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Some chemical problems in geology

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SOME CHEMICAL PROBLEMS IN GEOLOGY

BY

REGINALD SCOTT DEAN

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE
Rolla, Mo.
1916

Approved by V. H. Gottschalk
Professor of Chemistry.

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(Some Chemical Problems in Geology)

INTRODUCTION.

This thesis is in the main a compilation of the views held at this institution in regard to the problems discussed as interpreted by the author. No claims for originality are made except in the manner of presentation as the material used has been obtained by conference and class room work with Professor V.H. Gottschalk and Professor G.H.Cox and also to some extent with H.A.Buehler, State Geologist. On the other hand the material is an expression of these ideas as assimilated by the author and hence may in certain cases differ radically from the views held by those mentioned above.

It is hoped that this thesis may serve as an outline for future study of the subjects discussed and its main value is as such rather than as a contribution to the knowledge of chemical geology. With this in mind the bibliographies have been prepared with some care although they are by no means complete.

SOME CHEMICAL PROBLEMS IN GEOLOGY.

THE NATURE AND FORMATION OF IRON DISULFIDE.

(Some Chemical Problems in Geology)

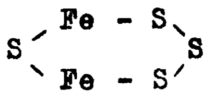
Bibliography of Iron Disulfide.

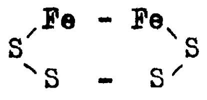
Allen, E.T. Am. Jour. Sci. Ser.4, Vol.33: 169. (1912)

Prepared pyrite and marcasite by (1) action of H_2S on ferric salts (2) by the action of H_2S on ferrous salts (3) by the action of soluble thiosulfates on ferrous salts. This work was done in sealed tubes at 230°. Pyrite and marcasite shown to bear a temperature relation to each other, pyrite being stable above 420° and marcasite below that temperature. Marcasite also shown to be favored by acidity of solution.

Arbeiter, E. Chem. Zeit. 37: 457 thru C.A.7: 547.

Treated pyrite and marcasite with H_2O_2 finding that in pyrite 3 atoms of S go to H_2SO_4 and one to S, while in marcasite one atom goes to each form. Suggests the following formulae

Pyrite 

Marcasite 

Berzelius. Jahresbericht 6: 165 thru Bischof vol.1.

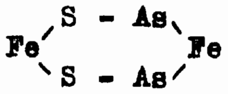
Prepared iron pyrites by heating oxide of iron hydrous or anhydrous, or carbonate, in a stream of hydrogen sulfide at a temperature between 100° C. and red heat.

Bergeat, A. Neues Jahrb. Min. Geol. 39 (1914) thru C.A. 8: 2681.

Finds pyrite with barite and sphalerite crystallized out on the ocean bottom. $CaCO_3$ acted as a precipitating agent.

Beutell, A. Centr. Min. 1912: 225.

Gives the following formula for arsenopyrite



Benedeck, L.Z. Z. Kryst. Min. 48: 447.

Gives the following experiment to show that all the iron of pyrite is ferrous. When heated in a stream of CO_2 to red heat it loses half its sulfur. When heated in H_2O vapor at 300 - 400° FeO results.

Buehler, H.A. and Gottschalk, V.H. Economic Geology 7: 15 (1912).

Studies on the oxidation of sulfides.

Doss, Bruno. Neues Jahrb. Min. Geol. 3: 662.

Describes a mineral of the composition FeS_2 perhaps variable which apparently has been derived from a colloid. It is black, magnetic, soluble in acids and bromine water, and decomposed by boiling water, giving FeS and S.

Thought to represent the colloid condition of pyrite and to be formed by the action of S set free by S bacteria on hydro-troilite ($FeS\ H_2O$) which is known to occur in these miocene clays. S is shown to be present in clays by extraction with CS_2. Doss named the mineral Melnikovite.

Ibid, Z. Pract. Geol. 20: 453.

Shows by metallographic methods that melnikovite changes to pyrite.

Durocher J. Compt. Rend. 32: (1851) 823.

Obtained pyrite by mingling $FeCl_3$ vapor and H_2S.

Doelter, C. Zeit. Kryst. Min. 2: 30 (1886)

Obtained pyrite by heating hematite, magnetite and siderite with H_2S and water at 70° for 72 hours.

Feld, W. Zeit. Angew. Chem. 34: 97 (1911)

Feld prepares pyrite by passing SO_2 thru a solution of $FeSO_4$. On investigation he finds that FeS_2 is formed when S and FeS are boiled together in a neutral or slightly alkaline solution and that $Na_2S_2O_3$ helps the reaction. It is to be noted in this connection that Feld got his mixtures of FeS and S by precipitating ferric salts with alkaline polysulfides. Clarke says, when iron salts are precipitated from an alkaline solution ferrous sulfide and sulfur are thrown down (?) (See Stokes). If the solution is then neutralized or made feebly acid the precipitate is readily transformed into the bisulfide. Probably Feld has misinterpreted his results and the FeS_2 resulted from the action of the acid on the Fe_2S_3 thrown down.

Geitner, Ann. 129: 350 (1864)

Obtained FeS by heating metallic iron with a solution of SO to 300° C.

Glatzel, F. Berliner Chem. Gesell. 23: 37 (1890)

Obtained FeS (crystals of pyrite) by treating $FeCl_3$ with P_2S_5.

Moissan, H. Traité de Chimie Minérale, Vol.4.

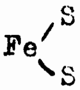
General Reference. Gives directions for preparing Fe_2S_3 and states that Fe_2S_3 is decomposed by acids yielding FeS_2 H_2S and a ferrous salt.

Konschegg and Malfatti, Z. Anal. Chem. 45: 747 (1906)

Konschegg and Malfatti show that the green solution obtained by the action of alkaline polysulfides on ferrous salts does not necessarily contain colloidal FeS as has usually been supposed but rather contains a higher sulfide of iron which being acid in character dissolves and gives an alkaline sulfo-ferrate.

Loczka, J.   Berg. Hutt. Zeit. 52: 209.

