphide and sodium hydrate on the quantity of mercuric sulphide which a given mixture of the solvents would take up. It is almost impossible to make experiments of this kind with the same accuracy which can easily be attained in precipitations because, if one or more drops of either fluid reagent is added to a mass consisting of mercuric sulphide partially dissolved in the menstruum, it is not practicable to say how long a time will elapse before the additional drop will have become saturated. Approximate results are however readily obtained, and these appear in the present case to be sufficient.

It was found that, provided a small quantity of free hydrate exists in the mixture, the solubility of HgS depends solely upon the quantity of Na^2S in the solution. The average of fourteen experiments made with varying proportions of sodic hydrate gives 1HgS to $2.03\text{Na}^2\text{S}$. From the nature of the experiments a slight excess in the quantity of solvent employed is to be expected. One experiment was made by mixing mercuric sulphide and sodic sulphide in the proportion of two molecules of the latter to one of the former, and adding a few drops of caustic soda. A mere trace of mercuric sulphide remained undissolved, and this completely disappeared on the addition of a single drop of a solution of sodic sulphide, so that less than one drop completed the solution.

Chemists of course regard cases of solution such as that under discussion as due to the genesis of soluble double salts, which are formed according to ordinary laws of composition. The

ner's potassium compound. He found mercuric sulphide insoluble in sodic hydrate or in the simple sulphide of sodium, but highly soluble in mixtures.

Alkaline pentasulphides convert amorphous quicksilver sulphide digested with them into cinnabar (Gmelin-Kraut, *Handbuch der Chemie*, vol. iii, p. 756, where many references may be found), and this process implies a certain degree of solubility. Mr. Barfoed, however, found mercuric sulphide insoluble at ordinary pressures in sodium sulphhydrate to which sulphur had been added, and the solubility, in the pentasulphide is probably slight. The conversion of the black sulphide into the red, does not appear to imply more than a mere trace of solubility, for Messrs. H. Sainte-Claire Deville and Debray produced rhombic crystals of cinnabar by heating precipitated sulphide with chlorhydric acid to 100°C . in a closed tube (Fouqué and Michael-Lévy, *Synthèse des Min. et des Roches*, p. 313). No statement is made in the account of this experiment of any means being employed to produce any great pressure. Mr. S. B. Christy (this *Journal*, vol. xvii, 1879, p. 453) found that at pressures of from 150 to 500 pounds per square inch and temperatures of from 180 to 250 various liquids heated with precipitate mercuric sulphide convert it into vermilion. He experimented with polysulphides of potassium, potassic sulphhydrate, acid sodic carbonate charged with sulphydric acid, and a spring water containing acid sodic carbonate which he charged with sulphydric acid. He reached no conclusion as to the state of combination of the mercury in solution. The fact that glass is greatly attacked at high pressures and temperatures by alkaline solutions of course leaves many possibilities open. Prof. R. Wagner (*Journal für prakt. Chemie*, vol. xxviii, 1866, p. 23), has shown that mercuric sulphide is soluble in barium sulphide, and Prof. Roth (*Allgem. u. chem. Geol.*, vol. i, p. 264) thinks it probable that calcium sulphide possesses a similar power.

above experiments show that this soluble double salt can be represented only in the formula $\text{HgS}, 2\text{Na}^2\text{S}$. The soluble mixture given by Méhu answers to $\text{HgS} + 2.07 \text{Na}^2\text{S}$ and is thus, so far as it goes, confirmatory of the above experiments.

Solubility of HgS in Na²S.—The most carefully prepared solutions of sodium sulphide dissolve mercuric sulphide freely. This statement is directly contrary to that which some of the chemists referred to have made, and it would be a rash one if the evidence to be adduced for it depended simply upon bringing solutions of sodic sulphide into contact with mercuric sulphide; for it is impossible to make certain that there is no trace of free caustic alkali or of sulphhydrate in a solution of sodic sulphide, however closely its analysis may correspond to its theoretical composition. If, however, a solution of sodic sulphide containing sodic hydrate is treated with hydrogen sulphide, it is gradually converted into sodic sulphhydrate and passes through a point at which the only compound present is the monosulphide. If mercuric sulphide is dissolved in a mixture of sodic sulphide and caustic soda, and the clear filtrate is treated with hydrogen sulphide, the mercuric sulphide begins to be precipitated when very little free caustic alkali is left, and is continuously precipitated until the entire amount of sodium present is converted into sulphhydrate. The purest preparations of Na^2S which we have been able to make, dissolve mercuric sulphide less freely than mixtures of sodic sulphide and sulphhydrate. Different preparations, however, shown by most careful analysis to correspond very accurately to the formula Na^2S , give somewhat different results, possibly indicating a minute variation from absolute purity. It does not seem *a priori* improbable, that the soluble salt when the sodic sulphide is absolutely pure is $\text{HgS}, 3\text{Na}^2\text{S}$; and one of our preparations gave almost exactly this result. It may also be that mixtures of $\text{HgS}, 2\text{Na}^2\text{S}$, and $\text{HgS}, 4\text{Na}^2\text{S}$ are formed in proportions varying with other conditions than the purity of the sodium sulphide, such as temperature and concentration.

