A study of the precipitation of iron di-sulphide and its relation to certain types of deposits

Vachel Harry McNutt

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A STUDY OF THE PRECIPITATION OF IRON DI-SULPHIDE
AND ITS RELATION TO CERTAIN TYPES OF DEPOSITS.

by

Vachel Harry Mc Nutt.

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Approved by
Professor of Chemistry.

14246
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A STUDY OF THE PRECIPITATION OF IRON DI-SULPHIDE AND ITS RELATION TO CERTAIN TYPES OF DEPOSITS.

--INTRODUCTION--

For a long time investigators have puzzled much over the formation of pyrite and marcasite and have attempted logical explanations of the occurrence of these minerals in nature. Not only has the formation of these minerals been attempted, but various interesting differences have been noted and systematically studied. Within the last two or three years scientists have investigated more vigorously than ever before the problems presented by the di-sulphides of iron.

A thorough understanding of the conditions and agents governing the formation of iron di-sulphide is of interest to both chemists and geologists. To the chemist, it means the solving of an elusive scientific problem; to the geologist, because of the widespread occurrence of iron di-sulphide in nature, an understanding of its formation would doubtless be an important step toward a clearer conception of the origin of ore deposits.
Very few of the interesting points bearing upon the formation of iron di-sulphide will be treated in this paper. The laboratory tests made are considered to have been sufficiently thorough to substantiate the ideas set forth so that exhaustive tests were not necessary. While the field evidence was collected largely in the Joplin district of Missouri, the conclusions are sufficiently generalized to be applicable to any district in which pyrite and marcasite have been derived from cold solutions.

By "cold solutions" as herein used, is meant those solutions at room temperature as contrasted with "hot solutions" which range in temperature from near the boiling point of water upward.

Acknowledgement is due Mr. A. X. Illinski, Chemist for Missouri Bureau of Geology and Mines, for the accurate determination of sulphur in the artificially prepared products.
Bischof:

Because of the fact that pyrite is so often a constituent of igneous rocks, many of the early theorists assumed it was all formed by crystallization from molten magma. Bischof #, one of the greatest German investigators, was of the opinion that pyrite is the product of precipitation from water solutions. He further demonstrated the formation of iron mono-sulphide out of water solutions, by bacteriological investigations. Later study along geologic lines presents undeniable evidence that pyrite and marcasite are precipitated from water solutions, the natural processes involved being as yet an open question.

The two investigators who have recently published the results of experiments on the formation of iron di-sulphide are Feld and Allen. These men each succeeded in obtaining valuable data upon the subject. Each worked independent of the other and each upon a separate problem; incidentally their results were published about the same time. The work of both Feld and Allen, with those conclusions bearing upon the

# (Newer Investigations on Iron and Sulphur Bacteria (German edition) Vol. 1, p 917.)
subject at hand are here briefly given:

Feld:

After reviewing his work on the formation of iron di-sulphide from water solutions, Feld points out those factors he considers important and attempts an explanation of the genesis of pyrite deposits.

While testing a new process for the purification of illuminating gas, Feld discovered a method of forming iron di-sulphide from cold solutions. Further experiments along this line led to the formation of iron di-sulphide under varying conditions, which conditions are clearly explained. Feld also mentions factors which prevent the formation of iron di-sulphide, and generalizes the results of his research. Below are quoted some of the main statements:

"Iron di-sulphide is formed always and rapidly when iron mono-sulphide is heated in weakly acid or neutral solutions in the presence of an excess of sulphur or other substances containing sulphur".

"The presence of reducing substances accelerates the formation of iron di-sulphide out of mono-sulphide on boiling".

*(Zeitschrift fur angewandte Chemie, Vol. 24, p 97.)*
"If $\text{H}_2\text{S}$ is conducted into a cold solution of iron sulphate and a solution of thiosulphate, and the ferric salt is not present, there is an immediate precipitation of iron mono-sulphide mixed with sulphur".

