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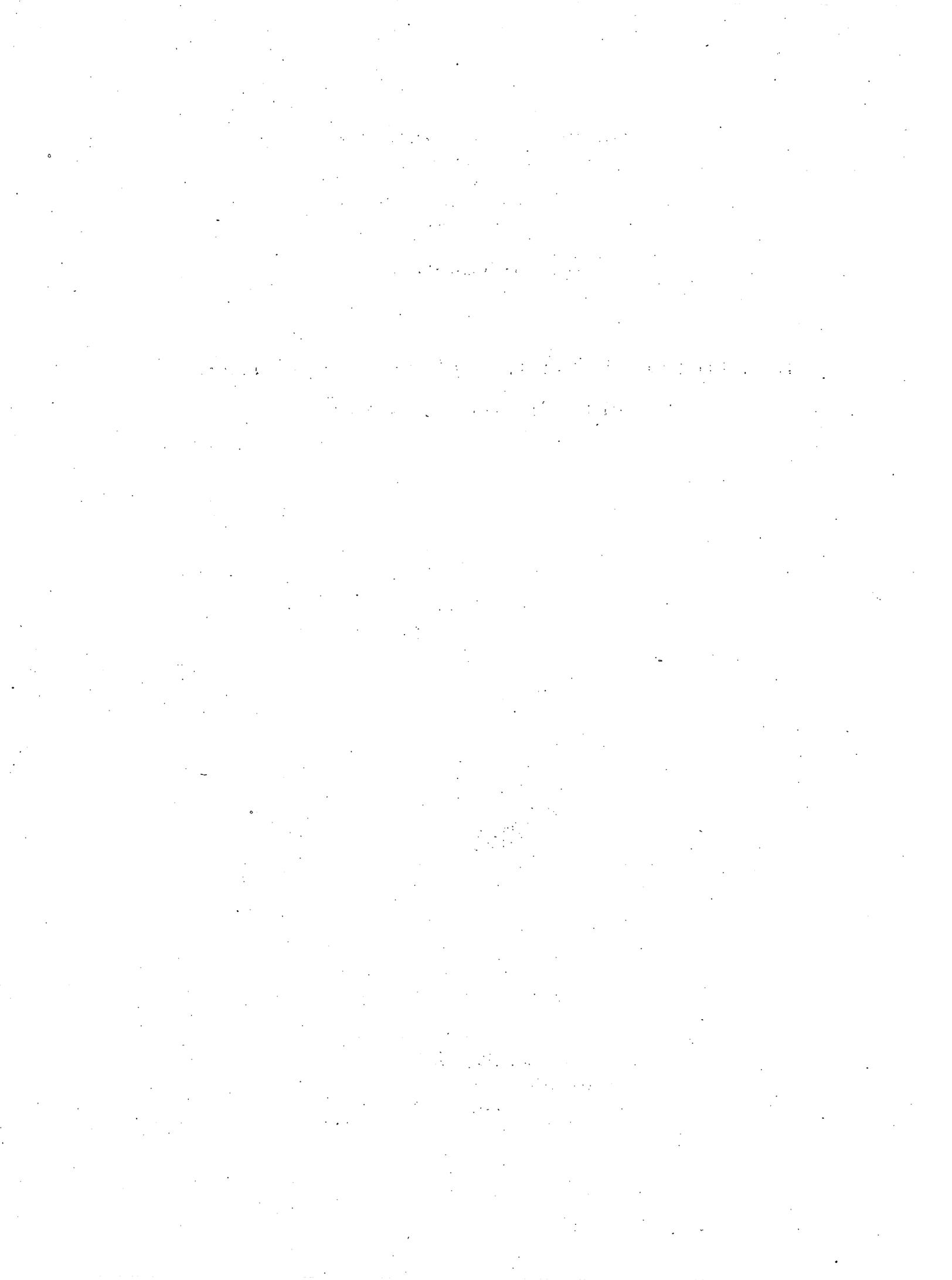
IRON-DEPOSITING BACTERIA AND THEIR
GEOLOGIC RELATIONS

BY

EDMUND CECIL HARDER



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PREFACE.

By F. L. RANSOME.

The enormous importance of bacteria in all that pertains to the nutrition and well-being of animals and of the higher plants is to-day a matter of wide recognition, even by those whose knowledge of the part played by these minute and wonderful organisms is far from exact. The investigations of Pasteur opened our eyes to their deadly power in disease and their enormous efficiency in processes of fermentation and decay. Realization of the influence of bacteria in affecting the character and fertility of soils, in bringing about rock decay, and in producing other geologic results has come more slowly.

It has been known, however, since 1836 that certain bacteria have the power of withdrawing iron from solution and causing its precipitation as ferric hydroxide. The precipitation of iron sulphide by bacterial processes has also been known for some time. The geologic applications of these discoveries, though predicted by some to be far-reaching, have been rather slowly made, and it is safe to say that many geologists have paid little attention to the possible extent of bacterial action in the deposition of iron ores. Lately, in connection with the studies in the geology of the Coastal Plain, now in progress under the direction of T. W. Vaughan, the part played by bacteria in the deposition of limestones has been specially investigated and found to be important. Similarly when Mr. Harder, who has devoted particular attention for some years to the occurrence of iron ores both in the United States and abroad, was detailed to study the Cuyuna Range, Minn., he found an opportunity in the laboratories of the University of Wisconsin to pursue investigations on the iron-depositing bacteria. The report here presented records the results of this research.

Opinions have differed as to the mode whereby the bacteria withdraw iron from solution. Some investigators have maintained that

the deposition of iron hydroxide is one of the vital processes of the organism and as such is effected directly by the action of the living cell; others that the precipitation is purely chemical and is incidental rather than essential to bacterial life; and still others that the accumulation is mechanical, particles of iron hydroxide present in the water being caught and held by mucilaginous parts of the bacteria.

In the course of his work Mr. Harder has found that in addition to the iron-depositing bacteria proper, chiefly the higher or thread bacteria, probably many of the common bacteria of soil and water are active in the precipitation of ferric hydroxide or basic ferric salts from solutions containing iron salts of organic acids. This result is believed to be new. Such bacteria apparently utilize some constituent of the salt other than iron, the iron hydroxide being left as a waste product.

Mr. Harder concludes that, according to present knowledge, there are three principal groups of iron-depositing bacteria—(1) those that precipitate ferric hydroxide from solutions of ferrous bicarbonate, using the carbon dioxide set free and the available energy of the reaction for their life processes; (2) those that do not require ferrous bicarbonate for their vital processes but that cause the deposition of ferric hydroxide when either inorganic or organic iron salts are present; and (3) those that attack iron salts of organic acids, using the organic acid radicle as food and leaving ferric hydroxide, or basic ferric salts that gradually change to ferric hydroxide.

In addition to recording much that is new concerning iron-depositing bacteria, Mr. Harder's report constitutes a valuable critical summary of previous work and should serve a useful purpose in bringing before geologists a digest of practically all that is known on the subject, supplemented by a carefully prepared bibliography.



IRON-DEPOSITING BACTERIA AND THEIR GEOLOGIC RELATIONS.

By EDMUND CECIL HARDER.

INTRODUCTION.

As early as 1836 it was found by Ehrenberg that organisms play an important part in the formation of ocherous deposits of bog iron ore. Since that time these organisms have been studied by various investigators, who have determined their position in the classification of lower plant forms, have investigated the life histories of some of them, and have studied their morphology and their physiologic processes. Nearly all of this work, however, has been done from the standpoint of the biologist, and the geologic significance has received only minor consideration.

For a number of years I have been engaged in a study of iron ores in different parts of the world and have paid special attention to the mode of origin of these deposits. I have been impressed with the difficulty of explaining the accumulation of large masses of ferric oxide by simple chemical processes. Certain iron-ore deposits, such as limestone-contact ores, ores formed by magmatic segregation, and some types of veins undoubtedly owe their origin to igneous agencies, but there are other deposits of enormous extent, such as sedimentary ores, bog ores, and deposits formed by surface concentration, which have no igneous associations and the origin of which has usually been attributed to simple oxidation and precipitation from solutions containing ferrous iron. It is with reference to the last class that I have endeavored to find a more efficient agent of precipitation under all conditions and have taken up the study of the organisms which precipitate iron oxide.

In order to pursue this investigation intelligently, it was of course necessary to study the

organisms both in the laboratory and in the field. It was necessary to show the widespread occurrence of the organisms, as well as to prove their effectiveness in precipitating ferric hydroxide from solution.

In the field work many iron springs, bogs, mines, and streams were examined for the presence of deposits of ferric hydroxide, and when found samples were taken to the laboratory and examined microscopically and some of them chemically. The morphology of the organisms was studied and laboratory cultures were made from them in attempts to study the physiology. Many different iron compounds were used in the laboratory work, organic as well as inorganic, and the activity of the organisms in precipitating ferric hydroxide from each compound was studied.

In general it was found that iron-precipitating organisms were present wherever iron-bearing waters occur, both underground in wells and mines and in surface waters. It was found that the ocherous scums which occur in such localities consisted mainly and in many places entirely of iron-precipitating organisms or their remains. These were found to belong chiefly to the class of organisms known as thread bacteria.

It was determined also that solutions of certain iron compounds, when inoculated with almost any type of natural water or of soil, showed a precipitation of ferric hydroxide by certain types of lower bacteria, thus indicating the almost universal presence in nature of organisms capable of precipitating iron from solution.

ACKNOWLEDGMENTS.

The investigations on which this report is based were made largely in the bacteriologic

laboratory of the Agricultural Experiment Station of the University of Wisconsin. Many helpful suggestions, as well as material aid, were given me by members of the bacteriologic staff of the university. I wish, however, especially to acknowledge my indebtedness to Prof. E. G. Hastings, head of the department of agricultural bacteriology, and to Prof. E. B. Fred, in charge of soil bacteriology, who kindly placed the laboratory and all its facilities at my disposal and who always aided me with willing criticisms throughout the course of the investigations. From Prof. C. K. Leith, of the geologic department of the University of Wisconsin, I received suggestions regarding the method of attack of the geologic problems involved. Prof. W. H. Hunter, of the department of chemistry, University of Minnesota, read and criticised the sections of the report which are largely chemical in nature. Mr. F. T. Thwaites, Dr. W. L. Uglow, Mr. A. D. Wheeler, Prof. E. B. Fred, and many others rendered assistance in collecting material for investigation.

THE IRON-DEPOSITING BACTERIA.

GENERAL CLASSIFICATION AND MORPHOLOGY.

Until recently the term "iron bacteria" was applied to a certain group of filamentous bacteria that have the power of precipitating ferric hydroxide from iron solutions. These organisms were classified by Migula under the general term *Trichobacteria* or "higher bacteria" to distinguish them from the *Haplobacteria* or "lower bacteria" to which ordinary coccus, bacillus, and spirillum forms belong. Besides the iron bacteria, such as *Crenothrix*, *Gallionella*, *Spirophajllum*, *Leptothrix*, and *Clonothrix*, there were included under "higher bacteria" certain soil and pathogenic bacteria, such as *Cladothrix*, *Streptothrix*, *Phragmidiothrix*, and *Actinomyces*, and a third group, the "sulphur bacteria," also a higher bacterial type, was classed independently as *Thiobacteria*. It was supposed that all iron bacteria belonged to the higher type, until about 1908, when Molisch discovered certain coccus forms that had the power of precipitating ferric hydroxide. Still more recently Mumford claims to have isolated a

bacillus that has the same power, and it seems quite probable that many other species of both lower and higher bacteria may be found that precipitate ferric hydroxide from iron solutions.

The higher bacteria are distinguished from the lower bacteria by their morphology and their methods of reproduction.¹ Lower bacteria occur as spherical, rod-shaped, or spiral forms and reproduce by simple cell division. Higher bacteria occur as long threads, which are usually composed of many individual cells, and which generally reproduce by the formation of conidia or swarm spores. In some species of higher bacteria conidia or swarm spores are produced by the division of cells which form part of the thread, whereas in other species small protrusions are said to form along the sides of the threads and in time separate themselves from the threads as conidia.

Higher iron bacteria present a variety of forms, such as single threads composed of cylindrical cells placed end to end and generally inclosed in sheaths; ribbon forms, twisted spirally; cylindrical threads showing false branching, or coiled threads or ribbon forms produced by the bending of the filaments in the middle and the twisting of the ends around each other like rope.

According to Migula's general classification, the iron bacteria may be grouped as follows:²

- A. Eubacteria (true bacteria).
 - 1. Haplobacteria (lower bacteria).
 - a. Coccaceae (2 species of iron bacteria known).
 - Siderocapsa treubii*.
 - Siderocapsa major*.
 - b. Bacteriaceae (1 species of iron bacteria described).
 - Bacillus M. 7*.
 - c. Spirillaceae (no known species of iron bacteria).

¹ Benecke, Wilhelm, *Bau und Leben der Bakterien*, pp. 487-498, Leipzig, 1912.

Rullman, W., *Eisenbakterien, Cladotricheen, Streptotricheen, und Actinomyceten*, in *Lafar's Handbuch der technischen Mykologie*, Auflage 2, Band 3, pp. 190-214, Jena, 1904-5.

Migula, W., *System der Bakterien*, Band 2, p. 1031, Jena, 1897-1900.

Molisch, Hans, *Die Eisenbakterien*, Jena, 1910.

Ellis, David, *The iron bacteria: Sci. Progress*, vol. 10, pp. 374-392, 1916.

² Adapted in part from Migula and in part from Benecke and Ellis.

A. Eubacteria (true bacteria)—Continued.

2. Trichobacteria (higher bacteria) (numerous species of iron bacteria).

- a. Thread bacteria consisting of sheaths with included cells generally plainly visible; reproduction by internally produced conidia or by the separation of motile or nonmotile cells.

Crenothrix polyspora.

Cladothrix dichotoma.

Clonothrix fusca.

Leptothrix ochracea (*Chlamydothrix ochracea*).

Chlamydothrix sideropous (*Leptothrix sideropous*).

Megalothrix discophora.

- b. Thread bacteria showing no division into separate cells; method of reproduction not definitely established but supposed to be by breaking off of parts of threads and perhaps by external abstriction of conidia.

Gallionella ferruginea (*Chlamydothrix ferruginea*).

Spirophyllum ferrugineum.

Nodofolium ferrugineum.

Conidiothrix. (?)

B. Thiobacteria (sulphur bacteria) (no known species of iron bacteria).

Siderocapsa was found by Molisch¹ to occur on the submerged leaves or stems of certain water plants on which it exists in the form of little irregular ringlike colonies. Frequently it forms a brown incrustation covering the entire submerged portion of the plants. It is a common coccus form and is said to be one of the most abundant of water bacteria. It is believed by Molisch to be an important agent in the formation of bog iron ores.

Bacillus M. 7 was discovered by Mumford² during an examination of iron-bearing colliery waters in England. He examined the brownish ochereous scum which formed in a basin into which the mine waters emptied and found that it consisted of a mass of ferric hydroxide of fine granular texture with some scattered threads of higher iron bacteria. After various inoculations of this granular material in culture media a bacillus was isolated which produced an enzyme that had the power of precipitating ferric hydroxide from either ferrous or ferric solutions. Mumford states that he succeeded in isolating the enzyme from the organism by filtration.

¹ Molisch, Hans, *Siderocapsa treubii* Molisch, eine neue weitverbreitete Eisenbakterie: Centralbl. Bakteriologie, Abt. 2, Band 29, p. 243, 1911; Die Eisenbakterien, Jena, 1910.

² Mumford, E. M., A new iron bacterium: Chem. Soc. Jour., vol. 103, pp. 645-650, 1913.

*Crenothrix*³ is the largest of the iron bacteria and is found most commonly at the bottoms of wells and in city water pipes. Less than 2 parts of iron per million in water is sufficient to support the activity of *Crenothrix*.

In its manner of growth and reproduction, *Crenothrix* is one of the most interesting of the iron bacteria. It is sessile; the attached end is thin and the organism gradually thickens toward the free end. The separate cells that make up a thread of *Crenothrix* are clearly distinguishable, being rod shaped and placed end to end in a sheath. Toward the upper end of the filament the cells are seen to divide, at first transversely and then longitudinally, so that a large number of small spherical cells are formed near the upper end of the filament. These are the conidia, which leave the parent sheath and form new threads. Frequently conidia are prevented from leaving the sheath, and then they germinate within the sheath and thrust their filaments through the walls, giving the appearance of numerous little branches extending from the parent filament.

*Clonothrix*⁴ and *Cladothrix*⁵ are forms related to *Crenothrix* but differ from it in showing false branching. This is caused by one cell pushing by the next above it and then dividing and pushing its way through the sheath. *Clonothrix* reproduces by the forma-

³ Cohn, F. J., Ueber den Brunnenfaden (*Crenothrix polyspora*) mit Bemerkungen ueber die mikroskopische analyse des Brunnenwassers: Beitr. Biologie Pflanzen, Band 1, Heft 1, pp. 108-131, 1875.

Zopf, W., Entwicklungsgeschichtliche Untersuchungen ueber *Crenothrix polyspora*, die Ursache der Berliner Wasserkalamität, Berlin, 1879.

Rössler, O., Ueber Kultivierung von *Crenothrix polyspora* auf festem Nährboden: Archiv Pharmacie, Band 233, pp. 189-191, 1895.

Adler, Oscar, Ueber Eisenbakterien und ihrer Beziehung zu den therapeutisch verwendeten natürlichen Eisenwässern: Centralbl. Bakteriologie, Abt. 2, Band 11, pp. 215-219, 277-278, 1903-4.

Schorler, B., Beiträge zur Kenntnis der Eisenbakterien: Centralbl. Bakteriologie, Abt. 2, Band 12, pp. 681-695, 1904.

Beythien, Hempel, and Kraft, Beiträge zur Kenntnis des Vorkommens von *Crenothrix polyspora* in Brunnenwässern: Zeitschr. Untersuchung Nahrungs- und Genussmittel, 1904, Heft 4, p. 215.

Rullmann, W., Ueber Eisenbakterien: Centralbl. Bakteriologie, Abt. 2, Band 33, pp. 277-289, 1912.

⁴ Schorler, B., Beiträge zur Kenntnis der Eisenbakterien: Centralbl. Bakteriologie, Abt. 2, Band 12, pp. 681-695, 1904.

⁵ Cohn, F. J., Untersuchungen ueber Bakterien: Beitr. Biologie Pflanzen, Band 1, Heft 3, p. 185, 1875.

Zopf, W., Zur Morphologie der Spaltpflanzen, Leipzig, 1882.

Ellis, David, An investigation into the life history of *Cladothrix dichotoma*: Roy. Soc. Proc., B, vol. 85, pp. 344-358, 1912.

tion of conidia resembling those of *Crenothrix* and by vegetative cells which slip out of the sheath. The threads are similar to those of *Crenothrix* but taper toward the free end while those of *Crenothrix* thicken toward the free end. *Cladothrix* is primarily a soil organism and does not belong to the iron bacteria proper, but it is capable of depositing ferric hydroxide on its sheath. It reproduces by motile and nonmotile conidia, resembling vegetative cells, which either leave the ends of the threads or are set free by the breaking up of the threads.

*Leptothrix*¹ is a simple thread form, usually free but sometimes attached at one end. The threads are straight or curved. They generally have the same width throughout and consist of a sheath inside of which rod-shaped cells lie end to end. Only rarely, however, can the cells in the sheath be distinguished, due to the coloring in the sheath, and besides many dead, empty sheaths are mixed with the living organisms. The sheaths are yellowish brown from ferric hydroxide. The organism commonly reproduces by fragmentation but may reproduce also by the separation of vegetative cells and by swarm cells.

Leptothrix is found abundantly in chalybeate springs, where it forms soft fluffy botryoidal masses attached to the bottom or sides of the basins. Less commonly it occurs underground in mines or tunnels where iron-bearing waters issue from the rocks. The occurrence of iron bacteria in deep mines has to my knowledge not previously been mentioned in the literature.

Megalothrix discophora, a form recently described by Schwerts,² somewhat resembles *Leptothrix* but differs from it in being thicker and in possessing a very thick sheath. Inside of this sheath is a narrow canal in which long cylindrical cells are occasionally seen. The

threads have a holdfast at one end by means of which they attach themselves to foreign objects. Some of them show dichotomous branching.

*Gallionella*³ in its typical form consists of spiral threads coiled together into double or quadruple coils like rope. The individual threads, which are yellow to brown, are cylindrical like those of *Leptothrix* but are generally much thinner. Cells have not been distinguished within them. Though usually tightly wound into coils, loosely wound threads are frequently seen and occasionally even single spiral threads.

Gallionella is said to occur in iron-bearing surface waters with *Leptothrix*, but more commonly it is associated with *Spirophyllum* in iron-bearing well waters and in certain mines where iron-bearing waters issue from the walls. In such places *Gallionella* and *Spirophyllum* form soft, spongy ochreous masses on the walls beneath the openings where iron waters issue.

*Spirophyllum*⁴ is perhaps the most abundant of the iron thread bacteria. It has the form of flat ribbon-like or tapelike threads twisted in the form of spirals. These spiral bands may occur as single filaments or they may be coiled together as in *Gallionella*. Reproduction in *Spirophyllum* is commonly by fragmentation but is said to take place also by means of conidia, which form budlike projections on the flat sides of the bands. This method of reproduction is questioned by some investigators.

Spirophyllum is abundantly distributed in nature. It occurs with *Leptothrix* in chalybeate springs and other iron-bearing surface

¹ Kützing, *Phycologia generalis*, p. 198, 1843.

Migula, W., *System der Bakterien*, Band 2, p. 1031, Jena, 1900.

Winogradsky, S., *Ueber Eisenbakterien*: *Bot. Zeitung*, Band 46, pp. 262-270, 1888.

Schorler, B., *Beiträge zur Kenntnis der Eisenbakterien*: *Centralbl. Bakteriologie*, Abt. 2, Band 12, pp. 681-695, 1904.

Ellis, David, A contribution to our knowledge of the thread bacteria: *Centralbl. Bakteriologie*, Abt. 2, Band 19, pp. 502-518, 1907; Band 26, pp. 321-329, 1910.

Molisch, Hans, *Die Eisenbakterien*, Jena, 1910.

² Schwerts, Henri, *Megalothrix discophora*, eine neue Eisenbakterie: *Centralbl. Bakteriologie*, Abt. 2, Band 33, pp. 273-276, 1912.

³ Ehrenburg, D. C. G., *Vorläufige Mittheilungen ueber das wirkliche Vorkommen fossiler Infusorien und ihre grosse Verbreitung*: *Poggendorf's Annalen*, Band 38, pp. 213-227, 1836.

Migula, W., *Ueber Gallionella ferruginea* Ehrenburg: *Deutsch. bot. Gesell. Ber.*, Band 15, p. 321, 1897.

Kützing, *Species algarum*, p. 250, 1849.

Ellis, David, A contribution to our knowledge of the thread bacteria: *Centralbl. Bakteriologie*, Abt. 2, Band 19, pp. 502-518, 1907; Band 26, pp. 321-329, 1910.

Schorler, B., *Die Rostbildungen in den Wasserleitungsröhren*: *Centralbl. Bakteriologie*, Abt. 2, Band 15, pp. 564-568, 1906.

⁴ Ellis, David, On the discovery of a new genus of thread bacteria (*Spirophyllum ferrugineum* Ellis): *Roy. Soc. Edinburgh Proc.*, vol. 27, pt. 1, pp. 21-34, 1907; A contribution to our knowledge of the thread bacteria: *Centralbl. Bakteriologie*, Abt. 2, Band 19, pp. 502-518, 1907; Band 26, pp. 321-329, 1910.

Lieske, R., *Beiträge zur Kenntnis der Physiologie von Spirophyllum ferrugineum* Ellis: *Jahrb. wiss. Botanik*, Band 49, pp. 91-127, 1911.

waters, alone or with *Gallionella* or *Leptothrix* in iron-bearing mine waters, and with *Crenothrix* in city water pipes. In the latter it occasionally becomes so abundant as to cause turbidity of the water and even a blocking of the pipes due to the deposition of ferric hydroxide.

*Nodofolium*¹ is described by Ellis as being related to *Spirophyllum*. It is said to consist of flat elliptical disks placed end to end so that each succeeding one is at right angles to the last, the whole forming a chain. Investigators who do not follow Ellis claim that *Nodofolium* is simply a form of *Spirophyllum*.

The name *Conidiothrix* is suggested by Benecke² for a simple thread form resembling *Leptothrix* which has been described by Ellis. It differs from *Leptothrix* in that its cell structure is not visible and in that it reproduces by conidia which form projections on the outside of the sheath. This form has not been definitely identified.

The separation of the higher iron bacteria into two groups, one characterized by internally produced conidia and the other by the external abstriction of conidia, seems to me questionable. Several investigators doubt the occurrence of external conidia, Ellis being practically the only author on record who states definitely that he has seen their formation and germination. In my work, during which I have examined iron bacteria from many different localities, I have never certainly identified external conidia, and although I have often noted nodular projections or attached bodies on bacterial threads, most of these projections have turned out to be granules of ferric hydroxide or other foreign particles. It is not impossible, however, that further work may prove Ellis's contention to be correct and that other investigators will be able to definitely confirm this method of reproduction among iron bacteria.

A number of other organisms besides iron bacteria are known which deposit ferric hydroxide in their coatings or in certain parts of their bodies.³ Among these are included algae, such as *Psichohormium*, *Oedogonium*, *Euglena*, *Glosterium*, and *Trachelomonas*, as well as pro-

tozoa, such as *Rhipidodendron*, *Phallansterium*, *Spongomonas*, *Carchesium*, and especially a certain flagellate called *Anthophysa*, a branch-like organism which commonly becomes heavily incrustated with ferric hydroxide. In my own work I have also found that the mycelia of various fungi often become impregnated with or coated by ferric hydroxide.

GENERAL PHYSIOLOGY.

Several explanations have been offered for the deposition of ferric hydroxide by iron bacteria. Some investigators believe that the precipitation is merely a chemical process, in no way connected with the internal activity of the cell, whereas others claim that the process is one of oxidation of ferrous to ferric compounds and that it is necessary for the life processes of the organisms.

Among the first to study the activities of iron-depositing thread bacteria were Cohn and Zopf. Cohn⁴ believed that the ferric hydroxide was deposited as a result of the activity of living cells and that the deposition occurred in the same manner as the deposition of silica takes place in the tests of diatoms. Zopf⁵ some years later stated that he found ferric hydroxide being deposited on empty sheaths from which all living cells had been removed. He was of the opinion, therefore, that the storing up of ferric hydroxide in the sheaths was merely the result of mechanical processes, the iron compounds being taken up by a mucilaginous coating on the sheaths.

Later Winogradsky⁶ investigated the physiology of iron bacteria. His experiments were conducted with *Leptothrix*, and in a publication of his results in 1888 he states that *Leptothrix* will live and grow only in solutions in which iron is present in the ferrous form, and that only where living cells are present in a sheath is there any coloration of the sheath due to the oxidation of ferrous salts. He also found that the sheaths would not take up mechanically any ferric hydroxide which may be present in the solution and believed that the

¹ Ellis, David, A contribution to our knowledge of the thread bacteria: Centralbl. Bakteriologie, Abt. 2, Band 26, pp. 321-329, 1910.

² Benecke, Wilhelm, Bau und Leben der Bakterien, pp. 489-492, Leipzig, 1912.

³ Mollsch, Hans, Die Eisenbakterien, pp. 53-58, 1910.

⁴ Cohn, F. J., Ueber den Brunnenfaden (*Crenothrix polyspora*) mit Bemerkungen ueber die mikroskopische Analyse des Brunnenwassers: Beitr. Biologie Pflanzen, Band 1, Heft 1, pp. 108-131, 1875.

⁵ Zopf, W., Zur Morphologie der Spaltpflanzen, Leipzig, 1882.

⁶ Winogradsky, S., Ueber Eisenbakterien: Bot. Zeitung, Band 46, pp. 262-270, 1888.

coloration is due to ferric hydroxide being given off by the cells and caught in the sheath which incloses them.

He concludes from this that the oxidation of ferrous compounds to form ferric hydroxide is necessary for the life and growth of the organisms and that this process furnishes energy to the cell for the assimilation of food. The food consists of organic compounds present in the water. Only a small amount of organic matter, however, was found to be necessary to sustain life. Winogradsky worked with solutions of ferrous carbonate (FeCO_3).

Molisch¹ (1892 and 1910), in a series of experiments, proved that *Leptothrix* will grow profusely in an iron-free medium, forming perfectly colorless sheaths. He found that peptone solutions were especially favorable for its development. If either iron or manganese compounds were present in the solutions, however, he found that they were oxidized and taken up by the sheaths. Likewise, Molisch states that *Leptothrix* forms thicker and longer threads when iron or manganese is present in solution and that sheaths containing live cells accumulate ferric hydroxide more abundantly. However, threads in which the cells have been killed by boiling in water are still capable of taking up ferric hydroxide in their sheaths. He determined further that where there was little chance of oxidation, a ferrous compound would accumulate in the sheath and cause the same luxuriant growth as ferric hydroxide. Therefore he concludes that though these organisms show a marked attraction for iron or manganese compounds, the reason for this is a physicochemical one, and the change of ferrous to ferric compounds is due to simple oxidation and is not connected with the life-processes of the cells as was claimed by Winogradsky. That dead, empty sheaths do not take up ferric hydroxide to a marked extent he explains by stating that living cells probably have some influence in keeping the sheath in a condition in which it is able to accumulate more material.

James Campbell Brown² made some interesting observations on the black slime which

collects in pipes, culverts, and other water channels. He finds that it consists mainly of a mixture of ferric hydroxide, manganese oxide, and organic matter and that it contains among other organisms abundant iron-depositing thread bacteria. He states that such slimes form only in acid waters, that they do not occur in neutral or alkaline waters, and that they frequently form in waters in which iron is not present as ferrous bicarbonate.

From his observations he concludes that where black slimes form in water channels iron is carried in solution in the form of soluble organic salts. He believes that the iron-depositing thread bacteria which are found in the slimes use the organic salts as food and set free ferric hydroxide, which is then deposited in the sheaths. The manganese oxide he believes is a simple oxidation product. A small amount of ferric hydroxide is perhaps also formed by simple oxidation and becomes mixed with the slime.

Ellis³ in 1907 published a paper in which he sets forth his belief that the deposition of ferric hydroxide around bacterial threads is purely mechanical. He does not believe that Winogradsky had a valid basis for his conclusions and thinks with Zopf that the accumulation is the result of the catching up of particles of ferric hydroxide present in the water by a mucilaginous covering which surrounds the sheaths. The presence of such a mucilaginous coating was demonstrated by Zopf⁴ in 1878. Ellis, like Winogradsky, worked principally with *Leptothrix* but also examined cultures of *Spirophyllum* and *Gallionella*, and believes that what is true of *Leptothrix* is true of all iron bacteria.

Lieske⁵ in a report published in 1911 gives the results of various experiments made with *Spirophyllum*. He finds that this organism will grow only in solutions containing ferrous carbonate and that other ferrous salts will not take the place of ferrous carbonate. He finds not only that much organic matter impairs the growth of *Spirophyllum* and may stop it alto-

¹ Molisch, Hans, Die Eisenbakterien, pp. 44-52, Jena, 1910; Die Pflanze in ihren Beziehungen zum Eisen, p. 71, Jena, 1892.

² Brown, J. C., Deposits in pipes and other channels conveying potable water: Inst. Civ. Eng. Proc., vol. 156, Sess. 1903-4, pt. 2, pp. 1-17, 1904.

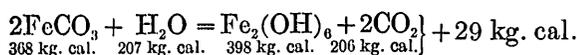
³ Ellis, David, A contribution to our knowledge of the thread bacteria: Centralbl. Bakteriologie, Abt. 2, Band 19, pp. 502-518, 1907.

⁴ Zopf, W., Entwicklungsgeschichtliche Untersuchungen ueber *Crenothrix polyspora*, die Ursache der Berliner Wasserkalamität, Berlin, 1879.

⁵ Lieske, Rudolf, Beiträge zur Kenntnis der Physiologie von *Spirophyllum ferrugineum* Ellis: Jahrb. wiss. Botanik, Band 49, pp. 91-127, 1911.

gether, but that where abundant carbon dioxide is present in water and organic matter is entirely absent this organism will grow profusely. He concludes from this that the carbonate radicle furnishes food for *Spirophyllum* and that the latter oxidizes ferrous carbonate to ferric hydroxide mainly for the purpose of obtaining carbon. He believes with Winogradsky that the oxidation may furnish energy to the organism for the assimilation of food, which in this case is carbon dioxide.

Lieske gives the following reaction as indicating what probably takes place in this process of oxidation:



Mumford¹ in a short paper published in 1913 describes experiments with *Bacillus M. 7*, a new type of iron bacterium discovered by him. He states that this organism forms a precipitate of ferric hydroxide in ferric as well as ferrous solutions. Organic compounds were used as a source of food. He found that ferric hydroxide was precipitated only under aerobic conditions and that under anaerobic conditions the ferric hydroxide already precipitated was simply somewhat dehydrated, forming limonite or bog ore. He ascribed these reactions to an enzyme which, he states, he succeeded in isolating from the organisms by filtration. This filtered enzyme produced the same phenomena as the living organism.

It is difficult to reconcile these various conflicting hypotheses regarding the physiologic activity of iron-depositing bacteria. Some of the discrepancies can probably be explained by the fact that some of the observers were working with different organisms and under different conditions, but other discrepancies seem to be due to faulty observation. Molisch worked with *Leptothrix* and found that it required organic matter but that it did not require iron in solution. Lieske, on the other hand, in working with *Spirophyllum*, finds that it requires ferrous carbonate in solution but that it can live in the absence of organic matter. Here are two different organisms that clearly show entirely different characteristics. Such an explanation, however, does not apply to the discrepancies between the observations of Mo-

lisch and Winogradsky. Both of these investigators were working with *Leptothrix* and yet their results differ radically. Similarly, James Campbell Brown, who finds that iron-depositing thread bacteria grow in solutions containing no ferrous bicarbonate, concludes that iron-precipitating organisms do not use inorganic iron compounds but must have soluble organic iron salts in solution. Such a conclusion is speculative, for although Molisch has shown that *Leptothrix* will thrive on certain organic iron salts in solution, Lieske has proved that *Spirophyllum* undoubtedly will not. Besides, very little is known definitely about the carrying of iron in solution in natural waters in the form of soluble organic salts, although indications of this possibility exist. The observations of Mumford also are open to doubt, for the reason that he did not use control cultures and the possibility of chemical oxidation taking place in his ferrous solutions has not been eliminated.

In general it seems reasonable to believe that certain iron-depositing organisms, such as *Spirophyllum*, require ferrous bicarbonate in solution and can not live without it; that others, such as *Leptothrix*, can live without any iron compounds, but if they are present can use either ferrous bicarbonate or soluble organic iron salts; and that still others, such as various lower bacteria (see pp. 29-31) will use the organic radicle of certain soluble organic iron salts when present but can not utilize any inorganic iron salts. The physiologic activity of iron-depositing organisms will be frequently referred to in the following discussion.

RESULTS OF THE PRESENT INVESTIGATION.

OCCURRENCE AND MORPHOLOGY OF IRON-DEPOSITING THREAD BACTERIA.

CRENOTHRIX POLYSPORA Cohn.

The common habitat of *Crenothrix polyspora* is in wells and in city water pipes in localities where the water contains an appreciable amount of iron in solution. It is so common in many places both in the United States and in Europe that it has become known as the "water-pest bacterium," because of its tendency to produce turbidity in water due to the precipitation of ferric hydroxide. In Ger-

¹ Mumford, E. M., A new iron bacterium: Chem. Soc. Jour., vol. 103, pp. 645-650, 1913.

many *Crenothrix* is commonly known as "Brunnenfaden" (well thread), on account of its frequent occurrence in wells, although various German investigators mention its occurrence in streams, canals, and other water bodies as well. In wells *Crenothrix* is described as occurring in dark-brown or black scumlike masses at the bottom or along the sides. The newer outer portions of such masses are usually lighter colored than the older portions. In distributing pipes *Crenothrix* occurs in association with *Spirophyllum* and *Gallionella*, which are attached to the interior of the pipes, where they often form hard iron crusts.

Most of the *Crenothrix* cultures for my investigations were obtained from the city water of Madison, Wis. (See Pls. I, II, and III.) This water, although its iron content is comparatively low, contains an abundance of *Crenothrix*, as well as *Gallionella* and *Spirophyllum*. It is obtained from several deep wells which penetrate the Cambrian sediments and end in the underlying granite more than a thousand feet below the surface. The following is a partial analysis of the mineral constituents of Madison city water by W. G. Crawford, of the University of Wisconsin:

Partial analysis of city water from Madison, Wis.

	Parts per million.
Silica (SiO ₂)-----	10.3
Ferric oxide (Fe ₂ O ₃)-----	1.8
Calcium (Ca)-----	62.5
Magnesium (Mg)-----	36.4
Bicarbonate radicle (HCO ₃)-----	324.5
Sulphate radicle (SO ₄)-----	15.5
Chlorine (Cl)-----	.4
Free carbon dioxide (CO ₂)-----	5.8

The analysis shows that the water contains an abundance of calcium and magnesium carbonates and is a typical "hard water." No attempt is made to combine the constituents into salts. The usual method of making such combinations is at best artificial, and here it seems preferable to show the actual facts. The carbon dioxide in the bicarbonate radicle is that which is combined with the bases, such as calcium, magnesium, and iron, to form carbonates or bicarbonates. The carbon dioxide present as free gas is shown separately. The sulphate radicle, which forms an appreciable percentage, is probably present combined with

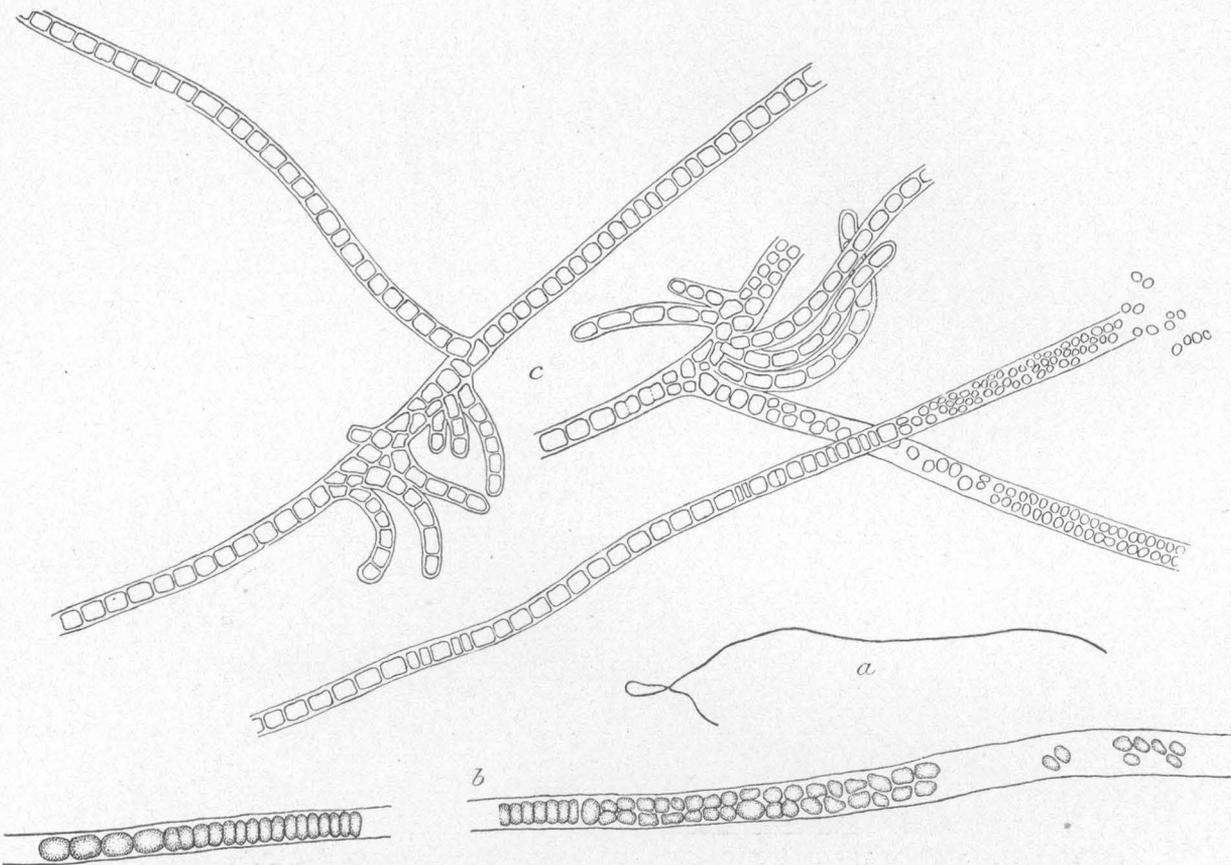
calcium and iron. The iron present is shown as ferric oxide, although in the water practically all of it is present in the ferrous form, mainly as carbonate or bicarbonate and perhaps as sulphate. It is not possible to tell in what relative proportion these salts occur. The actual quantity of metallic iron present in the water amounts to 1.26 parts per million. This seems a very small amount to cause the growth of iron bacteria, yet it was sufficient to produce turbidity in the water upon standing with free access of oxygen.