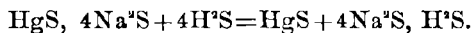
Insolubility of HgS in cold NaHS.—Repeated experiments and analyses undertaken during this investigation have shown that mercuric sulphide is totally insoluble in sodium sulphhydrate at ordinary temperatures, and that any preparation of this compound which will dissolve a trace of mercuric sulphide can be shown by analysis to fall short of complete saturation. A long time and an enormous quantity of hydrogen sulphide are required to completely saturate even a small amount of caustic soda with sulphur. As already mentioned, both Weber and Barfoed were aware of the insolubility of mercuric sulphide in sodium sulphhydrate at ordinary temperatures. It will be seen later that the behavior of these compounds varies with the tem-

perature. If mercuric sulphide is left in contact with cold sodic sulphhydrate for twenty four hours, just a trace of mercury goes into solution. This is due to the spontaneous loss of hydrogen sulphide which the sulphhydrate is well known to undergo.

The absolute want of power of a preparation of sodic sulphhydrate to dissolve a trace of mercuric sulphide is perhaps the best known test of its freedom from the alkaline monosulphide. This test does not show the absence of polysulphides, however, for we have frequently found mercuric sulphide totally insoluble in solutions of sodic sulphhydrate, which possessed a yellow color, and which were proved by analysis to contain an excess of sulphur. This corresponds to Barfoed's observation. The occurrence of alkaline polysulphides in nature, excepting near the surface of the earth, seems so improbable, that I have undertaken no investigations of the conditions under which they dissolve mercuric sulphide.

Solubility of HgS in mixtures of Na²S and NaHS.—For the purpose of determining the character of solutions of mercuric sulphide in mixtures of sodium sulphide and sulphhydrate, clear solutions of mercuric sulphide in sodium sulphide and sodium hydrate were made, all the reagents being carefully prepared for the purpose, and sulphuretted hydrogen was passed through the solution until a large permanent precipitate of mercuric sulphide formed. The mass was then filtered, and of course the filtrate represented an absolutely saturated solution of mercuric sulphide in a mixture of sodic sulphide and sulphhydrate. A portion of this solution was analyzed. The remainder was treated further with hydrogen sulphide, the precipitation being arrested before the separation of mercuric sulphide was completed, and the second filtrate, representing a second saturated solution of the metallic sulphide in a mixture of alkaline sulphide and sulphhydrates, but one containing much less mercuric sulphide, was also analyzed.

These analyses, which formed the conclusion of a tedious series of experiments, show beyond any reasonable doubt that there is a compound HgS, 4Na²S which is soluble in the presence of Na²S, H²S and which is decomposed by hydrogen sulphide in the presence of the sulphhydrate by the reaction,



Conclusion from the experiments.—It appears from the above that there are at least three double salts of the form HgS, $n\text{Na}^2\text{S}$, where n may be either 1, 2 or 4 and, judging from the analogy of the potassium compounds, there is probably also a compound of this group where n is $\frac{1}{2}$. The possibility of a case where n is 3 has also been adverted to. Thus mercuric sulphide readily enters into combination with sodic sulphide in various propor-

tions, while all the best known soluble compounds of mercuric sulphide and sodium have the same general formula. The presence of carbonates of the alkalies is also known, especially from Méhu's results, to be compatible with the existence of these compounds. The question therefore arises whether such double sulphides may not exist in natural waters.

Possible existence of Na²S in natural waters.—This question resolves itself into two. It is to be considered whether Na²S may exist in natural waters as such. In that case such waters must dissolve mercuric sulphide. It is also possible that alkaline monosulphides cannot exist as such in these waters, but that the affinity of sodic sulphide and mercuric sulphide is sufficient to overcome the obstacles to the formation of sodic sulphide, and that this compound will form when mercuric sulphide is present. The latter possibility is the more important one, but the former is manifestly one of interest to chemical geology.