Dissolves FeS_2 in H_2SO_4 and shows that all the iron dissolved is ferrous.   Suggests the formula



Poyne, J.E.   U.S. National Museum Proc. 39: 571.

Pseudomorphs of marcasite after pyrrhotite.

Pöschl, Viktor.   Zeit. Cryst. Min. 48: 572.

Pyrite is somewhat harder than marcasite.

Senarmont, De.   Ann. Ch. Phys. 22: 129 (1851)

Prepared FeS_2 by the action of alkaline polysulfides on ferrous salts.

Stokes, H.N.   Journ. Amer. Chem. Soc. 29: 304 (1907)

Shows by the reactions

$$FeS + Zn(OH)_2 \rightarrow Fe(OH)_2 + ZnS$$

$$Fe_2S_3 + 3Zn(OH)_2 \rightarrow 2Fe(OH)_3 + 3ZnS$$

that the precipitate by alkaline solutions of sulfides in ferric salts is Fe_2S_3.

Sirovich, G.   Atti. Accad. Lincei, 21: 352.

In the vicinity of marcasite deposit at Castelnuevo de Poto are formed Fe springs and H_2S pools.   Thus confirming the views of Allen.

Sidot, T. Comptes Rend. 32: 823 (1851)

Prepares FeS_2 by heating magnetite to redness in a stream of H_2S. The product which he obtained was probably troilite but Doelter has prepared pyrite in a similar manner.

Schondörf and Schroeder. Neues Jahrb. Min. Geol. 1911.

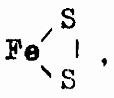
Describe pseudomorphs of marcasite after pyrrhotite.

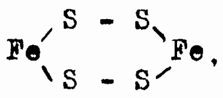
Wöhler. Ann. 27: 26 (1836)

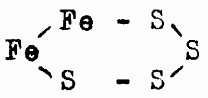
Obtained FeS_2 by heating a mixture of Fe_2O_3 and sulfur with NH_4Cl till the latter sublimed.

Iron Disulfide

The nature of iron disulfide: Many structural formulae may be written for pyrite and marcasite, among the commonest are:







These formulae rest largely on erroneous experimental evidence. Thus J.Loczka dissolves pyrite in sulfuric acid and finds that all the iron which is in solution is ferrous. B.Doss also dissolves iron disulfide in hydrochloric acid in an atmosphere of carbon dioxide and finds all the iron in the ferrous state. L.Bendeck heated iron disulfide in a stream of water vapor and obtained ferrous oxide. It is obvious that these experiments mean nothing as in each case the hydrogen sulfide liberated would be sufficient to accomplish the reduction.

It seems probable that the iron in pyrite is tetravalent belonging to the same series of compounds as the ferrates. These ferrates are formed by the action of potassium peroxide on iron hydroxide or by the action of chlorine on a suspension of iron hydroxide in potassium hydroxide solution. From the work of Konschegg and Malfatti it has been shown that the analogous sulfur compounds are formed when iron salts are treated with alkaline polysulfides, and exist in the dark green solution which is formed in this way. There is no reason to believe that while the ferrates and their anhydride FeO_2 are very unstable that the corresponding sulfur compounds and their anhydride FeS_2 might not be stable and even exist in nature as marcasite and pyrite. In fact this seems extremely probable from Senarmont's synthesis of pyrite; he obtained pyrite by the action of alkaline polysulfides on iron solutions at 180°. Allen has also prepared pyrite in this way. The reactions involved might be:

$$FeSO_4 + 2Na_2S_x = Na_2FeS_3 + Na_2SO_4$$

$$Na_2FeS_3 = Na_2S + FeS_2$$

From the analogy of this reaction with that of the sulfides of arsenic and antimony we might expect to obtain FeS_2 also by the proper neutralization of the green sulfo-ferrate solution. Whether this can be done or not has not been determined. The synthesis of pyrite by Glatzel is also worthy of note at this point; he obtained pyrite by the action of phosphorus pentasulfide in ferric chloride which would seem to indicate a higher sulfide of iron.

We may then give a less forced explanation of the structure of pyrite than has heretofore been given, viz, that the iron is tetravalent and the formulae is $S=Fe=S$

The formation of iron disulfide in nature from cold waters: In spite of the large amount of work that has been done on the subject there is as yet no definite solution to the problem of the formation of pyrite and marcasite in nature. The literature on the subject is very confusing; we find that pyrite and marcasite may be formed in a large number of ways, none of which seem to be particularly applicable to their natural formation from cold waters. It is the purpose of this paper to give a definite method by which ferric disulfide may be precipitated in cold waters under conditions which exist in nature.

Starting from the first, - in the formation of iron disulfide from natural waters we have the erosion of the igneous rocks and the solution of the iron and sulfur which go to form the pyrite and marcasite. It is very probable that pyrite itself is the principal constituent of igneous rocks from which the iron and sulfur are dissolved. The iron and sulfur then would be in solution in the form in which they are derived from the oxidation of pyrite. According to Gottschalf and Buehler, pyrite and marcasite may oxidize in various ways, viz.:

(1) $FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$

(2) $2FeS_2 + 3O = Fe_2O_3 + 4S$

(3) $FeS_2 + 3O + H_2O = FeSO_4 + H_2S$

(4) $FeS_2 + 6O = FeSO_4 + SO_2$

the first of the above reactions being by far the most important. With an excess of oxygen such as we would have in erosion we would naturally get further oxidation giving ferric sulfate and sulfuric acid thus

$$2FeSO_4 + O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O$$

the ferric sulfate so formed is however not stable in solutions which are as dilute as those with which we have to deal, and hydrolyses giving colloidal ferric oxide and sulfuric acid. For our purposes we may consider the colloidal ferric oxide as a simple suspension of very finely divided ferric oxide. We have then a solution containing sulfuric acid and very finely divided ferric oxide from which to precipitate the pyrite and marcasite.

The only precipitants which are worthy of mention are hydrogen sulfide and organic matter. It seems doubtful whether organic matter can precipitate the sulfides direct from the sulfates, and if any reduction did take place it could only result in the production of hydrogen sulfide as sulfuric acid is the only sulfate present. Hydrogen sulfide then is the only precipitating agent with which we have to deal.