Crenothrix polyspora is easily obtained from city water, in which it is present, by filtering. The best method is to attach a thoroughly cleaned and sterilized Berkefeld porcelain filter to a screw spigot and allow the water to pass through for 24 to 36 hours. At the end of this period a thin yellowish-brown deposit of ferric hydroxide will be found to coat the filter, unless the water is turbid, and then a heavy blackish-brown coating may be found. The latter, however, is not so desirable for cultures.

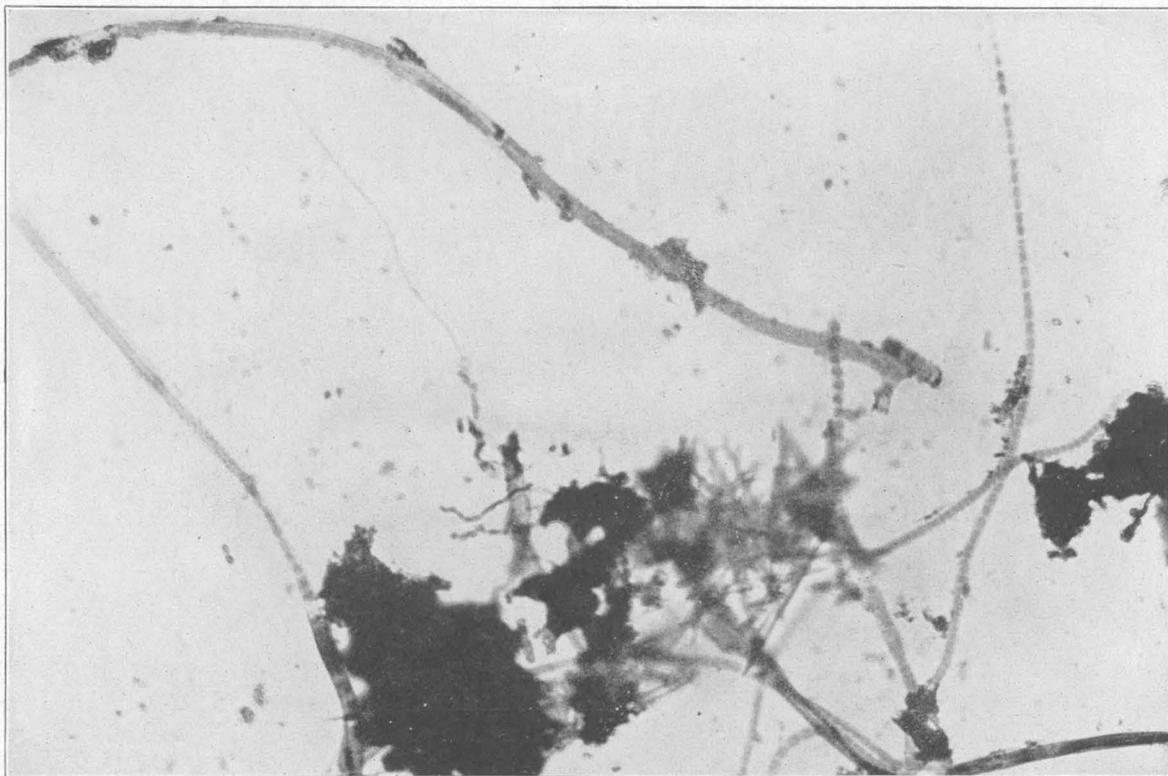
The filter, after being removed from the spigot, should be immersed in a sterile solution of well water to which has been added, previous to sterilizing, about 0.1 per cent of powdered ferrous carbonate (FeCO₃) and about the same amount of sodium or potassium acetate. This solution should be placed in a large beaker (preferably about 3,000 cubic centimeters), and the filter should be suspended so as to hang freely in the liquid. The beaker should be covered in order to prevent dust from settling on the solution.

For incubating the cultures it is best to place them in an ice chest at a temperature of about 6° to 8° C., for this retards the growth of molds, which otherwise rapidly develop on the surface of the filter and prevent the growth of other organisms. Within a few days *Crenothrix* will be found to develop on the filter and can be obtained for examination under the microscope by scraping material from the surface of the filter with a platinum needle. Impure cultures prepared in this manner may be kept for several weeks.

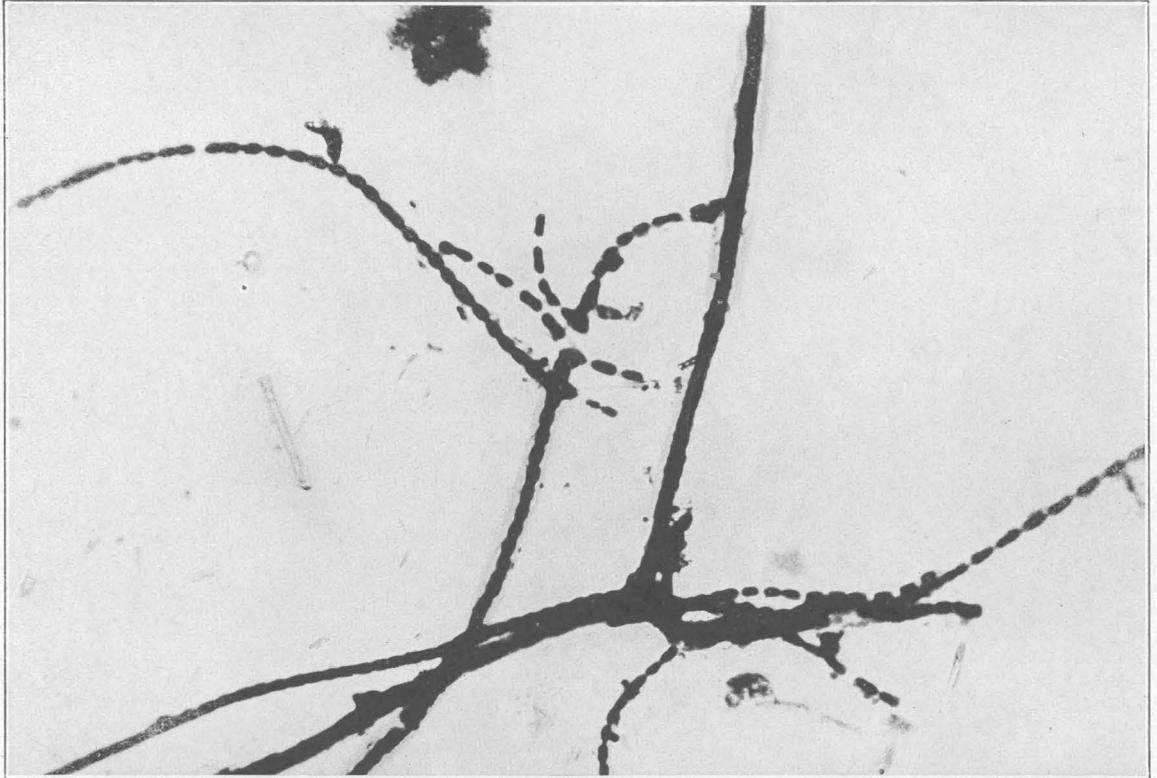
Pure cultures of *Crenothrix polyspora* are difficult to obtain, not only because of the difficulty of finding artificial media in which *Crenothrix* will grow but also because the threads are so large that it is difficult to make



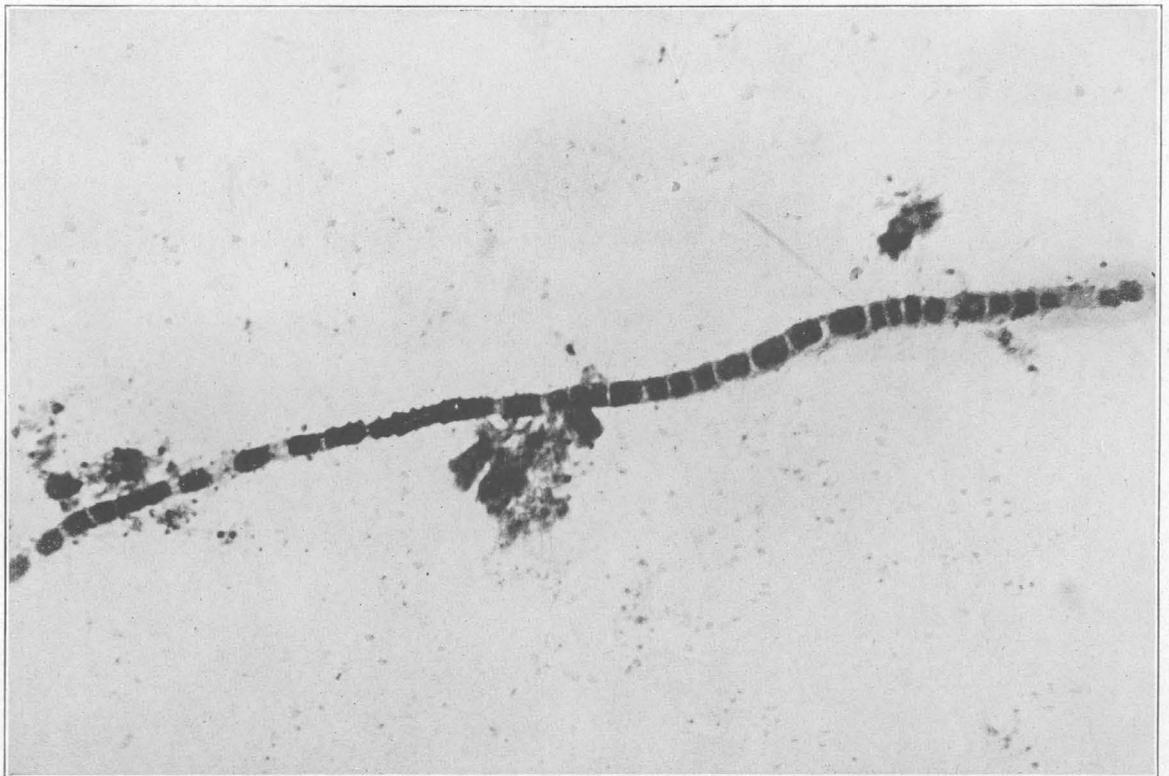
4. *a*, THREAD OF CRENOTHRIX POLYSPORA, $\times 80$; *b*, UPPER PORTION OF THE SAME THREAD, $\times 940$, SHOWING CONIDIA IN THE UPPER PART OF THE SHEATH AND ORDINARY VEGETATIVE CELLS IN THE LOWER PART; *c*, PORTIONS OF THREADS OF CRENOTHRIX POLYSPORA, $\times 550$, SHOWING VEGETATIVE CELLS, CONIDIA, AND GERMINATION OF CELLS WITHIN THE SHEATHS.



B. PHOTOMICROGRAPH OF THREADS OF CRENOTHRIX POLYSPORA FROM CITY WATER, MADISON, WIS., $\times 450$.
Material obtained on filter. Some threads show ordinary vegetative cells; others show conidia. Stained with gentian violet.



A. PHOTOMICROGRAPH OF THREADS OF CRENOTHRIX POLYSPORA FROM CITY WATER, MADISON, WIS., $\times 450$.
Material obtained on filter. Threads show vegetative cells and germination of cells within the sheath. Stained with carbol fuchsin.



B. PHOTOMICROGRAPH OF THREAD OF CRENOTHRIX POLYSPORA FROM CITY WATER, MADISON, WIS., $\times 640$.
Shows ordinary vegetative cells and disklike cells formed by transverse division of ordinary cells. Shows also a thickening of the thread toward the upper part of the sheath (on the right). The sheath is faintly seen. Stained with gentian violet.

transfers of the organism without taking other forms which may be attached to them. Rössler¹ claims to have obtained pure cultures of *Crenothrix* on sterilized bricks immersed in water to which a small amount of ferrous sulphate was added. However, he does not state how he obtained his material for inoculation nor does he mention the presence in the solution of any other nutrient material besides ferrous sulphate. Molisch² repeated these experiments, but without success, and states that he has not been able to cultivate *Crenothrix* in any kind of artificial media even in impure cultures. He concludes that the growth of *Crenothrix* is dependent on special conditions which are difficult to reproduce in the laboratory. Recently, however, Rullmann³ succeeded in producing cultures of *Crenothrix* both in liquid media and on agar plates.

As already mentioned, *Crenothrix* occurs as unbranched threads (see Pls. I, II, and III, and figs. 1 and 2), one end of which is attached while the other end is free. A gradual thickening takes place from the attached end to the free end with the result that the free end commonly has three or four times the width of the attached end. The individual cells making up the thread suffer the same decrease in width toward the attached end as the sheath inclosing them and hence appear much more elongated at the attached end.

Crenothrix threads are generally colorless and can only be seen with the microscope when the light is greatly reduced. The separate cells are then clearly distinguishable, as is also the sheath which incloses them. The threads vary in length up to several millimeters, but usually under the microscope one does not see threads that exceed 0.5 millimeter in length. In diameter the threads vary between 2 and 9 micra.⁴ Only very young threads or the attached ends of the older threads are as thin as 2 micra, and the maximum diameter, 9 micra, is only found in old sheaths when complete formation of conidia has taken place. The diameter of the threads is ordinarily between

3 and 5 micra near the attached end and between 5 and 6 micra at the free end.

The individual vegetative cells (see Pls. I, A, II, B, and III, B) forming the thread range in width from 2 to 5 micra and in length from 2 to 9 micra. The normal shape of the cells is cylindrical, the length being about twice the diameter. Just after cell division, however, which takes place transversely, the length and diameter are nearly equal. In the lower portion of the thread many of the cells have a rectangular outline with the square ends, whereas in the upper part of the thread the ends are rounded. The sheath inclosing the cells is generally thin, in some specimens being hardly distinguishable from the cell walls themselves.

In spore formation the division of cells takes place both transversely and longitudinally—that is, there is cell division in three directions. (See Pls. I and II, A.) This process results in the formation of a large number of spherical or more or less irregular spores or conidia, which increase in size

somewhat after their formation so that different spores range in diameter from less than 2 micra to 4 micra. The division of cells into spores as a rule takes place at the end of the thread, but frequently it occurs at different points in the upper part of the thread, so that small round spores may be inclosed between cells as yet undivided. (See fig. 1.)

The spores are nonmotile conidia. They are washed from the ends of the sheaths, distributed by currents of water, and eventu-



FIGURE 1.—Portion of a thread of *Crenothrix polyspora* showing formation of conidia. The lower part of the thread consists of ordinary vegetative cells. In the upper part are disk-shaped cells and conidia. Drawing with camera lucida. $\times 550$.

¹ Rössler, O., Ueber Kultivierung von *Crenothrix polyspora* auf festem Nährboden: Archiv Pharmacie, Band 233, pp. 189-191, 1895.

² Molisch, Hans, Die Eisenbakterien, p. 29, Jena, 1910.

³ Rullmann, W., Ueber Eisenbakterien: Centralbl. Bakteriologie, Abt. 2, Band 33, p. 283, 1912.

⁴ The micron equals 0.001 millimeter.

ally become attached and germinate into new threads. It often happens that conidia germinate before they have a chance to leave the sheath, and then the new threads push their way through the sheath, forming a radiating mass of threads which appear like branches of the old thread all coming out at one place. (See Pls. I, A; II, A; and III, B.) In many threads germination takes place at several points.

Though the young *Crenothrix* threads are colorless, older threads are commonly coated with a thick brown deposit of ferric hydroxide, which frequently has a thickness of several times the diameter of the original threads. (See fig. 2.) Younger threads never have this coating and rarely show even a yellowish tint to indicate the presence of ferric hydroxide.



FIGURE 2.—Portion of a thread of *Crenothrix polyspora* showing thick coating of ferric hydroxide. Thin young threads are formed by germination of conidia in parent sheath. Drawing with camera lucida. $\times 1,080$.

except the spores. The mount may then be stained with gentian violet or methylene blue, which will restrain the vegetative cells and also to some extent the sheath. The most satisfactory method of staining *Crenothrix* is to prepare a weak staining solution consisting of 1 part concentrated carbol-fuchsin to 10 parts of distilled water. The slide on which the organism is mounted should be allowed to remain in this solution for 12 or 14 hours. It is frequently advantageous to treat the material

with a dilute solution of hydrochloric acid before staining.

LEPTOTHRIX OCHRACEA Kützing.

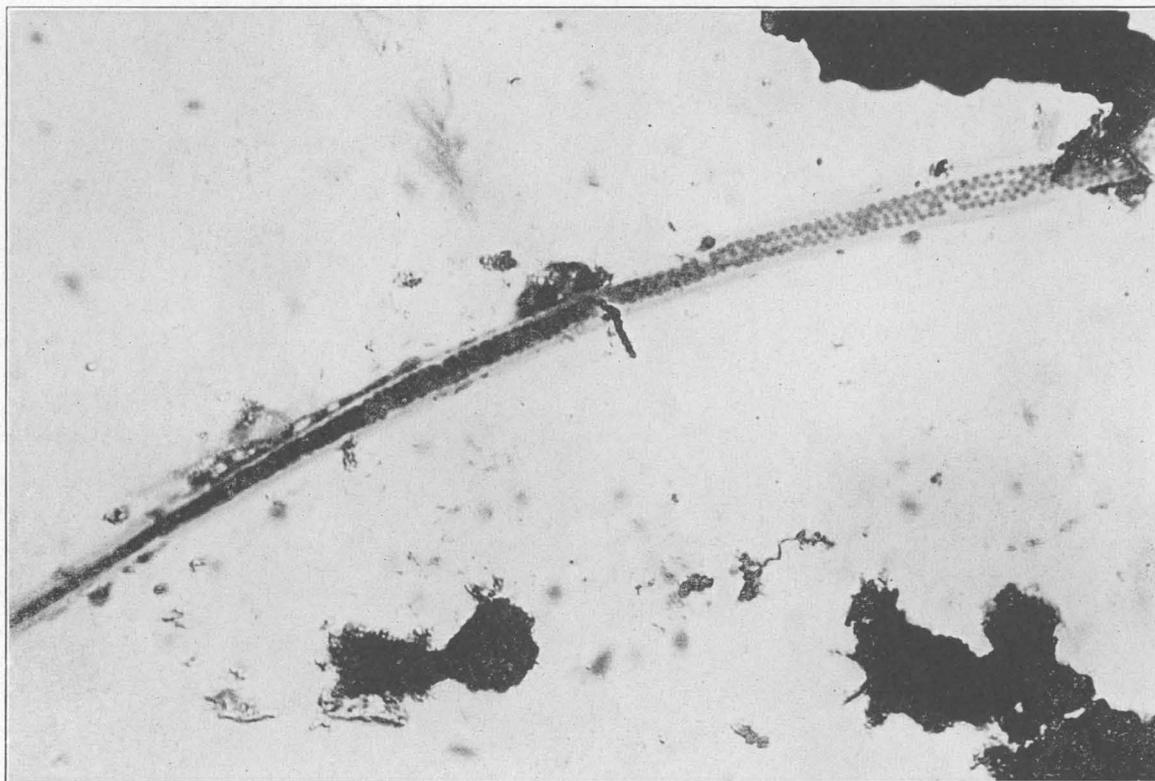
Leptothrix ochracea Kützing, also known as *Chlamydothrix ochracea* Migula, is found mainly in iron-bearing surface waters of bogs, streams, and springs, but I have found it also in mine waters in the Cuyuna iron range of central Minnesota and in the lead and zinc region of southwestern Wisconsin. In some iron springs *Leptothrix* is extremely abundant, but in others not even a trace of it can be found. This irregularity in its distribution is probably due to a difference in composition of the spring waters, perhaps influenced by other contributing factors. In streams and bogs it is found principally where the water is stagnant.

I found *Leptothrix* growing profusely in a chalybeate spring on a small creek west of Lake Kegonsa, about 14 miles southeast of Madison. (See Pl. IV.) The water of this spring contains an abundance of ferrous iron in solution and has a distinct iron taste. It issues from the hillside about 10 feet above the level of the creek, forming a little basin 2 or 3 feet in diameter. At the top of the slope at various points in the vicinity are outcrops of Madison sandstone (Lower Ordovician), and the water probably derives its iron from this formation either from disseminated pyrite or from siderite. The iron is probably present in solution as ferrous carbonate (or bicarbonate), judging from the following partial analysis, made by G. W. Crawford, of the University of Wisconsin:

Partial analysis of water from spring on creek west of Lake Kegonsa, Wis.

	Parts per million.
Silica (SiO ₂)	18.9
Ferric oxide (Fe ₂ O ₃)	5.2
Calcium (Ca)	78.1
Magnesium (Mg)	32.5
Bicarbonate radicle (HCO ₃)	354.4
Sulphate radicle (SO ₄)	.0
Chlorine (Cl)	.4
Free carbon dioxide (CO ₂)	11.6

A large volume of water is given off by the spring and there is a constant flow winter and summer. The water does not freeze in the winter. As there is no sulphate radicle pres-



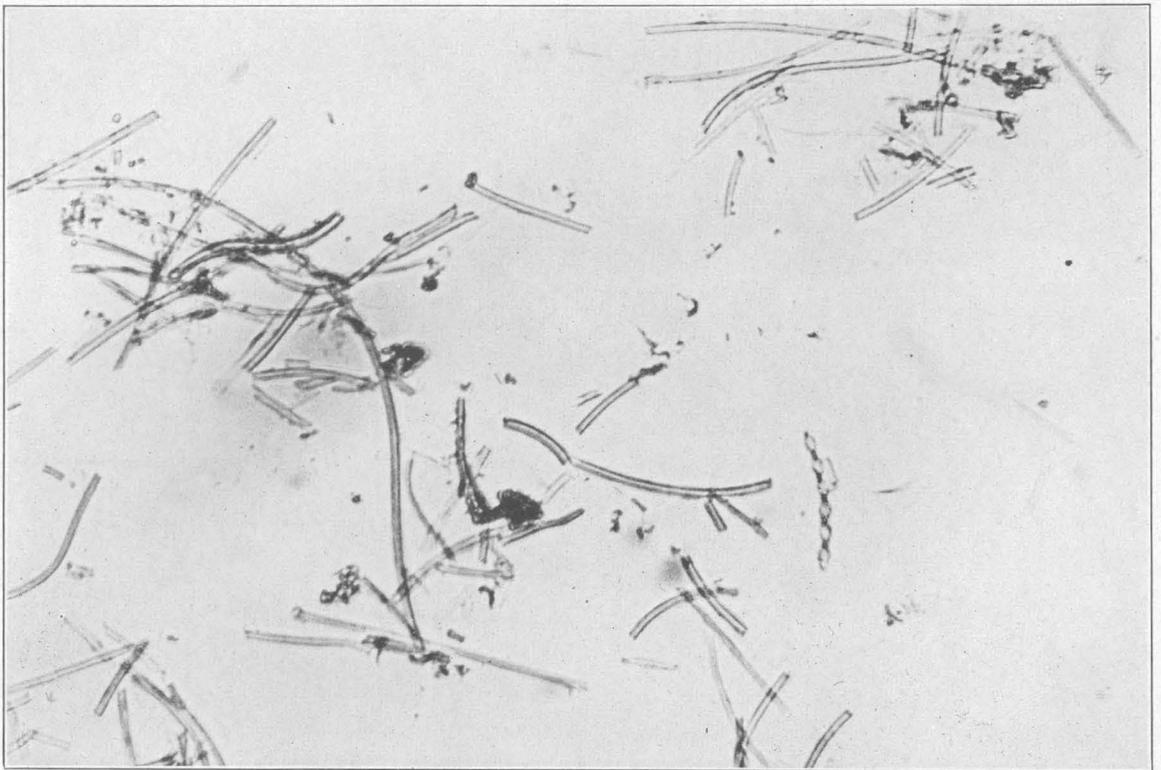
A. PHOTOMICROGRAPH OF THREAD OF CRENOTHRIX POLYSPORA FROM CITY WATER, MADISON, WIS., $\times 640$. Shows the formation of conidia from vegetative cells. Conidia occur in the upper part of the sheath (on the right) and vegetative cells in the lower part (on the left). Sheath is faintly outlined. Stained with gentian violet.



B. PHOTOMICROGRAPH OF THREAD OF CRENOTHRIX POLYSPORA FROM CITY WATER, MADISON, WIS., $\times 640$. Shows the germination of cells within the sheath. Sheath is also well shown in small threads. Stained with gentian violet.



A. PHOTOMICROGRAPH OF OCHEROUS SCUM IN IRON SPRING NEAR LAKE KEGONSA, MADISON, WIS., $\times 640$. Shows simple straight and curved threads of *Leptothrix ochracea*. Unstained.



B. PHOTOMICROGRAPH OF OCHEROUS SCUM IN IRON SPRING NEAR LAKE KEGONSA, MADISON, WIS., $\times 640$. Shows threads of *Leptothrix ochracea* and one of *Spirophyllum ferrugineum*. Thread of very regularly twisted *Spirophyllum* on the right. Unstained.

ent, and as the chlorine is negligible, it seems that in this spring at least all the calcium, magnesium, and iron are present in the form of carbonate (or bicarbonate). The iron, although given as ferric oxide in the analysis, is all present in the ferrous form, as is shown by the fact that the water as it issues from the spring is beautifully clear but upon standing soon becomes turbid on account of the oxidation of the iron by atmospheric oxygen. After a few days a distinct yellowish-brown deposit has formed at the bottom of vessels in which the water is kept and at the end of a week or two the iron is so completely precipitated that less than 0.2 part per million of ferric oxide remains in the solution, although the original content was 5.2 parts per million, as shown in the analysis. The 5.2 parts ferric oxide are equivalent to 3.69 parts metallic iron.

Leptothrix forms soft, fluffy brown botryoidal masses attached to the bottom and sides of the spring. The masses may be an inch or more in thickness and form a sort of lining locally along the sides and bottom of the spring. They consist of an almost pure culture of *Leptothrix* threads, both living and dead, but with these here and there are threads of *Spirophyllum*, all interwoven into a thick matting.

During the course of several visits to this spring I had an opportunity of noting the effect of seasonal changes on the growth of the iron bacteria. The most abundant growth apparently occurred in the spring and early in the summer; late in the fall the growth seemed to be at its lowest, being less marked even than in midwinter. During the period of lowest growth *Spirophyllum* seems to be somewhat more abundant relatively than during periods of luxuriant growth.

At the Rowe mine, an open-pit iron mine near Riverton, in the Cuyuna district in central Minnesota, a number of springs of iron-bearing water issue directly from the ore at the east end of the pit. The ore is a mixture of limonite and more or less hydrated hematite, but the water issuing from it probably contains ferrous iron in solution and supports an abundant growth of *Leptothrix* and various algae in little depressions on the surface of the ore.

In spring water from Middleburg, Va., procured for me by Dr. E. B. Fred, of the University of Wisconsin, I found *Leptothrix* occurring in abundance associated with some *Spirophyllum* and various types of algae. The spring is 1 mile northwest of Middleburg. The iron-bearing water issues from red clay probably derived by decomposition from Triassic red shale (Newark), outcrops of which occur within 50 feet of the spring. The waters flow into Wauquipin Creek, a tributary of Goose Creek, which empties into Potomac River 10 to 15 miles distant.

In the Kennedy mine, in the Cuyuna iron ore district, *Leptothrix* occurs abundantly on some of the lower levels. (See Pl. V.) On the 262-foot level two long crosscuts penetrate a succession of iron ore, ferruginous chert, cherty siderite rock, and green chloritic schist. The walls of these crosscuts, where they consist of cherty siderite rock and green schist and where water is abundant, support a luxuriant growth of *Leptothrix* associated with some *Spirophyllum* and *Gallionella*. Locally also pools of water on the floors of the crosscuts are filled with yellowish-brown to dark-brown masses of these organisms.

Microscopically the material is seen to consist very largely of *Leptothrix*, but here and there threads of *Gallionella* and *Spirophyllum* are common. Most of the *Leptothrix* threads are light yellowish-brown and transparent, but some are dark brown and have a thick irregular coating of ferric hydroxide. With careful handling very long threads of *Leptothrix* were obtained, some of which had a thick brown coating of ferric hydroxide at one end, though the other end was smooth and transparent, there being a gradation between the two ends. A few nearly colorless threads were seen which showed cell structure very plainly. Some of the cells were elongated cylindrical, some short cylindrical, and some were platelike. Whether these threads were really *Leptothrix* or whether they were some form of almost colorless algae or fungi it is not possible to say. In size and general form they were like *Leptothrix*. Other threads of *Leptothrix* occur which have little projections along them at intervals. These projections are probably little lumps of ferric hydroxide, but they resemble very closely the

conidia described by Ellis in connection with the form for which Benecke¹ has suggested the name *Conidiothrix*.

A sample of the scum of iron oxide collected from the walls of the drifts of the Kennedy mine and dried at 105° C. was analyzed by W. G. Crawford, of the University of Wisconsin, with the following results:

Analysis of scum of iron oxide from Kennedy mine, Minn.

[Dried at 105° C.]

Ferric oxide (Fe ₂ O ₃) -----	70.56
Silica (SiO ₂) -----	7.27
Lime (CaO) -----	3.41
Magnesia (MgO) -----	.40
Combined water (H ₂ O) -----	13.75
Loss above 105° C. (besides combined water) --	4.60
	99.99

This analysis shows that the material precipitated by the iron bacteria is practically pure ferric hydroxide, for the impurities may be attributed to small rock particles which were unavoidably included in the sample in collection. On the supposition that the iron is all present in the form of ferric hydroxide or limonite, 11.95 per cent of water is required to combine with 70.50 per cent of ferric oxide, making a total of 82.51 per cent limonite, or of 49.3 per cent metallic iron. This amount leaves 1.8 per cent of combined water unaccounted for, which probably means that the ferric oxide is in a slightly higher state of hydration than in the mineral limonite. The loss above 105° C., besides the combined water, is probably mainly carbon dioxide, derived from the oxidation of the carbon present in the bacterial sheaths. The silica, lime, and magnesia are accounted for by the presence of rock particles.

Besides finding *Leptothrix* in iron springs and mines I have found it in river waters and in bogs. In river waters I have found it especially common where pools of more or less stagnant waters occur along the banks between boulders or outcrops of rock. In some places it seems that these rocks yield iron for its growth.

In bogs ferric hydroxide frequently occurs as a thin iridescent film on the surface of the water. This film results from the oxidation of iron compounds in solution in the water. With

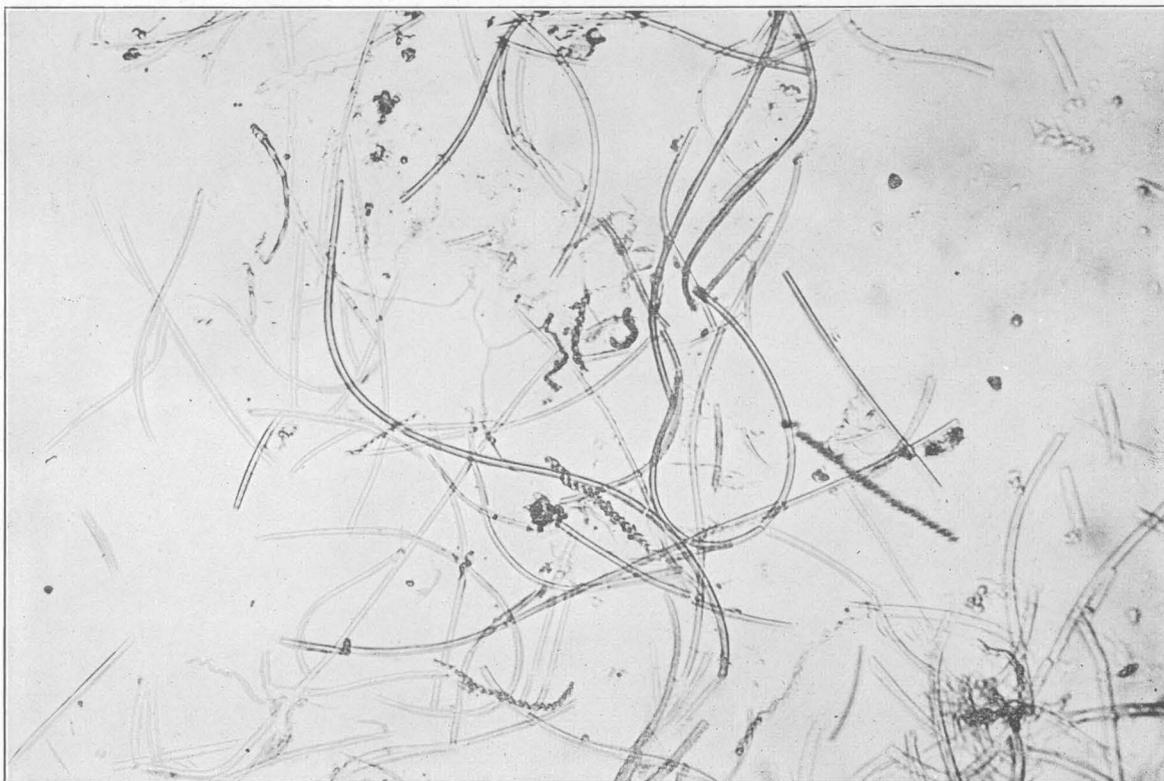
such occurrences there is almost always associated a yellowish-brown scum or ooze along the sides and bottom of the pools of water. This scum generally consists of *Leptothrix* associated with more or less algae. It is well known that, on account of the abundant presence of decaying organic matter, bog waters can take a considerable amount of iron into solution. A thin layer of water near the surface, which is in direct contact with the oxygen of the air, probably suffers oxidation, and the iron in solution is changed to ferric hydroxide and forms the surface film. Below the surface it seems reasonable to suppose that the iron is kept in solution to some extent by products of decaying organic matter but that some of it is taken up by the iron bacteria and that ferric hydroxide is deposited on their sheaths. This material gradually accumulates and eventually forms deposits of bog iron ore.

On account of the abundant presence of ferric hydroxide in the sheaths, cultures of *Leptothrix* (and also of *Spirophyllum* and *Gallionella*) may be kept in water for an almost indefinite length of time for purposes of study. It seems that although the organisms die the sheaths retain their natural form.

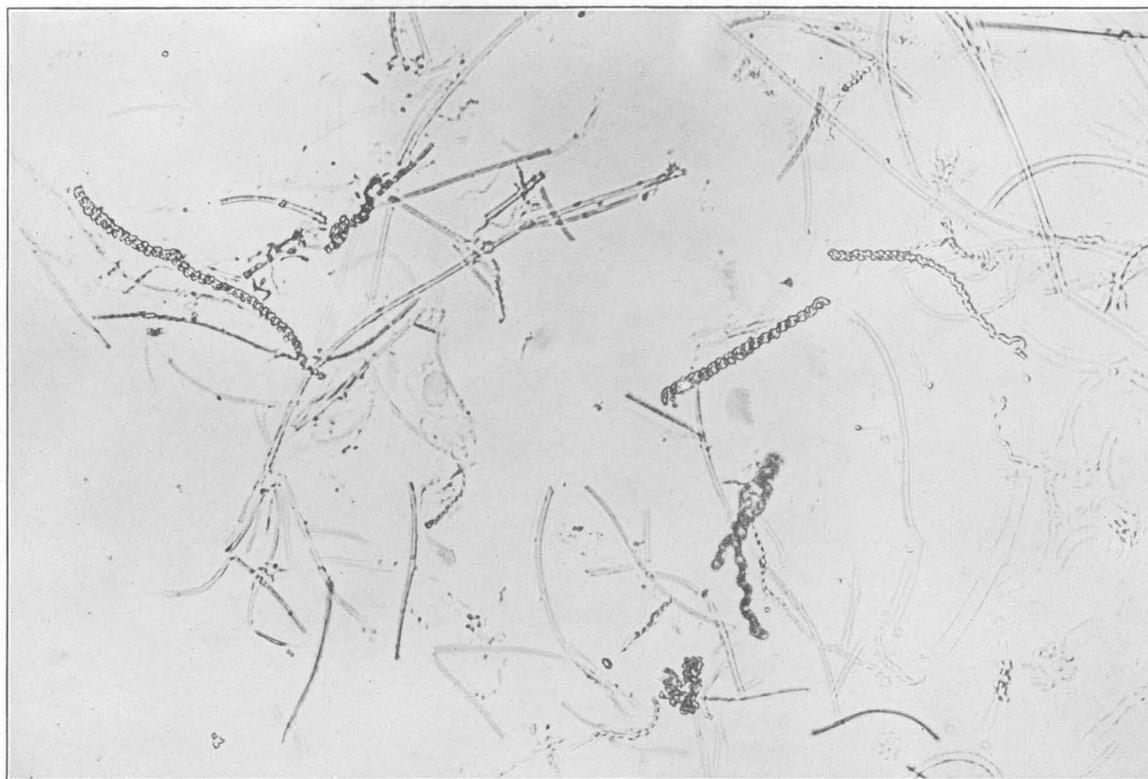
Leptothrix ochracea has been grown in the laboratory by a number of investigators. The first laboratory cultures of *Leptothrix* were obtained by Winogradsky.² He used for the purpose a glass cylinder about 8 inches tall and placed in the bottom of this crushed hay which had been previously cooked. On this material he sprinkled some freshly precipitated ferric hydroxide and then filled the cylinder with well water. As soon as gas formation occurred, little ocher-colored flakes and masses appeared on the surface of the water and on the sides of the glass cylinder. In 8 or 10 days a thick, yellowish-brown deposit was found to cover the sides of the cylinder and on the surface of the water large zoogloea of the same color formed and gradually sank to the bottom. The ocher-colored masses were found to consist almost entirely of organisms, amorphous flocculent ferric hydroxide being very uncommon. Among these organisms *Leptothrix* was almost always present. The difficulty with this culture method was that be-

¹ Benecke, Wilhelm, *Bau und Leben der Bakterien*, 1912.