"If $\text{H}_2\text{S}$ is conducted in a slow stream for three or four days, through an iron solution containing thiosulphate, the formation of iron di-sulphide becomes so copious as to manifest itself in the physical behavior of the precipitate. While the precipitate is at first voluminous and black and dissolves in dilute hydrochloric acid, even after twenty-four hours, it settles in a sharply defined layer, in spite of the bubbling through of the gas. After a few days the precipitate is almost completely insoluble in hydrochloric acid".

Feld also states,

"Basic substances, even such weak bases as magnesium oxide (MgO) prevent the formation of iron di-sulphide". This last statement he confirms by experiments with solutions containing an excess of calcium carbonate, from which he was unable to to obtain any precipitate insoluble in hydrochloric acid.

Allen:

Allen's paper deals at length with the conditions

effecting the precipitation of pyrite and marcasite in nature. Much importance is given to the problem of differentiating pyrite and marcasite, studying the conditions under which each forms in the laboratory, and attempting to show a parallelism between laboratory observations and the occurrence of these minerals in natural deposits. Allen does practically all of his research with hot solutions under pressure. It is evident that Allen has crystallized both pyrite and marcasite and has produced crystals sufficiently large to be determined by crystallographic measurements as pyrite and marcasite. Below is given a part of the first paragraph of Allen's summary:

"The formation of iron di-sulphide was accomplished (1) by the action of hydrogen sulphide on ferrous salts; (2) by the addition of sulphur from solution to amorphous ferrous sulphide or pyrrhotite; (3) by the action of soluble polysulphides on ferrous salts; (4) by the action of soluble thiosulphates on ferrous salts. The first three methods may be generalized as "the action of sulphur on ferrous sulphide": (a) in acid solutions; (b) in nearly neutral solutions; (c) in alkaline solutions. Marcasite was obtained with certainty only by method (1). Low temperature and acid
solutions favor the precipitation of marcasite. A solution of one percent sulphuric acid at one hundred degrees gives pure marcasite. Less acid solutions at higher temperatures give mixtures of pyrite and marcasite. The other methods (2, 3, and 4, above mentioned) give pyrite, which under certain conditions may be mixed with amorphous di-sulphide.

It is evident that the work of both Feld and Allen has been of decided value. Feld has succeeded in precipitating amorphous iron di-sulphide from cold solutions and Allen, by the use of heat and pressure, has crystallized pyrite and marcasite in the laboratory.

-ORIGINAL INVESTIGATION-

After reading Feld's paper, it seemed that further work along this line would be interesting and of value. In the work done by Feld, there seems to have been no attempt to make use of those reagents which are abundant in nature. If we wish to understand the factors concerned in the formation of pyrite and marcasite deposits, or if we hope to offer a satisfactory explanation of conditions, we must assume agents and conditions with which these minerals are commonly associated in natural deposits.
Feld has generalized too broadly in presenting his paper to geologists; his work is of value to chemists and to such geologists, who by further experimentation, carry the work to a point where it has special significance. Some generalizations were made which seem not to be substantiated by occurrences of pyrite and marcasite; these will be mentioned in another place.

In following Feld’s experiments, effort has been made to duplicate conditions described in his paper and also, to perform a series of experiments, which if successful, would offer a logical explanation of the formation of pyrite and marcasite. These experiments were made to determine whether or not basic substances such as calcium salts would exercise a preventative effect upon the formation of iron di-sulphide and further, to observe the effect of calcium thio-sulphate upon the formation of the di-sulphide.

Three groups of six experiments each were prepared. The solutions were made up to 250 cc. and put into air-tight flasks. Hydrogen sulphide was then conducted
into the flasks in such a manner as to allow the gas from the first flask to pass directly into the second and so on, requiring for the six experiments only one generator. (See diagram 1, page 21). About twenty bubbles of hydrogen sulphide per minute were allowed to pass through the solutions for eleven days. Below is a brief description of the experiments and the artificially prepared products.