From the above it would seem that pyrite and marcasite are formed from the action of hydrogen sulfide on finely divided ferric oxide in slightly acid solutions.

This is borne out by experimental evidence as will be shown. C.Doelter obtained iron disulfide by heating hematite with hydrogen sulfide and water at 70-90° for 72 hours. Allen has obtained the disulfide by treating iron hydroxide or oxide with hydrogen sulfide in acid solution even at room temperature he attributed the action to be first the formation of FeS and S and the subsequent reaction of the two to give FeS_2 (on this point I cannot agree with him). It would seem then that the finely divided colloidal ferric oxide would react much more readily and some experiments on ferric oxid hydrosols indicated that this was the case. We have then a simple method by which iron disulfide may be formed in nature from cold waters.

The chemistry of the reaction may be worked out as follows: According to Stokes, if iron hydroxide is treated with hydrogen sulfide in alkaline solution, ferric sulfide (Fe_2S_3) is formed. Moissan also describes the preparation of ferric sulfide by passing hydrogen sulfide thru a boiling suspension of hydrated iron oxide, further Moissan states that if ferric sulfide is treated with dilute acids it leaves a residue of pyrite. It would seem then that ferric salts sometimes break up giving ferrous salts and salts in which iron has a valence of four and if an acid suspension of iron oxide were treated with hydrogen sulfide we would expect to obtain the pyrite direct instead of thru the intermediate Fe_2S_3. The equations for this might be written

(1) $Fe(OH)_3 \rightleftarrows Fe(OH)_2 + Fe(OH)_4$

(2) $Fe(OH)_2 + H_2S \rightarrow$ No reaction.

(3) $Fe(OH)_4 + 2H_2S \rightarrow FeS_2 + 4H_2O$

now writing the mass law equation for (1) we have

$$\frac{C^{Fe(OH)2} \times C^{Fe(OH)4}}{C^{Fe(OH)3}} = K$$

in which K is for ordinary conditions extremely small but if H_2S be added reaction, (2) cannot take place in acid solution and only reaction (3) will take place giving FeS_2 which is insoluble in water and is hence removed from the system and makes $C^{Fe(OH)4}$ smaller and to keep K constant more $Fe(OH)_3$ must break up. In this way one-half of the iron may be deposited as FeS_2 and the other half reduced to Fe" which may then be oxidized and the reaction completed.

This explanation is borne out by the syntheses of Allen and of Feld. The latter obtained iron disulfide by neutralization of a solution of ferric iron which had been precipitated with alkaline sulfides which according to Stokes would be nothing more than the action of acids on Fe_2S_3. Allen's syntheses are of practically the same nature; he, however, in one instance used FeS, S, and H_2S which is suggestive of the explanation offered by Allen and practically also by Feld and Doss, i.e., that the FeS_2 results from the combination of FeS and S.

This latter explanation seems particularly plausible if the sulfur and ferrous sulfide were in a colloidal condition so that they might mutually precipitate each other. That this may at times be the case seems probable from the work of B.Doss on the colloidal form of pyrite which he calls melnikovite. (F.T.Wherry suggests K-Pyrite). He concludes that this is formed by the action of S liberated by bacteria with hydro-troilite ($FeS.H_2O$). This explanation is inadequate in one place, i.e., how an indefinite colloidal combination can have crystal form and give such definite ratios. That this is not impossible however is shown later in the consideration of the natural iron oxides.

Factors controlling the formation of marcasite or pyrite: Allen has shown that the principal factors determining whether marcasite or pyrite is formed synthetically are temperature and acidity of solution. He has shown that in the synthesis of FeS_2 from solutions of iron salts, high temperatures and low concentration of acid favor the formation of pyrite, and low temperatures and high concentration of acid favor the formation of marcasite. There are various reasons however why these relations do not hold in nature. Among these may be mentioned the presence of another component which may effect the range over which each of these minerals exist, and thus allow the formation of pyrite from cold solutions (inversion point of marcasite-pyrite is 450° according to Allen). The deposition of marcasite in limestones where the solutions could not have been acid and sometimes its deposition from hot solutions cannot be accounted for readily from these facts but it seems probable that these relations may hold for original deposition.

The most important factor in determining the crystal form of the mineral is the crystal centers of neuclei. These may be of two kinds, crystals previously existing around which new ones may crystallize or nascent ultramicroscopic neuclei existing as colloid particles in the depositing solution. These particles have been derived from the dissolved mineral. Thus if a pyrite deposit is taken in solution and redeposited by secondary concentration the secondary mineral may be pyrite even though the deposition took place from a cold acid solution. It will be noted that this case has as a limiting condition, the transportation of pyrite and marcasite altogether as colloids.

SOME CHEMICAL PROBLEMS IN GEOLOGY

THE NATURAL FERRIC OXIDES

(Some Chemical Problems in Geology)

Bibliography of the Natural Ferric Oxides.

Bancroft, W.D. Journal of Physical Chemistry 5: 28.
Some notes on the color of natural iron oxides.

Bemmelen, J.M.Van. Die Absorption, Gesammelte
Abhandlungen ueber Kolloide und Absorption.
Dresden 1910. Verlag von T.Steinkopf.