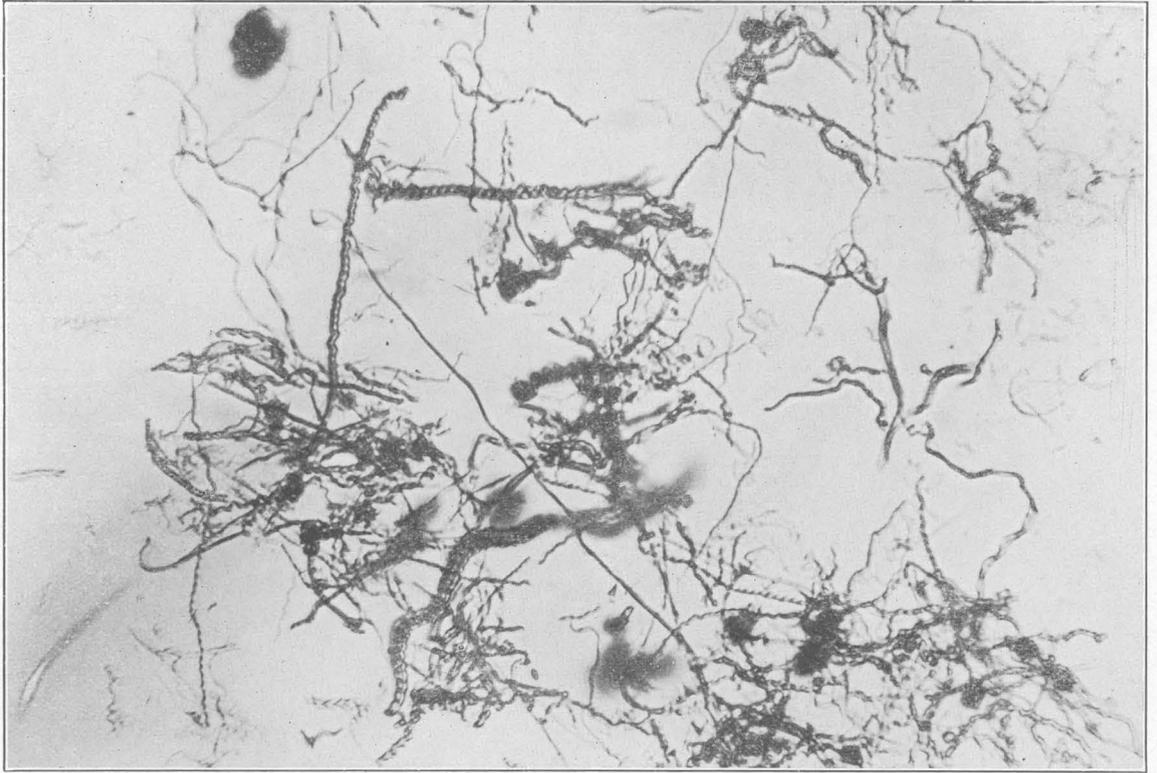
² Winogradsky, S., Ueber Eisenbakterien: *Bot. Zeitung*, Band 46, pp. 262-270, 1888.



A. PHOTOMICROGRAPH OF MATERIAL FROM 262-FOOT LEVEL, KENNEDY MINE, CUYUNA, MINN., $\times 640$.
 Threads of *Spirophyllum ferrugineum* are near the upper left corner and near the center. Threads of *Leptothrix ochracea* and *Gallionella ferruginea* are scattered; the latter show braidlike forms. Unstained.

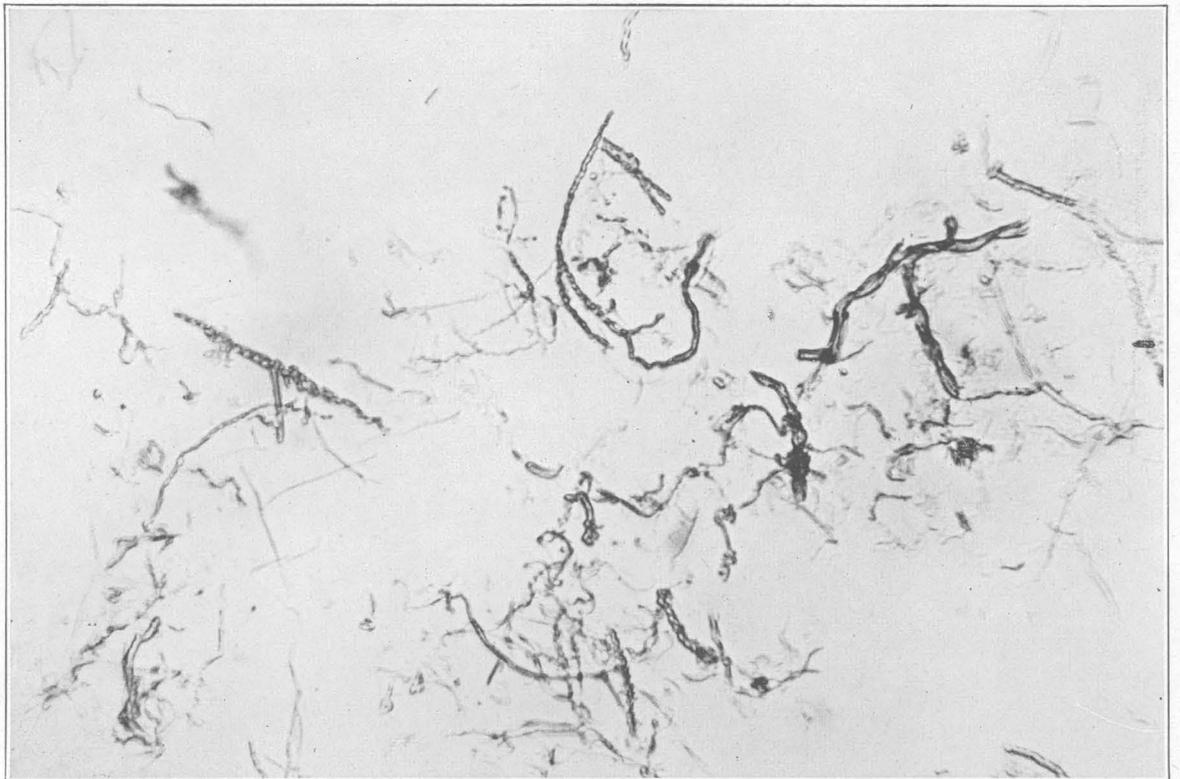


B. PHOTOMICROGRAPH OF OCHEROUS SCUM ON 262-FOOT LEVEL, KENNEDY MINE, CUYUNA, MINN., $\times 640$.
 Shows simple threads of *Leptothrix ochracea*, coiled, braidlike forms of *Gallionella ferruginea*, and a few spiral ribbon-like forms of *Spirophyllum ferrugineum*. Unstained.



A. PHOTOMICROGRAPH OF OCHEROUS, GELATINOUS SCUM FROM 100-FOOT LEVEL, FEDERAL MINE, HAZEL GREEN, WIS., $\times 640$.

Shows braidlike forms of *Gallionella ferruginea* and also single spiral threads of *Gallionella ferruginea*. Twisted ribbon-like forms of *Spirophyllum ferrugineum* are abundant. Unstained.



B. PHOTOMICROGRAPH OF OCHEROUS, GELATINOUS SCUM FROM 100-FOOT LEVEL, FEDERAL MINE, HAZEL GREEN, WIS., $\times 640$.

Shows ropelike forms of *Gallionella ferruginea*, one near the center consisting of four single threads; also single spiral threads of *Gallionella* and twisted ribbon-like forms of *Spirophyllum ferrugineum* of different sizes. Unstained.

sides *Leptothrix* numerous other bacteria as well as protozoa of many varieties developed, so that the culture was impure.

Adler¹ made some improvement by adding 0.05 per cent iron ammonium citrate to water from the city supply of Prague, which was taken from Moldau River, and allowing the solution to stand in a glass beaker. After some days yellowish flakes of *Leptothrix*, *Cladothrix*, and *Anthophysa* developed abundantly, as well as a few protozoa.

Molisch,² after many attempts, finally succeeded in getting pure cultures of *Leptothrix*. In an attempt to repeat Adler's experiments by using water from the city supply of Vienna, which was derived from springs, he was unsuccessful, and therefore he used water from Moldau River in all his experiments. His first experiments were for the purpose of obtaining an abundant growth of *Leptothrix* with the least possible development of other forms. He took various organic compounds of iron and manganese and dissolved them in water from Moldau River, in which *Leptothrix* was known to be present. The strength of the solutions used was usually about 0.05 per cent. The compounds with which he was most successful in obtaining growths of *Leptothrix* were manganpeptone, iron ammonium citrate, peptone with manganese carbonate, manganum phospholacticum, iron sulphide with peptone, and iron-ammonium tartrate. He found that in these solutions, which were kept in beakers in diffused light, little brown spots appeared near the surface in a few days and that after a week or two a thick matting formed over the surface. This was found to consist mainly of *Leptothrix*, but *Anthophysa* and *Cladothrix* were generally abundant, and other protozoa and algae also frequently developed.

Molisch then attempted the isolation of *Leptothrix* by growth on solid media. The medium which he found best adapted consisted of 1,000 cubic centimeters of water from Mol-

dau River, 0.05 gram of manganpeptone, and 10 grams of agar. This medium was inoculated with *Leptothrix* which was obtained from impure cultures and was incubated at 25° C. In a few days, among numerous other bacterial colonies, certain light-brown colonies developed which soon became dark rusty brown and upon examination were found to consist entirely of *Leptothrix*.

Montfort³ mentions the occurrence of heavy growths of *Leptothrix ochracea* in tanks containing moderately strong solutions of ferrous sulphate. He states also that the organism is easily grown in a 5 to 10 per cent solution of

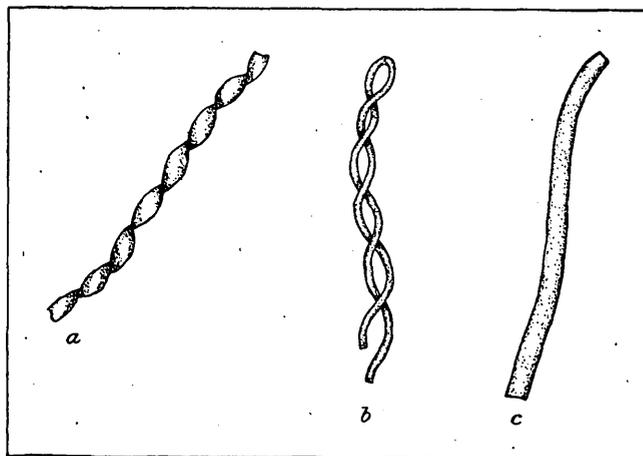


FIGURE 3.—Diagrammatic sketch of *Spirophyllum ferrugineum* (a), *Gallionella ferruginea* (b), and *Leptothrix ochracea* (c). Shows difference in size and structure of the organisms. \times about 1,080.

ferrous sulphate, and develops under such conditions in a few days. At my request Mr. Montfort sent me samples of the ferrous sulphate with which he had obtained cultures. However, I was unable to duplicate his results, although I made several attempts. The solutions gave an abundant yellowish-brown ochreous, flocculent precipitate, due to oxidation, which upon examination under the microscope gave no trace of any organic forms except occasional filaments of mold mycelium, some of which had a brown coating of ferric hydroxide. The precipitate consisted mainly of brownish-yellow mixed granular and flocculent material, probably partly basic ferric sulphate and partly ferric hydroxide.

Leptothrix ochracea (see Pls. IV and V and figs. 3, 4, 5, and 6) commonly occurs as un-

¹ Adler, Oscar, Ueber Eisenbakterien und ihrer Beziehung zu den therapeutisch verwendeten natürlichen Eisenwässern: Centrbl. Bakteriologie, Abt. 2, Band 11, pp. 215-219, 277-278, 1903-4.

² Molisch, Hans, Die Eisenbakterien, Jena, 1910.

³ Montfort, W. F., Dry feed of chemicals in water purification: Am. Waterworks Assoc. Jour., vol. 2, pp. 204-205, 1915.

branched threads of the same width throughout and with usually no visible differentiation

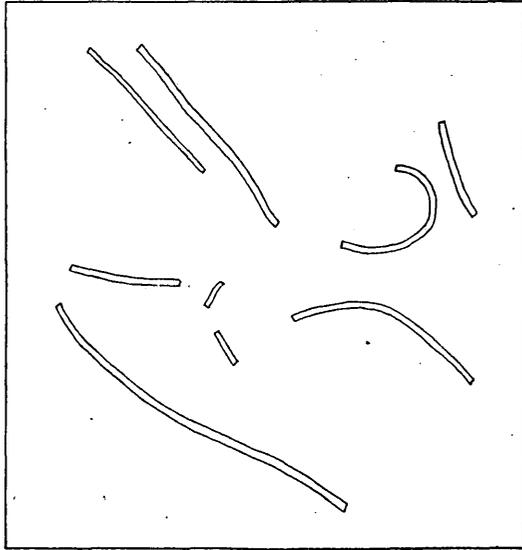


FIGURE 4.—Portions of threads of *Leptothrix ochracea* showing straight and curved forms. Drawing with camera lucida. $\times 550$.

between the two ends. Ellis¹ described *Leptothrix* threads as being free at both ends and being held in place only because numerous threads intertwine with each other to form a thick matting which becomes attached to foreign objects. Benecke,² on the other hand, states that some of the threads are sessile and that then they show a thickening toward the attached end. *Chlamydothrix sideropus*, a related species, has a well-developed holdfast.³

Threads of *Leptothrix ochracea* almost invariably have a light yellowish-brown color, due to the presence of ferric hydroxide in the sheaths, which enables them to be studied without staining. They are very difficult to stain. I have tried staining with gentian violet, carbol fuchsin, and methylene blue, both with and without previous treatment with dilute hydrochloric acid, and the results have been very unsatisfactory. By careful treatment with dilute hydrochloric acid, however, and then stain-

ing for 10 or 12 hours in a dilute solution of carbol fuchsin, I have succeeded in staining the sheaths, but I have not been able by any method to bring out clearly the cell structure.

The average width of the threads of *Leptothrix* is about $1\frac{1}{2}$ micra, but they range in width from 1 micron to 2 micra. The longest thread that I have noted measured about 120 micra, or about one-eighth of a millimeter, but doubtless the threads grow to a much greater length, being broken during the manipulations necessary for microscopic examination. Generally the threads are slightly curved or undulatory, but some short threads are quite straight. Rarely *Leptothrix* may be twisted spirally into a corkscrew form.

In fresh cultures of *Leptothrix* I have occasionally seen threads that show a differentiation into cells. The cells are usually long cylindrical in shape with slightly rounded ends. They vary greatly in length, but generally the length is many times the width. By far the greater mass of threads in ordinary cultures, however, shows no cell structure whatever, which may be due to the cells being obscured by the ferric hydroxide that colors the sheath

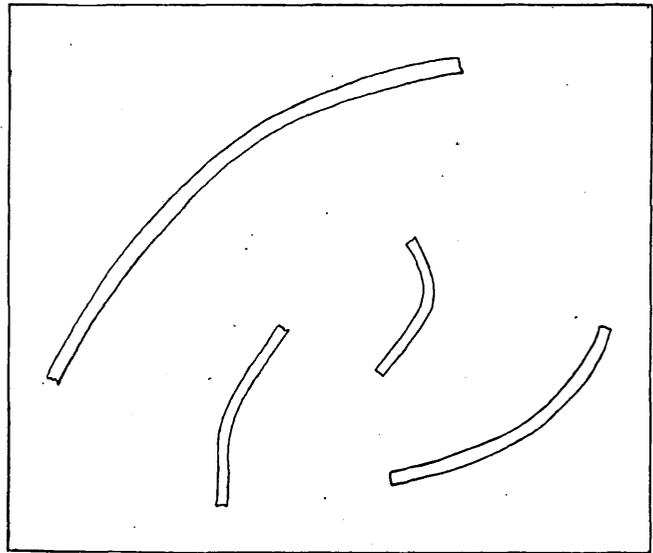


FIGURE 5.—Portions of threads of *Leptothrix ochracea*. Drawing with camera lucida. $\times 1,080$.

or to the sheaths being empty. Molisch⁴ states that by treatment of the threads with a 2 to 5 per cent solution of hydrochloric acid he was able to dissolve the ferric hydroxide from the sheath and thus brought out very plainly the

¹ Ellis, David, A contribution to our knowledge of the thread bacteria: Centralbl. Bakteriologie, Abt. 2, Band 19, pp. 503-505, 1907.

² Benecke, Wilhelm, Bau und Leben der Bakterien, p. 489, 1912.

³ Molisch, Hans, Die Eisenbakterien, pp. 14-16, 1911.

⁴ Molisch, Hans, op. cit., p. 22.

cell structure in threads that under ordinary conditions showed no cell structure whatever. I have attempted this with many cultures but without success, perhaps because the cultures used were too old.

Leptothrix ochracea is said by Molisch¹ to reproduce in three ways—by fragmentation (that is, by the breaking off of small fragments of threads which in time grow into new threads), by the forcing out of end cells from the thread, and by swarm cells. The swarm cells are cylindrical rods with rounded ends 0.6 to 0.8 micron in width and attain a maximum length of 14 micra. Some of them are threadlike and consist of several cells. Their movement is

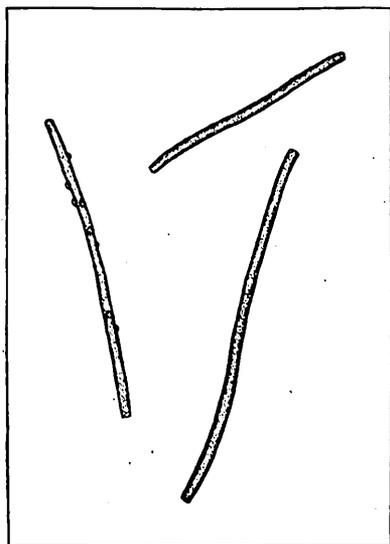


FIGURE 6.—Portions of threads of *Leptothrix ochracea*, one of them showing nodular projections. Drawing with camera lucida. $\times 1,080$.

backward and forward, as well as rotational around the longer axis. The swarm cells after they leave the cell swim around and finally attach themselves and form new threads. Frequently they attach themselves to old threads and thus simulate branching forms. Swarm cells are said to stain readily with aniline dyes.

Ellis,² in his descriptions of *Leptothrix*, states that it reproduces by the formation of conidia. He described *Leptothrix* as a simple thread, straight or curved, which shows no cell structure. The conidia form small spherical projections on the sides of the threads and gradually detach themselves and are carried away

by currents to other places, where they germinate and produce new threads. According to Ellis, this is the common mode of reproduction for *Leptothrix*. Molisch, however, states that he has never seen these conidia and doubts their existence, believing that the projections observed by Ellis may have been lower bacteria which have attached themselves to the *Leptothrix* threads, or that perhaps they were swarm cells of *Leptothrix* itself. Benecke,³ in reviewing the facts, suggests that the form described by Ellis may be a new species related to *Gallionella*, and proposes the term *Conidiothrix* for it if such a form is proved to exist by further investigations.

In several of the cultures which I have collected recently, notably a culture of *Spirophyllum* and *Gallionella*, from the 100-foot level of the Federal mine, near Hazel Green, in southwestern Wisconsin, I have found a form resembling that described by Ellis. It consists of a thread similar to *Leptothrix* in size and general form. (See Pl. VII, A, and fig. 6.) However, no threads were found which gave any semblance of cell structure, but many threads showed small, rounded projections at irregular intervals along the thread. Whether these projections were attached particles of ferric hydroxide or other foreign material, or whether they were really conidia, was difficult to determine. They seemed, however, to be part of the thread, not having any distinct partition wall separating them from the thread. It is also rather significant that in only a few out of many cultures of *Leptothrix* which I examined have I found these forms. On the other hand, many of the cultures contain threads of *Leptothrix*, some of them thickly coated with ferric hydroxide, which show little projections and irregularities, consisting, without much doubt, of ferric hydroxide. It is therefore difficult to say whether the form mentioned above is the same as that described by Ellis as *Leptothrix* or whether all the projections are simply foreign bodies, as is suggested by Molisch. I have never found these bodies in a germinating condition, nor have I found them where they have been completely separated from the parent thread by abstriction.

In view of the fact that some investigators, such as Molisch and Benecke, describe *Lepto-*

¹ Molisch, Hans, op. cit., p. 43.

² Ellis, David, op. cit.

³ Benecke, Wilhelm, op. cit.

thrix as having well-developed cell structure, whereas others, such as Ellis, have not been able to find any evidence of cell structure, there is some question as to whether there may not exist two similar forms both widely distributed, the one showing cell structure and the other consisting of simple undifferentiated threads resembling those of *Gallionella* and *Spirophyllum*. Careful work is necessary not only to determine whether the latter form exists, but if so, whether it reproduces by the external abstriction of conidia or simply by the breaking off of parts of the threads. The method of reproduction has to be definitely determined for *Spirophyllum* and *Gallionella* as well.

GALLIONELLA FERRUGINEA Ehrenberg.

The term *Gallionella* was applied by Ehrenberg¹ in 1836 to all the organisms which are concerned in the formation of the brown iron scums of bogs and springs. That the brown scum at the bottom of certain wells was composed of organisms was also recognized by him and these organisms are mentioned as being a related type. He classified the iron organisms as infusoria and thought that they were related to the diatoms, which he had studied and which he also believed to be infusoria. Thus iron bacteria were at one time classed as unicellular animals, but later it was recognized that they were really plants and for some time they were grouped with the algae. Gradually as the investigations progressed it was determined that more than one species of iron bacteria were concerned in the formation of iron scums, and thus *Leptothrix*, *Crenothrix*, and more recently *Spirophyllum* and *Clonothrix* were recognized as distinct types. At present the term *Gallionella* is restricted to the ropelike form that consists of double spirally twisted threads.

Up to the present time I have found *Gallionella* in only three localities, namely, in the Federal mine, near Hazel Green, in southwestern Wisconsin, where it occurs in great abundance in association with *Spirophyllum*; in the Kennedy mine, in central Minnesota, where it is found in minor amount with predominating *Leptothrix* and some *Spirophyllum*; and in

the filtrate from water from the city supply of Madison, Wis., where it is associated with *Spirophyllum* and *Crenothrix*.

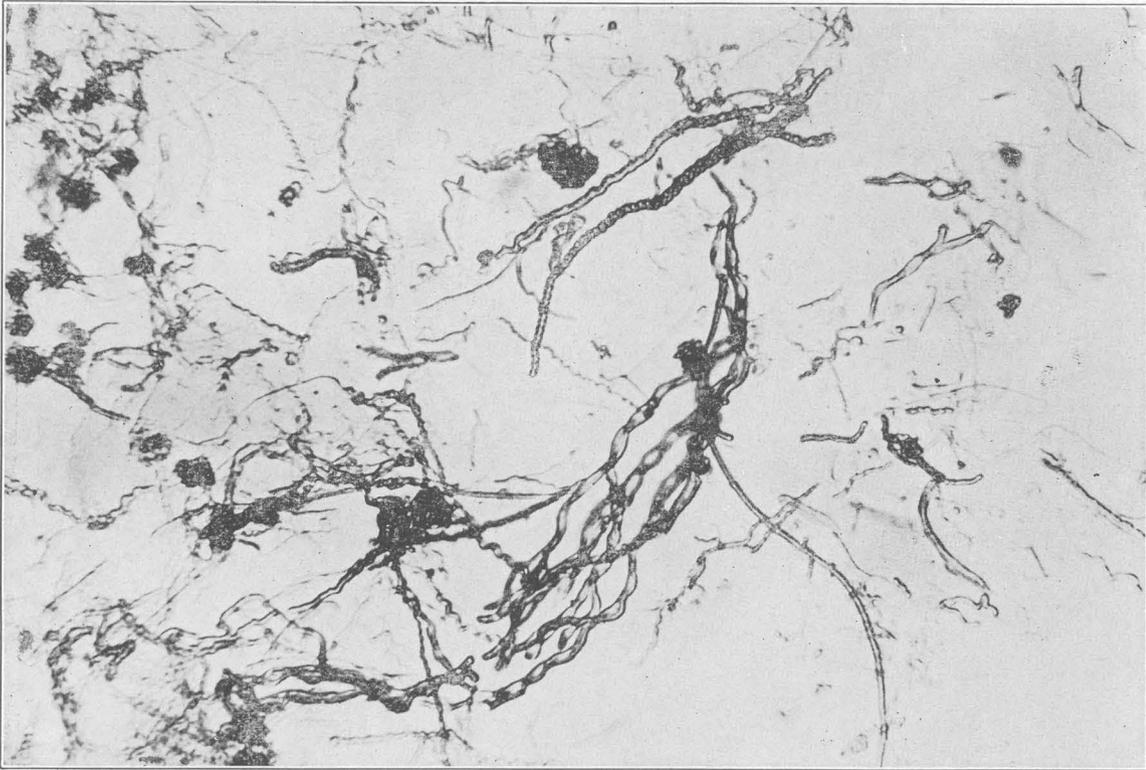
The material in the Federal mine and the Kennedy mine occurs in brown gelatinous masses, which are attached to the walls of the tunnels beneath small openings from which streams of iron-bearing water issue, and which is also found in pools along the floors of the drifts.

The cultures from the Federal mine (see Pls. VI and VII, A), when examined microscopically, were found to contain abundant *Gallionella* of various forms and sizes. Perhaps the most common form is a short twisted ropelike thread consisting either of two or four single threads closely twisted together. The twisting is accomplished by the bending of single threads in the middle and twisting the ends around each other. There are also present very loosely twisted forms and single spiral or corkscrew-like threads, resembling a single strand from a rope when untwisted. The ropelike forms of *Gallionella* vary considerably in width from end to end, the thick end being usually that where the loose ends of the threads project. Different individuals also vary in width and length, not only among the ropelike forms but also among the single threads, which show a considerable range in size.

In the cultures from the Kennedy mine (see Pl. V) *Gallionella* is not very abundant, and most of it has the ropelike form. Many individuals are quite thin and transparent, not much thicker than the associated *Leptothrix* threads, whereas others are thick and heavily coated with brown ferric hydroxide. Some show the free ends of the separate threads projecting at one end, but most of them are short thick braids. Some have the same width throughout, but others taper toward one end.

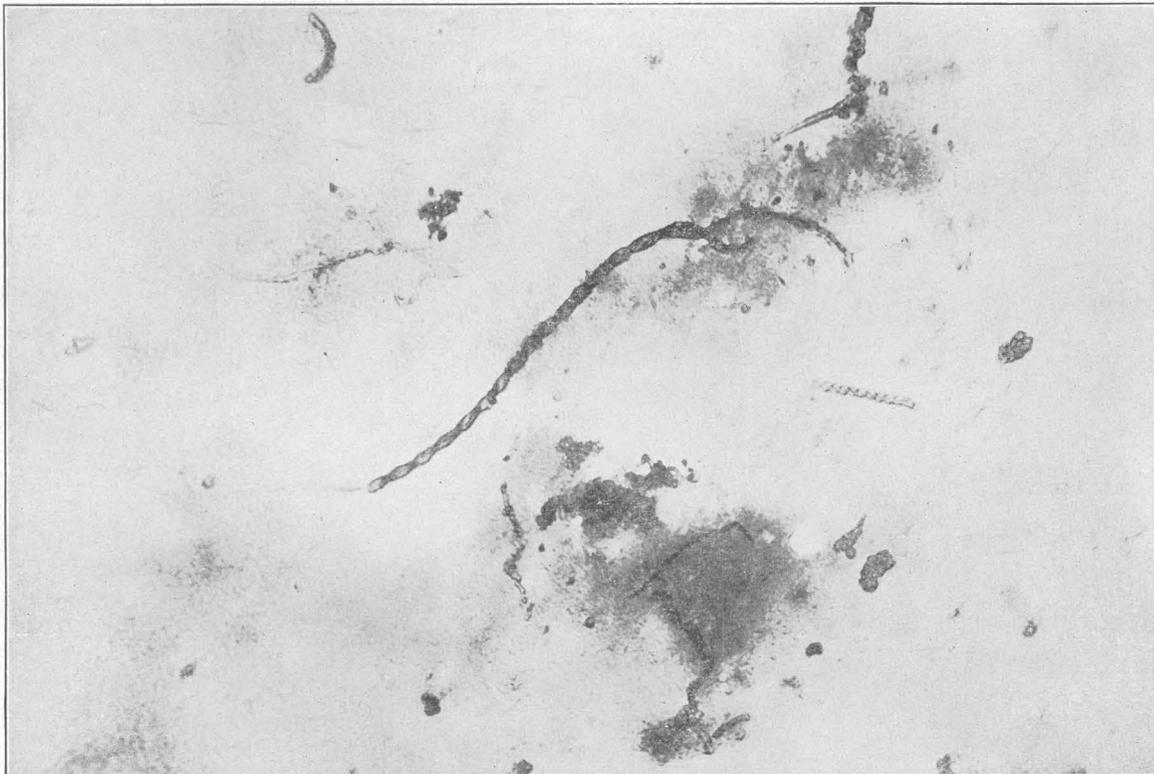
Spirophyllum, *Gallionella*, and *Crenothrix* occur together in the distributing pipes of the water system of Madison, Wis. Upon filtering with a porcelain filter a dark-brown mud is frequently obtained, especially when the water is turbid. Upon examination with a microscope this mud is seen to consist largely of flocculent textureless masses of ferric hydroxide with scattered strands of *Spirophyllum* and *Gallionella* and here and there short pieces of *Crenothrix* threads. The *Crenothrix*

¹ Ehrenberg, C. G., Vorläufige Mittheilungen ueber das wirkliche Vorkommen fossiler Infusorien und ihre grosse Verbreitung: Poggendorf's Annalen, Band 38, pp. 213-227, 1836.



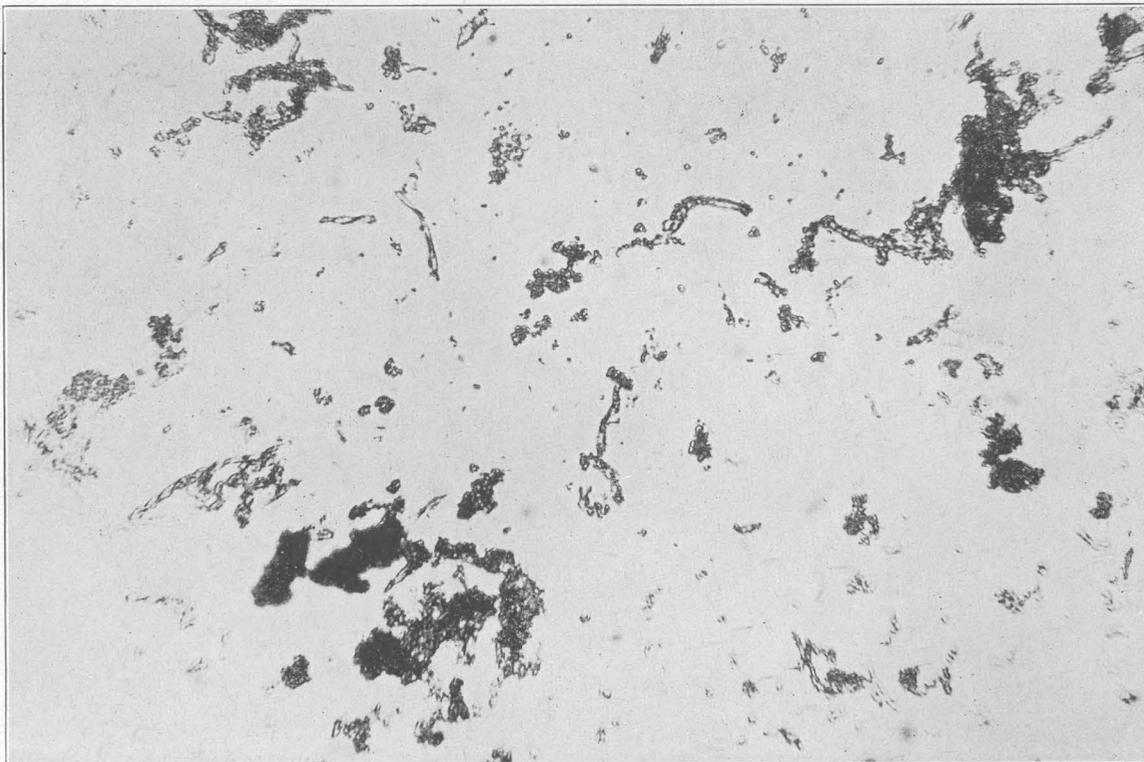
4. PHOTOMICROGRAPH OF OCHEROUS, GELATINOUS SCUM FROM 100-FOOT LEVEL, FEDERAL MINE, HAZEL GREEN, WIS., $\times 640$.

Shows irregularly twisted ribbon-like forms of *Spirophyllum ferrugineum*, a few braidlike forms of *Gallionella ferruginea*, and a thread of *Leptothrix ochracea* with nodular projections. On the right is a double form of *Spirophyllum*. Unstained.



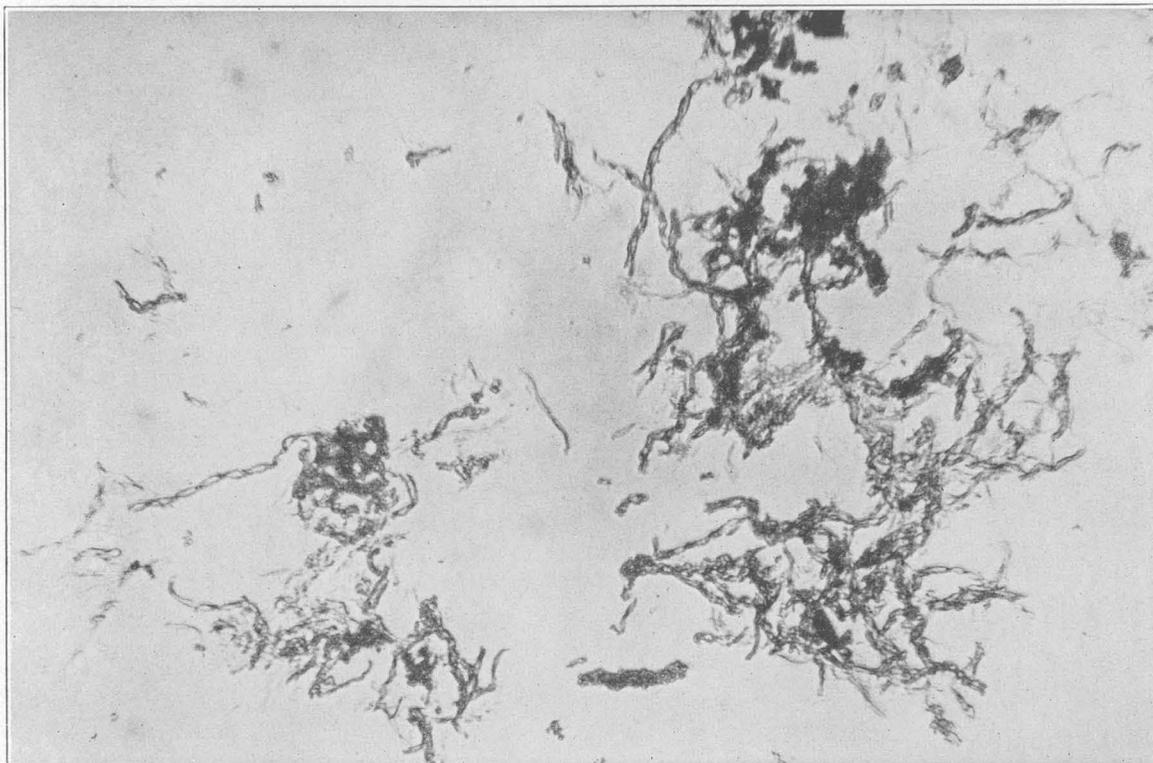
B. PHOTOMICROGRAPH OF DOUBLE TWISTED RIBBON-LIKE FORM OF SPIROPHYLLUM FERRUGINEUM FROM CITY WATER, MADISON, WIS., $\times 640$.

The dark masses are gelatinous ferric hydroxide. Unstained.



A. PHOTOMICROGRAPH OF OCHEROUS SCUM FROM 300-FOOT LEVEL, JUDSON MINE, ALPHA, MICH., $\times 640$.

Short twisted ribbon-like forms of *Spirophyllum ferrugineum* mixed with irregular masses and scattered specks of granular and gelatinous ferric hydroxide. Some *Spirophyllum* is coated with granules of ferric hydroxide. On the left is a double twisted form. Unstained.



B. PHOTOMICROGRAPH OF OCHEROUS SCUM FROM 200-FOOT LEVEL, JUDSON MINE, ALPHA, MICH., $\times 640$.

Shows numerous small, irregularly twisted forms of *Spirophyllum ferrugineum*. Near the bottom is a short form thickly coated with granular ferric hydroxide. The dark irregular masses are gelatinous ferric hydroxide. Unstained.

will grow and develop into long threads when placed in culture media, as previously described, but apparently no growth of *Spirophyllum* and *Gallionella* takes place on the filter.

Water pipes in cities where the water contains an appreciable amount of iron in solution are a common habitat of *Gallionella*, *Spirophyllum*, and *Crenothrix*. In some places the precipitation of ferric hydroxide by the iron bacteria is so abundant that crusts are formed around the inside of the distributing pipes. These crusts increase in thickness until they completely fill the pipes and block the passage of the water. The material composing the crusts has been examined and has been found to contain large numbers of bacterial casts, so that little doubt exists as to its origin.

It is claimed by some investigators that the growth of *Crenothrix* and associated iron bacteria in city water pipes is not dependent on the original iron content of the water but is due to iron taken into solution from the pipes, and that the most abundant growth takes place in newly laid pipes. Doubtless the solution of iron from distributing pipes is a contributing factor, yet it seems evident that some iron must be in solution originally or iron bacteria would be found in all city waters and not confined to certain localities, in most of which the water is known to have a high original iron content. I have tried to find *Crenothrix* and other iron bacteria in distributing pipes where the water was obtained from lakes and had a low iron content but have been unsuccessful.

Schorler,¹ while examining some iron crusts from pipes from the city of Dresden, found that pipes which were thickly encrusted on the inside with iron oxide and which had been in use for 30 years had suffered no corrosion on the inside underneath the iron crust. This condition he thought indicated that the iron forming the incrustation came from some source other than the pipes themselves and that the deposition on the walls occurred through the medium of iron bacteria, which here found a favorable place for growth. In this locality Schorler found that the organism responsible for the precipitation was principally *Gallio-*

nella, casts of which he found to be abundant in the iron crust.

Gallionella ferruginea may be likened to a hairpin the two ends of which have been twisted around each other. (See figs. 3, 7, and 8, and Pls. V, VI, and VII, A.) Sometimes such a twisted form may be bent again in the middle and the two ends be twisted around each other, thus forming a rope of four single strands. (See Pl. VI, B.) In some individuals the twisting is very loose, in others close. (See figs. 7 and 8.) I have found different coiled forms to range in width from 1 to 3½ micra. In individual coils the difference in width between the two ends may be as much as 1 micron. The longest coiled form that I

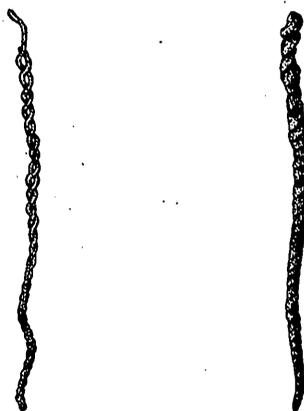


FIGURE 7.—Loosely twisted, ropelike form of *Gallionella ferruginea*. Drawing with camera lucida. × 1,080.

FIGURE 8.—Closely twisted, ropelike form of *Gallionella ferruginea*. Drawing with camera lucida. × 1,080.

have observed was about one-fourteenth millimeter in length, or 70 micra.