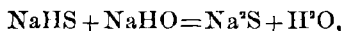
A train of thermochemical reasoning, upon which it is not necessary to enter here, makes it extremely probable that, at temperatures exceeding 80°, a certain amount of sodic sulphide may form by the decomposition of neutral sodium carbonate and sodium sulphhydrate in the presence of acid sodium carbonate. The behavior of such mixtures to mercuric sulphide at the temperature indicated is also such as it would be if the sodic sulphide actually formed; but a full and sufficient proof of the reaction which theory indicates as probable seems very difficult and has not yet been accomplished. It is certain, however, that a tendency exists to the formation of sodium sulphide under these conditions. When in addition to this tendency, the affinity of mercuric sulphide for sodic sulphide is brought into play, it can be proved experimentally that sodic sulphide is formed. We found that at a temperature of about 90° a mixture of the two carbonates and the sulphhydrate dissolves mercuric sulphide freely without a sensible evolution of gas. If the solvent does not contain sodic sulphide, it must contain the sulphhydrate. Hence it becomes important to ascertain the behavior of mercuric sulphide to sodic sulphhydrate at moderately elevated temperatures.

While sodic sulphhydrate will not dissolve a trace of mercuric sulphide at ordinary temperatures, if mercuric sulphide is added to a solution of sodium sulphhydrate which stands upon the water-bath, hydrogen sulphide is evolved and mercuric sulphide goes into solution. The fact that hydrogen sulphide is evolved demonstrates that sodic sulphide must be formed. Cooling does not reprecipitate the mercuric sulphide, and the compound dissolved is therefore of the form HgS, $n\text{Na}_2\text{S}$. Though the solubility of mercuric sulphide in warm solutions

of the alkaline sulphhydrates at ordinary pressures has, so far as I know, never been explicitly stated, I have no doubt that chemists have observed it and that, in consequence of this observation, the general statement of the solubility of mercuric sulphide in alkaline sulphhydrates has remained in chemical literature in spite of the observation of Weber and Barfoed. The preparation in which I originally observed this important reaction was one from which mercury had already been removed by precipitation with hydrosulphuric acid. The experiment was afterwards repeated by Dr. Melville with several preparations of sulphhydrate which had been accurately analyzed and had been tested in numerous ways. Now in a mixture of the carbonates and sulphides of sodium at the temperature of the water-bath, either sodic sulphide or sodic sulphhydrate is present, or, more probably, both coexist. If, then, mercuric sulphide is added to such a solution, either sodic sulphide combines directly with mercuric sulphide, or sodic sulphhydrate is decomposed by mercuric sulphide setting free hydrogen sulphide, which must be immediately absorbed by neutral sodic carbonate. Hence in any case the salt dissolved in the mixture must be of the form $\text{HgS}, n\text{Na}^2\text{S}$.

Effects of dilution—Laboratory experiments are usually made with solutions which are much more concentrated than those found in nature. Hence the effect of dilution on solutions of $\text{HgS}, n\text{Na}^2\text{S}$ are important. Whether mercuric sulphide is dissolved in a mixture of sodium monosulphide and sodium hydrate, or of the former and sulphhydrate, dilution with cold water precipitates mercuric sulphide.

The cause of this precipitation, which is attended by some curious phenomena to be described hereafter, is clear. It is known through the investigations of Messrs. Kolbe, Thomsen and others, that while in moderately concentrated solutions



this reaction is partially reversed on dilution; or that, in the presence of much water, sodic sulphide is decomposed by water, the proportion of the sulphide undergoing this decomposition increasing gradually with the dilution. It is evident that the decomposition of $\text{HgS}, n\text{Na}_2\text{S}$ is effected in the same way, more and more of the monosulphide being converted into the sulphhydrate as the dilution increases, probably without any limit. Since mercuric sulphide decomposes hot sodic sulphhydrate, the effect of dilution in hot solvents will evidently be less than in cold ones.

Brunner* found that dilution of solutions of his salt precipitated a black mass in which, on examination with the

* Loc. cit.

lens, minute globules of mercury were visible. The quantity of mercury was extremely small, so that the precipitate on analysis corresponded very closely indeed to the composition expressed by the formula HgS . Gmelin-Kraut* appear to have some independent confirmatory evidence on this point. If metallic mercury is precipitated in diluted solutions, of course sulphur is liberated; and, as shown above, sodium hydrate must also be present. Now when these two substances are brought in contact, sodic hyposulphite forms. Accordingly Brunner found hyposulphite in the solution forty years before the decomposition of sodic sulphide in dilute solution had been elucidated.