In review of previous work he states "Wittenstein found that the precipitated iron oxide crystallized after long standing under water. Z.Roussin obtained a crystalline powder from the action of KOH on "Nitrosulfures de fer", it had the composition $Fe_2O_3H_2O$. G.Resseau also noted that at high temperatures the amorpheus Fe_2O_3 crystallizes when in a medium of molten KOH or alkali chloride and gives crystals of the formula $Fe_2O_3H_2O$. Further if this hydrate which is formed at high temperatures be again heated it loses water. Also H.Brunck and H.Graebe found $Fe_2O_3.H_2O$ in hexagonal crystals in Fe_2O_3 which had been in molten KOH. In trying out Wittenstein's results Van Bemmelen was unable to obtain a crystalline product, but found that loss of water could be helped by lowering the temperature but no crystalline material could be obtained even at -20° after long standing. He found that the water contained in the gel of ferric oxide differed considerably at different temperatures and vapor pressures. The relation is shown in the following table:

Temperature	Vapor Pressure	Mol.H_2O Frozen	Mol.H_2O Unfrozen
15°	dried	7.4	7.7
15°	9.37 = 84% after 2 weeks	7-6.1	7-6.4
15°	70% after 3 months	4.8-4.2	4.5-4.2
15°	00 mm after 2 months	2.0-1.5	2.0-1.46
100°	in room air	.97-.9	-.96
100°	00 mm	.87	1.37-.96

He obtained crystals of the formula $Fe_2O_3.H_2O$ from ferrite solutions and found that the crystals were pseudomorphic after the ferrites having been formed from the decomposition of the ferrites. In regard to the constitution of the natural mineral göthite he found that it did not lose water in dry air at 15°, 68°, 100°, 130°, 150°, 170°, 190°, 210°, 230°, 250°, First at 280° it loses a noticeable amount of water; at 300° it is all lost in five to six hours the last mol remaining tenaciously.

Dana, J.D. A System of Mineralogy.

He describes the following species: Hematite, Fe_2O_3. Rhombohedral, H=5.5-6.5. G=4.9-5.3. crystals=5.20. Turgite $2Fe_2O_3\ 3H_2O$ no crystal form, H=5.6, G=4.29-4.49. Göthite Fe_2O_3 H_2O orthorhombic H=5-5.5, G=4.0-4.4, crystals 4.37. This may be made artificially by heating a solution of $FeCl_3$ (30-85 parts in 100), the crystals so obtained have the formula $Fe_2O_3.H_2O$ and are orthorhombic. Limonite $2Fe_2O_3$ $3H_2O$ not crystallized, H=5.5, G=3.6-4. Xanthosiderite Fe_2O_3 $2H_2O$, H=2.5, G not given. Formed when Fe_2O_3 is precipitated from hot solutions. Limnite Fe_2O_3 $3H_2O$.

Taylor, W.W. The Chemistry of Colloids.

p.161. The structure of gels, as emulsoid sols are two phase liquids and as gels are obtained from them by cooling or evaporation the conclusion is natural that gels also possess the same structure as the emulsoids; two solutions the one more concentrated then the other forming the inclosing walls of the cells which contain the other more dilute solution. The only difference is that the one solution, if not both, is more concentrated than before and thus confers the greater viscoscity and rigidity. The structure then is cellular, the walls being a highly viscous solution enclosing a more dilute one. This is confirmed by observations in many directions, at least so far as the cell walls are concerned, especially by J.M.Van

Bemmelen and above all by Bütschli who closely examined the microstructure of a series of precipitates and gels. Now all these microstructures are more or less after the honeycomb pattern and several other observers have confirmed Bütschli's observations". Von Veimarn considers the structure secondary: he says, "There are however precipitates so fine grained that in the microscope the form of the grain appears round owing to diffraction and other phenomena".

The Nature of a Gel.

As gels are formed from the evaporation and cooling of emulsoid sols as well as by coagulation of them there is no reason to believe that any structure which a gel may possess was not inherent in the emulsoid sol from which it was formed. The real key to the structure of a gel then is the nature of the sol. On this point there are two existing views which are worthy of our consideration. The one in which the sol is supposed to be made up of two solutions of the substance one more dilute than the other in which the more concentrated one forms the walls of the cells in which the other is contained. Just why the two solutions do not mix is not said and indeed the whole matter seems a trifle absurd. The second view which is much more logical is the one held by P.P.Von Veimarn. He holds, that sols differ from solutions on the one hand and suspensions on the other only in the matter of dispersity, and gels are merely concentrated sols. The view of Von Veimarn with some modifications will as readily explain the observed facts in regard to the microstructure of gels as will the two solution theory, because as he pointed out grains when sufficiently small appear round regardless of their actual shape. Without considering the relative value of either of these theories or the deductions that may be made from them, let us present a new theory which we may call the electron theory. According to this theory as in Von Veimarn's, there is a constant gradation between suspensions, sols, and solutions, but starting where Von Veimarn's theory leaves off, let us take up some of the reasons why some things form suspensions, some sols, and some solutions with a given medium while one substance may form all three classes with different mediums. If we take a given solid there must be electronic equilibrium within it, with a comparatively small number of partially neutralized (half-bound) electrons on the surface: (use the word "free" to indicate this latter kind), but if we break the solid the equilibrium no longer exists and there must be a larger number of "free" electrons and the more we break it the more "free" electrons relatively do we have. If then a dispersing medium be added, as water, the "free" electrons of the particles attract the medium and attach a sufficient amount of it to themselves to satisfy their charges, the substance then becomes dispersed in the medium each particle being held apart by the attracted medium in which it is enveloped. Diagramatically this is shown in Fig.I.

The difference between a suspension, a sol, and a solution is only a difference in the degree of subdivision and consequent amount of medium held relative to the weight of the particle which determines the ease of agglomeration.

If a substance has so little electronic attraction between the molecules that the medium may separate the molecules from each other completely, we have formed a solution. If the molecules separate in bunches or if they are exceptionally large we have a sol and if the material will break up into very large aggregates we have a suspension. If the cohesion between the molecules is sufficiently large neither a solution or a suspension will form. The nature of a gel will be the same as a sol and will consist of small particles each one enveloped in a cell of water which it holds by means of its electronic charges. The microstructure of a gel then would be as Van Bemmelen and Bütschli have found it, the apparent cell walls being the surfaces of discontinuity between the various portions of adsorbed water around the particles. So much for the theory; now let us see what we may deduce from it.

The particles in the gel may be crystalline or may not be crystalline; if they are crystalline they will be left as a cryptocrystalline aggregate when the water is dissipated. It seems probable that chert may be formed in this way and is hence at least partly cryptocrystalline. If the particles are not crystalline the result will be an amorphous mass. The breaking down of a gel would be most easily affected by neutralizing the charges which hold the water. This might be done in a number of ways, viz. electrolytes, ultraviolet light, charged air or water, X rays, etc. It will be noted that any of these ways involve the addition of free charges.