The single threads which compose these ropes or coils are very thin and have the same width throughout, although different individuals vary in size. The common range is from less than 0.5 to about 0.75 micron. The longest single thread I have noticed was about 0.05 millimeter in length. Most of the single threads which occur are probably detached parts of coils, for they generally show the spiral form. As in *Spirophyllum*, no differentiation has ever been noticed between the two ends of the threads of *Gallionella*, nor has any cell structure ever been distinguished. The organisms appear to be simple threads.

Gallionella has a yellowish-brown to brown color. The ropelike forms are quite dark

¹ Schorler, B., Die Rostbildungen in den Wasserleitungsröhren: Centralbl. Bakteriologie, Abt. 2, Band 15, pp. 564-568, 1906.

brown, much darker than similar forms of *Spirophyllum*.

The methods of reproduction of *Gallionella* have not been thoroughly studied. Migula¹ describes the reproduction as taking place by the breaking off of parts of the threads, these being carried away by water currents to other localities and growing into new threads. Ellis² claims that in addition to the above method of reproduction *Gallionella* also multiplies by the external abstriction of conidia similar to *Spirophyllum* and the form which he describes as *Leptothrix*. In connection with *Gallionella* and *Spirophyllum* he describes the formation of abundant little projections all over the surface of the threads. In some individuals their development is so profuse as to almost conceal the parent thread. These little projections after becoming separated from the thread are said to germinate and form new threads. I have frequently seen *Gallionella* and especially *Spirophyllum* covered with small light-brown spherical or somewhat irregular bodies of fairly uniform size such as Ellis describes but have never become convinced as to whether they are conidia or particles of ferric hydroxide. Upon treatment with hydrochloric acid they disappear, as they would if they consisted of ferric hydroxide, yet it is true also that the entire thread is destroyed in a very short time by similar treatment.

Schorler,³ in connection with his investigations on the formation of crusts of iron rust by *Gallionella* in the city water pipes of Dresden, found numerous strands of *Gallionella* in the outer portion of the crust, whereas the older interior portion of the crust consisted of a structureless mass of ferric hydroxide. He found that the individual strands of *Gallionella* had granular coatings of ferric hydroxide, which increased in thickness with the age of the strand and gradually caused its structure to disappear. He describes the development of small hexagonal crystals of hydrated ferric oxide on the sides of the older threads and states that they gradually increase in size and incorporate within them the surrounding granules of ferric hydroxide. Their growth results in the gradual disappearance of the

strands and the development of the textureless ferric hydroxide mass typical of the older portion of the crust.

From this and other descriptions it appears that various investigators have noticed the formation of granules and projections on *Gallionella* and *Spirophyllum* threads, but only Ellis has connected them with the formation of conidia.

SPIROPHYLLUM FERRUGINEUM Ellis.

Spirophyllum ferrugineum Ellis appears to be the most widespread of the iron bacteria. It occurs abundantly in iron-bearing surface waters, as well as in underground waters. It is almost always associated in greater or less abundance with other iron-depositing thread bacteria and frequently occurs where other iron-depositing thread bacteria are absent. With *Leptothrix* it is found in springs and clear stream waters, even where *Leptothrix* grows very profusely. With *Crenothrix* and *Gallionella* it is found in city water systems, and with *Gallionella* or *Leptothrix* it is found in mine waters. In some iron springs and mines almost pure cultures of *Spirophyllum* occur, *Leptothrix* and *Gallionella* being entirely absent.

I first encountered *Spirophyllum* abundantly in cultures obtained from the Federal mine, a zinc mine located near Hazel Green, in southwestern Wisconsin. (See Pls. VI and VII, A.) The mine workings are in the lower part of the Galena limestone, and zinc, lead, and iron sulphides occur with calcite in veins in the limestone.

Waters issue from fissures and openings at numerous points in the mine. Where the culture was obtained a little stream of iron-bearing water issued from a small fissure in the rock wall a short distance below a horizontal vein containing sphalerite, marcasite, and calcite. Below the opening, attached to the rock wall and forming a streak to the floor, was a soft gelatinous brown deposit of ferric hydroxide which had a maximum thickness of one-half inch and a maximum width of 2 inches. A short distance from this point a basin in the rock floor was filled with water and contained a thick brown deposit of ferric hydroxide. The material forming the streak beneath the fissure opening upon examination proved to

¹ Migula, W., System der Bakterien, Band 2, p. 1031, 1900.

² Ellis, David, op. cit., pp. 505-507.

³ Schorler, B., op. cit.

consist largely of *Spirophyllum* and *Gallionella*, with some *Leptothrix* or perhaps *Conidiothrix*. (See pp. 17-18.) Various forms of *Spirophyllum* were present, the most common being a wide, irregular, loosely twisted form. (See Pl. VI.) Other types are very regularly twisted and have the appearance of strings of beads. Their variation in size is considerable, some being almost as narrow as a single thread of *Gallionella*, whereas others are as wide as rope forms of *Gallionella*. Both single and double threads occur.

Subsequently I obtained almost pure cultures of *Spirophyllum* on the 200 and 300 foot levels of the Judson mine, south of Crystal Falls, Mich. (See Pl. VIII.) This mine is located on a steeply dipping deposit of red hematite inclosed in slate walls. The foot-wall consists of dark-gray pyritic slates. Water issues from numerous small fissures throughout the mine and yellowish-brown gelatinous masses of iron bacteria are abundant along the drifts, both where they cut the slate and where they cut the ore.

It seems probable that all the water issuing in the mine has at one time or another passed through the slate, and by its dissolving action on the disseminated iron sulphide and iron carbonate has become heavily loaded with iron. No analysis of the water has been made as yet, but it seems probable that the iron is in solution mainly as ferrous bicarbonate, though perhaps a part of it may be in the form of ferrous sulphate. These waters issuing from the mine openings either in the ore deposit or along the slate walls give abundant opportunity for the growth of bacteria.

The question naturally arises, How do the iron bacteria come into the mines? Are they carried by the waters themselves through intervening soil and rock or are they brought down into the mine on mine timbers, tools, or machinery? I have seen cultures of iron bacteria in places in mines where it seems quite improbable that they could have been brought by any other agency than the water itself, and it does not seem at all impossible that they may have been carried downward by surface waters through the larger openings in the soil or rock for many hundreds of feet. This opens the interesting possi-

bility that iron bacteria may be active in fissures or other large underground openings entirely unconnected with mines and may thus be instrumental in the formation of many of the fissure deposits and replacement deposits of iron ore which are so common. Their presence in such localities is of course difficult to prove unless they should be actually found in underground openings which are penetrated during mining operations. Such a phenomenon to my knowledge has not been observed, but it might easily escape notice unless particular attention were called to it.

The cultures obtained from the Judson mine showed only *Spirophyllum*, and these were mainly in the form of short pieces of filaments. A peculiarity about these cultures, however, was that most of the filaments were thickly covered with small spherical bodies of the same brownish color as the filaments. (See fig. 9.) Whether these little bodies are granules of ferric hydroxide or whether they are conidia, as described by Ellis, has not been determined.

The occurrence of *Spirophyllum* associated with *Leptothrix* and *Gallionella* at the Kennedy mine, on the Cuyuna range in central Minnesota, has already been described.

In addition to these underground localities I have found *Spirophyllum* in a number of places in iron-bearing surface waters, but it occurs in clear, fresh waters rather than in stagnant bog waters like those in which *Leptothrix* is often found.

In the Vermilion iron-ore district of northern Minnesota I obtained cultures of *Spirophyllum* from two iron springs, both issuing at the bases of extensive ridges, composed largely of banded jasper and associated greenstone. One of these springs is at the base of Soudan Hill, on the south shore of Vermilion Lake; the other is at the western foot of Jasper Peak, a few miles south of Soudan.

At the spring on Vermilion Lake the water issues from an iron pipe at the base of a ridge consisting mainly of greenstone and jasper and some slate. It empties into a small basin from which it flows down a short slope into the lake. Brown scum occurs in the basin and for some distance along the little rivulet down toward the lake. Where the water is quiet the brown scum lies on the bottom and elsewhere it is

attached to the sticks, grass blades, and other material lying in the water. The water has a strong iron taste.

At the spring at Jasper Peak the water comes directly out of the hillside into a small basin from which it flows through a series of larger pools into a marsh. Jasper Peak consists mainly of banded jasper and associated greenstone. A yellowish-brown scum of iron bacteria occurs at the bottom of the basin at the mouth of the spring and also in the pools in the marsh. It is not gelatinous but rather in the form of a fluffy precipitate.

When examined microscopically the scum of iron oxide from both of these localities is seen to contain an abundance of threads of *Spirophyllum*, but with these threads is associated a large amount of brown flocculent, textureless material in large and small irregular masses. (See Pl. IX, A.) The textureless masses probably consist largely of ferric hydroxide, but whether this material is precipitated by simple chemical action or whether its formation is due perhaps to the activity of lower forms of iron-depositing bacteria has not been determined. Probably it results from simple oxidation. The *Spirophyllum* in these cultures is of medium size and has regular but not very close twisting. In general the threads are clear and do not have the deposits of granular material on them that is so characteristic of the cultures from the Judson mine. However, many of the granular masses of ferric hydroxide can be seen to contain spiral threads, these forming a sort of nucleus around which the ferric hydroxide collects.

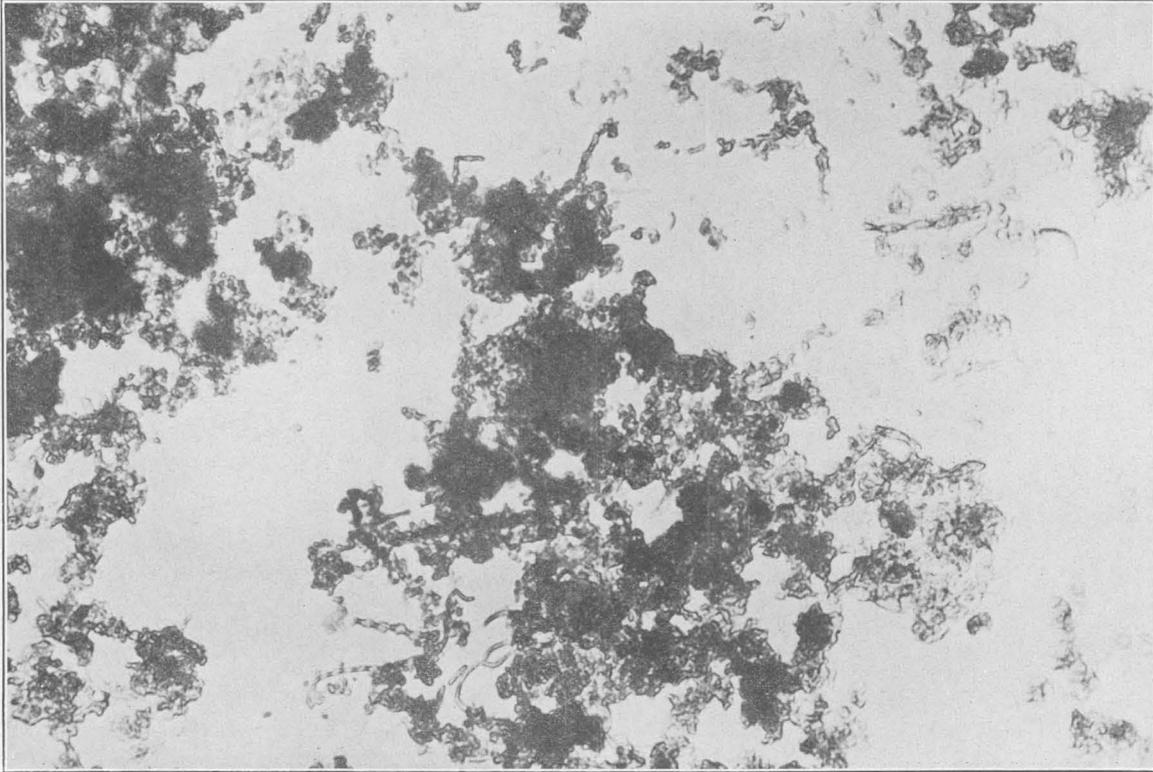
In the Rowe and Hillcrest mines, in the Cuyuna iron range, both of which are open-pit mines in red and brown hematite, seepages of iron-bearing waters issue from glacial sand and gravel which overlie the iron ore. The iron is taken into solution by the water while it is percolating through the sand and gravel, probably being derived from iron silicates, carbonates, and sulphides disseminated through the glacial material.

Thin coatings of yellowish-brown scum cover the pebbles over which the water flows and this material upon examination is seen to consist of *Spirophyllum* associated with more or less granular and flocculent ferric hydroxide, which is probably a chemical precipitate. In localities like these iron bacteria develop in a

surprisingly short time, deposits being formed by them within a week after the glacial sand and gravel are laid bare by stripping operations.

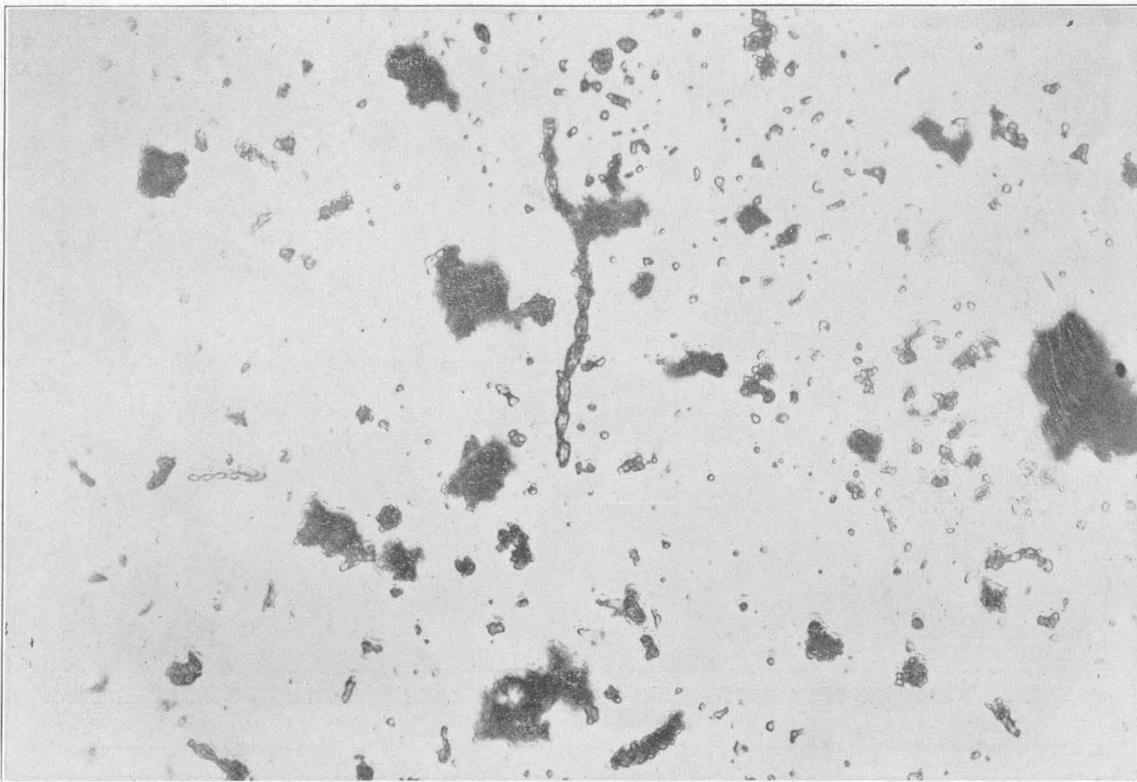
In the Pennington open-pit mine a very curious form of *Spirophyllum* was found. The water, which issues in the form of a small spring directly from the ore, apparently contains enough ferrous iron in solution to support a growth of iron bacteria. The material collected was brown in color and contained some *Spirophyllum* and algae. Upon standing for a week or so it became black, but over its surface a light-brown scum formed, which upon examination was found to consist of an almost pure culture of a variety of very small *Spirophyllum*. The threads are ribbon-like but very narrow and very loosely and irregularly twisted and are intergrown into a thick matting mixed with considerable granular ferric hydroxide. A great many of the threads show no twisting at all, and double ropelike threads are rare. There seems to be a great uniformity in the size of the threads, though here and there occur larger threads which resemble the ordinary *Spirophyllum* seen in other cultures.

At several points in the Pennington pit there are steel bars and rails which during the closed season for mining operations become submerged by water that accumulates in the pit. On several of these bars and rails I found beautifully developed porous tubercles of iron rust, which upon microscopic examination proved to contain abundant casts of *Spirophyllum*. (See Pl. IX, B, and fig. 13.) The greatest diameter of the tubercles is 2 inches or more at the base, and they rise from the surface of the bar or rail from a quarter to perhaps half an inch. The surface of such tubercles is formed by a thin, smooth, brittle film, and the interior consists of porous cellular ocherous material which on handling breaks up into fine powder. It is this material which contains abundant casts of *Spirophyllum*. Many of the casts still show the original texture of the threads clearly under the microscope, some of them being single and some double threads. Most of them, however, are thickly coated with granules of ferric hydroxide and appear like thick brown cords with rough surfaces. Some of these are twenty or more times the thickness of the original *Spirophyllum*. Frequently



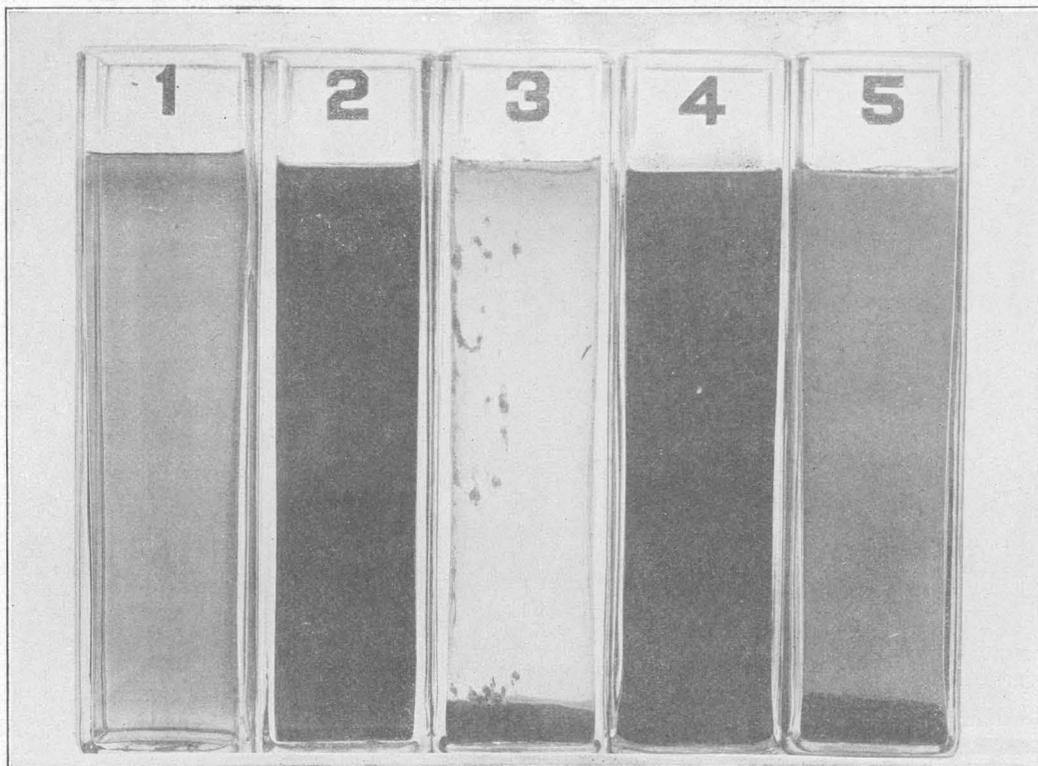
A. PHOTOMICROGRAPH OF OCHEROUS SCUM FROM IRON SPRING NEAR VERMILION LAKE, SOUDAN, MINN.,
× 640.

The dark irregular masses are ferric hydroxide. With it are mixed numerous forms of *Spirophyllum ferrugineum*, some double and some single. Unstained.



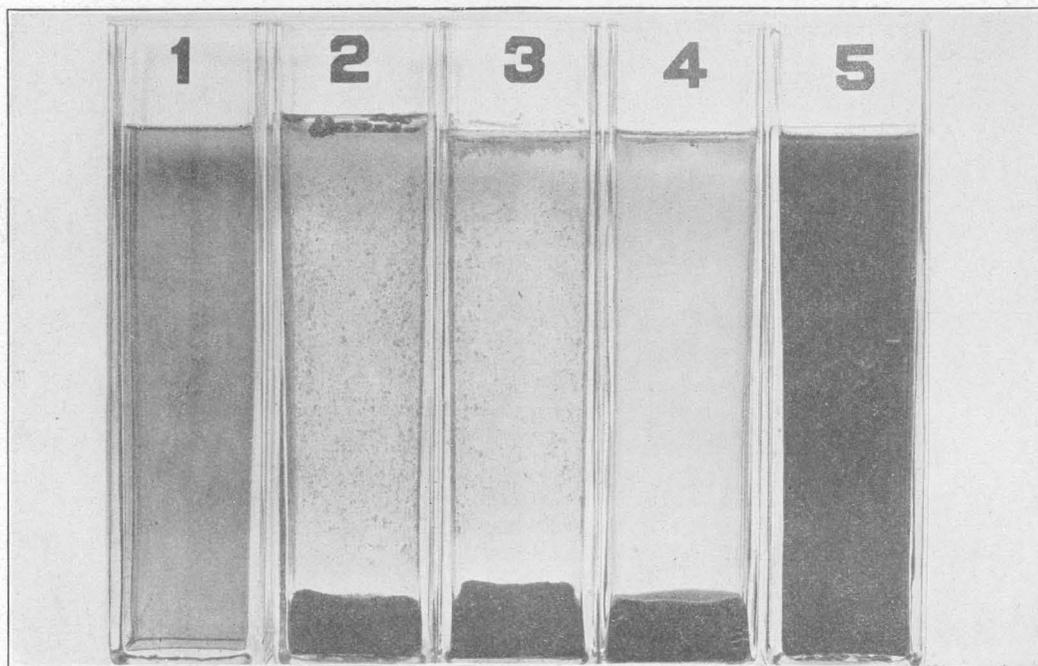
B. PHOTOMICROGRAPH OF LIMONITE POWDER FROM TUBERCLE OF IRON RUST, × 640.

Shows a number of scattered forms of *Spirophyllum ferrugineum* and irregular masses and scattered specks of granular iron rust. Unstained.



A. CULTURES SHOWING THE PRECIPITATION OF FERRIC HYDROXIDE FROM SOLUTIONS OF FERRIC AMMONIUM CITRATE.

- 1, Water with freshly dissolved ferric ammonium citrate; 2, water from Lake Mendota, Wis., with ferric ammonium citrate after standing one month; 3, city water, Madison, Wis., which contained ferric ammonium citrate but from which the iron has been precipitated as ferric hydroxide; 4, water with hay infusion containing freshly dissolved ferric ammonium citrate; 5, water with hay infusion which contained ferric ammonium citrate but from which the iron has been precipitated as ferric hydroxide.



B. CULTURES SHOWING THE PRECIPITATION OF FERRIC HYDROXIDE FROM SOLUTIONS OF FERRIC AMMONIUM CITRATE.

- 1, Water with freshly dissolved ferric ammonium citrate; 2, water from Lake Mendota, Wis., which contained ferric ammonium citrate but from which the iron has been precipitated as ferric hydroxide; 3, city water, Madison, Wis., which contained ferric ammonium citrate but from which the iron has been precipitated as ferric hydroxide; 4, water from iron spring near Lake Kegonsa, Wis., which contained ferric ammonium citrate but from which the iron has been precipitated as ferric hydroxide; 5, distilled water with ferric ammonium citrate after standing one month.

they are intertwined to form networks. Besides the threads and cordlike forms an abundance of small specks and granules of ferric hydroxide occur, and also large irregular masses of granules which do not show the cordlike forms.

Spirophyllum was originally cultivated in the laboratory by Lieske.¹ In his first attempt he used sand and old leaves obtained from a stream in which *Spirophyllum* occurred. He placed this material in a vessel, added to it a thin iron wire, and then filled the vessel with water from the public supply of the city of Dresden. In this manner he obtained an abundant growth of *Spirophyllum*. Later he used an Erlemeyer flask containing water from the same system to which had been added a small amount of extract of old leaves and thin iron wire or coarse filings. After three or four days *Spirophyllum* had developed. By making transfers to sterile flasks he was able to obtain approximately pure cultures.

He finally obtained pure cultures in a specially prepared culture medium through which carbon dioxide was passed. The medium had the following composition:

Composition of culture medium used by Lieske.

(NH ₄) ₂ SO ₄	grams	1.5
KCl.....	do	.05
MgSO ₄	do	.05
K ₂ HPO ₄	do	.05
CaNO ₃	do	.01
Distilled water.....	cubic centimeters	1,000

Erlemeyer flasks of 100 cubic centimeters each were filled up to 2 centimeters with this medium and after sterilization were allowed to stand in atmospheric air for two days. Coarse iron filings, which had been dry sterilized at 160° C. for one hour, were then added, 0.05 gram being used for each flask. The flasks were then inoculated with a small amount of culture of iron bacteria, placed under a bell jar in a cool place, and carbon dioxide was added up to 1 per cent. This resulted in the formation of ferrous bicarbonate in the solution to the amount of about 0.01 per cent. *Spirophyllum* developed in four days. By repeated transfers to sterile flasks pure cultures were obtained.

¹ Lieske, Rudolf, Beiträge zur Kenntnis der Physiologie von *Spirophyllum ferrugineum* Ellis: Jahrb. wiss. Botanik, Band 49, pp. 91-127, 1911.

Spirophyllum occurs as flat unbranched ribbon-like filaments twisted spirally about the longer axis. There appears to be no differentiation between the two ends of the filaments, and apparently no variation in the width or the thickness of the filament from end to end. Along the edges, however, they are somewhat thicker than along the center. Like *Leptothrix*, *Spirophyllum* is always colored yellowish brown to brown from the ferric hydroxide in the filament. I have not been able to stain it satisfactorily with any of the common aniline stains.

The closeness of the spiral twisting of *Spirophyllum* varies with the individual; possibly there may be several species. Some filaments are very loosely twisted, but others are very

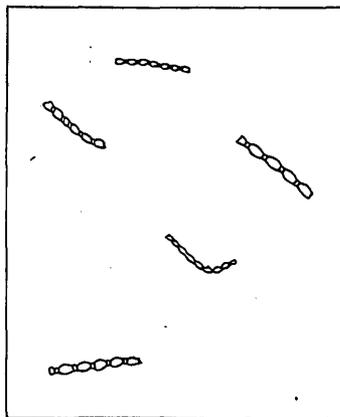


FIGURE 9.—Various forms of *Spirophyllum ferrugineum*. Drawing with camera lucida. $\times 550$.

closely twisted. In some the twisting is irregular, varying in closeness in different parts of the filament, whereas in others it is very regular and diagrammatic. (See figs. 9, 10, and 11, and Pls. IV, B; V, A; VI, A; VII; VIII, A; and IX, A.) This difference may indicate a separation into different species. In some cultures there are numerous filaments which are bent in the middle and the ends of which have been twisted about each other around a common axis, as in *Gallionella*. In such an individual the two ends frequently form a fork, thus giving it the appearance of a single branching filament. (See Pl. VII, A.) More often, however, the two filaments forming such a thread can be traced with more or less distinctness. (See Pl. VII, B.)

In the cultures examined I have found *Spirophyllum* to vary in width from 1 to 3

micra, the average width being perhaps a little over 2 micra. The longest filaments that have come to my notice were about 0.1 millimeter in length. However, the filaments are very brittle and, like those of *Leptothrix*, are easily broken during mounting operations.

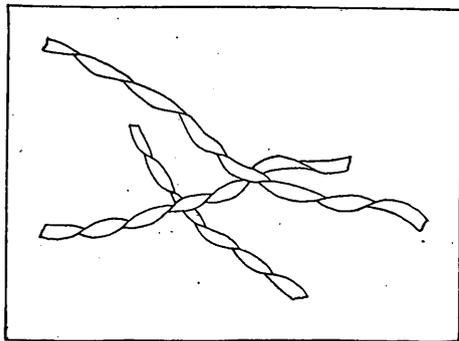


FIGURE 10.—Irregularly-twisted forms of *Spirophyllum ferrugineum*. Drawing with camera lucida. $\times 1,080$.

Up to the present time no cell structure has ever been observed in *Spirophyllum* by any investigator. The organism appears to consist of simple, flat, ribbon-like filaments, undifferentiated in its parts and without visible interior structure.

According to Lieske¹ the only method of reproduction of *Spirophyllum* is by fragmentation—that is, by the breaking off of pieces of filaments and their growth into new filaments. Ellis,² however, claims that *Spirophyllum* reproduces by means of conidia, which grow as small spherical bodies on the flat sides of the filament and gradually become detached and are carried away, eventually germinating and forming new filaments. Ellis gives descriptions of the conidia and of their germination. Lieske, who did much careful work on the growth and isolation of *Spirophyllum*, does not credit these observations of Ellis, believing that what Ellis saw were probably foreign bodies attached to filaments of *Spirophyllum*.

During my own observations I have found many cultures of *Spirophyllum* in which not a trace of the formation of conidia was visible. However, certain other cultures that I have examined, especially those from the Judson mine, show filaments of *Spirophyllum* which are covered with small spherical, elliptical, or

oval bodies, sometimes so thickly as to conceal the filament itself. (See fig. 12 and Pls. VIII and IX, A.) These bodies are colored brown just like the filament and average about two-thirds of a micron in diameter. I have not seen these bodies in the process of germination, so that I can not say whether they are conidia or whether, as seems more probable, they are small, chemically precipitated granules of ferric hydroxide. Although usually ferric hydroxide is precipitated in the form of structureless gelatinous masses, it is frequently found in the granular form as well. It also seems possible that these bodies might be lower iron-depositing bacteria of the coccus or bacillus types which live under the same conditions as *Spirophyllum* and might readily become attached to the filaments in large numbers.

Spirophyllum was first described as a separate species by Ellis³ in 1907. Previously it had been included under the species *Gallionella* first described by Ehrenberg in 1836, which included also other types of iron bacteria. After *Leptothrix*, *Crenothrix*, *Clonothrix*, and others had been described as distinct genera, Ellis found that the organisms still grouped under the term *Gallionella* were of two types very closely related in occurrence and general characteristics. One of these consisted of a double twisted cylindrical thread and the other of a twisted ribbon-like thread. He named the latter *Spirophyllum ferrugineum*, applying the name *Gallionella* only to the cylindrical threads. Molisch,⁴ in his work published in 1910, does not accept Ellis's classification and believes that the two types distinguished by Ellis are merely different forms of the same organism. He calls the ribbon-like form *Gallionella ferruginea* var. *lata*. Lieske, in his work with

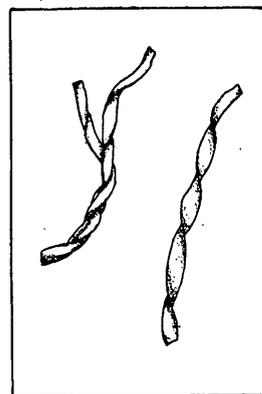


FIGURE 11.—Single and double twisted ribbon-like forms of *Spirophyllum ferrugineum*. Drawing with camera lucida. $\times 1,080$.

¹ Lieske, Rudolf, op. cit.

² Ellis, David, A contribution to our knowledge of the thread bacteria: Centralbl. Bakteriologie, Abt. 2, Band 19, pp. 507-512, 1907.

³ Ellis, David, On the discovery of a new genus of thread bacteria (*Spirophyllum ferrugineum* Ellis): Roy. Soc. Edinburgh Proc., vol. 27, pt. 1, p. 21, 1907.

⁴ Molisch, Hans, Die Eisenbakterien, 1910.

Spirophyllum, does not commit himself with regard to the classification but seems rather inclined to believe that *Spirophyllum* is a distinct genus. He gives the differences between *Gallionella* and *Spirophyllum* as follows: (1) *Spirophyllum* is ribbon-shaped whereas *Gallionella* is cylindrical. (2) *Spiro-*

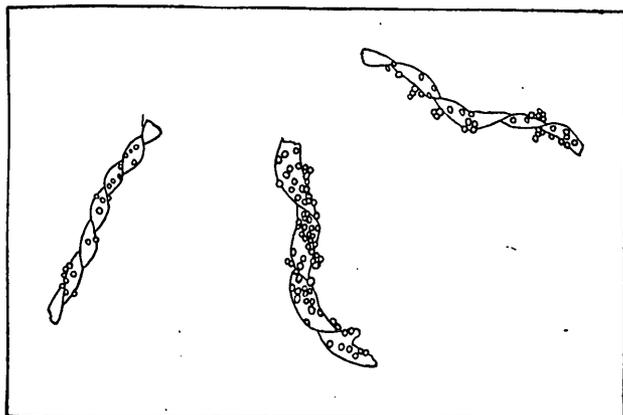


FIGURE 12.—Irregularly twisted forms of *Spirophyllum ferrugineum* with granular coatings probably consisting of ferric hydroxide. Drawing with camera lucida. $\times 1,080$.

phyllum is not found with two strands twisted around each other, but only as single strands. (3) *Spirophyllum* is twisted around its own longitudinal axis whereas *Gallionella* is twisted around an axis outside of the thread. (4) *Spirophyllum* grows into longer threads than *Gallionella*. (5) In cultures of *Spirophyllum* the typical form always develops and transitions to *Gallionella* are never seen. Lieske apparently never observed double strands of *Spirophyllum* probably because he was working mainly with artificial cultures. In nearly all cultures growing under natural conditions double strands are very common. *Spirophyllum*, therefore, is twisted about an axis outside of the thread just as is *Gallionella*. The other differences between the two forms, however, exist.

After examining cultures of iron bacteria from many different localities it appears to me that Ellis's view is probably reasonable. Although the two forms are undoubtedly closely related, there seem to be no gradational forms from one to the other and one form may be present in cultures to the exclusion of the other. There is, however, a danger of confusing double strands of *Spirophyllum* with those of *Gallionella*. Usually the ribbon-like form of the threads is clearly seen, but oc-

asionally, where the twisting is very close, the double threads greatly resemble those of *Gallionella*.

OTHER IRON-DEPOSITING BACTERIA.

Besides the group of iron thread bacteria, the most important members of which have just been described, two groups of lower iron-depositing bacteria are commonly present in soils and natural waters—(1) those which precipitate ferric hydroxide or basic ferric salts, and (2) those which precipitate ferrous sulphide. To the first group belong *Siderocapsa treubii* and its relatives described by Molisch as being abundant in natural iron-bearing waters from which they deposit ferric hydroxide, and also certain other lower bacteria that occur in soils and natural waters and that precipitate ferric hydroxide or basic ferric salts from solutions of organic iron salts. To the second group belong the sulphate-reducing bacteria and the hydrogen sulphide forming bacteria which are commonly present wherever decaying organic matter is found.

It has been known for a long time that many natural iron-bearing waters contain types of bacteria such as have been described which

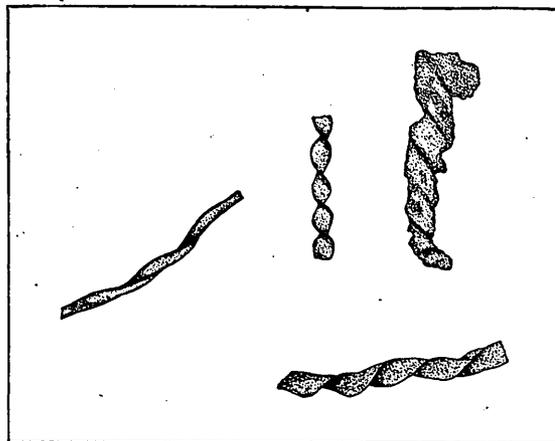


FIGURE 13.—Various forms of fossil *Spirophyllum ferrugineum* from tubercle of iron rust. $\times 1,080$.

deposit ferric hydroxide, but it has not been known that practically all soils and all natural waters contain bacteria which are capable of precipitating ferric hydroxide or basic ferric salts from solutions of certain organic iron salts. These organisms are not iron bacteria proper in the sense that they require iron in

solution for their development. It appears rather that they use other constituents present in the iron salts and that ferric hydroxide is thrown down as a waste product. In the course of my experiments I have noted the presence of such organisms in various natural waters, such as well water, lake water, river water, and spring water, and have also found them in different kinds of soil, such as silt, loam, clay, and sand. It seems probable that many of the common types of soil and water bacteria are active in the precipitation of ferric hydroxide or basic ferric salts from solutions which contain organic iron salts.

Up to the present time I have succeeded in isolating several individual types which precipitate iron. Although I have worked with different organic and inorganic solutions and have prepared cultures in liquid media that precipitated the iron from solutions of several organic iron salts, all the organisms which I have isolated and studied have been grown on solid media containing ferric ammonium citrate. Most of the other iron salts that I have used are unsatisfactory to work with, some, especially the inorganic salts, because they oxidize or hydrolyze too readily, and others because they render the media unfavorable for growth because of their toxic nature, harmful reaction, or other characteristics.

In experimenting with the precipitation of iron from solution by organisms it is, of course, necessary to use iron salts, which are readily soluble and which are not precipitated on account of oxidation when exposed to the atmosphere or when subjected to sterilization. Besides, the solutions must not be either too acid or too alkaline to sustain organic life. In my work I have used the following organic iron and manganese salts in culture media:

Organic iron and manganese salts used in culture media.

	Reaction to litmus.
Ferric ammonium citrate.....	Very slightly acid.
Ferric citrate.....	Acid.
Iron acetate.....	Acid.
Iron lactate.....	Slightly acid.
Ferric oxalate.....	Acid.
Albuminized iron.....	Neutral.
Manganese citrate.....	Acid.
Manganese acetate.....	Slightly acid.

Of these salts I have found ferric ammonium citrate to be the most satisfactory, because (1)

it is readily soluble, (2) it does not produce an unfavorable reaction, and (3) it is resistant to ordinary oxidation processes.

The solutions of inorganic iron salts tested in attempts to produce cultures of ferric hydroxide precipitating bacteria were ferrous sulphate, ferrous ammonium sulphate, ferrous carbonate, and ferric chloride. Deposits of ferric hydroxide formed in these solutions under some conditions but the formation was always readily explained as due to simple hydrolysis or to oxidation and hydrolysis rather than to the action of organisms.

The bacteria which produce hydrogen sulphide and those which reduce ferrous sulphate and thus precipitate ferrous sulphide from solution have also long been known, and many of them have been isolated and studied. The formation of ferrous sulphide by the bacteria which produce hydrogen sulphide is due to the action of hydrogen sulphide on iron salts in solution or on ferric hydroxide previously precipitated, whereas with the sulphate-reducing bacteria the formation is due to the removal of oxygen from the sulphate and this results in the precipitation of the sulphide directly.

Hydrogen sulphide is formed by bacteria in two ways—by the decomposition of sulphur-bearing proteins and by the reduction of sulphur. Many decay-producing bacteria have the power of changing organic sulphur compounds to hydrogen sulphide. When free sulphur is present with decomposing organic matter it is attacked through the action of bacteria and reduced to hydrogen sulphide as well. Hydrogen sulphide reacts with any iron salts present and forms ferrous sulphide.