As Brunner experimented with HgS , Na^2S , I thought it best to compare the action of HgS , $4\text{Na}^2\text{S}$. A very concentrated perfectly clear solution of freshly prepared mercuric sulphide in a mixture of sodic sulphhydrate and caustic soda, containing very little of the latter, was suddenly diluted with cold water to 200 times its volume and rapidly filtered. Minute globules of mercury could be seen with the black sulphide on the filter. On digestion (after thorough washing) with very dilute nitric acid, a solution was obtained from which sulphydric acid precipitated black sulphide. The decomposition thus appears to be the same in each of the compounds, HgS , Na^2S and HgS , $4\text{Na}^2\text{S}$.

Influence of foreign substances.—The fact that sodium carbonates do not prevent the solution of HgS in Na^2S is evident both from Méhu's result and from our own. Experiments show that borax solutions precipitate a portion of the mercury from solution, but not the whole. The precipitation does not appear to be progressive, like that accompanying dilution, but to reach a sharp limit beyond which further additions produce no effect. A large amount of borax added to a concentrated solution of Na^2S and NaHS does not rob it of the power to dissolve HgS . It is easy to imagine reactions by which borax may precipitate a portion of the mercuric sulphide. But the behavior of solutions of borax to sulphydric acid and to alkaline sulphides is very peculiar and, so far as I am aware, has not been thoroughly investigated.† Very concentrated solutions of sodium chloride do not precipitate mercuric sulphide from strong solutions in mixtures of sodic sulphhydrate, and they even appear to delay but not to prevent, precipitation by dilution.

Solubility of Fe^2S .—The sulphide which is most frequently associated with that of mercury is pyrite or marcasite, indeed these minerals in greater or smaller quantities are to be found in nearly every hand specimen of ore, and occur very abundantly in most quicksilver mines. On making the experiment

* *L. c.*, vol. iii, p. 851.† Gmelin-Kraut, *l. c.*, vol. ii, p. 160.

I found that pyrite, marcasite or precipitated ferrous sulphide when warmed with a solution of sodic sulphide diminished in quantity, while the solution changed color. The filtrates gave strong reactions for iron.

Pyrite dissolves in cold solutions of sodium sulphide without any evolution of gas. The solvent power seems to increase with the temperature. Pyrite like cinnabar appears totally insoluble in cold sodium sulphhydrate, and, like cinnabar, pyrite dissolves to some extent in hot solutions of the sulphhydrate. Pyrite is also soluble in solutions of sodium carbonate partially saturated with sulphydric acid, both hot and cold. Quantitative determinations have been made, but are omitted here for the sake of brevity.

Marcasite is more easily soluble than pyrite, and the simple precipitated sulphide goes into solution most readily of all. I think there can be no doubt that pyrite and marcasite form double salts with sodium sulphide entirely analogous to the soluble compounds of mercuric sulphide. Marcasite is more easily attacked than pyrite, just as metacinnabarite is more susceptible to the action of reagents than cinnabar.

Solubility of gold.—The association of gold and pyrite is world wide. According to Gahn* there is no pyrite which does not yield traces of gold when carefully tested. This indeed does not accord with my experience, for extremely careful tests of some pyrite in my laboratory have failed to reveal any indication of gold. Gold is associated with quicksilver, however, at Steamboat Springs, at some points on the gold belt of California, at the Manzanita mine, at the Reddington mine, and some other localities both in California and in foreign countries. From these facts I concluded that gold should be soluble in sodic sulphide. On warming chemically pure, precipitated gold-dust with a solution of sodic sulphide, the glittering scales of gold gradually disappeared. The filtrate after proper manipulation yielded a purple precipitate with phosphorous acid.

A solution containing 843 parts of Na_2S (by weight) dissolves one part of gold at the ordinary temperature of the atmosphere. Gold also dissolves at ordinary temperatures in sodic sulphhydrate, and in solutions of sodic carbonate partially saturated with sulphydric acid. The solubility appears to be increased and facilitated by heat.

Solubility of other sulphides.—Cupric sulphide dissolves less readily than pyrite in sodic sulphide and in mixtures of the sodic carbonates and sodic sulphhydrate. Unlike pyrite, it also dissolves in thoroughly saturated sodic sulphhydrate. Zinc sulphide is also soluble and behaves much as pyrite does. Quantitative determinations of the solubility of these substan-

* Bischof's Chem. Geol., vol. iii, p. 939.

ces have also been made. The solubility of the sulphides of arsenic and antimony in sodic sulphide and in the sulphhydrate is of course well known. In the presence of neutral sodic carbonate sulphides of arsenic and antimony dissolve in sodic sulphhydrate without the evolution of gas, because the sulphydric acid set free reacts upon the carbonate.