The charges may be in part neutralized giving a series of hydrated compounds.

The water of a gel would not be lost at 100° but would come off only at a higher temperature as with a solution.

When a gel is formed by the imbibition of water by a solid colloid there is always considerable decrease in volume and consequently gels should possess a greater density than would be calculated from their constituents.

The Natural Ferric Oxides.

Various minerals are described by Dana varying in composition between Fe_2O_3 and $Fe_2O_3 3H_2O$. Among these are turgite, göthite, xanthosiderite, linnaeite, limonite, and hematite. Of these minerals only göthite and hematite show crystalline form. Now according to Van Bemmelen, the water content of hydrated iron oxides varies with the temperature and vapor pressure; consequently we would not expect definite minerals, but rather a series which vary continuously in composition from Fe_2O_3 to $Fe_2O_3 3H_2O$ which is what we have in nature. It is probable that these minerals other than göthite and hematite do not have a definite composition but are members of a continuous series of "adsorption compounds" or gels of Fe_2O_3 and H_2O. That they are "adsorption compounds" or gels is shown by their indefinite character, their failure to lose water at 100°, their densities being greater than that which would be calculated by the method of mixtures; thus the density of turgite is 4.49 and that calculated by the method of mixtures is 4.25, göthite has a density of 4.37 and the calculated density is 3.65; and limonite has a density of 3.8 while the calculated density is 3.13.

The crystalline member of the series göthite is interesting as few "adsorption compounds" or gels (as this appears to be) show a definite crystalline form. But if there is no difference between a solution and a sol except in the matter of dispersity, there is no difference between an adsorption compound of water and a compound with water of crystallization except one of degree and they may grade imperceptibly into one another. Thus it seems not improbable that in göthite we have one of these gradation phases in which the particles are still sufficiently near molecular size to afford crystalline form but whose properties are more like those of a gel. The other possibility in regard to göthite is, that it is an amorphous gel occurring pseudomorphically crystalline, but if this be the case, it is not obvious what it is pseudomorphic after. The same considerations will explain the color; thus, the color depends on the size of the particles and the distance between them and just as a concentrated solution of ferric chloride is red or brown and a dilute solution is yellow so ferric oxid containing little water is brown or red while the more hydrated oxides are yellow.

In this connection, the formation of the oxides in nature might be commented upon. It seems only logical that they should be carried colloidally and precipitated by the means which precipitate a colloid, namely, the presence of a colloid of opposite sign or an electrolyte. If the iron is in solution in any form it will in contact with air soon oxidize to the ferric state when it will hydrolyze giving colloidal ferric hydroxide and free acid. This colloidal ferric oxide then is subject to precipitation by calcium carbonate clay, etc. This process may account for the precipitation of some such extensive iron bearing horizons as we have in the silurian.

SOME CHEMICAL PROBLEMS IN GEOLOGY

THE REDUCTION OF SULFATES TO SULFIDES

(Some Chemical Problems in Geology)

The Reduction of Sulfates to Sulfides.

The reduction of sulfates to sulfides is a matter of primary importance in geological chemistry. The sulfides form by far the greater portion of the metallic ore minerals, among which might be mentioned galena (PbS), sphalerite (ZnS), chalcocite (Cu_2S), etc. In all theories of origin of these ores some method must be given for the production of the sulfides: in so far as ore bodies derived from sediments are concerned, the agency appealed to for the original deposition of the ore has been the reduction of sulfates by organic matter in some form or other.

Bain and Van Hise, Ore deposits of the Mississippi Valley.
Buckley and Buehler, Geology of the Granby Area, Missouri Geological Survey, Vol.IV.
Buckley, Geology of the disseminated lead deposits.
Cox, Illinois lead and zinc.

It is of interest that this phenomena which is of the highest importance in the origin of these ores has been given so little careful study. The geologist has not concerned himself with the conditions necessary for the reduction of sulfates but has assumed this reduction by material of all kinds under any conditions which were convenient. A few experiments will readily convince one that the reduction is not as simple as one would expect from the equations written in the various geologic theories, but is one requiring very special conditions. Reduction of sulfates to sulfides is not an easy matter by other means than organic matter, none of the common reducing agents, as nascent hydrogen or sulfur dioxide effect the reduction. There is one case given in Watts' Dictionary, in which lead sulfate was reduced partially to lead sulfide by being heated in a stream of ammonia. The reduction by the electric current has never been accomplished, and as far as reduction by organic material is concerned any information which we may glean from the literature is indefinite and hazy. There is the famous case first noted by Bischof and which John Percy attempted to repeat but without success: of this Percy says in a series of lectures on chemical geology given before the Royal College of Mines and published in the Chemical News, "There is the well known experiment recorded by Bischof and often repeated by the artificial production of iron pyrites in a bottle containing the remains of an unfortunate mouse which had been left some years in a solution of green copperas. Distinct cubes of iron pyrites, very small it is true, are said to have been formed. I hoped to have been able to present to you a repetition of the experiment. For some years I kept the remains of a rat in green copperas, but unfortunately the air got access. I did not find the slightest trace of iron pyrites but as I said the experiment was defective and therefore I attach no importance to it". It is possible of course that John Percy caught the wrong rat but in any event we certainly could not have very large deposits of sulfides formed by the reduction of sulfates thru the agency of dead rats unless rats were extremely plentiful in bygone ages.