A number of species of bacteria have been isolated which act on sulphates, reducing them to sulphides. Among these are *Proteus vulgaris*, *Vibrio hydrosulfureus*, and *Spirillum desulfuricans*. Some sulphate-reducing bacteria have the power of reducing also thiosulphates and sulphites. When the compounds thus attacked are iron compounds ferrous sulphide is formed directly and precipitated. If sulphides of other metals are formed they may be attacked by carbon dioxide, and hydrogen sulphide may be formed. Hydrogen sulphide will then react with the iron salts to form ferrous sulphide.

Cultures were made in liquid and solid media of the bacteria which reduce sulphates and those which produce hydrogen sulphide. Ordinary synthetic nutrient media were used for sulphate reducers, and ferrous sulphate was added for reduction to sulphide. Cultures of bacteria which produce hydrogen sulphide were made in solutions containing decomposing organic matter, organic iron salts such as iron lactate or iron tartrate being used as indicators of hydrogen sulphide formation.

Experiments on the precipitation of ferric hydroxide and ferrous sulphide from solutions of iron salts by various species of lower bacteria are described on the following pages.

EXPERIMENTS ON PRECIPITATION OF IRON FROM SOLUTIONS BY BACTERIA.

PRECIPITATION OF FERRIC HYDROXIDE AND BASIC FERRIC SALTS FROM FERRIC AMMONIUM CITRATE SOLUTIONS.

It was noted by Prof. E. B. Fred, of the University of Wisconsin, that when ferric ammonium citrate was added to jars containing water and marsh mud in which bacteria of various kinds were abundant, the deep reddish-brown color which it imparted to the solution disappeared after a few weeks, owing to the precipitation of the iron. It was supposed that this precipitation was caused by the activity of ordinary iron-depositing thread bacteria, and upon this supposition I started a series of cultures.

The first experiments were performed with the object of determining whether pure natural waters had the same effect in precipitating the iron from ferric ammonium citrate solutions as impure muddy cultures, and whether this action varied with different kinds of natural waters. For this purpose three glass jars were each filled with 500 cubic centimeters of water, the first one being filled with water from Lake Mendota, the second with water from the city wells of Madison, Wis., and the third with hay extract—that is, water in which hay had been boiled. To each of these jars 2.5 grams of ferric ammonium citrate was then added. They were allowed to stand at room temperature (about 18° C.) for one month and were then photographed. (See Pl. X, A.) The results are well shown in the photograph. Jar No. 1 shows the appearance of the freshly pre-

pared ferric ammonium citrate solution in clear water, and jar No. 4 shows the same in hay extract. Jar No. 2 contains water from Lake Mendota with ferric ammonium citrate. It shows that decided bacterial action has taken place after one month, but no precipitate has formed. This jar was allowed to stand for another month and at the end of that time the iron had been completely precipitated. Jar No. 3 contains water from Madison city supply, which has had the same treatment as jar No. 2. It will be seen that in this jar the iron had been completely precipitated after one month, the solution being perfectly clear and transparent. Tufts of ferric hydroxide are attached to the inside surface of the jar and a thick deposit of ferric hydroxide with perhaps some basic ferric salts occurs at the bottom. Jar No. 5 contains extract of hay which has had the same treatment as jars Nos. 2 and 3. It will be seen that here also complete precipitation of the iron has taken place within one month, leaving a clear solution, which, however, is somewhat darker on account of the hay extract it contains.

Having obtained these results it was thought best to duplicate the experiment with slight variations. A set of four jars was therefore prepared, each being filled with 500 cubic centimeters of a different type of water. Two and one-half grams of ferric ammonium citrate were added to each. Two of these jars contained water from Lake Mendota and from the Madison city supply as before. A third, however, was filled with water from an iron spring near Lake Kegonsa, about 14 miles southeast of Madison. This spring contained an abundant growth of *Leptothrix*. A fourth jar was filled with distilled water. The jars were allowed to stand at room temperature and were photographed after five weeks. (See Pl. X, B.)

Jar No. 1 again shows the appearance of the freshly prepared solution of ferric ammonium citrate in clear water. Jar No. 2 and jar No. 3 show the action of water from Lake Mendota and from the Madison city supply respectively on ferric ammonium citrate in solution. Both waters precipitated the iron after four weeks. The masses of ferric hydroxide and perhaps some basic ferric salts are seen at the bottoms of the jars. Jar No. 4 contained iron spring water. The precipitation of ferric hydroxide

took place in this jar also after about four weeks. Jar No. 5 contains distilled water with ferric ammonium citrate in solution. Some bacterial action has taken place after five weeks, as is shown by the darkening of the solution. Complete precipitation of ferric hydroxide in this jar, however, did not take place until after about seven or eight months.

In order to see whether soil would have the same effect as natural waters on iron ammonium citrate in solution, several flasks containing 500 cubic centimeters of water with 2.5 grams of ferric ammonium citrate in solution were each inoculated with 20 grams of a different kind of soil—a black loamy soil, brown sandy soil, or clayey soil. Precipitation of ferric hydroxide took place in these jars after about two weeks, which showed a more rapid action with soils than with natural waters.

Although the results of the preceding experiments seemed to show fairly conclusively that the precipitation was due to biologic agencies rather than to chemical processes, it seemed best to make sure of this point. There are some iron salts, especially inorganic but also organic, in which precipitation occurs on account of oxidation or on account of hydrolysis, the precipitates consisting either of ferric hydroxide or of basic organic or inorganic ferric salts. In order to show conclusively that the precipitating action was due to biologic agencies, the following experiment was performed. Two sets of five flasks of 1,000 cubic centimeters capacity were prepared with culture solutions, one set being a duplicate of the other. Each of the flasks contained 500 cubic centimeters of water in which 2.5 grams of ferric ammonium citrate were dissolved. The differences between the culture solutions in the different flasks were as follows: The first flask in each set contained water from the city supply of Madison, Wis.; the second, water from Lake Mendota; the third, water from the iron spring near Lake Kegonsa; the fourth, water inoculated with 20 grams of garden soil; and the fifth, distilled water. One of these sets was sterilized, so as to stop all organic action, whereas in the other set the organisms were allowed to develop freely, as in the previous experiments. The flasks are shown in Plate XI, those of the lower row being sterilized duplicates of those of the upper row. The sterilization consisted in heating the flasks and

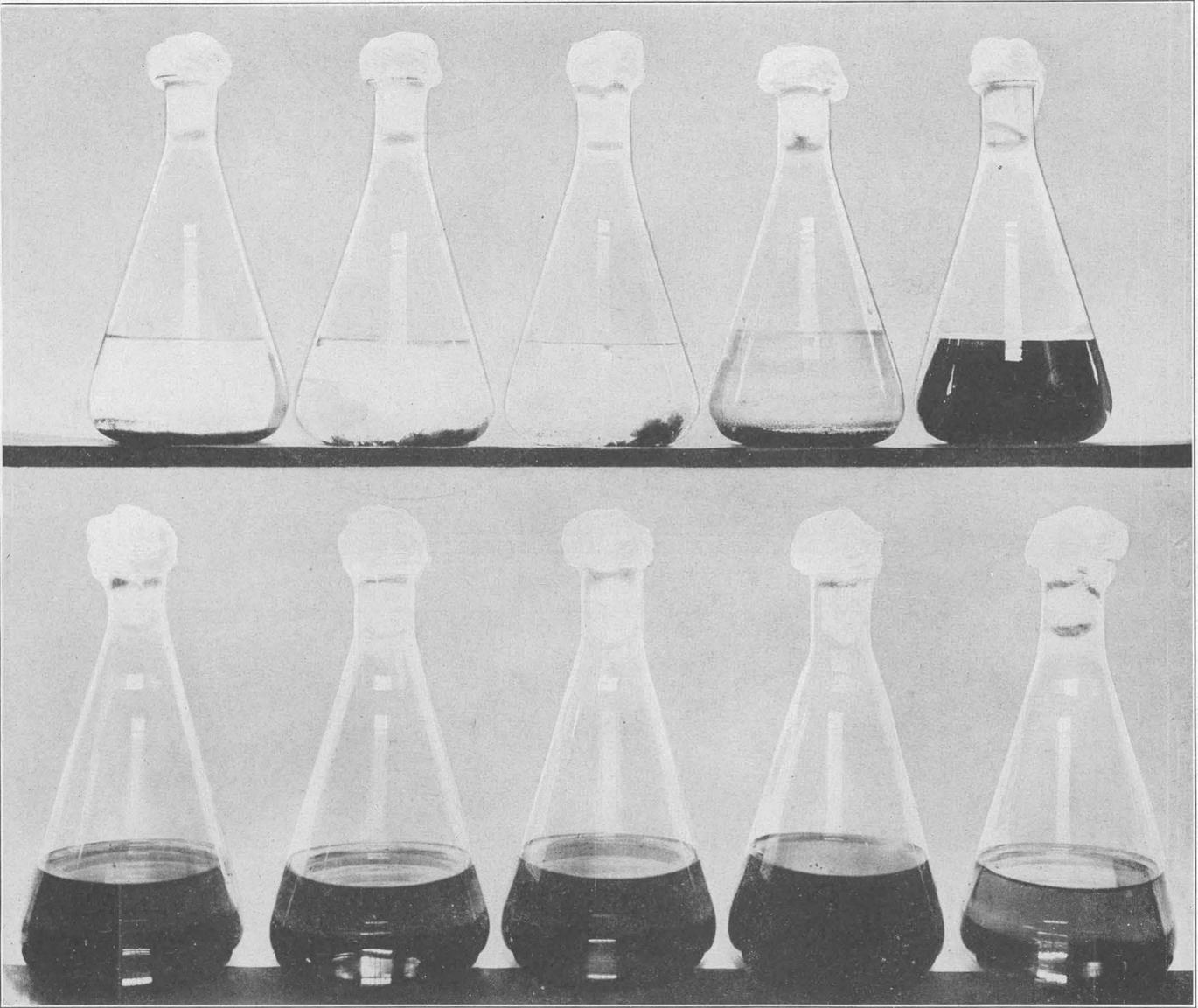
contents in an autoclave at 130° C. for 15 minutes.

Both sets of flasks were allowed to stand at room temperature for four months, at the end of which time the photograph was taken. As may be clearly seen, the contents of the lower row of flasks have suffered no change, whereas in the upper row the contents of all the flasks except the fifth have suffered complete precipitation of the iron in solution. The fifth flask, which contains distilled water, shows only a darkening of the solution. The time of precipitation varied in the different flasks. The water from the city supply of Madison precipitated the iron from solution in about two months, the water from Lake Mendota in about seven weeks, the iron spring water in about one month, and the soil infusion in about two weeks.

This experiment showed conclusively that the sterilized material did not suffer precipitation of the iron in solution. There still remained the possibility, however, that during the process of sterilization the iron salt in solution might have suffered some change which rendered it less subject to hydrolysis. To investigate this possibility several of the sterilized solutions, after having stood for four months, were reinoculated with a small amount of fresh soil infusion. This resulted in the precipitation of the iron within a very short time and showed beyond doubt that the precipitation of the iron was due to biologic agencies.

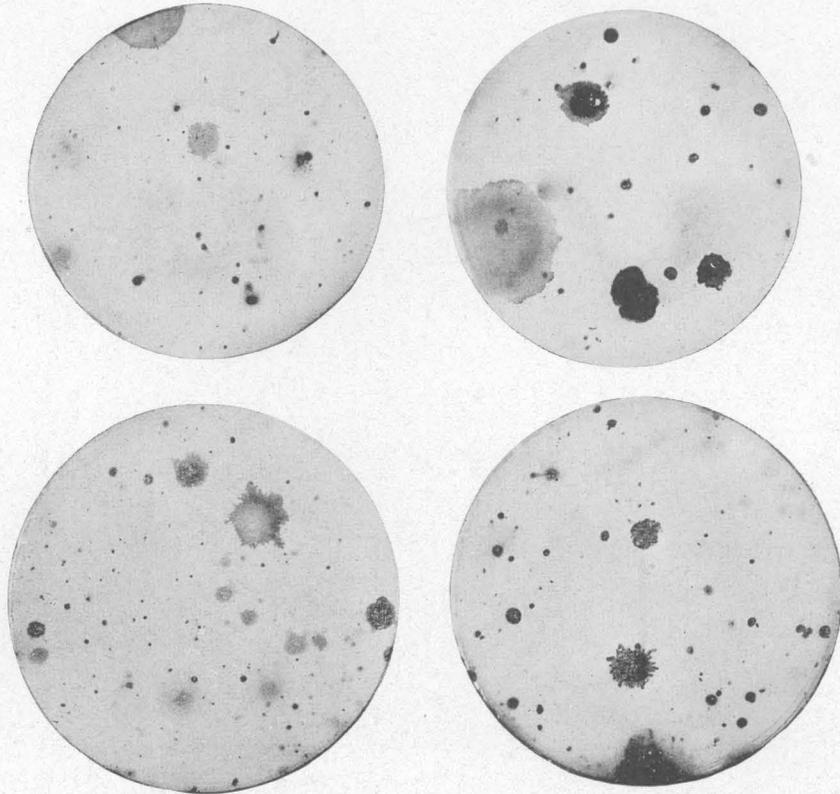
While these experiments were being conducted the precipitates were frequently examined. The material forming the deposits was reddish brown and flocculent and resembled the ferric hydroxide which is precipitated when ammonium hydroxide is added to a solution of a ferric salt, such as ferric chloride or ferric nitrate. It usually settled to the bottom of the containing vessel and after standing for some time became compacted into a fluffy, gelatinous deposit. After prolonged standing it contracted and changed from reddish brown to dark brown in color.

At the outset it was supposed that upon microscopic examination this material would be found to consist mainly of matted threads of iron bacteria such as I had already seen in gelatinous iron scums from many localities. I found, however, that the precipitate ap-

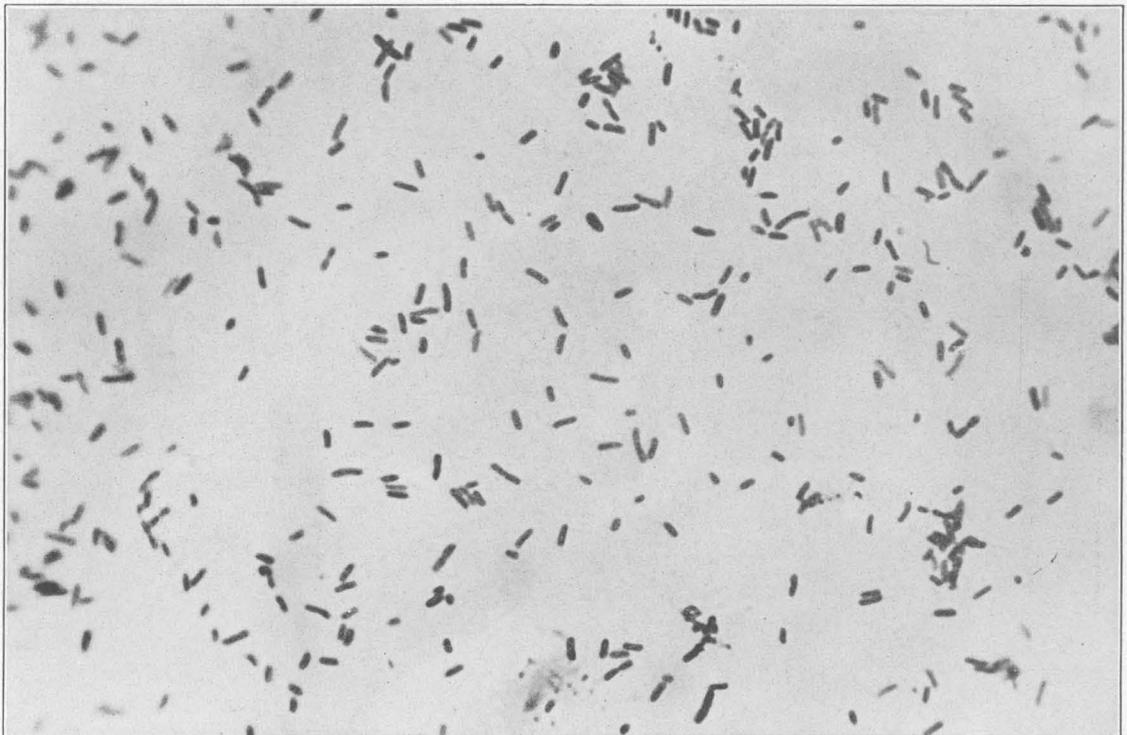


CULTURES SHOWING THE EFFECT OF STERILIZATION IN THE PRECIPITATION OF FERRIC HYDROXIDE FROM SOLUTIONS OF FERRIC AMMONIUM CITRATE.

Upper row, natural waters which contained ferric ammonium citrate but from all but one of which the iron has been precipitated as ferric hydroxide by bacteria; lower row, different waters containing ferric ammonium citrate in solution which were sterilized before bacteria had an opportunity to precipitate the iron. The flasks of the lower row are duplicates of those of the upper row. The first flask in each row contains Madison city water; the second, water from Lake Mendota; the third, iron-spring water; the fourth, water with soil; and the fifth, distilled water.



A. PETRI DISHES SHOWING COLONIES OF LOWER BACTERIA WHICH PRECIPITATE FERRIC HYDROXIDE FROM AGAR CONTAINING FERRIC AMMONIUM CITRATE.



B. PHOTOMICROGRAPH OF A PURE CULTURE OF ONE TYPE OF LOWER BACTERIA WHICH HAS THE POWER OF PRECIPITATING FERRIC HYDROXIDE FROM SOLUTIONS OF FERRIC AMMONIUM CITRATE, $\times 1,310$.

Stained with carbol fuchsin.

peared light brown, transparent, and was apparently colloidal. There were no traces of iron bacteria in the material, except that in the flask containing iron spring water a few threads of *Leptothrix* were found. These threads probably develop in ferric ammonium citrate solutions to some extent, as was determined by Molisch.¹ Many of the threads, however, were probably present in the water before the ferric ammonium citrate was added. Upon prolonged standing I found that mold mycelia frequently developed in the gelatinous material and sometimes became quite abundant. There appear to be several varieties of molds which grow in these solutions, but I have not attempted to identify or describe them.

A partial analysis was made by W. G. Crawford, of the University of Wisconsin, of the precipitate formed from a solution of ferric ammonium citrate in water from the city supply of Madison with the following result:

Analysis of precipitate formed from solution of ferric ammonium citrate.

[Dried at 105° C.]

Ferric oxide (Fe ₂ O ₃)	72.50
Combined water (H ₂ O)	7.11
Loss above 105° C. (exclusive of combined water)	20.12
	99.73

The material was examined qualitatively for traces of citrate in order to determine if basic ferric citrate was present in the precipitate. The indications of its presence were very slight, however. It appears from the analysis, therefore, that the material is one of the less hydrated forms of ferric oxide, approaching goethite in composition. A percentage of 72.50 ferric oxide requires 8.15 per cent combined water to form goethite. However, the analysis only shows 7.11 per cent of combined water, which probably means that the material is between goethite (Fe₂O₃.H₂O) and turgite or hydrohematite (2Fe₂O₃.H₂O) in composition. It is possible, however, that insoluble basic ferric citrate is precipitated with the ferric hydroxide, but that upon standing the citrate radicle is gradually used up by the bacteria, finally leaving only ferric hydroxide in the precipitate. The composition of the precipi-

tate would, therefore, change with the time it is left standing and probably also with the treatment it receives previous to analysis, such as washing.

The large percentage of loss above 105° C. besides the combined water is difficult to explain, because of the small amount of organic matter visible in the precipitate when examined microscopically. It is possible, however, that besides the mold mycelia there are present abundant remains of lower bacteria which developed in the solution and which would be difficult to identify with the microscope.

The series of experiments performed up to this time made the following points evident: (1) That the precipitation of iron from solutions of ferric ammonium citrate is due to some biologic agency; (2) that the precipitate is hydrated ferric oxide with perhaps a small amount of basic ferric citrate; and (3) that it consists of a colloidal, textureless mass in which bacterial forms are unrecognizable. The latter fact seems to indicate that, as the ferric hydroxide is not taken up by the cells of the organisms causing the precipitation, it is probably only a waste product, other constituents of the salt, such as citric acid or ammonia, being utilized and the ferric hydroxide thrown down.

In order to determine whether oxygen is necessary for the precipitation of ferric hydroxide or whether the action could take place under anaerobic conditions, carbon dioxide was run continuously for several weeks through ferric ammonium citrate solutions inoculated with soil. This produced a saturation of the solution with carbon dioxide and caused the removal of practically all traces of oxygen. The precipitation, however, took place as before.

Solutions prepared and inoculated with soil in the same manner as those mentioned above were placed under a bell jar and all the air removed, so as to produce a vacuum capable of supporting a mercury column 23.5 inches high. This reduction of air did not seem to affect the precipitation, which occurred after about the same period of time had elapsed as was required for similar cultures in the open air.

What remained now to be done was to isolate the organisms which threw the iron out of

¹ Molisch, Hans, *Die Eisenbakterien*, pp. 34, 35, 1910.

solution and to study their morphology and the conditions under which they are active. It required considerable experimental work before I succeeded in cultivating the organisms on solid media.

The first attempt was made with 1.5 per cent washed agar, containing no nutrient material. To this substance 0.5 gram of ferric ammonium citrate was added for every 100 cubic centimeters of agar. Plates were poured from this medium and were inoculated from various impure cultures. They were then allowed to incubate at room temperature for several weeks. Numerous colonies of different kinds of microorganisms developed on the plates, but none caused the precipitation of ferric hydroxide from the agar.

The second attempt was made by adding nutrient material in the form of soil and hay extract such as is used in media for protozoa. The agar was so prepared that 1,500 cubic centimeters of 1.5 per cent agar contained 50 cubic centimeters of hay and soil extract and 7.5 grams of ferric ammonium citrate. Plates were poured from soil infusion prepared by adding 20 grams of soil to a 400 cubic centimeter sterile water blank, then transferring 25 cubic centimeters of this infusion to another 400 cubic centimeter sterile water blank, and so on to the fifth dilution. Inoculations were made from the fourth and fifth dilutions, 1 cubic centimeter being used for each plate. Abundant growth of various organisms occurred on the plates after several days, but again there was no precipitation of ferric hydroxide.

In the third attempt, which was successful, Heyden Nährstoff agar was used as a medium and ferric ammonium citrate was added to it in the proportion of 1 gram of ferric ammonium citrate to 100 cubic centimeters of agar. Inoculations were made from soil infusion prepared as already described. The plates were incubated at a temperature of 28° C. for three or four days, and by that time showed an abundant development of microorganisms. (See Pl. XII, A.) Even after the second day certain of the colonies were seen to develop a dark-brown halo around them, and after five or six days these colonies became very dark brown and opaque and developed an iridescent sur-

face owing to the precipitated ferric hydroxide. The plates inoculated with soil infusion of the fourth dilution gave much more satisfactory results than the plates inoculated with soil infusion of the fifth dilution.

Several kinds of colonies of bacteria precipitating ferric hydroxide developed under these conditions. The most typical ones were irregular flat colonies with ragged corrugated or feathery edges, most of them lying on the surface of the agar. These precipitated ferric hydroxide almost immediately after they began to develop, and after five or six days became coated with a brittle, dark-brown crust of ferric hydroxide, whose surface was shining and generally iridescent.

Another type of colony around which ferric hydroxide begins to precipitate soon after it develops is large and flat but differs from the preceding type in having smooth edges and a

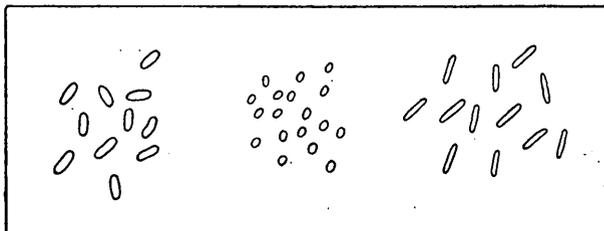


FIGURE 14.—Various forms of lower bacteria which have the power of precipitating ferric hydroxide from solutions of ferric ammonium citrate. \times about 1,350.

moist surface. This type does not become as dark and opaque as the preceding one.

There are a few other types of colonies of microorganisms which begin to precipitate ferric hydroxide soon after they appear on the agar. They are mainly small circular colonies which do not show any distinctive characteristics.

After a considerable period a great many other colonies on the plates begin to develop dark areas around them. Among these are small, raised, fluffy white colonies of *Actinomyces* and several varieties of small, raised cream-colored bacterial colonies. Some of these develop a small dark spot in the center. Bacteria from a number of the colonies were examined microscopically and it was found that there were several distinct species of organisms, some of them bacillus and some coccus forms. (See fig. 14.)

Slopes of Heyden Nährstoff agar, to which ferric ammonium citrate had been added, and also of bouillon agar similarly treated were inoculated from various colonies and the resulting streak cultures showed abundant formation of ferric hydroxide. Slopes of Heyden Nährstoff agar to which no ferric ammonium citrate had been added were similarly inoculated but showed practically no growth. Slopes of Heyden Nährstoff agar which contained manganese citrate also showed no growth. On the other hand, slopes of Heyden Nährstoff agar to which sodium citrate had been added showed considerable growth upon inoculation, and the same was true of plain bouillon agar, either with or without the addition of sodium citrate.

Pure cultures were made by inoculating another set of plates with organisms from one of the colonies which showed the most abundant formation of ferric hydroxide. These plates showed two distinct types of colonies as follows: (1) Circular, flat colonies with irregular corrugated edges formed on the surface of the agar. These colonies were quite thin and resembled the colonies already described as forming on plates of impure cultures. The formation of ferric hydroxide by the organism composing these colonies began in a few days. (2) Within the agar colonies of another type developed. These were very small, light-brown, lenticular colonies which commenced the formation of ferric hydroxide only after a week or two. There is little doubt that these two types of colonies were produced by the same species of microorganism, the difference being due to the different conditions under which they grew.

The organism composing these pure cultures was examined under the microscope and was found to be a short bacillus averaging about 1.4 micra in length, and about 0.5 micron in thickness. (See Pl. XII, B.) It was found to be difficult to stain, owing probably to the presence of ferric hydroxide in the cell walls. Upon prolonged treatment with carbol fuchsin, however, it assumed a distinct red color.

An attempt was made to determine the composition of the material precipitated from solution by a pure culture of this bacillus. For this purpose two flasks were prepared

with the following culture solutions, the first being a synthetic medium and the second an ordinary nutrient medium:

Media used to obtain a pure culture in solution of the bacillus shown in Plate XII, B.

Flask No. 1.

K ₂ HPO ₄	grams--	0.5
MgSO ₄	do.....	.5
NH ₄ NO ₃	do.....	.5
CaCl ₂	do.....	.2
NaNO ₃	do.....	.5
Ferric ammonium citrate.....	do.....	10.0
Distilled water.....	cubic centimeters--	1,000

Flask No. 2.

Heyden Nährstoff.....	grams--	7.5
Distilled water.....	cubic centimeters--	250

Heated for 2 hours in a steamer and filtered; 1,000 cubic centimeters distilled water and 10 grams ferric ammonium citrate then added to filtrate.

The solutions were both sterilized in the autoclave and then were inoculated from pure cultures. The synthetic solution showed precipitation of the iron after an incubation period of about five weeks at room temperature (about 17° to 19° C.) The Heyden Nährstoff solution showed no precipitation of iron even after a period of four and a half months. The precipitate from the synthetic solution was analyzed by W. G. Crawford, University of Wisconsin, with the following results:

Analysis of precipitate from flask No. 1.

[Dried at 105° C.]

Ferric oxide (Fe ₂ O ₃).....	65.00
Phosphoric acid (P ₂ O ₅).....	7.60
Combined water (H ₂ O).....	27.20
Chlorine (Cl).....	Trace.
Sodium (Na).....	¹ Trace.
Potassium (K).....	None.
Calcium (Ca).....	None.
Magnesium (Mg).....	None.
Ammonia (NH ₃).....	None.
Nitrate radicle (NO ₃).....	None.
	99.80

A comparison of this analysis with the analysis of a similar precipitate obtained with impure cultures from a solution of ferric

¹ With spectroscope.

ammonium citrate to which no other nutrient material had been added (see p. 33) shows marked differences. In the analysis of the precipitate obtained from the impure culture the ferric oxide amounts to 72.50 per cent as compared with 65 per cent in the analysis under consideration, and there is in the pure culture 7.60 per cent of phosphoric acid, which is entirely lacking in the impure culture. The presence of phosphoric acid is easily explained as being due to the presence of phosphate in the synthetic medium. Phosphorus almost invariably comes down with ferric oxide or alumina upon precipitation. Another difference, however, and one much more difficult to explain, is that in the analysis from the impure culture combined water amounts to 7.11 per cent and the loss, exclusive of water, to 20.12 per cent, whereas in the analysis of the precipitate from the pure culture in the synthetic medium the combined water amounts to 27.20 per cent and the loss due to volatilizing other substances is nil. There may be several explanations for this difference. In the first place, the presence of phosphoric acid in addition to the iron oxide may require a much larger percentage of combined water than iron oxide alone. The presence of this substance, however, does not account for the absence of other constituents, such as organic matter, included under loss. This difference, however, may be accounted for in part by the fact that the precipitate from the synthetic medium, on account of its slimy consistency, required washing by decantation for three weeks in order to clean it and to prepare it for analysis. This washing may have resulted in dissolving out any basic citrate and other material that may have been present and which in the precipitate from the impure culture was not removed in the comparatively short period of washing (1 hour). According to Crawford, the water obtained from the precipitate from the synthetic medium varied with the amount of heat applied, being only 19 per cent when the medium was heated to 300° C. but increasing to 27.20 per cent when it was heated on platinum to as high a temperature as could be obtained. No distillation of carbon was noted. The material is therefore apparently a hydrous ferric phosphate of indefinite composition.

PRECIPITATION OF FERRIC HYDROXIDE AND BASIC FERRIC SALTS FROM OTHER SOLUTIONS CONTAINING ORGANIC IRON.

At the same time that the experiments were being performed with ferric ammonium citrate a number of other organic iron salts were used as culture media with varying results. In the first place a series of cultures was prepared by inoculating different solutions containing organic iron with soil in order to see what effect the organisms in the soil had on the different salts in solution. The following organic iron salts were used, 2 grams of the salt being dissolved in 300 cubic centimeters of water in each experiment and the solution inoculated with 20 grams of sandy soil.

Appearance and reaction of solutions containing organic iron inoculated with soil.

Ferric ammonium citrate	Solution clear, light brownish red. Slightly acid.
Ferric citrate	Solution clear, yellow with brownish tinge. Acid.
Ferric oxalate	Solution clear, light lemon-yellow. Acid.
Iron lactate	Solution clear, light reddish brown. Slightly acid.
Iron acetate	Solution dark reddish brown. Acid.
Iron albuminate (5 per cent Fe ₂ O ₃)	Solution clear, light brownish red. Neutral.
Manganese citrate	Solution colorless. Acid.
Manganese acetate	Solution colorless. Slightly acid.

These cultures were kept in wide-mouthed bottles plugged with cotton, a small circular piece of sterilized filter paper being immersed in the solution in each bottle in order to cover the layer of soil at the bottom so as to prevent the precipitate that formed from mixing with the soil. They were allowed to incubate at room temperature for two months. Ferric ammonium citrate was used along with the other salts to serve as an indicator of the nature of the changes taking place in the other solutions. The organic manganese salts were used in order to determine whether the organisms would precipitate manganese from solution as well as iron. The following results were obtained:

From the ferric ammonium citrate solution flocculent, brownish-red ferric hydroxide was precipitated in about two weeks and formed

tufts on the sides of the bottle and a thin layer on the filter paper. Mold mycelia developed abundantly in this upon standing. A thin brittle brownish film formed over the surface of the solution. The solution became colorless but remained turbid.

In the ferric citrate solution precipitation was only partial at the end of two weeks but was complete in about three weeks. The precipitate consisted of flocculent black material, which formed a layer about one-fourth inch thick on the filter paper. The nature of the precipitate is unknown. It may have been hydrous ferrous sulphide. A dark-brown to black thin brittle film developed on the surface of the solution and from it a matting of black filaments, probably mold, extended down into the solution. Mold mycelia also developed abundantly in the black precipitate on the filter paper, as shown by microscopic examination. The solution became clear and colorless.

The ferric oxalate solution gave a very thin, light-brown deposit on the filter paper and on the sides of the bottle in about one and one-half weeks. The nature of the deposit was not determined. A thin brown brittle film formed on the surface of the solution. The solution became slightly turbid and retained a brownish tinge even after standing for two months.

In the iron lactate solution the precipitation did not begin until after two or three weeks and was not complete even after two months. The precipitate was brownish-red and flocculent and settled very slowly on the filter paper, so that at the end of two months the deposit was nearly one-half inch in thickness. Small masses attached themselves to the sides of the bottle. The solution remained light brownish owing to fine, suspended, flocculent material. Upon microscopic examination the precipitate was seen to consist mainly of colloidal material with here and there mold mycelia, some of which had a brown coating. The precipitate probably consisted of ferric hydroxide and more or less basic iron lactate.

From the iron acetate solution a flocculent reddish-brown material was precipitated in about a week and formed a fluffy layer about three-fourths inch thick on the filter paper. After a period of several weeks molds developed abundantly in this deposit and some

became coated with a thick brown deposit. The precipitate probably consisted chiefly of a mixture of basic ferric acetate with some ferric hydroxide. It seems likely, to judge from later experiments, that the precipitation in this experiment resulted from hydrolysis rather than from bacterial action.

The solution of iron albuminate began to ferment a day or two after it was prepared. It gradually became black and a thick brown scum formed on the surface. The changes probably resulted from complex processes of decomposition due to the presence of albumin.

No precipitation occurred in the solutions of manganese salts, but molds developed abundantly. In the manganese citrate solution mold mycelia developed as black filaments forming a matting below a light-brown brittle surface film. This growth eventually dropped to the bottom and formed a dark-gray deposit on the filter paper. Besides mold mycelia this deposit was found to contain filaments of algae and protozoa. In the manganese acetate solution the mold grew as a white, woolly matting on the filter paper. The deposit gradually became darker and more compact. The solution remained clear in both experiments.

The results in general showed that precipitation of ferric hydroxide and basic ferric salts took place in solutions of other organic iron salts besides ferric ammonium citrate but that the time and manner of precipitation varied in different solutions. They also showed that manganese was not precipitated from solution in the same manner as iron, although microorganisms developed abundantly in solutions of organic manganese salts.

It now became necessary to determine whether the precipitation from these iron solutions was due to chemical action or to the activity of organisms. For this purpose another set of solutions was prepared in the same way as the set just described except that iron albuminate was omitted. After inoculation with soil the cultures were sterilized in an autoclave. The sterilization produced a slight change of color in some of the solutions, and in the iron acetate solution it caused the formation of a reddish-brown flocculent precipitate due to hydrolysis. This precipitate probably consisted mainly of basic ferric acetates and

appeared to be similar to that formed in the iron-acetate culture already described. The solutions were allowed to stand for six weeks at room temperature, and during this period did not alter their appearance. At the end of six weeks the solutions were reinoculated by adding 1 cubic centimeter of fresh soil infusion to each, and were allowed to stand under the same conditions as before for another period of six weeks.

Precipitation in the ferric ammonium citrate solution took place in about one week after the inoculation, but in the other solutions the precipitation was slower. At the end of six weeks, however, precipitates had formed in all the iron solutions, and molds were growing in the manganese solutions. The precipitate from the ferric citrate solution was flocculent and brownish yellow in color and formed a coating over the layer of soil. The precipitates from the other iron solutions (iron lactate, ferric oxalate, and ferric ammonium citrate) were very similar to those which occurred in the previous cultures that had not undergone sterilization. In general they formed brown, flocculent deposits.

After obtaining precipitates from solutions containing organic iron inoculated with soil, under different conditions as described above, several attempts were made to obtain precipitates from solutions of these salts in natural waters. However, no precipitation occurred, although some of the cultures were allowed to stand for six months at room temperature. At the end of this period only a slight turbidity was noticeable in some of them.

Attempts to isolate bacteria which might cause precipitation of ferric hydroxide or insoluble basic ferric salts from ferric oxalate and iron lactate solutions were also unsuccessful. Pure cultures of bacteria obtained from agar containing ferric ammonium citrate were transferred to slopes of Heyden Nährstoff agar containing ferric oxalate and iron lactate, but no growth took place. Later plates of the same agar and also of plain bouillon agar were inoculated directly with a fresh infusion of soil, but no colonies either of bacteria or molds formed on the plates, although plates of agar containing ferric ammonium citrate that were inoculated at the same time from the same soil infusion showed abundant

growth. Whether this experiment indicates that bacteria do not grow in the presence of ferric oxalate and iron lactate and that the precipitation in the solutions was due to the action of molds which do not grow readily on solid media is difficult to say. It is very desirable that further work should be done along this line with other organic iron salts, such as iron tartrate, iron formate, iron butyrate, iron malate, iron ammonium tartrate, iron magnesium citrate, and others. Only in this way is it possible to determine how general is the precipitation of insoluble iron compounds from solutions of organic iron salts by microorganisms. From the experiments performed it seems reasonable to suppose that it is fairly general and that in certain cases bacteria are responsible and in other cases molds.

PRECIPITATION OF FERRIC HYDROXIDE AND BASIC FERRIC SALTS FROM SOLUTIONS CONTAINING INORGANIC IRON.

Several attempts were made to obtain, in solutions of inorganic iron salts, cultures of bacteria from soil and natural waters other than the iron thread bacteria already described. It seemed possible that *Siderocapsa*, described by Molisch¹ as being a very abundant water bacterium, or *Bacillus M. 7*, described by Mumford,² might be cultivated in artificial media containing inorganic iron salts. It seemed possible also that other lower bacteria might exist in the soil or natural waters which could use constituents present in certain inorganic iron salts with the result that ferric hydroxide or basic ferric salts would be precipitated. Such a process would be analogous to that just described as occurring when ferric hydroxide or basic ferric salts are precipitated from solutions of organic iron salts through the action of microorganisms.

However, my attempts to obtain such cultures have all been unsuccessful. Although precipitation of insoluble ferric compounds occurred in nearly all the inorganic iron solutions used, this precipitation seemed to be due to oxidation and hydrolysis or to hydrolysis alone, rather than to biologic processes. A

¹ Molisch, Hans, Die Eisenbakterien, pp. 11-14, 1910.

² Mumford, E. M., A new iron bacterium: Chem. Soc. Jour., vol. 103, pp. 645-650, 1913.

brief statement concerning the solutions used and the results obtained is given below.

The inorganic iron salts used in the experiments were ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$), ferrous carbonate (FeCO_3), and ferric chloride ($\text{Fe}_2\text{Cl}_6 \cdot n\text{H}_2\text{O}$). All of these solutions when allowed to stand where oxygen from the atmosphere was accessible became oxidized or hydrolyzed, forming yellow or yellowish-brown ochreous precipitates consisting either of ferric hydroxide or of a mixture of ferric hydroxide and basic ferric salts.

Attempts to make bacterial cultures in ferrous sulphate solutions were made with different strengths of solutions from very dilute to saturated. Yellowish-brown flocculent ochreous precipitates formed in all of them, and these were examined with the microscope from time to time for evidences of the presence of microorganisms. The precipitates in general had a granular appearance under the microscope, the granules being brownish yellow in color and somewhat rounded and fairly regular in size and shape. However, mixed with this granular material, many of the precipitates showed large irregular masses of a light-colored, textureless colloidal substance, resembling in appearance, though not in color, the precipitates formed in solutions containing organic iron or those formed by adding ammonium hydroxide to inorganic ferric salts, such as ferric chloride. The only organic forms found in the precipitates were scattered threads of mold mycelia, which were found in one or two of them after standing for several weeks.