Natural solutions and precipitations.—The foregoing experiments show that there is a series of compounds of mercury of the form $\text{HgS}, n\text{Na}^2\text{S}$ one or the other of which is soluble in aqueous solutions of caustic soda, sodic sulphhydrate or sodic sulphide, and apparently also in pure water, at various temperatures. These solutions subsist, or subsist to some extent in the presence of sodic carbonates, borates and chlorides. There is the strongest evidence that the waters of Steamboat Springs contain mercury in this form, and that the waters of Sulphur Bank have contained mercury in the same form, if indeed they do not still carry it in solution. Bisulphide of iron, gold and zincblende form double sulphides with sodium, which appear to be analogous to those of mercury. Copper also forms a soluble double sulphide, but combines more readily with sodic sulphhydrate than with the simple sulphide. All of these soluble sulphosalts may exist in the presence of sodic carbonates.

Mercuric sulphide is readily precipitated from these solutions. Any substance is more soluble in hot solutions than in cold ones, provided that increase of temperature does not resolve the fluid molecules into others which are less soluble; as happens with sodium chloride, neutral sodium carbonate, etc. Diminishing temperature is thus a cause of precipitation, and diminishing pressure appears to act in a similar way. There are also other methods of precipitation which may be carried out under natural conditions. If a natural solution of mercury comes in contact with strong solutions of borax, or with sulphydric acid, or any stronger acid, it will lose a portion of the mercuric sulphide in solution. At Steamboat Springs and Sulphur Bank large quantities of sulphuric acid are formed near the surface and, percolating downward, must precipitate mercury in some form. The acid waters penetrate to a depth of at least 20 or 30 feet and this explains the fact that the waters reaching the surface carry so little quicksilver. These same causes must also produce precipitation of the other ores and of gold from solutions.

Another method by which mercuric sulphide may be precipitated, as has been seen, is mere dilution. Now, ascending solutions of quicksilver must sometimes meet with springs; and when they do so, metacinnabarite, or black sulphide will be precipitated, and with it also a small amount of quicksilver. In nearly all mines a small quantity of "virgin" quicksilver

is found and in most it constitutes a very small proportion of the entire ore.* Accompanying this precipitation is the formation of hyposulphite, which actually occurs in the waters of Steamboat Springs. Dilution of solutions of quicksilver with extraneous spring waters thus explains the occurrence of metacinnabarite, found in at least four of the mines of California, and in New Zealand, and of native quicksilver. Native quicksilver however occurs in many mines in which no metacinnabarite has ever been seen. This does not preclude the supposition that the metal has been isolated by dilution; for black sulphides in the presence of solutions of mercury might readily be converted into the allotropic modification, and I know of no reason for denying that much of the cinnabar of the ore deposits may have been deposited in the amorphous state. Cinnabar and metacinnabarite are sometimes found mixed, as if the conversion to the red form were incomplete; and there is other evidence from observation that mercuric sulphide is slightly soluble in the waters of some of the cold mines.

While dilution will produce metallic mercury and a *causa vera* of its existence is thus detected, there may be other ways besides this in which it is produced in nature. Thus sulphydric acid precipitates a mixture of quicksilver and mercuric sulphide from mercurous salts. Whether soluble mercurous salts can occur in nature, excepting near the earth's surface, is another question. But even light is well known to decompose this feeble sulphide, and it is not impossible that the decomposition of organic matter, which is associated in most cases with cinnabar deposits, and seems to be specially abundant in the mines in which metallic mercury most prevails, may yield ammonium sulphide and metallic mercury.

Conclusions.—The conditions of the solution and precipitation of ores traced in this paper appear beyond doubt those mainly instrumental in forming the deposits of Steamboat Springs and Sulphur Bank. Most of the other quicksilver mines in California show ores and gangue minerals of similar composition to these, and many of them are accompanied more or less closely by warm springs containing much the same salts in solution. Some of the gold veins also appear to bear so considerable a resemblance in many particulars to these deposits as to lead to the belief that they too were formed by precipitation from solutions of soluble double sulphides.

That pyrite, gold and other ores are sometimes produced in nature by other methods is absolutely certain; for some auriferous pyrite is known to have resulted from the reduction

* It is a very curious fact that from ancient times to the beginning of the last century virgin quicksilver was supposed to possess qualities superior to that of the metal reduced from cinnabar. Brückmann, Magn. dei in loc. subt.

of iron sulphate by organic matter. This particular process is probably confined to short distances from the surface; for I know of no indication of the formation of iron sulphate far from the oxidizing influence of the atmosphere. But there may be other solvents yet for these and other minerals which can form at great depths and, if such there be, I am convinced they are cases in which they, and not those which it has been my good fortune to trace in the foregoing pages, have been instrumental in the segregation of ores.

U. S. Geological Survey, Dec., 1886.