An experiment of considerably more weight is given by Bischof, Chemical and Physical Geology, p.15, Vol.I, "Alkaline and earthy sulfates are reduced by carbonaceous substances in the wet way into sulfurets. This decomposition takes place in mineral waters which contain sulfates especially sulfate of soda and organic matter: when kept for some time in corked bottles they acquire an odor of sulfuretted hydrogen. This decomposition is affected not only by organic matter dissolved in water but also by accidental impurities such as pieces of straw, etc.*** Shortly afterward I had the opportunity of making a similar observation at the inclosure of a mineral spring. As the hollow wooden tube thru which the spring previously issued was taken away and the loose earth removed, dark yellow iron pyrites of metallic luster were found in it. They were seldom crystalline and contained pieces of vegetable stalk or splinters of wood which appear to have given first occassion to its formation. It scratched glass plainly and analysis showed it to be pure iron pyrite. The water contained $\frac{1}{33333}$ sulfate of soda. I found the key to the explanation of this phenomenon by other experiments. In order to prevent the precipitation of iron in mineral waters, I filled a large number of bottles and put into each a small quantity of sugar, closed them with a cork pitch and leather in the usual manner; after 13 months, black flocks had separated which were sulfuret of iron; after $3\frac{1}{2}$ years I opened several of the bottles. The contents of all smelt more or less strongly of sulfuretted hydrogen and the same black powder had separated and sometimes also in black flocks. The analysis of this black powder collected in more than 30 bottles showed that it had nearly the composition of iron pyrites *************. The mineral water itself was scarcely clouded with barium chloride after separation of the black powder. The sulfate of soda which in the unaltered water amounted to $\frac{1}{10000}$ had therefore been decomposed by the sugar."

We have no reason to doubt the authenticity of this experiment, but it was performed on natural waters the composition of which is not known: we might attribute the formation of pyrite to one of a dozen causes other than direct reduction by sugar. Bischof is clear however on the point that the reduction is brought about by organic compounds and not by carbon.

Jenney a hundred years later seems to have taken the equations written by Bischof and others in which the symbol C was used to indicate the reducing organic material of unknown nature as literal and in an article printed in "Ore Deposits", published by the American Institute of Mining Engineers, he seems to consider the reduction may be brought about by such inert material as charcoal: quoting from this article, "In the reduction of the metallic sulfates to sulfides by carbon, the action in each case is deoxydation with the formation of CO_2 according to the following equations:

$$ZnSO_4 + 2H_2O + 2C = ZnS + 2H_2CO$$

$$PbSO_4 + 2H_2O + 2C = PbS + 2H_2CO$$

The complete reduction of ferrous sulfate to pyrite or to marcasite requires that free sulfuric acid be present

$$2FeSO_4 + 2H_2SO + 5H_2O + 7C = 2FeS_2 + 7H_2CO$$

The carbonates of lead and zinc and iron in the presence of alkaline sulfates are reduced by carbon to the corresponding sulfides galena, blende and pyrite.

$$PbCO_3 + Na_2SO_4 + 2H_2O + 2C = PbS + Na_2CO_3 + 2H_2CO$$

$$ZnCO_3 + CaSO_4 + 2H_2O + 2C = ZnS + CaCO_3 + 2H_2CO$$

$$2FeCO_3 + 4CaSO_4 + 5H_2O + 7C = 2FeS + 4CaCO_3 + 5H_2CO$$

****

The reactions which take place when the hydrocarbons form the reducing substances are more complex *************. Oxygen seems to be needed to complete the reaction by petroleum of the paraffin series.

$$12ZnSO_4 + C_nH_{2n+2}O = 12ZnS + 16H_2CO + H_2O$$

Where the petroleum is partly oxidized ferric sulfate forms pyrite in the presence of free sulfuric acid. The reaction may be written as follows:

$$3Fe_2(SO)_3 + 3H_2SO_4 + C_xH_xO = 6FeS_2 + 16H_2CO + 2H_2O$$

*******************. Hydrogen and carbon have affinities for oxygen stronger than those of any other chemical elements under conditions normally occurring in ore bodies ********************." He gives the following table of relative reducing powers:

Hydrogen - - - - - - - - - - 100

Marsh Gas - - - - - - - - - - 50.0

This article is party erroneous and altogether misleading; the table of reducing powers which he gives and which has been considered very valuable by many geologists is hardly worthy to be the work of a college freshman and while it is undoubtedly correct in so far as it shows the relative amounts reduced if the reaction goes to completion in the manner in which he has calculated it, it is very misleading in that 99% of the reactions will not go at all.

In Bulletin 606, U.S. Geological Survey, Siebenthal gives the following: "The reduction of sulfates by organic matter, though generally accepted as a fact, does not seem to have been actually demonstrated by any experiment yet reported that negatives the possibility of the evolution of hydrogen sulfide from organic matter by the agency of bacteria or even the possibility of the direct reduction of the sulfates by sulfur bacteria. The writer has been orally informed by Dr. E.T.Allen of the Geophysical Laboratory of the Carnegie Institution, by Professor H.A.Buehler, of the Missouri Geological Survey and Dr.Chase Palmer of the United States Geological Survey that they have not succeeded in reducing sulfates by organic matter. Clarke put cupric sulfate, ferrous sulfate, sulfur dioxide, and powdered coal in a flask which was shaken daily for 122 days, but there was no formation of copper sulfide at the end of the experiment from which he concludes that carbon alone would not precipitate the sulfide. Hoppe-Seyler describes the reduction of a sulfate by nascent methane derived from the fermentation of cellulose but the fermentation was probably caused by bacteria and hydrogen sulfide may have been thus evolved in and have caused the reduction of the sulfate."

From this it is seen that the reduction of sulfates to sulfides is not an easy matter except thru the agency of bacteria.

There is a vast amount of literature on the reduction of sulfates by bacteria, a short bibliography of which is given here.

Saltet, R.H. J.C.S. 76: 265.

The reduction of sulfates to H_2S takes place in two stages the sulfates are partially reduced to sulfites or other oxygenated sulfur compounds by Bacillus desulfuricans and these are afterwards reduced to H_2S by other species of bacteria.

Etard, A. and Oliver, L. C.N.46: 255.

The authors show that certain algae have the power of reducing sulfates in solution.

Planchud, M. C.N.48: 34.

Certain algae acting as a ferment have the power of reducing sulfates; this reduction never takes place in the presence of lifeless organic matter.

Delden, A.Van. J.C.S. 86: 67.