It seems possible, of course, that the flocculent granular precipitate itself was the result of bacterial action, as is the flocculent, reddish-brown precipitate which forms in the organic iron solutions. However, with the inorganic iron salts sterilization apparently has no effect on the precipitating action, except that with some of them it hastens precipitation.

Montfort,¹ as has been stated (p. 9), claims that *Leptothrix* develops in solutions of ferrous sulphate, but I have not been able to identify it in my cultures. Up to the present time I have found no microorganisms with the

exception of molds in any cultures prepared with inorganic iron salts except those containing ferrous bicarbonate.

The precipitation of ferric hydroxide and basic ferric salts from solutions of ferrous sulphate differed from that taking place in organic iron solutions likewise in that it was not complete. A flask containing 750 cubic centimeters of water in which were dissolved 3.5 grams of ferrous sulphate was allowed to stand under oxidizing conditions for 6 months. An abundant precipitate of yellowish-brown ochreous material formed during this period, but much ferrous sulphate remained in solution at the end of this time, as was shown by the flocculent, light-green precipitate of ferrous hydroxide ($\text{Fe}(\text{OH})_2$), which formed upon the addition of ammonium hydroxide to the solution.

An interesting experiment was performed with solutions of ferrous ammonium sulphate inoculated with soil. Three bottles each containing a solution of 2 grams of ferric ammonium sulphate in 300 cubic centimeters of water were inoculated with 20 grams of soil. One of the bottles was left where oxygen of the atmosphere had free access to the solution, but the other two, one of which was sterilized, were attached to an apparatus generating carbon dioxide, and the solutions they contained were kept saturated with carbon dioxide. Precipitation began in the first bottle within 15 or 20 minutes after the solution was prepared, and in two or three days a deposit of yellowish-brown ochreous material covered the layer of soil and the inside of the bottle. The solutions saturated with carbon dioxide, however, showed no precipitation and no cloudiness, although they were left for several weeks connected with the apparatus that generated carbon dioxide. When they were finally disconnected, however, and the solutions became accessible to oxygen of the atmosphere a yellowish-brown, ochreous precipitate formed in a short time in both the sterilized and unsterilized solutions. This experiment showed that the precipitation of ferric hydroxide from solutions of ferrous ammonium sulphate was due to simple oxidation and hydrolysis.

Mumford describes the isolation of a bacillus from the water of the tunnels on the Bridge-water Canal, near Worsley, Lancashire. Eng-

¹ Montfort, W. F., Dry feed of chemicals in water purification: Jour. Am. Waterworks Assoc., vol. 2, pp. 200-206, 1915.

land, which is strongly charged with iron, owing to the entrance of iron-bearing colliery waters. He states that he made cultures of this organism in solutions of both ferric ammonium citrate and ferrous ammonium sulphate, and found that it precipitated ferric hydroxide in 24 to 36 hours at 37° C. The strength of the solutions used was 0.05 per cent, and they contained 0.005 per cent of peptone. He states that in both solutions the precipitation took place only under aerobic conditions and that the precipitation was complete, no iron remaining in solution. Under anaerobic conditions he found that precipitation did not take place, but that freshly precipitated ferric hydroxide was changed under these conditions to black compact bog ore.¹

The results obtained by Mumford with ferric ammonium citrate solutions are similar to those which I have already described as obtained with various solutions containing organic iron, except that in my experiments I was able to cause the precipitation both under aerobic and anaerobic conditions. In my experiments, also, the complete precipitation required a longer period of time. The results obtained with ferrous ammonium sulphate, however, are difficult to understand, because, as I have shown, precipitation takes place in this solution under oxidizing conditions, whether organisms are present or not, whereas in the absence of oxygen precipitation apparently does not take place. It is difficult to see under what conditions Mumford conducted his experiments in order to determine that it was the organism and not simple oxidation that caused the precipitation.

Experimentation with solutions of ferrous bicarbonate is somewhat difficult, because of the difficulty of getting ferrous carbonate into solution, and because of the small amount capable of being taken into solution even under favorable conditions. It is difficult also to retain it in solution because of its susceptibility to oxidation. A common way of obtaining solutions of ferrous bicarbonate is to place iron filings in water which is kept saturated with carbon dioxide. In this manner ferrous bicarbonate may be obtained in solution up to

about 0.01 per cent.² It is much more satisfactory, however, to work with natural iron-bearing waters. The oxidation and precipitation, however, take place very rapidly in such waters. A natural solution of ferrous bicarbonate which contained 5.0 parts per million of ferric oxide in the form of ferrous bicarbonate was left in a bottle with a rubber stopper. It soon became cloudy, and a yellowish-brown precipitate began to form in about an hour and continued forming for several days. After about 10 days only 0.2 part per million of ferric oxide remained in solution. The precipitate which formed was examined microscopically and was found to consist of light yellowish-brown semitransparent gelatinous ferric hydroxide with strands of iron thread bacteria, chiefly *Leptothrix*. The presence of the gelatinous ferric hydroxide would seem to indicate that the precipitation at least in part was due to simple oxidation. The presence of *Leptothrix* is explained by the fact that it occurred in the spring from which the water was taken.

A dilute solution of ferric chloride in natural water was allowed to stand at room temperature for several months with free access of oxygen of the atmosphere. A brownish-yellow precipitate, probably ferric hydroxide, similar to that which forms in inorganic ferrous solutions, formed in it. There was no evidence of bacterial action. This precipitate is notable, for normally upon the oxidation of ferric chloride by the addition of ammonium hydroxide a brownish-red, flocculent precipitate of ferric hydroxide forms. After two or three months apparently no ferric chloride remained in solution.

PRECIPITATION OF FERROUS SULPHIDE FROM SOLUTIONS CONTAINING IRON.

The precipitation of ferrous sulphide (FeS) from iron-bearing solutions occurs abundantly under the influence of microorganisms. It takes place under reducing conditions and usually in the presence of abundant decaying organic matter. The formation is usually due to the action of hydrogen sulphide (H₂S),

¹ Mumford, E. M., A new iron bacterium: Chem. Soc. Jour., vol. 103, pp. 645-650, 1913.

² Lieske, Rudolf, Beiträge zur Kenntnis der Phytologie von *Spirophyllum ferrugineum* Ellis, einen typischen Eisenbakterium: Jahrb. wiss. Botanik, Band 49, pp. 91-127, 1911.

formed under these conditions, on ferrous salts in solution, but may be due also in part to the reduction of iron salts of sulphurous or sulphuric acid. Ferrous sulphide may be formed in four distinct ways.¹ (1) Hydrogen sulphide is commonly produced by the decomposition of sulphur-bearing proteins in organic matter, due to the action of various decay-producing bacteria. By reaction with a ferrous salt in solution ferrous sulphide is precipitated by it. (2) Certain bacteria, commonly known as sulphate reducers, have the power, in the presence of decaying organic matter, of taking the oxygen away from sulphites, sulphates, or thio-sulphates, and reducing them to sulphides. If these compounds happen to be compounds of iron, ferrous sulphide is formed directly. (3) If, however, some other sulphide, such as calcium sulphide (CaS), is formed in this manner, it may react with carbon dioxide and water to form hydrogen sulphide, according to the following reaction:²



The hydrogen sulphide thus formed may then react upon ferrous salts in solution, precipitating ferrous sulphide. (4) Certain bacteria, in the presence of decaying organic matter, act directly upon free sulphur, reducing it to hydrogen sulphide, which may precipitate ferrous sulphide (FeS), if iron salts are present.

Hydrogen sulphide is formed from decaying sulphur-bearing proteins, either by processes of reduction or by the splitting off of the hydrogen sulphide molecule as a hydrolytic cleavage product. The power of producing hydrogen sulphide from protein is common not only to practically all the putrefying bacteria but is possessed also by various other bacteria which use proteins as food. The formation is accelerated by the absence of oxygen, and is also favorably influenced by the presence of peptone.

The production of hydrogen sulphide from organic matter may be shown by hanging lead

foil in a flask in which some organic matter is decomposing. Hydrogen sulphide will combine with lead, producing lead sulphide (PbS), which will form as a black coating on the lead foil. In solid media iron salts are used as indicators of the presence of hydrogen sulphide. Thus, 3 per cent of iron tartrate or iron saccharate in bouillon-peptone-gelatin indicates the presence of hydrogen-sulphide producers by the formation of iron-sulphide halos around the colonies.³

The method of the formation of hydrogen sulphide from decaying protein is not definitely known. If formed as a product of reduction it may result from special activities inherent to the protoplasm of the microorganisms or it may be due to the reducing action of other products, such as hydrogen, which microorganisms form. Where hydrogen sulphide forms as a direct cleavage product, it is supposed that the molecule was present in the protein as such and was released by bacterial action. However, the composition of protein is very imperfectly understood, and its decomposition is largely a matter of conjecture.

The reduction of sulphates, thiosulphates, and sulphites by sulphate-reducing bacteria commonly produces metallic sulphides but is usually accompanied also by the formation of considerable quantities of hydrogen sulphide. This is probably due to the fact that carbon dioxide present acts upon the metallic sulphides immediately upon their formation, producing hydrogen sulphide. A considerable number of bacteria probably have the power of reducing sulphates, among which the best known⁴ are *Vibrio hydrosulfureus* and *Bacterium hydrosulfureum ponticum*, isolated from the Black Sea muds by Selinsky and Brussilowsky, *Proteus vulgaris* and *Bacillus mycoides*, shown by Nadson to reduce calcium sulphate to calcium sulphide in the presence of a limited supply of oxygen, *Spirillum desulfuricans*, proved by Beijerinck⁵ to reduce sulphates energetically, and *Microspira aestuarii*, a form similar to *Spirillum desulfuricans*, isolated by Van Delden. Of these organisms the first two besides reducing sulphates also re-

¹ Omelianski, W., Der Kreislauf des Schwefels, in F. Laffar's Handbuch der Technischen Mycologie, Band 3, pp. 214-220, 1904-1906.

Lipman, J. G., Microbiology of soil, in Marshall's Microbiology, pp. 288-290, 1912.

Phelps, E. B., Microbiology of sewage, in Marshall's Microbiology, pp. 217-218, 1912.

² Lipman, J. G., op. cit., p. 290.

³ Omelianski, W., op. cit., pp. 214-216.

⁴ Idem, pp. 216-218.

⁵ Beijerinck, M., *Spirillum desulphuricans*: Centralbl. Bakteriologie, Abt. 2, Band 1, p. 1, 1895.

duce thiosulphates when no organic sulphur is present, and the last two, one of which (*Spirillum desulfuricans*) is a fresh-water form and the other a salt-water form, reduce sulphates, thiosulphates, and sulphites. Another organism, *Bacterium sulfureum*, has been found which reduces sodium thiosulphate. Judging from the fact that some of the sulphate-reducing organisms work more effectively in the absence of organic sulphur compounds, such as proteins, it appears that many of them are capable of decomposing organic sulphur compounds as well as of reducing sulphides.

Thiosulphates and sulphites, according to Beijerinck, are reduced also when added to fermenting sugar solution or other yeast cultures, showing that yeasts as well as bacteria have the power of sulphate reduction.

Brussilowsky¹ isolated three varieties of bacteria which are chiefly concerned in the reducing processes characteristic of the black ferrous sulphide-bearing muds of limans. These grew on meat-peptone-agar and produced the characteristic odor of the liman mud. The principal one isolated was *Vibrio hydrosulfureus*. When oxidized gray liman mud in which this organism occurs was sterilized it was found to keep indefinitely, but upon inoculation with pure cultures it showed reduction and again turned black. A great many other anaerobic bacteria probably have the same power, the functions not being confined to a few species.

An artificial medium for sulphate-reducing organisms was prepared by Brussilowsky by mixing a 2 per cent solution of aluminum chloride (AlCl_3) with a little ferric chloride and a little of a 0.33 per cent solution of thiosulphate, and adding ammonium hydroxide to make it alkaline. This, when inoculated with a bouillon culture of the bacteria, showed ferrous sulphide formation in 24 hours.

Nadson produced a reduction of sulphates with *Bacillus mycoides* and *Proteus vulgaris*, under anaerobic conditions and in the presence of peptone.

Beijerinck prepared cultures of sulphate reducers by using a medium consisting of ordinary ditch water and a small quantity of mineral salts, such as sodium carbonate, calcium,

or magnesium sulphate, and ferrous ammonium sulphate, and traces of organic compounds such as sodium malate or asparagin. He found that small quantities of organic compounds were necessary in order to supply carbon for the organism. Impure cultures in the absence of oxygen and at a temperature of 25° to 30° C. showed reduction of sulphate, accompanied by the formation of an appreciable amount of hydrogen sulphide in 12 to 24 hours. Pure cultures of *Spirillum desulfuricans* were obtained by him on plates of agar and gelatin prepared with the above medium. The organism isolated is a slightly coiled *Spirillum* about 4 micra in length and 1 micron in thickness.

Microspira aestuarii was isolated later from salt water by Van Delden. Its close resemblance to *Spirillum desulfuricans* led to the belief that it might be the same form living under different conditions. The addition of gradually increasing quantities of common salt to the culture solutions, however, was found to have entirely different effects on the two organisms.

It was found that in pure cultures of these two microorganisms the amount of hydrogen sulphide formed was very large, amounting to several hundred milligrams per liter of culture solution. Pure cultures also thrive and react on sulphates in the presence of a larger percentage of organic material, such as bouillon, than impure cultures, because there is no competition with ordinary putrefying bacteria, which otherwise crowd out the sulphate reducers.

A good medium to use for the detection and isolation of sulphate reducers is the one used by Prof. E. B. Fred, of the University of Wisconsin, for class work, as follows:

Culture solution for sulphate-reducing bacteria.

Water	liter	1
Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$)	grams	2
Sodium lactate	do	5
Dibasic potassium phosphate (K_2HPO_4)	do	.5
Ferrous sulphate (FeSO_4)		Trace.

This medium may be placed in bottles and to it should be added a small amount of garden soil (1 gram) or of marsh slime (0.1 cubic centimeter). The bottles should be filled with the medium and then corked and rendered airtight by immersing the mouth and stopper in

¹ Omelianski, W., op. cit., pp. 220-224.

hot paraffin. Upon incubating at 37° C. for three or four days a blackening of the solution takes place, owing to the formation of ferrous sulphide by the reduction of the sulphates present. After a period of several weeks the solution may be tested for sulphates by adding a little barium chloride (BaCl₂) to a small amount of the liquid culture poured into a test tube. If sulphates are still present a white precipitate of barium sulphate (BaSO₄) forms. In time all the sulphates present will be reduced.

Pure cultures of the organisms may be obtained by using an agar medium. This is prepared by adding 15 grams of agar to 1 liter of the liquid medium described above. The sulphate agar medium may be inoculated from the bottle cultures. After incubating for a few days colonies with black halos will develop. Organisms from these colonies may then be reinoculated into sterile liquid media or on to other plates and pure cultures thus obtained.

The following medium developed by Fred was found to be very satisfactory for obtaining cultures of sulphate-reducing organisms:

Culture medium for sulphate-reducing bacteria.

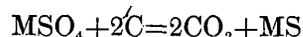
Iron lactate (Fe(C ₆ H ₅ O ₅),3H ₂ O).....grams..	5.0
Ammonium sulphate ((NH ₄) ₂ SO ₄).....do....	2.0
Dibasic potassium phosphate (K ₂ HPO ₄)_do....	.5
Distilled water.....cubic centimeters..	1,000

A solid medium may be prepared with this solution by adding it to a 15 per cent bouillon gelatin and sterilizing in an autoclave at 10 pounds pressure for 15 minutes. Colonies of sulphate-reducing bacteria growing on plates prepared from this medium will develop the characteristic dark halo due to the formation of ferrous sulphide.

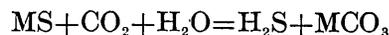
The physiology of sulphate-reducing bacteria is not yet thoroughly understood. Some investigators have claimed that the reducing action is not a property of any particular species of bacteria but that it is due to nascent hydrogen, which is liberated by many anaerobic organisms. Others believe that the action is due to methane liberated during the fermentation of cellulose by certain groups of organisms, the reaction being



Beijerinck rejects these explanations and cites a number of experiments in which hydrogen or methane producing bacteria did not reduce sulphates and in which sulphate reducers did not reduce other substances, such as nitrates. This indicates that the property of reducing sulphates is a special characteristic of certain bacteria, which use the oxygen taken from the sulphates for the production of energy within their cells by the oxidation of carbon to carbon dioxide. The reaction may be as follows:



The sulphide may then be acted upon by carbon dioxide and water, and the production of hydrogen sulphide results according to the following equation:



It is claimed that hydrogen sulphide is also produced by bacteria by the reduction of free sulphur in the presence of organic matter.¹ It was noticed that sulphur present in cultures containing decomposing organic matter gradually disappeared and that hydrogen sulphide, or, if iron salts were present, ferrous sulphide, formed abundantly. Thus Winogradsky found that the sulphur granules of dead cells of sulphur bacteria, such as *Beggiatoa*, gradually disappeared during decomposition with the formation of hydrogen sulphide. Later it was found that flowers of sulphur were attacked under the same conditions and that hydrogen sulphide was formed abundantly.

Beijerinck prepared two flasks with meat bouillon containing 1 per cent iron lactate as indicator. The oxygen present was removed by boiling and then flowers of sulphur were added to one of them. After inoculation with impure bacterial cultures and incubation for 24 hours both solutions became black through the formation of ferrous sulphide, but though the ferrous sulphide formation in the flask containing no free sulphur soon reached a limit that in the other flask continued for a long time and a large quantity of the black precipitate was formed. The formation of hydrogen sulphide from free sulphur is believed to be a secondary process, resulting from the various

¹ Omelianski, W., op. cit., pp. 219, 220.

reactions which take place in decomposing organic matter.

Associated with the hydrogen sulphide forming and the sulphate-reducing bacteria is an important and very interesting group of organisms known as the *Thiobacteria* or sulphur bacteria. A considerable number of morphologically different varieties of bacteria belong to this group, the principal members being the colorless varieties *Thiothrix* and *Beggiatoa* and the red or violet-colored varieties known collectively as *Rhodobacteria*. The sulphur bacteria have the power of oxidizing hydrogen sulphide to free sulphur and sulphuric acid, thus obtaining energy for the assimilation of food. The sulphuric acid formed immediately unites with bases present to form sulphates. The food of these bacteria is derived from organic matter, while the oxygen necessary for the oxidation of hydrogen sulphide is derived from free oxygen dissolved in the water.

As sulphur bacteria require both hydrogen sulphide and oxygen, and as an increase in hydrogen sulphide in solution results in an expulsion of oxygen, there is a certain horizon in the solution where the oxygen, which comes down from the surface, and the hydrogen sulphide, which comes up from the decaying organic matter on the bottom, are both present in the right proportions for these organisms to thrive on. At this horizon they form a platelike film, and it is below this film that sulphate-reducing and hydrogen sulphide forming bacteria are most active.

Jegunow¹ found that in limans (see p. 63), where the water is shallow and the mud is grayish and slightly oxidized, the sulphur bacteria lie on the bottom. With increasing depth and decrease of oxygen, the sulphur bacteria are forced to leave the bottom and form a thin layer through the water, while the mud becomes black in consequence. He believes that such a layer of bacteria is probably found over the entire Black Sea at a depth of about 200 meters.

Laboratory cultures made of black liman muds in water in a high glass jar showed a cloudy platelike swarm of organisms 0.2 to 0.3 millimeter thick in the water. The height of

this layer above the mud depended on the amount of hydrogen sulphide formed. When it sank down to the mud the mud became gray through oxidation, but upon the exclusion of oxygen it again became black and the swarm layer rose in the water.

The sulphates formed abundantly by the sulphur bacteria from hydrogen sulphide are attacked by the associated sulphate-reducing bacteria and are again reduced to sulphides and hydrogen sulphide, thus making a complete cycle. If ferrous or manganese sulphide are formed, they are precipitated.

GEOLOGIC IMPORTANCE OF IRON-DEPOSITING BACTERIA.

IRON IN THE EARTH'S CRUST.

In a study of the deposition of sedimentary iron-ore deposits there are four important points to consider: (1) The source and the manner of solution of iron compounds, (2) the transportation of iron compounds, (3) the manner of deposition of iron compounds, and (4) the conditions under which iron compounds are deposited.

Iron is abundant in the earth's crust in both the ferrous and ferric forms. Ferrous iron occurs in nearly all rocks. In the original crystalline rocks, such as granite, diorite, gabbro, pyroxenite, and peridotite, ferrous iron forms an important constituent of the ferromagnesian silicates, mainly biotite, amphibole, pyroxene, olivine, and chlorite. It is also present in the oxides of iron, magnetite and ilmenite, which form a noticeable percentage of the more basic crystalline rocks. In sedimentary rocks ferrous iron is present in original undecomposed silicates that occur in shales and graywacke, in secondary silicates, and also in secondary iron carbonate, which occurs in varying abundance in nearly all sedimentary rocks. In metamorphic rocks ferrous iron occurs mainly in the secondary iron silicates, especially in biotite, amphibole, chlorite, and garnet, but to some extent it is also present as recrystallized iron carbonate.

Ferric iron occurs in original crystalline rocks, mainly as the oxides magnetite, hematite, and ilmenite, but it is also found in smaller amounts in some of the silicates, such as biotite, amphibole, pyroxene, and epidote.

¹ Jegunow, M., Bakterien-Gesellschaften: Centrabl. Bakteriologie, Abt. 2, Band 2, p. 20, 1896.

In sedimentary rocks it is found mainly as the oxides hematite and limonite, and in some iron silicates, such as glauconite, and in metamorphosed sediments it occurs as the oxides hematite and magnetite and in the silicates biotite, amphibole, and garnet.

In addition to these minerals, iron is present in nearly all rocks in the form of the sulphides pyrite or marcasite, and occasionally in basic igneous rocks as pyrrhotite.

Thus iron is one of the most abundant and widely distributed metals on the surface of the earth, the only metal exceeding it in abundance being aluminum. In Clarke's average analysis of the earth's crust to a depth of 10 miles,¹ ferrous and ferric oxide, considered together, rank third in abundance of all the oxides, being exceeded only by silica and alumina. The principal constituents in the average rock and in the average igneous rock as given by Clarke, rank as follows:

Composition of average rock of the earth's crust and of average igneous rock.

	Average rock. ^a	Average igneous rock.
SiO ₂	59.77	59.83
Al ₂ O ₃	14.89	14.98
CaO.....	4.86	4.84
MgO.....	3.74	3.81
FeO.....	3.39	3.46
Na ₂ O.....	3.25	3.36
K ₂ O.....	2.98	2.99
Fe ₂ O ₃	2.69	2.65
H ₂ O.....	2.02	1.89
All other constituents.....	2.41	2.19
	100.00	100.00

^aIn the average rock which, according to Clarke, represents the earth's crust to a depth of 10 miles, the following percentages of igneous and sedimentary rocks are taken: Igneous, 95 per cent; shale, 4 per cent; sandstone, 0.75 per cent; limestone, 0.25 per cent.

DECOMPOSITION OF IRON-BEARING MINERALS.

When the rocks forming the earth's crust suffer disintegration and decomposition in their change to soil the iron compounds are dissolved by the action of the acids that are present in surface and ground waters. These acids are principally carbonic acid (H₂CO₃) and various organic acids, such as butyric, propionic, formic, lactic, acetic, citric, tartaric, valerianic, and the little-known humic acids.

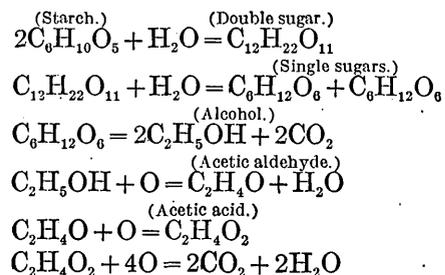
¹ Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 32, 1916.

Van Hise² mentions the common occurrence in the soil of certain other organic acids, such as crenic, apocrenic, and ulmic acids. Inorganic acids are present in the soil in small quantities and occur more or less locally. The principal ones probably are nitrous, nitric, sulphuric, and perhaps hydrochloric. Phosphoric and silicic acids also are present, but they are not important in processes of rock decay.

The presence of these gases and acids in the soil results from two conditions: First, and most important, is the decay of organic matter, due to bacterial action, and, second, is the decomposition of inorganic material, due to chemical agencies, which in part also owe their origin to bacterial action.

Carbon dioxide, which is the most important of these agents in the process of rock decay, is in part derived from the decomposition of carbonates, due to the action of acids, but mainly it is derived from the decay of organic carbon compounds under the action of various fermenting and decay-producing microorganisms, such as bacteria, yeasts, and molds.

The carbon in animals and plants may be in the form of carbohydrates, fats, or proteins. Carbohydrates, in which form by far the most carbon occurs in nature, are decomposed to carbon dioxide and water by the action of certain hydrolytic enzymes, commonly produced by various organisms, the decomposition taking place in a series of steps as is shown by the following formulae, which illustrate acetic fermentation as an example. Decomposition to other fatty acids, such as lactic, tartaric, and butyric, goes on along similar lines.



The change from starch to the double sugars, maltose, saccharose, or lactose, is due to the action of the enzyme diastase produced by all green plants, many molds, and a few bacteria. The decomposition from double sugars to single

² Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, pp. 461-462, 1904.

sugars is due to the action of the enzymes maltase, invertase, and lactase, each acting on a special sugar. These three enzymes differ in distribution but in general are present in green plants and in various microorganisms. Single sugars are acted upon directly by fermenting enzymes, the change to alcohol being due mainly to the action of yeasts, and the further decomposition of alcohol to fatty acids and carbon dioxide taking place under the action of bacteria and molds. The principal acids formed in this manner in the soil are butyric, propionic, acetic, formic, and lactic acids. The end products of the fermentation are large quantities of carbon dioxide and water.

Though these changes are the typical ones through which most carbohydrates pass in the process of decomposition, many irregularities and variations occur. Cellulose, for example, which is probably the most abundant carbohydrate in the soil, is decomposed by a special group of microorganisms known as cellulose fermenters. During the decomposition it may be changed directly to fatty acids, or it may be changed first to sugar and then to different gases, such as methane, hydrogen, and carbon dioxide.

The carbon in fats and proteins also suffers the change to fatty acids and carbon dioxide. The decomposition of the proteins, however, is very complex, and many little known compounds, including those of nitrogen, sulphur, and phosphorus, are formed during the process.

The carbonaceous material that resists decomposition by fermenting and decay-producing microorganisms collects in the soil in the form of humus. Humus consists mainly of cellulose, which is the most difficult of the different forms of organic carbon to decompose. The further decomposition of humus goes on very gradually, and during the process the different gases and organic acids already mentioned are produced, as well as humic acids. The composition of humic acids is not well understood, but it is now supposed that they are colloidal mixtures of various complex organic acids or of their acid salts.¹ Humus, therefore, acts as a constant source of soil acids and gases. Humic acids and their acid salts (humates) may be so abundant as to cause acidity of the soil in places where bases are not

present in sufficient quantity to neutralize the acids produced.

Inorganic acids in the soil are in part derived from the decomposition of certain minerals, such as sulphides, sulphates, and chlorides, and when so derived are local in their occurrence. Nitrous and sulphuric acids, however, are produced also during certain very important soil processes known as nitrification and sulphur oxidation.

The nitrogen content of proteins, urea, and other nitrogenous organic compounds is changed during decomposition by ammonifying bacteria into the form of ammonia (NH_3). The ammonia is acted upon by nitrifying bacteria, and the nitrogen is oxidized first to the nitrous and then to the nitric form. During the first part of the process nitrous acid is formed from ammonia, and this immediately reacts upon bases present in the soil to form nitrites, which are then oxidized to nitrates. Thus the nitrogen, and the bases with which it combines, were first present in a relatively insoluble form and have been changed by bacterial action to soluble nitrates, in this manner hastening rock decomposition.

Sulphur oxidation in general is very similar to nitrification. During the putrefaction and decay of sulphur-containing organic matter by ordinary putrefying bacteria, sulphur is liberated in the form of hydrogen sulphide (H_2S). This gas is oxidized by a special group of bacteria, the sulphur bacteria, first into free sulphur and then into sulphuric acid. The sulphuric acid immediately reacts upon the bases present to form sulphates, which for the most part are more or less soluble.

Thus it is clear that processes of bacterial decomposition are of unusual importance in promoting rock decay. They not only result in the formation of most of the carbon dioxide produced in the soil but also of many organic and a few inorganic acids, which locally become of importance in promoting decomposition.

By far the most abundant of the acids in the soil is carbonic acid or carbon dioxide. Although relatively weak, its abundance and continued action cause most metals, including iron, to be taken into solution in the form of carbonates. Nearly all ferrous compounds, but especially ferrous carbonate, are readily acted upon by carbonic acid dissolved in meteoric

¹ Lipman, J. G., Microbiology of soil, in Marshall's Microbiology, p. 250, 1912.

water, are taken into solution in the form of carbonate or bicarbonate, and are carried thus as long as the waters contain an excess of carbon dioxide in solution. Moody¹ says that carbonic acid exerts a greater corrosive influence on iron than equivalent amounts of hydrochloric or sulphuric acids. Some compounds of iron, however, especially ferric oxide, are practically insoluble in waters that carry only carbon dioxide, and in the solution of these compounds various other soil acids and decaying organic matter become effective. There is little doubt, therefore, that all iron compounds, even the most insoluble, such as ferric oxide, are acted upon to some extent by soil waters, especially if decaying organic matter is present. The intensity of the action differs in different places according to the composition of the water, and this depends more or less upon the character of the soil or rocks through which the water passes and upon the presence of vegetation. The influence of rock composition is well illustrated by certain rocks which are rich in ferric oxide and contain locally particles or bunches of sulphide of iron. In the neighborhood of the decomposing iron sulphide the ferric oxide is commonly reduced, by the liberated sulphuric acid, to the ferrous form, which is indicated by a change in color from yellow or red to white or green. The influence of vegetation is shown in some bog limonite deposits, where in places near abundant decomposing organic matter, such as rotting logs, the yellow bog scum is often bleached to a white or green color. This reduction is probably in part due to organic acids, which are abundant under these conditions, and in part to the action of decomposing organic matter, which requires oxygen and takes some of it from the ferric oxide. Kindler,² as early as 1836, called attention to the fact that decaying vegetable matter has a marked effect on the solubility of ferric hydroxide. He noticed that ferruginous quartzose sand was rendered colorless around decaying roots and in a few months became as white as if it had been treated by an acid. A root one-sixth of an inch in diameter, upon decaying, whitened the sand to a distance of 1 to 2 inches around it. This action is ascribed to organic acids pro-

duced during the decay. Ferric hydroxides are in this manner reduced to the protoxide, which at the same time combines with carbon dioxide to form carbonate. Iron carbonate becomes soluble and remains in solution in the presence of excess carbon dioxide.

The decomposition of iron sulphides, which is caused principally by partial oxidation, probably results in the formation of soluble ferrous and ferric sulphates. These sulphates may be carried in solution for some time if conditions are favorable. They are not very stable, however, and upon further oxidation and hydrolysis for the ferrous or simple hydrolysis for the ferric sulphate, they readily change to ferric hydroxide or to insoluble basic ferric sulphates.

•According to the extent to which organic acids are present iron may be carried in solution as salts of these acids. It is not impossible that such organic salts as iron formate, iron butyrate, iron lactate, or iron citrate may occur in iron-bearing waters. Aschan³ is of the opinion that great quantities of iron are carried in solution as soluble ferrohumes and ferrihumes and that humus compounds are largely instrumental in the formation of bog iron ore deposits, being active both in the solution of iron compounds and in their subsequent precipitation. He believes that the dark color of streams that pass through regions of abundant vegetation is largely due to the presence of humus compounds.

Once the iron is reduced to a form in which it is soluble in water it may be taken into solution and carried a greater or less distance depending upon the change in composition suffered by the water. It is generally supposed, probably with sufficient reason, that iron is carried in solution mainly as ferrous bicarbonate and is kept in solution as long as the waters retain an abundance of carbon dioxide. Among the iron-bearing waters analyzed many have been found which contain no sulphate or other acid radicle besides the carbonate, thus showing conclusively that at least in these waters iron was carried as the soluble carbonate. It is quite possible, however, that iron is carried to some extent also in other forms, perhaps as ferrous or ferric

¹ Moody, G. T., The rusting of iron: Chem. Soc. Jour., vol. 89, pp. 720 et seq., 1906.

² Poggendorff's Annalen, Band 37, p. 203, 1836.

³ Aschan, Ossian, Die Bedeutung der wasserlöslichen Humusstoffe für die Bildung der See und Sumpferze: Zeitschr. prakt. Geologie, Jahrg. 15, p. 56, 1907.

sulphate or as compounds of some of the organic acids.

The waters of many streams, springs, and lakes contain much iron in solution, as has been shown by analysis, by the fact that flocculent precipitates of ferric hydroxides occur in them, that iridescent films of limonite form on their surface, and by the fact that objects with which they come in contact commonly become coated with limonite. Thus, although it is undoubtedly true that ferric oxide, which is soluble with great difficulty, forms in abundance by the oxidation of other iron compounds and along with alumina and other insoluble substances becomes concentrated in residual soils, still it is certain that acids capable of taking and retaining iron salts in solution are abundantly present in soil waters and a large amount of iron is undoubtedly carried away by surface waters and redeposited elsewhere.

TYPES OF SEDIMENTARY IRON ORES AND IRON FORMATIONS.

GENERAL FEATURES.

Iron may be precipitated from natural solutions under ordinary conditions of sedimentation either by chemical or by biologic agencies. The precipitates may occur in any one of the following forms: Ferric hydroxides, ferrous carbonate, hydrous ferrous and ferric silicates of several kinds, iron phosphates, basic ferric sulphates, ferrous sulphide, and perhaps iron disulphide.

In the formation and accumulation of deposits of ferric hydroxide biologic agencies play a most important part, though chemical action is undoubtedly of great importance as well. Iron sulphide also may be formed either chemically or by the action of microorganisms. Ferrous carbonate and iron silicates, however, are not definitely known to be precipitated by organisms. They are probably chemical precipitates, the presence of organic matter being commonly an important factor in their formation. Iron phosphates and basic ferric sulphates are chemical precipitates.

Iron may be precipitated under many conditions. Usually it is taken into solution by ground waters that contain carbon dioxide in their passage through soil and rock, and in general it remains in solution as long as the

water retains an excess of carbon dioxide. Under ordinary conditions ground waters lose their carbon dioxide and become saturated with oxygen soon after they reach the surface, and the iron is deposited as ferric hydroxide. Iron bacteria are nearly always present under these conditions and not only aid in the precipitation but play an important part in the accumulation of the precipitated material. If the iron-bearing waters reach the surface in localities where abundant vegetation and decaying organic matter are present they may not become saturated with oxygen, but the solvent carbon dioxide may be taken up by the growing plants. In such localities the iron is precipitated as ferrous carbonate. If alkaline silicates are abundant in the water ferrous silicates may be formed. If phosphorus is present it is usually precipitated with the iron.

In localities where conditions are such that the iron is not chemically oxidized, when the iron-bearing waters come to the surface and when carbon dioxide is formed in sufficient abundance to retain the iron in solution, iron bacteria may be the agency in precipitation. Such conditions probably exist to some extent also in larger underground openings, such as caves and fissures, and under these circumstances certain subsurface concentration deposits of brown iron ore may be formed. When iron is carried in solution in the form of soluble humates or other salts of organic acids, iron-precipitating bacteria may also play an important part in its deposition.

The accumulation of iron precipitates usually takes place in quiet waters, such as bogs, marshes, lakes, and lagoons. Often, however, deposition occurs where iron-bearing waters issue from the ground and where they usually flow quite rapidly in little streams and rivulets. Some of the iron precipitated under this condition is doubtless carried along mechanically as little flocculent masses and is finally deposited in quiet water, where it may accumulate. Much of it, however, is doubtless lost in the mass of other sediments, so that only a relatively small proportion of the iron dissolved and carried in solution by ground waters is actually accumulated in the form of iron-ore deposits.

Sedimentary iron ores and iron ores derived directly from iron-bearing sediments by concentration are of great importance commer-

cially. Deposits of this nature occur on nearly all the continents, and probably more than 90 per cent of the iron ore that is being produced at the present time is of this type. Such ores consist of hematite, limonite, or iron carbonate, the first two being by far the most important.

DEPOSITS ORIGINALLY LAID DOWN MAINLY AS FERRIC HYDROXIDE.

Ferric hydroxides or hydrated ferric oxides are probably the most important iron compounds that play a part in processes of sedimentation. The following table shows the composition of anhydrous ferric oxide and of the ferric hydroxides which are known to occur in nature:

Chemical composition of ferric oxide and the ferric hydroxides that occur in nature.

	Fe	O	H ₂ O
Hematite (Fe ₂ O ₃).....	70.0	30.0	0.0
Turgite (2Fe ₂ O ₃ ·H ₂ O).....	66.3	28.4	5.3
Goethite (Fe ₂ O ₃ ·H ₂ O).....	62.9	27.0	10.1
Limonite (2Fe ₂ O ₃ ·3H ₂ O).....	59.8	25.7	14.5
Xanthosiderite (Fe ₂ O ₃ ·2H ₂ O).....	57.1	24.5	18.4
Limnrite (Fe ₂ O ₃ ·3H ₂ O).....	52.3	22.4	25.3

Most of the deposits of bedded hematite, as well as deposits of bog ore and beds of brown iron ore, were probably originally laid down in the form of limonite, associated with other ferric hydroxides and ferrous carbonate and locally accompanied by minor quantities of other iron compounds, such as phosphate, silicates, or sulphide. The ferric hydroxides that are probably most abundantly associated with limonite in freshly deposited iron sediments are xanthosiderite and limnrite, both of which have been found in bog ores of recent origin which also carry impurities such as organic acids, phosphoric acid, and clastic material. In older iron-ore beds the hydroxides that contain less water appear to be more commonly associated with limonite, and in many of them only slightly hydrated hematite is the most important constituent. Deposits which are composed mainly of a mixture of various ferric hydroxides are commonly known as limonite or brown iron ore deposits.

Hematite and limonite of sedimentary origin are distributed in many parts of the world, and

one or both of them occur in many important iron-ore deposits and iron-bearing formations. Among deposits which are formed wholly or in part by ferric oxide or hydroxide of original sedimentary origin are the Clinton hematite beds of the eastern United States, the Wabana iron-ore beds of Newfoundland, the iron-bearing formation of the Lake Superior region, the hematitic quartzite and associated bedded hematite of Minas Geraes, Brazil, the banded jasper and associated hematite of India, the extensive Jurassic oolitic limonite ores of Lorraine and Luxembourg, and the widely distributed bog and lake ores.

Beds and lenses of iron ore of Clinton (Silurian) age occur in many parts of the Appalachian region in eastern United States, extending from New York as far south as Alabama.¹ The ores are interbedded with shale and sandstone. In some places only one bed is found, but in other places three or four beds occur one above the other and separated from each other by clastic sediments. In many places lenses of clastic material occur within iron-ore beds. The iron-ore layers themselves range in thickness from a few inches to 40 feet, and single beds may extend along the strike of the rocks for many miles. As most of them occur in a region of folded rocks they have attitudes ranging from horizontal to vertical.

The Clinton ore beds are composed principally of three classes of ore—(1) oolitic, (2) fossil, and (3) finely granular or textureless ore. By far the larger part of the ore beds is formed by oolites, but locally fossils are very abundant in the ore beds, and in places may even form the principal part of them. Finely granular material is nearly everywhere present in small amount, and in places forms definite lenses within the oolitic or fossiliferous material. Locally ferruginous pebbles occur near the base of the ore beds.