The experiments in Group 1, were performed to test the action of calcium salts in the formation of iron di-sulphide. Group 2, was the same as Group 1, with the exception that more ferrous sulphate was used with the hope of obtaining a larger amount of the precipitates. Group 3, was the same as Group 1; the object being to obtain precipitate sufficient for chemical analyses.

Group 1, Experiment 1.

(Duplication of one of Feld's experiments)

Solution:

2 gr. Na$_2$S$_2$O$_3$; 2 gr. FeSO$_4$; 250 cc H$_2$O.

Precipitate:

A heavy brownish black precipitate which settled to the bottom and could be easily separated by decantation. Some free sulphur floated on top. The
precipitate was then thoroughly washed with carbon bi-sulphide in order to remove all uncombined sulphur; after drying in the air the precipitate was allowed to stand twenty four hours in 1 : 4 HCl. The filtrate from this treatment shows very little iron. The bulky residue after HCl treatment indicates FeS₂. The precipitate showed no evidence of crystalline structure.

Group 1, Experiment 2.

Solution:

2 gr. FeSO₄; 50 cc. saturated solution CaS₂O₃; 200 cc. H₂O.

Precipitate:

The precipitate settled to the bottom of the flask, as in experiment 1; shows less amount of both precipitate and free sulphur. The precipitate showed a decided tendency to stick together. After washing with CS₂, the precipitate was treated with HCl as above; very little of the precipitate was soluble, indicating that amorphous FeS₂ could be formed in the presence of CaS₂O₃.

Group 1, Experiment 3.

Solution:

2 gr. FeSO₄; 1 gr. Na₂S₂O₃; 0.5 gr. CaCO₃; 250 cc. H₂O.
Precipitate:

The precipitate was very finely divided and brownish black in color; some of it was still in suspension at the end of eleven days. Only part of it could be separated by decantation. This precipitate was given the usual treatment with CS$_2$ and with HCl. Some of the precipitate went into solution but most of it remained insoluble. While other precipitates appeared amorphous, this one seemed to contain numerous small yellow crystals. These were examined closely under a high power microscope but being opaque and so small could not be identified with certainty as crystals. Several were asked to examine this precipitate and all were of the opinion that small crystals were present. The precipitate showed a more decidedly yellow color than the others and further tests confirmed the idea that it was FeS$_2$. This is regarded as one of the most important experiments performed; it seems to point toward crystallization from cold solution. The result of this experiment disagrees with Feld's observation that weak bases prevent the formation of FeS$_2$. 

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Group 1, Experiment 4.

Solution:

2 gr. FeSO₄; 50 cc. saturated solution CaSO₄;
0.5 gr. CaCO₃; 200 cc. H₂O.

Precipitate:

Precipitate is less in amount than in experiment 3. It could not be washed entirely free by decantation. Brownish black to black in color. After washing the precipitate with CS₂, it was treated with 1:4 HCl; about half went into solution. Physical tests indicate that a part of the precipitate was amorphous FeS₂.

Group 1, Experiment 5.

Solution:

2 gr. FeSO₄; 1 gr. Na₂S₂O₃; 0.5 gr. CaSO₄. 2 H₂O;
250 cc. H₂O.

Precipitate:

The precipitate was not easily separated by decantation; it adhered closely to the scaly gypsum used. After the treatment with CS₂ and with HCl some of the precipitate remained insoluble; about two thirds had gone into solution. The precipitate resembled amorphous FeS₂.
Group 1, Experiment 6.

Solution:

2 gr. FeSO$_4$: 50 cc. saturated solution CaS$_2$O$_3$; 0.5 gr. CaSO$_4$: 2 H$_2$O; 200 cc. H$_2$O.

Precipitate:

Only a small amount of precipitate, not easily separated by decantation was formed. The precipitate was black in color; the solution from which it was precipitated was colored a pale green. The residue from HCl treatment was rather heavy and appeared to be amorphous FeS$_2$.