The optimum temperature for microspira desulfuricans is between 25 and 30° but even at 37° H_2S is produced abundantly.

Hartley, W.N. J.C.S. 76: 437.

The sulfates in fresh and sea water mud are reduced to carbonates and H_2S by the fermentation of cellulose thru the agency of bacteria.

There are various objections to the theory that bacteria play a very important part in the natural reduction of sulfates to sulfides among which may be mentioned the fact that they have only a small temperature range, they are killed by weak acid solutions, etc.

I am of the opinion that sulfates could be reduced to sulfides could the proper reducing agent be found. I am informed by Professor Gottschalk that students often obtained sulfides by reduction with alcohol when following the regular qualitative scheme for the separation of the Pb, Cu, Bi, Cd group, i.e., the sulfides are dissolved in dilute nitric acid and taken to SO_2 fumes with H_2SO_4, it is then diluted and the alcohol added and the lead sulfate filtered off. The alcohol is then boiled off the filtrate and it was at this point that a black precipitate often appeared which was supposed to be lead or copper sulfide. However, I have tried this at least a dozen times and have had others try it as many more and in no case has any precipitate formed. Other reducing agents as nascent hydrogen have no effect on the sulfates whatever. It is possible that the reduction may be brought about by induced reaction. In regard to this there are two possibilities, that the reducing organic material, e.g. cellulose is autoxydized, breaking up air into ozone and antozone as in the Brodie-

Schönbein theory. The ozone would then combine with the oxygen of the sulfate giving off molecular oxygen and leaving the sulfide. Or that the oxydation of the cellulose produces a reducing substance which reduces sulfates to sulfides.

An experiment with the autoxydation of P shows that the former is entirely improbable. We are left therefore with two possibilities that sulfates cannot be reduced by cellulose without the aid of bacteria, or that they are reduced by the oxydation products of cellulose. It is interesting to note in this connection that I once obtained a reduction of Na_2SO_4 by sugar and yeast, but this may have been due to bacterial action. At another time some sawdust was allowed to remain damp for two months and then a water extraction of it made; the brown humus solution so obtained was sterilized and mixed with Na_2SO_4 but no H_2S had formed even after three weeks standing.

In conclusion it may be said that if the formation of sulfides by the reduction of sulfates is appealed to in a theory of ore formation the burden of the proof rests upon the one who suggests it.

SOME CHEMICAL PROBLEMS IN GEOLOGY

RELATIONS OF PYRITE TO MARCASITE AND SPHALERITE TO WURTZITE

Relation of Pyrite to Marcasite and Sphalerite to Wurtzite.

Allen, Crenshaw and Johnston have found pyrite and marcasite to bear a monotropic relation to each other, pyrite being the stable form at all temperatures. It would follow then that marcasite would change into pyrite at all temperatures, the rate being presumably too slow to be noticeable up to 400° and becoming reasonably rapid at 450°. The presence of acid favors the formation of marcasite. A representation of such a monotropic relation is given in Fig.1. The following table from Allen, Crenshaw and Merwin shows the percentage of pyrite obtained in synthetic products at observed temperatures and acid concentrations:

Mineral Sulfides of Iron, American Journal of Science, Series 4: 33: p.169 (1912)

Formation of Marcasite and Pyrite, American Journal of Science, Series 4: v.38; p.393 (1914)

Temperature:	Initial acid concentration:	Final acid concentration:	Average acid concentration:	% Pyrite
200°	0.10	1.14	0.62	4.%
	0.75	1.35	1.05	3.7
	1.00	1.88	1.44	2.7
	1.00	1.73	1.38	2.9
	1.25	1.83	1.54	2.25
	1.50	1.78	1.64	18.5
	1.75	2.32	2.03	11.
	2.00	2.50	2.25	5.0
	2.00	2.42	2.21	3.0
	2.50	3.00	2.75	26
	2.75	3.05	2.90	21
300°	0.10	1.08	0.59	49.5
	0.50	1.20	0.85	45.5
	1.00	1.90	1.45	37
	1.00	1.90	1.45	36
	1.50	2.22	1.86	25
	2.00	2.20	2.19	28
	2.00	2.38	2.20	20
	2.50	2.40	2.50	21
	2.50	2.50	2.60	25
	3.00	2.60	2.92	26

It will be noted that the amounts of pyrite formed are proportional to the acid concentration and the following table taken from Allen, Crenshaw, and Johnston shows the effect of temperature on the formation of pyrite and marcasite:

Taken				Found
Temperature	$FeSO_4 7H_2O$ S	Free acid	Water sat H_2S	% Pyrite
300°	5 grams	0.5 grams	100cc	57.5
300°	" "	" "	" "	56.5
200°	" "	" "	" "	32.0
100°	" "	" "	" "	6.0
100°	" "	" "	" "	10.0

It is not obvious why mixtures of the two minerals are formed at any given temperature and acid concentration since it would appear that the marcasite would either change entirely into pyrite or no change would take place instead of having in every case a product containing both minerals.

Assuming that the relation is reproducible, i.e., that time does not enter. In explanation of this it seems probable that solid solutions are formed between the two minerals in either one or two series. These might be represented by two types of curves either of which will satisfy the known conditions for pyrite and marcasite. The first possibility is shown in Fig.2. The second possibility is shown in Fig. 3. This would give two series of solid solutions, one of pyrite in marcasite and the other of marcasite in pyrite which would exist together over a certain range above which we would have pure pyrite and below which we would have marcasite. This might well be the case from the experimental evidence except that we would not predict irreversibility from this diagram.

In support of the solid solution theory of pyrite and marcasite the field evidence is especially convincing. Some crystals found in the Jefferson City dolomite near Rolla, Missouri, in which the fundamental form was the cube with slight modification by the octahedron: the faces were curved due to what may be called sub-parallel intergrowth. (Private communication of E.T.Wherry.) These crystals were pyrite so far as their external form was concerned but the Penfield test (Brush and Penfield, "Determinative Mineralogy") showed them to be at least in part marcasite and that they represent a solid solution and not a simple mixture of the two minerals is shown by their electromotive force measured against copper this is found to be .28 volt while Gottschalk and Buehler find .22 volt for pyrite and .37 volt for marcasite. If it were a simple mixture, only the potential of the most noble mineral would be obtained. Dr.E.T.Wherry, of the United

States National Museum considers the crystals to represent paramorphs of marcasite after pyrite but this is obviously impossible as pyrite is the stable form and any change would be in the opposite direction: further a paramorph would not show an intermediate potential.