The ore is mainly ferric oxide and contains calcium carbonate and silica as impurities.

¹ Burchard, E. F., Butts, Charles, and Eckel, E. C., Iron ores, fuels, and fluxes of the Birmingham district, Ala.: U. S. Geol. Survey Bull. 400, 1910.

Burchard, E. F., Preliminary report on the red iron ores of east Tennessee, northeast Alabama, and northwest Georgia: U. S. Geol. Survey Bull. 540, pp. 279-323, 1914; The red iron ores of Tennessee: Tennessee Geol. Survey Bull. 16, 1913.

Newland, D. H., and Hartnagel, C. A., Iron ores of the Clinton formation in New York: New York State Mus. Bull. 123, 1908.

The water content of the hard ore which has not suffered surface weathering is remarkably low, being on the average only about 0.5 per cent. Even in the weathered surface ore the water content averages only from 2 to 3 per cent. Roughly the composition of the hard unweathered ore is as follows:

Composition of hard unweathered Clinton iron ore.

Fe ₂ O ₃	52
CaCO ₃	34
SiO ₂	10
Al ₂ O ₃	3.5
H ₂ O.....	.5

Upon weathering the calcium carbonate is removed, causing a proportionate increase of the remaining constituents and commonly increasing the ferric oxide content to 70 per cent. There is an increase in water in the weathered ore because of hydration.

The spherules in the Clinton oolitic ore on being examined microscopically are seen to consist of a nucleus of quartz or shell fragment around which are concentric alternate layers of hematite and silica or of hematite and calcite. Many spherules contain a green mineral, supposed to be an iron silicate, in the center. The matrix separating the spherules is largely calcite and detrital quartz.

Three principal hypotheses have been offered for the origin of the Clinton iron ore. The one most generally accepted is that the beds were originally laid down, together with the inclosing rocks, in much the same form in which they now occur.¹ The iron is supposed to have been precipitated as ferric hydroxide and later, owing to compression, to have been dehydrated. The oolites were probably formed immediately after deposition, while the ferric hydroxide was still in a flocculent form. The replacement of much of the calcium carbonate in the fossils present is believed to have taken place during the deposition. The second hypothesis is that the present hematite layers represent original beds of limestone, which have been replaced at some later period by iron brought in by percolating waters. By this hypothesis it is difficult to explain the regularity of the beds as well as the absence of similar

replacement phenomena with reference to other limestone beds in the region. According to the third hypothesis² the ore beds were originally laid down as glauconite, which was subsequently leached of some of its impurities and oxidized to hematite. As evidence is given the fact that unaltered remnants of a green mineral, supposed to be an iron silicate, occur in some of the spherules composing the oolitic ore.

The Wabana iron ore³ is found in beds which outcrop on Bell Island in Conception Bay in the eastern part of Newfoundland. The beds dip northwestward underneath the waters of the bay at angles that range from 8° to 10°. Many individual beds range in thickness from mere seams to 30 feet or more. They are scattered through about 1,000 feet of strata, but they are more or less grouped into zones which are separated by zones of barren rock. The thickest one of the barren zones is 600 feet in thickness. Though the individual ore layers differ in thickness from place to place, the ore zones are very continuous. The inclosing rocks are indurated sandstones, shales, and slates of Arenig to Llandeilo age (Ordovician).

The principal ore mineral is hematite, with which chamosite, an aluminous ferrous silicate, is abundantly associated. Siderite forms a considerable proportion of the ore beds locally and quartz occurs as detrital fragments. Fossil fragments of shells, mainly brachiopods, consisting of calcium phosphate, occur throughout the ore and tubes of boring algae are very abundant.

The great mass of the ore has an oolitic texture, being composed of fine spherules of mixed hematite and chamosite, generally somewhat flattened parallel to the bedding. Microscopically the individual spherules are seen to consist of alternate layers of hematite and chamosite arranged concentrically about a center which may be detrital quartz, a shell fragment, or chamosite. Locally the spherules may consist almost entirely of chamosite and elsewhere of hematite. The matrix between the spherules is generally chamosite, but hematite, quartz, or siderite may replace it in part or entirely.

¹ McCallie, S. W., Report on the fossil iron ores of Georgia: Georgia Geol. Survey Bull. 17, 1908.

² Hayes, A. D., Wabana iron ores of Newfoundland: Canada Geol. Survey, Dept. Mines, Mem. 78, 1915.

³ Smyth, C. H., jr., On the Clinton iron ore: Am. Jour. Sci., 3d ser., vol. 43, p. 487, 1892.

The range in composition of the Wabana iron ores is as follows:

Mineral composition of Wabana iron ores.

	Per cent.
Hematite.....	50-70
Chamosite.....	15-25
Siderite.....	0-50
Calcium phosphate.....	4-5
Quartz.....	0-10
Calcite.....	0-1

In contrast to the Clinton ores and to the oolitic limonite of northern France and southern Germany described later, these ores contain little or no calcium carbonate but instead contain abundant calcium phosphate.

The ores are supposed to be primary bedded deposits, originally laid down with the inclosing clastic sediments in much the same form in which they occur now, the hematite and chamosite being deposited at the same time but perhaps under slightly different conditions. The spherules are supposed to have resulted from the action of surface tension on the fine unconsolidated sediments. Boring algae presumably played an important part in the ore formation. Tubes of these organisms penetrate both spherules and matrix and seem to have thrived during the ore deposition. It is thought that they may be responsible for part of the oxidation to hematite.

In the Lake Superior region extensive beds of iron-bearing formation of pre-Cambrian age are found, interlayered with metamorphosed clastic sediments such as slate and quartzite and with volcanic flows.¹ The beds have a maximum thickness of 1,000 feet or more and in places are known to be continuous along the strike for more than 200 miles. The iron-bearing formation as exposed consists mainly of hematitic and limonitic chert and slate and iron ore. These rocks in many places grade downward at different depths along the bedding into sideritic chert and slate, or into greenalite rock, a ferrous silicate rock. Metamorphosed phases of the various types of the iron-bearing formations which have been altered by igneous intrusions or regional deformation occur locally.

The hematitic and limonitic chert and slate were probably derived mainly by oxidation

¹ Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, 1911.

from the sideritic chert and ferrous silicate rock, and the iron ore is believed to have been derived from the hematitic and limonitic chert by the leaching and removal of silica under the influence of meteoric waters. The iron-bearing formation was, therefore, for the most part laid down originally as sediments that consolidated into sideritic chert, sideritic slate, and greenalite rock. In association with these rocks, however, there were locally deposited beds and lenses of original ferric oxide or hydrated ferric oxide and silica which upon consolidation formed a rock very similar in all respects to the hematitic and limonitic chert formed by the secondary alteration of the sideritic chert and greenalite rock. In places layers of original relatively pure hematite ore are found with these beds, which in their character and manner of origin probably resemble the Clinton and Wabana iron ores.

In the State of Minas Geraes, in southeastern Brazil, there are extensive beds of so-called "itabirite," an iron oxide bearing quartzite, that contains intercalated beds and lenses of ferruginous schist and of pure hematite.² The itabirite in general is a thinly laminated rock that consists of alternating layers of quartz sand and iron oxide. In places, however, these two constituents are irregularly intermixed, forming a granular rock. The itabirite and associated iron ore and schist are interbedded with metamorphosed sedimentary rocks of probable pre-Cambrian age. The iron-bearing formation varies greatly in thickness, being less than 20 feet thick in some parts of the region and more than 4,000 feet thick in other parts. It is underlain by a great thickness of sericitic quartzite which in turn overlies granite and gneiss. At the contact of the iron-bearing formation and quartzite is a thin layer of argillaceous schist. Above the iron-bearing formation is a schist bed of great thickness, which in the upper part becomes quartzitic. In the lower part of this schist are local beds and lenses of limestone and itabirite. In places beds of manganese ore also occur near the contact of the

² Leith, C. K., and Harder, E. C., The hematite ores of Brazil and a comparison with the hematite ores of Lake Superior: Econ. Geology, vol. 6, pp. 670-686, 1911.

Harder, E. C., The "itabirite" iron ores of Brazil: Econ. Geology, vol. 9, pp. 101-111, 1914.

Harder, E. C., and Chamberlin, R. T., The geology of central Minas Geraes, Brazil: Jour. Geology, vol. 23, pp. 341-378, 385-424, 1915.

iron-bearing formation and the overlying schist.

The iron content of the itabirite in general ranges between 30 and 50 per cent, and the interlayered iron ores range from 50 to 70 per cent in metallic iron. In fact the itabirite, with diminishing quartz, grades into iron ore. Both hard and soft ores occur, the former being of very high grade and commonly averaging 69 to 70 per cent metallic iron and less than 0.02 per cent phosphorus for an entire deposit. High-grade hard-ore beds have a maximum thickness of 750 feet and a maximum length of 4,000 feet, but the lower grade soft ores form deposits several thousand feet in thickness and more than 2 miles in length.

The iron ores and associated itabirite and schist are believed to be primary sediments. The iron was probably deposited as ferric hydroxide by chemical and biological agencies at the same time as the associated clastic material.

The Archean rocks of British India consist of a basement of gneisses and crystalline schists. These are overlain by what is known as the Dhárwar series of metamorphosed sediments, consisting of conglomerate, quartzite, slate, phyllite, crystalline limestone, and different kinds of schist. Both of these series have suffered deformation and have been intruded by granitic and other rocks. The Dhárwar series locally contains beds of iron-bearing rocks, such as banded hematitic and magnetitic jaspers and ferruginous quartzites and schists associated with beds and lenses of pure iron ore.¹ Scattered areas of Dhárwar rocks occur in many parts of the peninsula of India, and iron-ore deposits are found in them both in the north and south.

The iron-ore deposits range in size from mere seams to great tabular lenses, some of the largest of which are 300 feet in thickness and cover many acres. The ore is generally hard and massive, but locally where associated with slate or phyllite it is soft, laminated, and schistose. It consists of a mixture of hematite and magnetite and contains as impurities

¹ Weld, C. M., The ancient sedimentary iron ores of British India: *Econ. Geology*, vol. 10, pp. 435-452, 1915.

Holland, T. H., Geology of the neighborhood of Salem, Madras Presidency: *Geol. Survey India Mem.* 30, pt. 2, pp. 103-168, 1901.

quartz and chlorite or pale-green amphibole (grünerite). Some of the ore contains as much as 68 per cent metallic iron and only about 2 or 3 per cent of impurities. As silica and amphibole increase the ore grades into hematitic and magnetitic quartzite and jasper.

The ores are supposed to be original sediments that were precipitated chemically as ferric hydroxide and later metamorphosed to their present form.

Beds of siliceous iron ore and associated ferruginous rocks similar to those of Brazil and India occur in Dunderland, in the northern part of Norway.

Jurassic limonite, or "minette" ore, is of widespread distribution in northern France and southern Germany, and is of great importance commercially.² The ore occurs as lenticular beds interlayered with shale, sandstone, and marl of Middle Jurassic (Dogger) age, not far above the underlying Lias marls. The seven principal ore beds vary in thickness, the maximum being 20 feet, and occur within a vertical distance of 75 to 150 feet. They are separated from one another by beds of marl and limestone. The sedimentary beds are nearly horizontal but have a very gentle dip to the west, and the iron-ore layers conform in structure with the sediments.

The ore beds consist mainly of oolitic limonite, soft and earthy, different beds having different colors, such as gray, brown, red, green, and yellow. With the limonite occur some calcite, siderite, secondary magnetite, and iron silicates, mainly glauconite, but berthierine, chamosite, and thuringite also have been found. The spherules that make up the oolitic ore are about the size and shape of millet seed or smaller, and consist of ferric hydroxide with a skeleton of silica. They are cemented by silica, lime, and clay shale.

² Einecke, G., and Köhler, W., Die Eisenerzvorräte des Deutschen Reiches: The iron-ore resources of the world, p. 670, Stockholm Internat. Cong. Géol., 1910.

Dondelinger, V. M., Die Minette im Grossherzogtum Luxemburg: *Idem*, p. 43.

Nicou, L., Les ressources de la France en minerais de fer: *Idem*, p. 3.

Cayeux, L., Les minerais de fer oolithique de France, 1909.

Kohlmann, W., Die Minettenablagerungen des lothringischen Jura: *Stahl und Eisen*, 1902, pp. 493-503; 554-570, 1273-1287, 1340-1357.

Van Werwecke, L., Bemerkung ueber die Zusammensetzung und Entstehung der lothringisch-luxemburgischen oolithischen Eisenerze: *Zeitschr. prakt. Geologie*, 1901, p. 396.

The oolitic limonite is of low grade and contains abundant impurities. The range in composition of ore from different beds is as follows:

Range in composition of Jurassic limonite of France and Germany.

	Per cent.
Fe-----	34- 40
SiO ₂ -----	7- 16
Al ₂ O ₃ -----	2- 8
CaO-----	6- 19
P-----	0.3-0.7
CO ₂ +H ₂ O-----	14- 22

Hypotheses have been offered for the origin of the Jurassic limonite similar to those advanced for the origin of the Clinton ores. It was formerly held that the ores were replacements of oolitic limestone beds, due to the action of iron-bearing waters. More recently, however, hypotheses have been advanced claiming that the ores were deposited as original iron-bearing sediments. Some investigators believe that the ore was originally deposited as oolitic siderite and that it has subsequently been oxidized in large part to limonite. Others, who have found iron silicates in the ore beds as well as silica in the ore spherules, claim that, in part at least, the ore is an alteration product of original iron silicates, perhaps glauconite. Still others hold that the beds were deposited essentially in their present form, mainly as limonite, but with admixtures of iron carbonate and iron silicates.

Bog iron ore is found in many parts of the world. It consists essentially of an earthy yellow to red or dark-brown mixture of ferric hydroxides, mainly limonite but with associated limonite and xanthosiderite. With these hydroxides occur some silicate, sulphate, and locally carbonate of iron, besides organic matter and clastic material, such as sand and clay. Bog iron ore is usually high in phosphorus, which is present as the iron phosphate, vivianite,¹ and locally wad or bog manganese also is an abundant constituent. The organic matter consists of humus substances and of plant remains, such as leaves and sticks, which may be in part or entirely replaced by limonite.

Bog iron ores are of two kinds—(1) those formed in lakes by water currents and known

as lake ores,² and (2) those formed in place in still water and occurring either as surface layers lying on soil or below a layer of porous surface soil and resting on clayey impervious subsoil.

Lake ores have been described from localities in Ontario and Quebec in Canada and from the eastern United States, as well as from Sweden and other places in northern Europe. The Canadian deposits, which are typical, consist mainly of layers of flat disklike or irregular concretions of ferric hydroxide that extend along the shores of lakes in which vegetation is abundant and into which streams carry iron-bearing water. The layers may attain a foot or two in thickness and are usually thickest at the water's edge and thin out toward the lake, few concretions being found where the water is more than 2 feet deep. The concretions themselves range from less than an inch to a foot or more in diameter. They contain quartz grains as impurities and are apparently formed around sand grains as nuclei by the rolling action of waves and currents. In the lower portion of such a layer of concretions, broken concretions with soft limonite and sand usually occur, and with them a green ferrous salt, perhaps a silicate or a sulphate, is generally found. Locally instead of concretions a layer of soft or hard, yellow, porous, bedded limonite occurs in the shallow water, and in still other places limonite occurs as cement in sand. In the deeper water of the lakes into which iron-bearing waters flow the distribution of the deposits is usually irregular, but in many places 6 to 8 feet of ochereous, slimy mud occurs at the bottoms of the lakes. Iron carbonate is usually absent in lake ore deposits.

The second type of bog ore usually forms in marshes, peat bogs, or other shallow surface depressions. These deposits may occur immediately at the surface but are more commonly found below several feet of porous surface soil and in many places are mixed with humus or peat. They form horizontal tabular bodies, as a rule of small circumference and of no great thickness. Some deposits have a pisolitic texture, consisting of small spherules of

¹ Van Bemmelen, J. M., Hoitsema, C., and Klobbie, E. A., Ueber das Vorkommen, die Zusammensetzung und Bildung von Eisenanhäufungen in und unter Mooren: Zeitschr. anorg. Chemie, Band 22, pp. 313-379, 1700.

² Moore, E. J., The occurrence and origin of some bog iron deposits in the district of Thunder Bay, Ontario: Econ. Geology, vol. 5, pp. 528-537, 1910.

porous yellow ocher, the interstices of which are filled with hard brownish-black limonite; others consist of layers of concretions or nodules embedded in sand or sandy clay, and commonly contain much iron carbonate and vivianite; and still others form solid, thin, tabular bodies consisting of sand and clay impregnated and cemented by limonite. Where much peat is present irregular nests of bog ore that consist almost entirely of white, amorphous iron carbonate are numerous.¹ Such deposits are common in the Netherlands and northern Germany.

Bog iron ores are distributed through many parts of the world but are especially abundant in the glaciated northern regions of North America, Europe, and Asia.² In these regions percolating waters dissolve iron from the glacial drift, where it is abundantly present as magnetite as well as iron silicates. Shaler states that in the glacial drift in New England 1 to 3 per cent of magnetite is found. The iron may be carried in solution as soluble carbonate, as sulphate, or combined with organic acids, and may be precipitated chemically or biologically. Chemical precipitation takes place either by removal of the solvents, by reaction with other materials in solution, or by oxidation. Biologic precipitation occurs through the action of microorganisms. Deposition usually takes place in small lakes or marshes, which are abundant in glaciated regions. The form in which the iron is precipitated depends on a number of factors, such as the form in which the iron is being carried in solution, the amount of oxygen present, the amount of organic matter present, and the presence of other materials in solution. Usually the conditions are so varied, however, that a mixture of iron salts is deposited, including ferric hydroxides, iron silicates, iron phosphate, and in places iron carbonate, iron sulphate, or iron sulphide, and perhaps ferrihumates or basic ferric salts. The deposition is described in more detail on pages 75-82.

Very few localities are known in which deposits of ferric hydroxide are at present form-

¹ Van Bemmelen, J. M., Hoitsema, C., and Klobbie, E. A., *op. cit.*

² Dake, C. L., The formation and distribution of bog iron ore deposits: *Am. Inst. Min. Eng. Bull.*, July, 1915, pp. 1420-1436.

Shaler, N. S., General account of the fresh-water morasses of the United States: *U. S. Geol. Survey Tenth Ann. Rept.*, pt. 1, p. 305, 1890.

ing in marine marshes, and it is supposed that the salts in solution in sea water interfere with the precipitation of ferric hydroxide. However, locally on the east coast of Brazil there are small areas of Tertiary marine sediments in which beds of sandy limonite are abundant, and in Huelva Bay, on the south coast of Spain, limonite is being deposited at present from iron-bearing mine waters. The "red mud," a terrigenous oceanic deposit which occurs locally on the borders of the continents in place of the more widespread "blue mud," also contains considerable ferric hydroxide.³ Such deposits are forming along the coast of Brazil and in the Yellow Sea and are caused by abundant ocherous material being brought by the rivers to the ocean. Whether the precipitation of ferric hydroxide in these localities occurs in the waters of the rivers before they reach the sea or in the marine waters it is not possible to say.

DEPOSITS ORIGINALLY LAID DOWN MAINLY AS FERROUS CARBONATE.

Probably next in importance to ferric hydroxide as an original iron-bearing sediment is ferrous carbonate (FeCO_3). This compound has a theoretical composition of iron protoxide 62.1 per cent (Fe 48.2 per cent), and carbon dioxide 37.9 per cent.

Ores originally deposited mainly as iron carbonate include the clay ironstones and "black band" ores of the "Coal Measures" in both the United States and Europe, the oolitic siderite of the Jurassic in the Cleveland Hills and other parts of England, the cherty siderite and much of the hematite in the great pre-Cambrian iron-bearing beds of the Lake Superior district, and possibly a considerable part of the Jurassic oolitic limonite of northern France and southern Germany already described. Besides these ores there are large deposits of iron carbonate which have usually been regarded as originating by the replacement of limestone but many of which may be of primary origin. They include the beds of iron carbonate near Bilbao and in southern Spain, those of Erzberg in the Styrian Alps, and many others of minor importance.

Ironstone concretions and black-band ores of Carboniferous age occur in Ohio, Pennsyl-

³ Murray, J., and Hjort, J., The depth of the ocean, pp. 161 et seq., 1912.

vania, West Virginia, and elsewhere in the eastern United States and also in Great Britain and parts of Germany. In the eastern United States ores of this nature are found principally in strata of lower Pennsylvanian age (Pottsville and Allegheny), though scattered beds occur both above and below this horizon. The siderite beds, which vary somewhat in form and structure, are classed under four groups. The most important of these groups are the limestone ores, so called because they occur at or near the top of limestone strata. These beds range from a few inches to several feet in thickness and have a pockety character because of variations in thickness in short distances. The ore is dense and close-grained and has a gray or bluish-gray color. The second type of siderite ore is called block ore because it cleaves into blocks when mined. These beds are more persistent and of more uniform thickness than the beds of limestone ore but usually contain a considerable amount of sand as impurity. The third group includes the concretionary or kidney ores. The ironstone concretions, though not regularly bedded, occur at definite stratigraphic horizons as peculiar rounded masses scattered through zones of clay or shale 3 to 6 feet thick. The fourth group, the black band ores, consist of iron carbonate with more or less intermixed bituminous and earthy matter. They occur as layers a few inches in thickness, interbedded with carbonaceous shale in zones 10 to 15 feet in thickness. They are generally of higher grade than the other carbonate ores. Where beds of iron carbonate of any of these types are exposed to weathering they are altered to limonite for varying distances from the outcrop.

In Great Britain¹ three types of ironstone are mentioned, of which two are important—the black band ores, which are closely associated with coal seams, and the clay-band ores. Both types occur as beds or seams, lenslike in character and varying from a few inches to several feet in thickness. In central England there are a dozen or more important beds of black-band and clay-band ironstone in the Upper and Lower Coal Measures. The third type

¹ Louis, H., The iron resources of the United Kingdom of Great Britain and Ireland: The iron-ore resources of the world, Cong. géol. internat., Stockholm, p. 637, 1910.

of iron carbonate ore is the nodular ironstone that occurs in parts of Ireland. The average range in composition of iron carbonate ores of the Coal Measures of Great Britain is, iron 26 to 35 per cent, silica 10 to 20 per cent, and phosphorus 0.5 to 1 per cent.

These sedimentary iron carbonate beds are supposed to have been formed by chemical precipitation from iron-bearing waters under conditions where oxidation could not take place. The presence of coal beds and carbonaceous shales in association with the ore indicates the presence of abundant vegetation at the time of deposition. The precipitation of iron carbonate probably occurs in shallow lagoons or marshes along the sea coast, and is due to the absorption by plants of the excess of carbon dioxide which held it in solution. Some of it may have been precipitated as ferric hydroxide, which upon settling to the bottom and becoming mixed with decaying organic material, was reduced to ferrous carbonate. Kidney ores were not originally deposited as such, but represent later segregations of iron carbonate originally deposited with muds.

Oolitic siderite beds of Middle and Lower Jurassic age² are found in the Cleveland Hills and in Northamptonshire, Lincolnshire, and elsewhere in the eastern part of England. The principal beds in the Cleveland Hills occur in the Middle Lias (Lower Jurassic), which consists of about 125 feet of nearly horizontal shale, sandstone, and ironstone. Four beds of ironstone occur, and these range in thickness from 1½ to 12 feet and have a combined average thickness of 16 feet. The main seam, which ranges in thickness from 6 to 12 feet, consists of impure bluish oolitic siderite that averages iron 30 to 35 per cent, silica 6 to 12 per cent, and phosphorus pentoxide (P₂O₅) 1 to 3 per cent.

In Northamptonshire there is only one important bed of iron carbonate, which lies at the base of the Lower Oolite (Middle Jurassic). Its maximum thickness is 30 feet and its average thickness throughout the district is about 9 feet. It is siliceous siderite of gray, green, or blue color and is oxidized to sandy brown or yellow limonite where exposed to weathering. The siderite averages in compo-

² Louis, H., op. cit., p. 630.

sition from 30 to 35 per cent of iron, 12 to 14 per cent of silica, and 0.5 to 1 per cent of phosphorus.

The Lincolnshire ironstone bed occurs in the middle of the Lower Lias (Lower Jurassic). The thickness ranges from 10 to 25 feet, and averages about 12 feet. It lies nearly horizontal and where known consists mainly of calcareous brown hematite, having been oxidized by weathering agencies.

The oolitic siderites of England occur at approximately the same geologic horizons as the oolitic limonites of northern France and southern Germany, and this situation is somewhat suggestive of a similar origin. However, the Jurassic ores of England are mainly iron carbonate which is altered only at the surface to limonite, whereas the ores of France and Germany, where deep mining has taken place, do not seem to alter their character markedly with depth.

Probably the most extensive beds of iron carbonate known are those of the Lake Superior region already mentioned.¹ Though the iron-bearing formation as exposed at present in this region consists almost entirely of oxidized rocks, such as hematitic and limonitic chert and slate and iron ore, these rocks have been found to grade downward into cherty iron carbonate and silicate in a sufficient number of places to make the phenomenon appear fairly general.

The iron-bearing formation in the Lake Superior district is associated with basic volcanic rocks of Archean age and with metamorphosed sediments and volcanic rocks of lower, middle, and upper Huronian age. The beds are of great thickness and longitudinal extent, those of the upper Huronian being most widespread. Iron-bearing rocks of Archean

and lower Huronian age are found only in the Vermilion district in northern Minnesota, and iron-bearing rocks of middle Huronian age are found only in the Marquette district in northern Michigan. The upper Huronian iron-bearing formation, however, is found throughout most of the Lake Superior district.

The Archean iron-bearing formation is infolded in Keewatin greenstone, the relation between them indicating that the iron-bearing formation is the younger. In places, however, bands of the iron-bearing formation are interbedded with greenstone flows, indicating contemporaneous origin. The lower Huronian iron-bearing formation lies on conglomerate and is overlain by slate. It is of little importance. The middle Huronian iron-bearing formation is underlain by slate and overlain unconformably by conglomerate and quartzite. The upper Huronian iron-bearing formation is in general underlain by quartzite or graywacke and is overlain by a great thickness of quartzose, micaceous, chloritic, and carbonaceous slate with associated basic volcanic rocks. Extensive layers and lenses of iron-bearing formation entirely inclosed in the slate also occur in the upper Huronian, as in the Cuyuna and Crystal Falls districts.

The unaltered beds of the iron-bearing formation consist largely of cherty siderite, grayish white to gray or greenish gray in color. With the cherty siderite are interbedded, here and there, layers of sideritic slate of grayish or greenish color. The cherty siderite in detail consists of interlaminated dense, fine-grained chert and siderite, usually in very thin layers. The average composition of cherty siderite is, iron 25 per cent and silica 40 per cent.

In their general occurrence and their relation to the inclosing sediments the Lake Superior cherty and slaty siderite beds resemble other sedimentary iron carbonates. Because of this general similarity they were formerly regarded as having the same origin. More recently, however, on account of their great thickness and their conspicuous association with basic volcanic rocks, a hypothesis has been advanced that ascribes their origin, at least in part, to igneous agencies.² The iron is supposed to have been derived from basic igneous

¹ Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, 1911.

Irving, R. D., and Van Hise, C. R., The Penokee iron-bearing series of Michigan and Wisconsin: U. S. Geol. Survey Mon. 19, 1892.

Van Hise, C. R., Bayley, W. S., and Smyth, H. L., The Marquette iron-bearing district of Michigan: U. S. Geol. Survey Mon. 28, 1897.

Clements, J. M., Smyth, H. L., and Bayley, W. S., The Crystal Falls iron-bearing district of Michigan: U. S. Geol. Survey Mon. 36, 1899.

Clements, J. M., The Vermilion iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 45, 1903.

Bayley, W. S., The Menominee iron-bearing district of Michigan: U. S. Geol. Survey Mon. 46, 1904.

Harder, E. C., and Johnston, A. W., Preliminary report on the geology of east-central Minnesota including the Cuyuna iron-ore district: Minnesota Geol. Survey Bull. 15, 1918.

² Van Hise, C. R., and Leith, C. K., op. cit., pp. 499 et seq.

rocks, the eruption of which occurred at approximately the same time as the formation of the iron-bearing sediments. These eruptive rocks, which are rich in iron, are now represented by greenstones, which occur at various horizons from the Archean to the upper Huronian. The iron, according to Van Hise and Leith, may have been derived from the eruptives in three ways: (1) A part may have been derived through processes of weathering from lavas extruded on land areas. (2) Another part may have been given off by reactions between sea water and hot subaqueous eruptive rocks. (3) Most of it, however, probably came from hot magmatic solutions that were squeezed out of the lavas during solidification.

The precipitation of the iron carbonate and silicate from solution is believed to have been the result of simple chemical reactions between ferrous solutions, alkaline silicates, and carbon dioxide. The deposition of the iron-bearing sediments took place in marine waters, the ferruginous materials being distributed over large areas by currents. The conditions of deposition differed considerably in different parts of the district and in the different epochs, causing a great diversity in the occurrence of the iron-bearing sediments.

The iron carbonate deposits of Bilbao, in northern Spain, are scattered over an area about 30 kilometers in length and 2 to 8 kilometers in width.¹ They occur as irregular tabular masses in the upper part of a thick Cretaceous limestone overlain by calcareous shale. The masses are said to have a maximum thickness of 100 feet. Along the outcrop and for some distance in from the surface they are altered to hematite and limonite.

The iron carbonate is supposed to have been formed by the replacement of limestone by iron-bearing waters that percolated downward from the overlying shale. Their tabular shape and their occurrence at a definite horizon,

¹ Vidal, L. M., *Résumé des gisements de fer de l'Espagne: The iron ore resources of the world*, *Cong. géol. internat.*, Stockholm, p. 49, 1910.

Adamis, F. D., *Notes on the iron-ore deposits of Bilbao, northern Spain: Canadian Min. Inst. Jour.*, vol. 4, pp. 196-204, 1901.

Czyszkowski, M. S., *Exploration géologique de la région ferrifère de Bilbao-Somorrostro*, 1879.

John, *Die Eisenerzlagertstätten von Bilbao und ihrer Bedeutung für die zukünftige Eisenversorgung Grossbritanniens und Deutschlands: Glückauf*, vol. 46, pp. 2002-2013, 2045-2052, 1910.

however, suggest the possibility of their direct sedimentary origin.

The iron carbonate ore in northern Styria occurs in the so-called "graywacke zone," a complex of Paleozoic rocks lying between the granite, schist, and gneiss of the central part of the eastern Alps and the Triassic sediments of the northern part.² It is found over an area about 50 kilometers in length, east and west, as scattered deposits.³ The principal ore bed occurs at Erzberg and has a maximum thickness of 125 meters. Underlying it unconformably is the Sauberg limestone of Lower Devonian age, which consists of interlayered limestone and ankerite. The ankerite commonly passes over into siderite. Between the main ore bed and the limestone is a thin bed of dark sericitic schist. Overlying the ore bed unconformably are Lower Triassic rocks, which consist of first a conglomerate and then a grayish-green sandstone, which passes upward into red Werfener slates. The ore bed itself consists of dense fine-grained siderite and here and there contains more coarsely crystalline siderite along fissures and fractures. Local interbedded layers of shale and limestone are found in it.

The generally accepted hypothesis for the origin of this ore is that it was formed by the metasomatic replacement of limestone by iron brought in by percolating waters. The chief evidence cited is that small siderite deposits are irregularly distributed in the Sauberg limestone and that sulphides occur in the ore beds. However, the well-developed bedding of the iron carbonate and the fact that fragments of ore occur in the basal Triassic conglomerate above the ore bed would indicate that at least the principal ore bed is of sedimentary origin,² though the siderite in the Sauberg limestone may be a later replacement.

DEPOSITS ORIGINALLY LAID DOWN MAINLY AS IRON SILICATES.

Iron silicates of several kinds occur as sediments, the most widespread probably being glauconite. This mineral has no definite

² Singewald, J. T., jr., *The Erzberg in Styria: Eng. and Min. Jour.*, vol. 92, p. 22, 1911.

³ Uhlig, V., *Die Eisenerzvorräte Oesterreichs: The iron-ore resources of the world*, *Cong. géol. internat.*, Stockholm, p. 143, 1910.

chemical composition but is essentially a hydrous silicate of iron and potassium with some alumina. When pure it probably has approximately the composition represented by the formula $\text{Fe}''\text{KSi}_2\text{O}_6 \cdot \text{aq}$.¹ Alumina may replace a part of the iron. The iron is largely in the ferric form, but a variable though small amount of ferrous iron is always present. Glauconite is common in sedimentary rocks of many different ages but especially of the Cretaceous. It is usually more or less disseminated, but locally it forms pure beds and lenses.

Another important iron silicate found in sediments is the hydrous ferrous or ferros-ferric silicate, greenalite, which occurs along with cherty siderite as an original constituent locally in the Lake Superior iron-bearing formation.² Greenalite has the composition $\text{FeSiO}_3 \cdot n\text{H}_2\text{O}$ or $\text{Fe}''_2\text{Fe}'_3(\text{SiO}_4)_3 \cdot 3\text{H}_2\text{O}$. A part of the ferrous iron may be replaced by magnesium.

Besides these there are four other more or less related hydrous silicates of iron—thuringite, chamosite, berthierine, and bavalite—which are quite widespread. Only the first of these has a definite chemical formula, which is as follows: $8\text{FeO} \cdot 4(\text{AlFe})_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ (silica, 22.8 per cent; alumina, 17.2 per cent; ferric oxide, 13.5 per cent; ferrous oxide, 36.3 per cent; combined water, 10.2 per cent). The other three silicates differ from thuringite in that they contain a higher percentage of iron protoxide, only a small percentage of alumina, and little or no ferric iron.

Thuringite and chamosite are said to be the principal minerals in certain lenses of iron ore of Lower Silurian age in Bohemia and in Thuringia, Germany. Thuringite is olive-green in color and scaly, and chamosite is dark grayish green and either compact or oolitic. Chamosite is an abundant constituent of the Wabana iron ore of Newfoundland, in which it is associated with compact and oolitic hematite. Berthierine occurs in northern France as a constituent of the Jurassic oolitic ores, associated

with limonite, siderite, and other minerals.³ Bavalite is found in scattered deposits in Brittany, where it is interbedded with metamorphosed rocks.⁴

Glauconite occurs as dark-green granules widely distributed in sedimentary rocks and is also being deposited at the present time in many places on the ocean bottom. It forms a green granular sediment and is generally more or less mixed with other sedimentary material, especially fine sand and silt. The separate granules usually have the shape and size of foraminiferal shells, and many of them still have fragments of shells attached to the outside of them. Many also are distinct internal casts of Foraminifera. Very few glauconite grains exceed 1 millimeter in diameter.

At the present time glauconite is forming most abundantly in comparatively shallow waters and near the mud line surrounding the continental shores just beyond the limit of wave and current action.⁵ The depth at which it commonly forms ranges between 100 and 200 fathoms, but in some places it forms at depths as great as 900 fathoms. The entrance of large rivers interferes with its formation.

The common occurrence of glauconite inside shells of Foraminifera has led to the belief that these organisms are concerned in its formation. The dead organisms are supposed to drop to the bottom, whereupon the shells become filled with fine mud which in the presence of the sulphates in sea water is acted upon by the decaying organic matter in the shell.⁶ The iron supposed to be contained in the mud is reduced to sulphide, and this afterward oxidizes to ferric hydroxide, setting free sulphuric acid. The sulphuric acid acts upon the alumina, causing it to be removed in solution and at the same time colloidal silica is set free. The colloidal silica reacts upon the ferric hydroxide and in the presence of potassium salts, supposed to be derived from adjacent decomposing minerals, forms glauconite. Sediments with which glauconite is associated are said to contain invari-

¹ Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 517, 1916.

² Leith, C. K., The Mesabi iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 43, pp. 239 et seq., 1903.

Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, pp. 165, 521, 1911.

³ Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, pp. 516-518, 1916.

⁴ Dana, E. S., System of mineralogy, p. 658, 1914.

⁵ Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, p. 383, 1891.

⁶ Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 135, 1916.

Murray, J., and Renard, A. F., op. cit.

ably abundant orthoclase, muscovite, and other minerals from which potassium may have been derived. Other materials commonly found with glauconite in greensand are quartz, hornblende, magnetite, augite, zircon, garnet, and varying amounts of calcareous matter derived from shells.

Glauconite is disseminated in marine sediments of all geologic ages, forming strata which are known as greensand. In the Paleozoic rocks greensand is probably most abundant in Cambrian and Ordovician strata. Cambrian greensand is common in the north-central United States, where it is associated with siliceous limestone and fine calcareous sandstone beds. Ordovician ("Lower Silurian") greensand occurs in the Baltic provinces of Russia. In the Mesozoic rocks glauconite is particularly abundant in the Cretaceous formations both in Europe and North America. In England it occurs throughout the southern counties as well-defined beds generally interlayered with sand, marl, and clay. It is so abundant along certain zones that they are known as greensand horizons. The principal greensand horizons are in the upper part of the Lower Cretaceous and in the lower part of the Upper Cretaceous. The principal chalk beds occur above them in the Upper Cretaceous. In the Atlantic and Gulf coastal sediments of the United States greensand occurs in the Cretaceous and in the overlying Eocene deposits.¹ It is found more or less abundantly throughout the strata, being associated with coarse and fine sand, clay, and marl. Locally beds of pure glauconite occur.

Below is shown the range in composition of glauconite obtained from different localities.²

Range in composition of glauconite from different localities.

SiO ₂	40.00-53.61
Al ₂ O ₃	6.62-13.00
Fe ₂ O ₃	15.16-23.43
FeO.....	1.32-10.17
MgO.....	.95-2.97
CaO.....	.57-1.97
Ni ₂ O.....	.42-2.16
K ₂ O.....	3.49-9.54
H ₂ O.....	4.93-10.32

¹ Clark, W. B., Origin and classification of the greensands of New Jersey: Jour. Geology, vol. 2, pp. 161-177, 1894.

² Clarke, F. W., op. cit., p. 518.

The occurrence and character of the Lake Superior iron-bearing formation have already been described. Although cherty siderite is the principal rock in the unaltered iron-bearing formation, there are localities in the Penokee-Gogebic district where a considerable amount of greenalite occurs with it, along certain horizons, and other localities, as in the Mesabi district, where most of the formation is believed to have originally consisted of greenalite.³

Greenalite forms a dark-green, hard, compact rock with oolitic texture. The greenalite spherules have a maximum diameter of a millimeter or more and in shape they vary from spherical to oval or elliptical. They differ from spherules of Clinton hematite and Wabana ore in that they do not show concentric layering. They are usually homogeneous throughout and consist of green amorphous material which in places has a little siderite or chert or crystalline ferrous silicate intermixed. The matrix in which the spherules are embedded consists in places of chert and elsewhere of a light-greenish crystalline ferrous silicate, probably grünerite.

Greenalite rock may occur as beds of considerable thickness, but as a general rule it is thin bedded and is interlayered with thin beds of dense black ferruginous slate. Upon exposure to surface weathering the greenalite rock is altered to a peculiar granular, speckled, hematitic chert to which the name taconite has been given.

The following shows the range in composition of greenalite from the Mesabi district, Minn.⁴

Range in composition of greenalite from Mesabi district, Minn.

SiO ₂	46.12-61.90
Al ₂ O ₃37-1.09
Fe ₂ O ₃	5.01-15.00
FeO.....	10.23-30.93
MgO.....	2.33-5.35
CaO.....	.00-.28
H ₂ O.....	.75-2.50
H ₂ O+.....	4.17-6.41

The chamosite ores of Bohemia are found in the Brdagebirge, the principal deposits occur-

³ Leith, C. K., The Mesabi iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 43, pp. 101 et seq., 1903.