The experiments in Group 2 were identical with those of Group 1, with the exception that five instead of two grams of FeSO$_4$ were used. In this series of tests a peculiar phenomenon was noticed. After two days a copious black precipitate was formed; when hydrogen sulphide had been passing into the solutions for five days more than half of the precipitate that had formed had gone again into solution. This has caused considerable puzzling and no satisfactory explanation of it has yet been offered. The precipitates obtained in this group were not in sufficient quantity to permit of an analysis.
The experiments in Group 3 were performed, primarily, to obtain sufficient precipitate to test analytically. The reagents used were the same as those in Group 1; the time the experiments were carried on was however less than the time given to Group 1.

The precipitates in Group 3 were practically the same as those described under Group 1. Experiment number 3, did not show the same structure as exhibited in number 3, of Group 1. The precipitates from Group 3 were analyzed and are given below. In one column are the analyses and in the other is the figure for an equal amount of theoretically pure FeS₂.

<table>
<thead>
<tr>
<th>Analyses for sulphur.</th>
<th>Analyses of pure FeS₂.</th>
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<tr>
<td>No. 1.---- 0.2748.</td>
<td>---------------------0.2750.</td>
</tr>
<tr>
<td>No. 2.---- 0.1158.</td>
<td>---------------------0.1144.</td>
</tr>
<tr>
<td>No. 3.---- 0.1975.</td>
<td>---------------------0.2000.</td>
</tr>
<tr>
<td>No. 4.---- 0.1744.</td>
<td>---------------------0.1714.</td>
</tr>
<tr>
<td>No. 5.---- 0.2079.</td>
<td>---------------------0.2003.</td>
</tr>
<tr>
<td>No. 6.---- 0.0892.</td>
<td>---------------------0.0900.</td>
</tr>
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A glance at the above analyses is sufficient to convince one that the discrepancies are well within the limit of experimental error. Mr. Illinski has checked these results closely.
DISCUSSION

When Feld wrote his paper entitled, "On the Formation of Iron Bi-sulphide in Solution and the Genesis of Natural Pyrite Deposits", it seems that he has worked out the chemical probability and not regarded the natural evidence. The observation that basic substances prevent the formation of iron bi-sulphide is not justified by natural associations or occurrences of pyrite and marcasite deposits.

When we consider that the di-sulphides of iron occur so generally associated with ore deposits, and by far the most common occurrence of ore deposits is in limestones or dolomites, it is difficult to conceive how these solutions might travel for any appreciable distance through such easily soluble rocks and not dissolve and carry along relatively large amounts of calcium and magnesium carbonates.

The lead and zinc districts of both southwestern Missouri and Upper Mississippi Valley show large amounts of iron bi-sulphide associated directly with the ore and occurring in the great majority of cases in limestone or dolomite.
Recently while visiting some of the large caves in the Joplin district of Missouri, attention was called to certain calcite crystals. These crystals varied in length from two to ten inches and exhibited the usual scalenohedron and rhombohedron faces. A close examination of these crystals disclosed numerous inclusions of small marcasite crystals. When held to the light these small inclusions could be seen to be independent of each other and were contained within the calcite very much as impurities within a block of ice. (See diagram 2, page 21). This specimen proves conclusively the contemporaneous deposition of the calcite and the marcasite, or, that FeS₂ and CaCO₃ must have been carried by the same solution.

Even though experiments performed in the laboratory should not have confirmed the above occurrences, it must be admitted, that if these occurrences cannot be reconciled with a theory of origin of iron bi-sulphide, the theory is at fault. Experiments conducted in the laboratory confirm these natural occurrences and indicate that iron di-sulphide may be formed in an excess of such a substance as calcium carbonate.
In attempting to explain the genesis of natural deposits one must account for an adequate source of supply for those compounds assumed to enter into the chemical actions. This may be done in this case as follows:

Hydrogen sulphide.