These crystals are not particularly uncommon and were noted by Stokes*, who considered them merely intergrowths and found some specimens which clearly contained two kinds of crystals. This last observation seems indicative of the second form of curve as it is the only form of curve in which two kinds of crystals both solid solutions could exist together as the solid phase.

The sphalerite wurtzite case is very similar except that they bear an enantiotropic relation to each other the sphalerite changing to wurtzite at 1020°. The presence of acid favors the formation of wurtzite. The following table from Allen, Crenshaw, and Merwin shows the relation of acid concentration to the crystalline form of ZnS at 325°.

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*Bulletin 186, U.S. Geological Survey, page 35.

Initial H SO	Final H SO	Composition of product	
		% Wurtzite:	% Sphalerite.
3.0	0.9	0	100
3.0	1.1	0	100
5.0	2.0	0	100
6.0	2.3	60	40
7.5	3.0	30	70
9.0	3.3	50	50
9.0	4.2	100	0

This table shows that below a given acid concentration sphalerite is formed and then over a certain range the product is composed of two kinds of crystals and above this the product is pure wurtzite. The simplest explanation that can be offered for this is the formation of two solid solutions as suggested in the second case for marcasite and pyrite this is shown in the temperature concentration diagram in Fig.4, the dotted lines representing the curves for varying acid concentrations.

Figure I

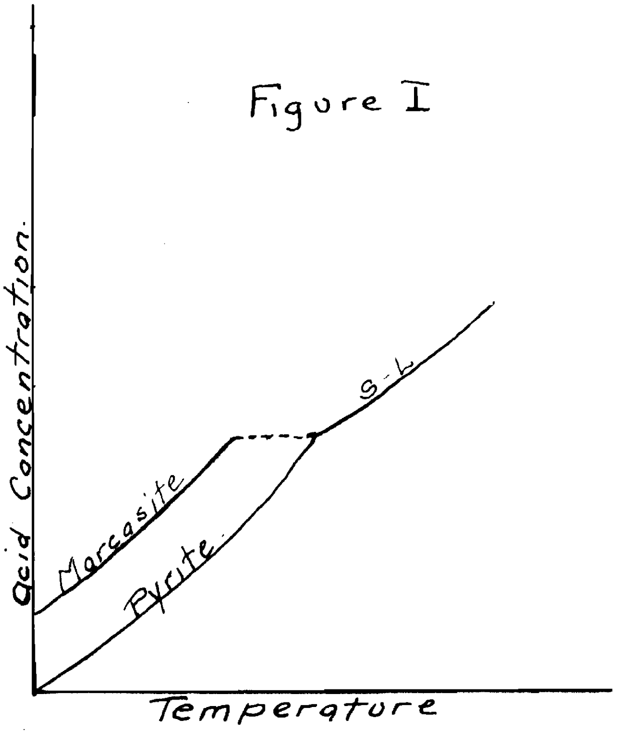

Figure 2.

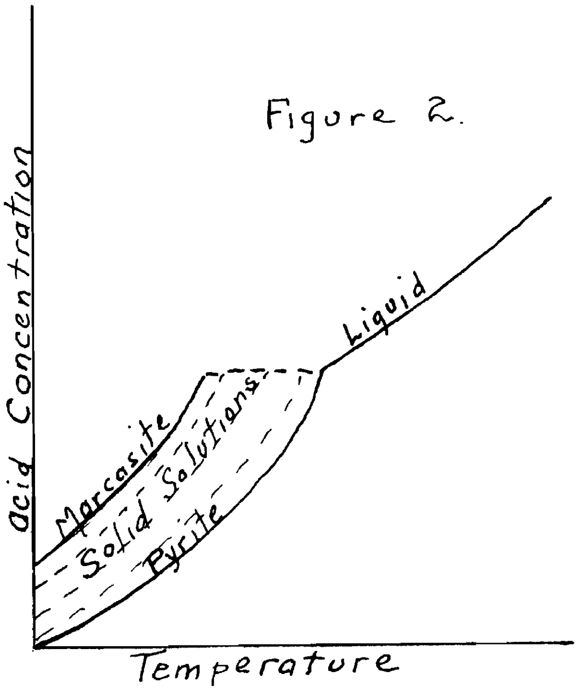

Figure 3.

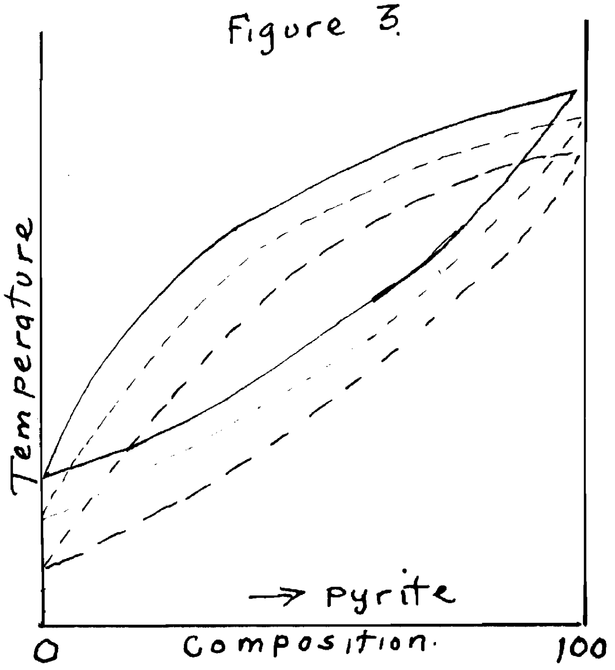

Figure 4.