It is generally conceded that natural solutions may contain large amounts of hydrogen sulphide; enough in fact, to be very active as a precipitating agent. Hydrogen sulphide is often the direct result of vegetable and animal decay. Many of the mineral waters contain hydrogen sulphide in large amount.

Calcium thiosulphate.

The presence of calcium thiosulphate is assumed in this paper to be an important factor in the formation of iron di-sulphide and may be accounted for as follows:

Calcium carbonate acted upon by hydrogen sulphide would result in the formation of \( \text{Ca(HS)}_2 \),

\[
(a) \quad \text{CaCO}_3 + 2 \text{H}_2\text{S} = \text{Ca(HS)}_2 + \text{CO}_2 + \text{H}_2\text{O}.
\]

The \( \text{Ca(HS)}_2 \), being unstable would likely break down into calcium sulphide and liberate some hydrogen sulphide,

\[
(b) \quad \text{Ca(HS)}_2 = \text{CaS} + \text{H}_2\text{S}.
\]
Large amounts of CaS being formed, upon slight oxidation would liberate sulphur,

\[(c) \text{Cas} \quad \text{H}_2\text{O} = \text{Ca(OH)}_2 \quad \text{S.}\]

More CaS constantly forming would unite with the sulphur to form the bi-sulphide of calcium,

\[(d) \text{CaS} + \text{S} = \text{CaS}_2.\]

Upon being oxidized, the calcium bi-sulphide would go readily into the thiosulphate form,

\[(e) \text{CaS}_2 \quad \text{3O} = \text{CaS}_2\text{O}_3.\]

Calcium thiosulphate is very soluble (1 pt. of H₂O at 3°) and is readily carried in solution.

This comparatively simple explanation takes into consideration and has to commend it, not only the chemical possibility, which the laboratory work indicates; but also the geologic probability of the association of those reagents assumed to be active in the formation of iron di-sulphide in natural deposits.

Another probability which suggested itself in this connection was that in solutions of polysulphides iron might exist as a soluble thio-ferrate e.g. Na₂FeS₃ or CaFeS₃; this on addition of an acid would give an unstable thio-ferric acid, H₂FeS₃, whose decomposition products would be H₂S and FeS₂. No experiments

* Comey, "Dictionary of Chemical Solubilities".
have been made in attempting to test this idea but it is the intention to undertake experimental work along this line.

Another factor which it seems might influence the precipitation of iron di-sulphide from solution would be the presence or absence of carbon dioxide gas. Waters flowing beneath the surface in a limestone region become charged with carbon dioxide. Carbon dioxide when passed into a solution of calcium carbonate will cause an acid reaction. This, it is thought, may have to do with the precipitation of FeS$_2$ by providing an acid solution even in the presence of an excess of CaCO$_3$.

It is plain that there are many factors not yet understood which influence the precipitation of FeS$_2$ and the genesis of pyrite and marcasite deposits, if ever clearly understood, will likely not be so simple a matter as has been argued in the past.

-CONCLUSIONS-

1. Pyrite and marcasite are formed from solutions containing basic substances. It might even be argued, from the wide-spread occurrence of iron bi-sulphides in lime-bearing rocks, that calcium carbonate may have
some beneficial action in the precipitation or the solution of pyrite and marcasite.

2. It seems likely that many deposits of iron bisulphide, especially those occurring in limestones or dolomites, were formed by the action of hydrogen sulphide upon a solution of ferrous sulphate and calcium thio-sulphate. The calcium thio sulphate is supposedly formed by the action of hydrogen sulphide upon a calcium carbonate solution.

3. That other solutions carrying thio-ferrates may be responsible of some of the FeS₂ in nature.

4. That CO₂ gas may have an important effect in acidifying solutions and thus producing an acid solution without having present strong mineral acids.

5. That the process of the formation of iron di-sulphide involves many complex conditions as yet poorly understood.
Diagram No. 1.

Hydrogen Sulphide Generator.

Diagram No. 2.

Calcite Crystal.