⁴ Idem, p. 108.

ring in the region of Nučitz.¹ Beds of this ore are located at the base and near the top of a certain horizon in the Silurian known as horizon "D."

The base of horizon "D" consists of graywacke and slate with sheets of diabase and diabase tuff and layers of iron ore which seem to be genetically related to the diabase. The iron ore is mainly oolitic hematite, but oolitic ferrous silicate (mainly chamosite) is abundantly associated with it. It occurs in lenticular beds which range from a thin film to 18 meters in thickness and is widely distributed. Near the surface the chamosite is altered to limonite.

In the upper part of horizon "D" also several zones containing beds of iron ore occur. The rocks consist mainly of graywacke and graywacke slate, the former containing light-colored quartzite layers. The ore beds are associated with the slates. They are lenticular in shape and in places, as in the vicinity of Nučitz, reach a maximum thickness of 22 meters. The ore is oolitic dark-green or bluish-green ferrous silicate with a more or less sideritic or slaty matrix. At the surface it is altered to limonite. The beds are lens-shaped and pinch out horizontally.

Near Schmiedefeld, in the Thuringian Forest, widely distributed beds of ferrous silicate occur in rocks of Lower Silurian age. They extend over many square miles and are so constant that they are taken as horizon markers. The lower bed, which is unimportant, is found just above a Cambrian quartzite and grayish-green argillaceous schist and is overlain by a few meters of micaceous quartzite schist. This is overlain by the main ore bed, 15 to 20 meters thick, above which are Lower Silurian clay slates.² The lower bed is only a few meters thick and locally is represented by two layers. It contains much hematite, usually oolitic. The upper bed is extensive and consists of chamosite and thuringite, the former being predominant. The chamosite is silver-gray to black in color and shows oolitic texture. At

the surface it alters to limonite. The thuringite is olive to dark green in color and fine scaly, dense, or oolitic in texture. A large quantity of iron carbonate occurs with the ferrous silicates.

The association of chamosite with hematite in the Newfoundland oolitic iron-ore beds has been mentioned on page 50.³ It is found in the spherules and in the interstices between the spherules composing the ore beds and occurs also in the matrix of the clastic sediments that inclose the ore beds. In the leaner portions of the ore layers chamosite is abundant in the spherules and either occurs concentrically interlayered with hematite or forms entire spherules itself. In this form it is usually dense and amorphous. In the matrix between the spherules and in the inclosing clastic rocks the chamosite is nonoolitic and shows a microcrystalline or finely crystalline texture. Occasionally it forms large tabular crystals.

Hayes⁴ gives the following recalculated average analyses of Wabana chamosite:

Recalculated average analyses of Wabana chamosite from Newfoundland.

SiO ₂	24.87	23.23	25.64
Al ₂ O ₃	19.45	22.85	19.75
Fe ₂ O ₃	6.66	1.00
FeO.....	34.52	38.99	39.74
MgO.....	3.34	3.25	2.98
H ₂ O.....	11.16	10.68	11.89

The color of chamosite varies from light to deep green and occasionally has a grayish tint. Tubes, supposed to be those of boring algae, are abundant in the ore beds. Where these tubes penetrate chamosite they are usually lined with a coating of hematite, which is believed to have resulted from the oxidation of the chamosite by the action of the algae.

DEPOSITS ORIGINALLY LAID DOWN MAINLY AS IRON SULPHIDE.

Iron disulphide (FeS₂; iron, 46.6 per cent; sulphur, 53.4 per cent) is abundant in sedimentary rocks, occurring both as disseminated specks and nodules and as beds and lenses. It is generally present as pyrite, but in some recent sediments the black iron disulphide, melnikowite, has been found also. Marcasite

¹ Beyschlag, F., Krusch, P., and Vogt, J. H. L., Die Lagerstätten der nutzbaren Mineralien und Gesteine, Band 2, pp. 528 et seq., 1913.

Uhlig, V., Die Eisenerzvorräte Oesterreichs: The iron-ore resources of the world, Cong. géol. internat., Stockholm, pp. 148 et seq., 1910.

² Beyschlag, F., Krusch, P., and Vogt, J. H. L., op. cit., Band 2, pp. 531 et seq.

³ Hayes, A. O., op. cit., p. 26.

⁴ Idem, p. 62.

more commonly occurs as a vein mineral. Ferrous sulphide (FeS) forms a constituent in some modern lacustrine and marine sediments.

Lenses of crystalline pyrite, of probable sedimentary origin but more or less recrystallized, occur interbedded with metamorphic rocks such as slate, schist, and quartzite, in Spain, France, Italy, Austria, Norway, and many other parts of the world. Beds of oolitic pyrite occur in the Ordovician rocks of Newfoundland, and in the Devonian rocks of Westphalia, Germany. Melnikowite has recently been described as occurring in Miocene clays in southeastern Russia.

More interesting probably than these, however, are the deposits of hydrous ferrous sulphide which characterize the black mud forming at present in the bottom of the Black Sea and neighboring limans and in bays on the island of Oesel, Gulf of Riga, and elsewhere. Iron sulphide, some of which is probably in the ferrous form, also characterizes the "blue mud" deposited locally in the ocean bottom.

In the Huelva region in southern Spain¹ lenses of pyrite occur in sedimentary rocks, mainly clay slate with some graywacke and limestone belonging to the Culm (Lower Carboniferous). The rocks are highly folded and faulted and have steep dips. The lenses have a maximum length of more than 1,100 meters and a maximum width of 180 meters. They occur at different horizons in the Culm and most of them are said to be closely associated with intrusive sheets of porphyry. On account of this association the pyrite lenses are usually described as being epigenetic in origin and as having been formed by hot solutions from the porphyry magma. Their interlayering with the sediments, however, and close concordance with them in strike and dip make a sedimentary origin not impossible. The Huelva pyrite lenses are important copper bearers and contain also some lead, zinc, arsenic, and silver, the occurrence of which is taken as additional evidence for their epigenetic origin.

At Agordo, in the Venetian Alps of northern Italy,² lenses of pyrite, similar to those in the Huelva region, occur interlayered with pre-Carboniferous metamorphosed argillaceous

schist, usually not far from masses of intrusive quartz porphyry. The lenses have a maximum length of 550 meters and a maximum width of 200 meters and show fine-grained texture and distinct layering. In metal content they resemble the Huelva pyrite lenses. Their origin must be explained along similar lines.

In the Carpathians at Szomolnok³ pyrite lenses occur in folded and metamorphosed sediments of the Culm, consisting of graphitic and chloritic schist and quartzitic sandstone. Intrusive diorite and porphyry occur in the schist. The pyrite lenses are found in distinct layers corresponding in structure with the metamorphosed sediments. However, they are usually explained as being of epigenetic origin, resulting from the diorite intrusions.

At Rammelsberg, near Goslar,⁴ on the northwestern border of the Harz Mountains in central Germany, a lens of pyrite occurs interlayered between two slate beds of Middle Devonian age, which stratigraphically overlie Lower Devonian coarse sandstone. The beds are folded into an overturned anticline of which the sandstone forms the center. The pyrite lens occurs on the lower limb of the anticline and has been folded with the inclosing slates, following the contortions of the slates closely. It generally ranges in thickness from 0.5 meter to 3 meters, and shows marked banding parallel to the lens, which in part is due to included thin layers of slate. The principal minerals are pyrite, zinc blende, chalcopryrite, galena, and arsenopyrite in a gangue of barite.

It is generally believed that the Rammelsberg pyrite deposit is a contact vein formed by magmatic solutions. Recently, however, fossils of *Goniatites* have been found in the pyrite bed, which has led to its reclassification by some authors as a sedimentary deposit.⁵

The oolitic pyrite bed in Westphalia occurs at Meggen on the Lenne.⁶ By some authors it is considered as of sedimentary origin and by others as a later introduction. The bed consists of pyrite and barite and averages about 10 feet in thickness. The pyrite occurs in fine

¹ Idem, pp. 329-331.

² Lindgren, Waldemar, Mineral deposits, pp. 606-610, 1913.

³ Beyschlag, F., Krusch, P., and Vogt, J. H. L., Die Lagerstätten der nutzbaren Mineralien und Gesteine, Band 1, pp. 311-323, 1910.

⁴ Idem, pp. 326-328.

⁵ Beyschlag, F., Krusch, P., and Vogt, J. H. L., op. cit., Band 2, pp. 630-637, 1913.

⁶ Stelzner, A. W., and Bergeat, A., Die Erzlagerstätten, Band 1, pp. 339-342, 1904.

layers, distinctly stratified and in places oolitic. Underlying it are graywacke slates and overlying it is a bed of dense nodular limestone, in part dolomitic, carrying inclusions of iron pyrite. Above the limestone are clay slates. The rocks are of Devonian age.

The oolitic pyrite beds which are associated with the Wabana hematite beds of Newfoundland are probably the most typical sedimentary pyrite beds known.¹ The pyrite-bearing zone is found just above one of the principal hematite beds (the Dominion bed), being separated from it by 1 to 10 feet of shale or sandstone. There are one to three beds of pyrite ranging in thickness from an inch to a foot or more and separated by fissile black shale. The beds thicken, thin, and die out within short distances, but the zone is persistent. Shale occurs above the pyrite beds. The pyrite nearly all has a distinct oolitic texture and together with the inclosing shale contains abundant graptolites and some brachiopods, showing its marine origin. Associated with the pyrite spherules are nodules and small irregular bodies of pyrite. Quartz occurs both as fragments and as a matrix between pyrite spherules.

In the southeastern part of Russia near Nowo-Usensk in the Government of Samara, clays containing iron sulphide were encountered in drilling natural gas wells.² The succession of strata passed through in these borings is as follows:

Section penetrated in borings near Nowo-Usensk, Samara, Russia.

	Feet.
Post-Tertiary:	
Brown clay	150
Clayey sand containing magnesium sulphate bearing water	35
Sandy clay	5
Miocene:	
Brown clay, in part sandy, with layers of gas-bearing sand	115

The Miocene brown clay is interesting in that it carries a black iron sulphide, melnikowite, which occurs finely disseminated through the clay, as well as in streaks and thin layers.

¹ Hayes, A. O., Wabana iron ore of Newfoundland: Canada Geol. Survey Mem. 78, p. 15, 1915.

² Doss, Bruno, Ueber die Natur und Zusammensetzung des in Miocenen Tonen des Gouvernements Samara auftretenden Schwefeleisens: Neues Jahrb., Beilage Band 33, pp. 662-713, 1912; Melnikowit, ein neues Eisenbisulphid und seine Bedeutung für die Genesis der Kieslagerstätten: Zeitschr. prakt. Geologie, Jahrg. 20, pp. 453-483, 1912.

Particles of it are commonly attached to fragments of fossil mollusks. As obtained from the bore holes the melnikowite was mainly in the form of dull, dense, compact fragments, generally with concentric structure. Associated with these fragments were found spherical, oval, grapelike, or kidney-shaped forms, the largest of which were 1 millimeter in diameter. The microscopic texture of the melnikowite is finely crystalline and the color black. Analysis has shown it to be iron disulphide (FeS_2), but it differs from marcasite and pyrite in being strongly magnetic and in various other physical properties.

The particles of melnikowite are somewhat impure, containing quartz and calcite grains, clay particles, or fine muscovite flakes. Much of the melnikowite also has associated with it particles and grains of finely crystalline pyrite, whose occurrence and gradation into melnikowite suggest strongly that the pyrite is a stable form into which the melnikowite is altering.

Black muds containing abundant organic material and impregnated with colloidal hydrous ferrous sulphide occur in many localities both in inclosed seas and in gulfs and bays connected with the open ocean.³ Among the best-known localities are the eastern Mediterranean Sea, Black Sea, Sea of Azov, Caspian Sea, Dead Sea, Aral Sea, and other inclosed bodies of water in southeastern Europe and western Asia. Similar muds, however, also occur around Oesel Island and elsewhere in the Gulf of Riga, at several localities in the southern Baltic Sea, around the mouths of the Elbe and the Weser, and along the Netherlands coast in the North Sea, as well as locally on the coast of Scotland. Many sulphur springs throughout Europe contain black muds that carry ferrous sulphide, and the "blue mud" of the ocean bottom along the edges of the continents is also characterized by iron sulphide, part of which is doubtless in the ferrous form.

The "blue mud" of the ocean bottom is blue or slate-colored, but the upper layer in contact with the water is oxidized to red or brown. The blue color is due to the presence of organic matter and sulphide of iron in a fine state of division. It has the smell of sulphureted hydrogen. The depth at which it occurs ranges from 125 to 2,800 fathoms. "Blue mud" con-

³ Doss, Bruno, Neues Jahrb., Beilage Band 33, pp. 689 et seq., 1912. (Numerous references cited.)

tains, besides terrigenous clastic material, abundant remains of Foraminifera, Radiolaria, diatoms, sponge spicules, and fragments of mollusk and echinoderm shells.

The "blue muds" surround nearly all the continents and occur in inclosed seas like the Mediterranean, and even in the Arctic Ocean. They occupy the largest area of the terrigenous oceanic deposits.¹

The following table shows the range in composition of the principal constituents of blue mud:

Range in composition of the principal constituents of blue mud.

SiO ₂	59.54-64.20
Al ₂ O ₃	13.55-19.42
Fe ₂ O ₃	7.15-11.23
Loss on ignition ²	4.92- 6.24

Small amounts of soda, potash, lime, and magnesia are also present.

Recent studies of muds from the bottom of the Black Sea and neighboring limans³ as well as from other inclosed seas of southeastern Russia, have shown that they contain an abundance of ferrous sulphide. As indicated by the dredgings two kinds of mud exist in the Black Sea at depths of 300 to 717 fathoms. One type is a sticky black mud containing hydrous ferrous sulphide (FeS·nH₂O) presumably as a gel. The other type is a less dense blue mud containing pelagic diatoms, a smaller quantity of ferrous sulphide, and concretions of iron disulphide. The blue mud is believed to underlie the black mud, and its existence proves that iron disulphide undoubtedly occurs at least locally in unconsolidated ferrous sulphide bearing muds.

In some of the limans and shallow lakes of southern Russia ferrous sulphide generally occurs as an intermixed paste or as lumps and concretions in black mud, or as coatings of other substances, but it is also found with moist black shore muds and sands.

The limans bordering the Black Sea are shallow, salty lagoons separated from the open

water by low, narrow bars.⁴ The bottoms of these lagoons are covered with a tough, black mud which owes its color to an abundance of ferrous sulphide. The mud is plastic and doughy, has a strong odor of hydrogen sulphide, and gives an alkaline reaction. It consists of clay particles, fine sand, and shells, which are impregnated with and held together by colloidal, hydrated ferrous sulphide and abundantly mixed with decomposing organic material derived from both plants and animals. The liman mud is used for healing purposes on account of its content of hydrogen sulphide, but when exposed to the air the ferrous sulphide oxidizes and the mud takes on a gray color. However, upon being reimmersed in brine it is again reduced, owing to the action of reducing bacteria, which are present abundantly.

Doss's explanation⁵ of the origin of sedimentary deposits of iron sulphide is as follows: Iron is dissolved from iron-bearing minerals and carried in solution as soluble ferrous carbonate (Fe(CO₃)₂) by surface waters to inclosed bays or lagoons in which decaying organic matter is abundant. Here the iron is precipitated, either directly as black colloidal hydrated ferrous sulphide by reaction with hydrogen sulphide liberated by bacteria from the decaying organic matter, or as ferric hydroxide by iron bacteria. Ferric hydroxide under reducing conditions and in the presence of hydrogen sulphide is changed to hydrated ferrous sulphide. By loss of water and the addition of sulphur, which occurs as free sulphur in the mud, the hydrated ferrous sulphide is changed to melnikowite (FeS₂). The melnikowite alters gradually to pyrite and the inclosing mud becomes hardened and cemented to clay and shale. Where iron sulphide was originally mixed with the mud it was later disseminated through the resulting rocks, but where more or less pure deposits occurred they resulted in the formation of beds and lenses of pyrite. Later metamorphism may cause the recrystallization of the pyrite lenses and alteration of the inclosing rocks to slate and schist. Thus all stages occur between the black ferrous sulphide muds forming in many inclosed basins and the recrystal-

¹ Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, pp. 229 et seq., 1891.

Murray, J., and Hjort, J., *The depth of the ocean*, pp. 161 et seq., 1912.

² Organic matter, sulphur, etc.

³ Andrussow, N., *La mer noire: Cong. géol. internat.*, Guide des exc., 7^e sess., Excursion 29, p. 7, 1897, cited by Hayes, A. O., op. cit., p. 90.

⁴ Omellanski, W., *Der Kreislauf des Schwefels*, in F. Laffar's *Handbuch der technischen Mycologie*, Band 3, pp. 222-223, 1904-1906.

⁵ Doss, Bruno, *Zeitschr. prakt. Geologie*, Jahrg. 20, pp. 460-461, 1912.

lized lenses of pyrite interbedded with slates and schists.

Many of the pyrite lenses in schists and other metamorphic rock, such as the deposits at Huelva and those of Agordo and Szomolnok, have been fairly definitely shown to be related, at least in part, to igneous intrusions. The igneous rocks may have caused the formation of the entire deposits or they may simply have caused the recrystallization of original lenses of iron sulphide and the introduction into them of their content of silver, lead, zinc, copper, and other metals. It must be remembered that deposits of iron sulphide are forming abundantly at the present time in association with argillaceous sediments, which upon metamorphism would yield just such rocks as those in which we find the lenses of pyrite containing copper, lead, and zinc sulphides. The facts that these lenses are distinctly conformable to the bedding of the rocks in which they occur, that many of them exhibit banding parallel to the bedding of the associated rocks, and also that many are far removed from igneous intrusions, are strong points in favor of their original sedimentary origin. The reason why only a few deposits of iron sulphide that are clearly of sedimentary origin, such as those of Russia and Newfoundland, have been described in the literature can perhaps be sought in their relative unimportance commercially, which is due to their lack of precious or semi-precious metals.

FORMATION OF SEDIMENTARY IRON-BEARING DEPOSITS.

DEPOSITION OF IRON BY MECHANICAL PROCESSES.

There are certain iron-ore deposits which have been formed almost entirely by mechanical processes. To this type belong the black sands, which consist of magnetite or hematite sand mixed with particles of other hard, heavy minerals, such as garnet, zircon, ilmenite, rutile, quartz, and chromite.

The processes which are most active in the formation of black sands are disintegration and transportation. The rocks that contain disseminated iron minerals upon being subjected to disintegration without much decomposition release the separate mineral particles, which are then carried away by streams and

finally sorted by currents and waves according to their density. Black sands may form on the seashore or on the shores of rivers or lakes. Their specific gravity prevents the particles from being carried very far from shore, though moderately swift flowing streams may carry them some distance, along with other coarse clastic material, and deposit them in their deltas.

In general black sand deposits are very impure on account of the admixture of non iron-bearing clastic particles. In many places also they are very high in titanium owing to the presence of abundant ilmenite. Deposits of magnetite sands are forming at the present time along the sea coast and along the larger rivers in Washington, Oregon, and California. Deposits of hematite sand are forming along streams in Minas Geraes, Brazil, the materials being derived from the disintegration of the extensive beds of hematite-bearing quartzite that occur in that region. Though most of the known black sand deposits are of recent origin, older beds of a similar character are met with locally, such as the black sand beds in Upper Cretaceous rocks in northwestern Montana.¹

Other iron-ore deposits that are formed largely by mechanical processes are the detrital talus deposits, consisting of blocks and fragments of ore, which commonly lie on slopes below outcropping cliffs of iron ore. They are generally designated by the name of rubble ore. Such deposits may become cemented by the filling of the spaces between the fragments and thus result in clastic breccias. To this type belong the "canga" ores of Brazil, which are derived from and associated with the bedded hematite. Some fragmental varieties of laterite which occur in India in association with the Dhárwar iron-bearing sediments may also be classed with this type.

DEPOSITION OF IRON BY CHEMICAL PROCESSES.

FORMATION OF DEPOSITS OF FERRIC HYDROXIDE.

Ferric hydroxides may be precipitated either from organic or inorganic iron solutions, the reaction being accompanied by hydrolysis in ferric compounds and by oxidation with hy-

¹Stebinger, Eugene, Titaniferous magnetite beds on the Blackfoot Indian Reservation, Mont.: U. S. Geol. Survey Bull. 540, pp. 329-337, 1914.

drolisis in ferrous compounds. The ferric hydroxides form a gradational series in which iron, in the form of Fe_2O_3 , is associated with water. This water (meaning "water above 105°C .") ranges from a few per cent, as in hydrated hematite, to an unknown upper limit, perhaps more than 30 per cent. These amounts of "water" probably range through all the possible varieties of combinations, as with most other hydrated oxides, from hydroxyl groups to firmly held hygroscopic moisture. In general the series of ferric hydroxides is probably analogous to the various hydrated forms of silica. A large number of ferric hydroxides have been prepared or are found in nature as minerals, but the exact composition of many of these is uncertain.¹

Much work was done on the constitution of ferric hydroxides during the nineteenth century, of which the most important was that of Muck,² Tomassi,³ van Bemmelen,⁴ and Ruff.⁵ Muck first and Tommasi later, by chemical precipitation from iron solutions, obtained two different classes of ferric hydroxides, the red hydroxides and the yellow hydroxides. The red hydroxides are obtained by precipitation from ferric salts with alkalis, whereas the yellow hydroxides are obtained by the oxidation of moist ferrous hydroxide or of ferrous carbonate. By drying freshly prepared precipitates of ferric hydroxide at different temperatures Tommasi obtained the following compounds, which he regarded as definite hydroxides:

Yellow hydroxides:

- $\text{Fe}_2(\text{OH})_6$Forms below 70°C .
 $\text{Fe}_2(\text{OH})_4\text{O}$Forms between 70° and 105°C .
 $\text{Fe}_2(\text{OH})_2\text{O}_2$Forms between 105° and 150°C .

Red hydroxides:

- $\text{Fe}_2(\text{OH})_6$Not obtained.
 $\text{Fe}_2(\text{OH})_4\text{O}$Forms below 50°C .
 $\text{Fe}_2(\text{OH})_2\text{O}_2$Forms between 50° and 92°C .

Upon further heating of the red hydroxides a brown anhydrous ferric oxide having a

specific gravity of 5.1 was produced, but the anhydrous ferric oxide resulting from heating the yellow hydroxides was reddish yellow in color and had a specific gravity of 3.95. Tommasi concluded from these data that there exist two distinct series of ferric hydroxides with different properties.

Van Bemmelen in his experiments with colloids showed that red ferric hydroxides are really colloidal substances without any definite chemical composition, the amount of water retained by them being dependent on the aqueous vapor pressure in the atmosphere, with which they are in equilibrium. Only at high temperatures are they converted to anhydrous ferric oxide. He believed that the red hydroxides do not differ in any essential way from the yellow hydroxides and that the latter also are colloids in perhaps a little more stable and concentrated form.

If these conclusions are correct it is difficult to understand under what conditions various stable ferric hydroxides found in nature are formed, and further how deposits of anhydrous or slightly hydrated ferric oxide are formed so abundantly under natural conditions when in the laboratory high temperatures are necessary for their formation.

Realizing the discrepancies between the conclusions of Tommasi and Van Bemmelen, Ruff took up the study of the ferric hydroxides. His first experiments were performed with red colloidal ferric hydroxide under ordinary conditions of pressure but with varying temperature. They confirmed more or less the work of Van Bemmelen. He found also that the freshly precipitated red ferric hydroxide, when allowed to stand for several years at ordinary temperatures, gradually lost water but before becoming entirely anhydrous began to take on water again and after 10 or 15 years changed to the normal stable ferric hydroxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

The second series of experiments of Ruff was performed with ferric hydroxide under varying pressures of about 5,000 atmospheres. By raising the temperature under these conditions of pressure he found that the colloidal red ferric hydroxides became converted into definite hydroxides all found in nature, the particular hydroxide formed depending on the temperatures. Between 30° and 42.5°C . the colloid

¹ Roscoe, H. E., and Schorlemmer, C., A treatise on chemistry, vol. 2, pp. 1197 et seq., 1913.

² Muck, Zeltschr. Chemie, 2d ser., vol. 4, p. 41, 1868. Cited by Roscoe, H. E., and Schorlemmer, C., op. cit., p. 1222.

³ Tommasi, D., Ricerche sulle formole di costituzione dei composti ferrici; Parte prima, Idrati ferrici, Florence, 1879. Also see Deutsche chem. Gesell. Ber., vol. 12, pp. 1929, 2334, 1879.

⁴ Van Bemmelen, J. M., Rec. trav. chim., vol. 7, pp. 36-119, 1889.

⁵ Ruff, O., Ueber das Eisenoxyd und sein Hydrate: Deutsche chem. Gesell. Ber., vol. 34, pp. 3417 et seq., 1901.

changed to a yellow granular powder having the water content and specific gravity of limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), between 42.5° and 62.5° C. it became yellowish red and took on the properties of goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and above 62.5° C. it became brick-red and had the composition of turgite ($2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Ruff did not obtain the anhydrous oxide, hematite, at high pressures below a temperature of 150° C. The yellow hydroxide, when treated under similar conditions with a range of temperature from 40° to 70° C., behaved like a stable compound and did not alter in content of water. The suggestion is made that this material may be represented in nature by the mineral xanthosiderite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$).

Ruff concludes from these data (1) that red colloidal ferric hydroxide under ordinary conditions is a colloid of indefinite composition, but that under high pressure and rising temperature it may change in a short time to various definite hydroxides; (2) that yellow ferric hydroxide is very probably a definite chemical compound that contains various amounts of adsorbed water; (3) that under ordinary conditions of temperature and pressure the red colloidal ferric hydroxide is slowly dehydrated and changed to anhydrous ferric oxide, but at the same time water is taken up by the anhydrous oxide and a change occurs to the stable ferric hydroxide, limonite; (4) that pure anhydrous ferric oxide does not form from ferric hydroxides except under exceptional conditions of temperature or pressure.

Nicolardot,¹ by whom the most recent work has been done on ferric hydroxides, has come to the conclusion that six modifications of ferric hydroxide exist which are all polymers of the simplest hydroxide. They all differ in chemical and physical properties and in the content of water. Two of the hydroxides, $(\text{Fe}_2\text{O}_3)_1(\text{H}_2\text{O})_{1.5-2}$ and $(\text{Fe}_2\text{O}_3)_1(\text{H}_2\text{O})_{1-1.5}$, are brown and are derived from the normal sesquioxide Fe_2O_3 , whereas the other four, all opalescent and yellow in color, are derived from the two anhydrides of $\text{Fe}_2(\text{OH})_6$ — $\text{Fe}_2\text{O}(\text{OH})_4$ and $\text{Fe}_2\text{O}_2(\text{OH})_2$. Each of these substances forms a series of hydroxides with variable water content, the hydroxides of one

series being transformed into the hydroxides of another series by the elimination of water.

Hydroxides of iron of various kinds, therefore, may be formed by precipitation with alkalis or by simple oxidation and hydrolysis from different iron compounds. Thus, solutions of ferric chloride and ferric nitrate, when treated with sodium, potassium, or ammonium hydroxides, give precipitates of red colloidal ferric hydroxide. Solutions of ferrous salts when treated with alkaline hydroxides give precipitates of light bluish-green ferrous hydroxide, which upon oxidation changes to yellow ferric hydroxide. Yellow ferric hydroxide is also formed by oxidation and hydration of ferrous carbonate and in the rusting of metallic iron. Freshly precipitated iron rust consists chiefly of ferric hydroxide but usually contains considerable quantities of ferrous hydroxide and ferrous carbonate.² When dried and exposed to atmospheric oxidation it soon loses its ferrous iron and consists entirely of ferric hydroxide, with the approximate composition $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

In some solutions of iron salts, such as ferrous or ferric sulphate, as well as certain iron salts of organic acids, iron may be precipitated by oxidation and hydrolysis (for the ferrous salts) or by hydrolysis alone (for the ferric salts) not as hydroxide, but in the form of basic salts. When a ferric sulphate solution is treated with an excess of alkali, as ammonium hydroxide, ferric hydroxide is precipitated. When, however, the precipitation is incomplete various basic ferric sulphates are formed. The same is true when a solution of ferric sulphate is boiled or when a solution of ferrous sulphate is allowed to oxidize in the air. Among the common basic ferric sulphates thus formed which are said to exist is $\text{FeSO}_4(\text{OH}) \cdot 7\text{H}_2\text{O}$, which is decomposed by water to form the insoluble salt $\text{Fe}_3\text{SO}_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$. Several of the basic sulphates occur as minerals, being formed by the oxidation of iron sulphides.³ Among these are vitriol ocher ($\text{FeSO}_4(\text{OH})_4 \cdot 2\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$), copiapite ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 \cdot 10\text{H}_2\text{O}$), and fibroferrite ($2\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 \cdot \text{Fe}_2\text{SO}_4(\text{OH})_4 \cdot 24\text{H}_2\text{O}$).

¹ Nicolardot, M. P., Recherches sur le sesquioxyde de fer: Annales chimie et physique, 8th ser., vol. 6, p. 334-393, 1905.

² Moody, G. T., The rusting of iron: Chem. Soc. Jour., vol. 89, pp. 720 et seq., 1906.

³ Roscoe, H. E., and Schorlemmer, C., op. cit., pp. 1214 et seq.

Pickering,¹ who has done some work on the constitution of basic ferric sulphate, states that only one basic ferric sulphate exists and that it has the formula $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, in which x ranges from 8 to 40. The molecular weight ranges from 1,341.34 to 1,916.10, according to the amount of water present.

The reason for these varying results is probably to be found in the fact that the precipitate which forms varies with the nature of the solution, the temperature, and the manner of precipitation. It probably consists of a mixture of one or more of the possible ferric hydroxides with one or more basic ferric sulphates and the proportion of each present varies under different conditions of precipitation.²

Mixed precipitates of all degrees of oxidation and hydration probably form under different conditions, the degree of complexity varying with the treatment. Thus simple boiling would result in the formation of a larger proportion of basic ferric sulphates, and treatment with alkalis would result in the formation of larger amounts of ferric hydroxides.

The further hydrolysis of basic ferric sulphates results in the formation of the stable ferric hydroxide, limonite.

Several of the iron salts of organic acids, such as iron acetate, iron oxalate, and iron lactate, give precipitates of flocculent basic salts. The precipitation results from simple oxidation, heating, or treatment with alkalis.

A solution of iron acetate, when treated with alkalis or when evaporated or boiled, gives a red flocculent precipitate, consisting probably of a mixture of ferric hydroxides and basic ferric acetates. The amount of ferric hydroxide present in the precipitate increases with temperature, with the strength of the precipitant, and with the time allowed for precipitation. When a solution of iron acetate is boiled in the presence of alkaline acetates, ferric hydroxide rather than basic ferric acetate is said to be precipitated.³ A number of basic ferric acetates have been described, among which are $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)(\text{OH})_2$, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2\text{OH}$, and

$\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_4 + 2\text{Fe}_2\text{O}_3$.⁴ Herz⁵ found that the basic ferric acetate, $\text{FeC}_2\text{H}_3\text{O}_2(\text{OH})_2$, is precipitated from solutions of pure ferric acetate ($\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$) when heated for 10 hours or more at a temperature of 44° C., and also from impure ferric acetate solutions when allowed to stand at ordinary temperature or when boiled for a short time. Under the latter conditions no precipitation occurred from pure solutions. This basic ferric acetate is a fine yellow colloidal precipitate. Often ferric hydroxide ($\text{Fe}(\text{OH})_3$) is said to form with it as small, brown, shining crystals.

A solution of iron oxalate upon treatment with alkalis also gives a brownish-red flocculent precipitate, which is probably a mixture of ferric hydroxides and basic ferric oxalates. An iron oxalate solution when boiled leaves a yellowish-brown salt with the composition $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 18\text{Fe}(\text{OH})_3$, but when the solution is only heated to 100° C. the precipitate is $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Fe}(\text{OH})_3 + 4\text{H}_2\text{O}$, showing an increase of $\text{Fe}(\text{OH})_3$ with the increase in temperature.⁶

Iron lactate upon treatment with alkalis gives a flocculent brownish-black precipitate, doubtless a mixture of ferric hydroxides and basic ferric lactates.

Comparatively little work has been done heretofore on the constitution of basic ferric compounds precipitated from solutions of organic iron salts and very little definite information is available with regard to these compounds. In general the precipitates formed are probably of indefinite composition, due to the variable content of water and to the varying amounts of ferric hydroxides mixed with them. As in the precipitation from solutions of ferrous and ferric sulphate the precipitates which form in solutions of organic iron salts vary in composition according to the conditions of precipitation.² If precipitation takes place through the agency of a strong alkali, such as sodium hydroxide (NaOH), more fer-

¹ Pickering, S. W., On the constitution of molecular compounds; the molecular weight of basic ferric sulphate: *Chem. Soc. Jour.*, vol. 43, pp. 182 et seq., 1883.

² Hunter, W. H. (Department of Chemistry, University of Minnesota), personal communication.

³ Bellstein, F., *Handbuch der organischen Chemie*, Auflage 3, Band 1, pp. 405-406, 1893.

⁴ Scheurer-Kestner, M. A., Sur quelques nouvelles combinaisons du fer et sur l'atomicité de cet élément: *Soc. chim. Paris Bull.*, vol. 5, pp. 342-352, 1863; Mémoire sur une nouvelle classe de sels de fer, et sur la nature hexatomique du ferricum: *Annales chimie et physique*, 3d ser., vol. 63, pp. 422-447, 1861.

⁵ Herz, W., Ueber den Verlauf der Zersetzung des Ferracetats: *Zeitschr. anorg. Chemie*, Band 20, pp. 16-20, 1899.

⁶ Bellstein, F., *Handbuch der organischen Chemie*, Auflage 3, Band 1, p. 644, 1893.

ric hydroxide is liable to be intermixed with the basic ferric salts than if a weaker alkali, such as ammonium hydroxide (NH_4OH), is responsible for the precipitation. Likewise the reaction with a weak alkali would result in the formation of relatively more ferric hydroxide than would result from simple boiling. It seems probable that more than one basic compound of each of the organic iron salts may exist. Thus there are probably several basic ferric acetates or basic ferric oxalates and these vary in quantity relatively to each other and to the ferric hydroxides in precipitates formed under different conditions. Care must be taken, however, in drawing conclusions from analyses of precipitates; because even if but one ferric hydroxide and but one basic salt of a given organic acid were present, their changing ratios under varying conditions might counterfeit the presence of other compounds in these mixtures.

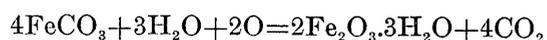
In solutions of organic iron salts of oxyacids, such as iron citrate, iron tartrate, or iron malate, basic ferric salts do not precipitate, because in these salts the iron forms part of an "inner complex salt." This is true also of salts of many of the acids which occur in the "composite" called humic acid, and is the reason why such salts may be carried in solution for long periods.

In the formation of sedimentary iron-bearing deposits in nature the precipitation of ferric hydroxide is mainly from ferrous solutions and occurs when these solutions come in contact with the oxygen of the atmosphere. The precipitation may result chemically from oxidation alone, but as a rule iron bacteria aid in the reaction. To some extent ferric hydroxide is also probably precipitated from ferric solutions which in nature are mainly solutions of organic salts, and here also iron precipitating bacteria may aid in the deposition.

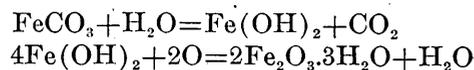
The hydroxide precipitated from solutions of ferrous salts is generally the stable yellow ferric hydroxide of fairly definite chemical composition, whereas that precipitated from ferric solutions is generally the red colloidal hydroxide, which, however, in time may change to the stable hydroxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, as shown by Ruff.¹

The most common form in which iron occurs in solution in natural waters is as ferrous bicarbonate, but ferrous or ferric sulphates probably occur, as well as salts of organic acids, which have generally been included under the terms ferrohumes and ferrihumes.

Ferrous bicarbonate may be derived from many different iron minerals. It is taken into solution through the agency of carbonic acid (H_2CO_3) and retained in solution by excess carbon dioxide. Such solutions may remain in circulation underground for long periods and eventually come to the surface as iron springs or seepages and may be carried by streams to lakes or lagoons. Upon the removal of the excess carbon dioxide and exposure to the atmospheric oxygen, oxidation and hydration take place according to the following reaction:²



This reaction may perhaps be better stated in two steps, thus:



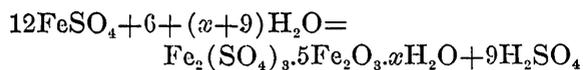
The flocculent yellowish-brown precipitate of ferric hydroxide ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) that is formed drops to the bottom, where it accumulates or where a part or all of it may become mixed with mud containing organic matter and be reconverted to ferrous carbonate. A part of the yellowish-brown precipitate may consist of iron in the more hydrated forms, such as $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. In this way the mixture of various ferric hydroxides and of ferrous carbonate in bog ores is accounted for. The iron sulphide and iron sulphate locally present in the deposits may be formed by the action of H_2S , given off by the decaying organic matter, on ferrous carbonate or by precipitation from iron sulphate solutions.

Iron sulphate is present in solution in meteoric waters owing to the decomposition of sulphides of iron or to the action of sulphuric acid on other iron minerals. The iron present in this form may be precipitated by simple oxidation as a mixture of ferric hydroxides and basic ferric sulphates, or by reaction with cal-

¹ Ruff, O., op. cit.

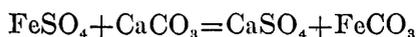
² Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, p. 826, 1904.

cium carbonate present in solutions as ferrous carbonate, which then may be oxidized to limonite. Van Hise says that basic ferric sulphate may be precipitated from ferrous sulphate solution according to the following reaction:¹

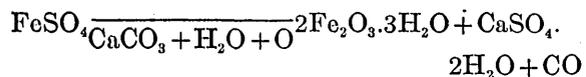


In reality, however, the reactions which take place are probably much more complex and the result is a mixture of compounds rather than a single basic salt.

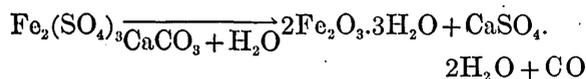
The reaction between ferrous sulphate and calcium carbonate to form ferrous carbonate is as follows:²



The calcium sulphate is deposited as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the ferrous carbonate may be oxidized to ferric hydroxide according to the reaction given above. In the presence of abundant oxygen the two reactions might occur almost simultaneously thus:



If ferric sulphate is present in solution the precipitation of ferric hydroxides may occur thus:



The occurrence of iron in solution in natural waters as salts of organic acids has received but little study, and the literature with reference to it is largely speculative. It is commonly supposed that the iron is in the form of soluble salts of certain little-known soil acids termed humic acids. It does not seem impossible, however, that it may also be carried as salts of other organic acids known to be present in the soil, such as formic acid, lactic acid, butyric acid, citric acid, or tartaric acid.

The iron which is present in solution in the form of organic salts upon precipitation is probably largely thrown down as ferric hydroxide together with various insoluble or-

ganic ferric compounds, which, however, in a comparatively short time will also change to ferric hydroxide. According to Aschan,³ who has studied this subject, the principal organic iron salts occurring in natural waters are salts of humic acids, such as ferrohumes and ferrihumes. He believes that humic acids are the principal constituents of the soluble derivatives of humus, which he calls humus hydrosols (gels in colloidal solution). Humus hydrosols are of unknown and variable composition and are supposed to contain, besides humic acids, various other soil substances such as humates of different composition. They are believed to play an important part in the decomposition of rocks and minerals, as well as in the precipitation of such substances as iron and aluminum. The humus hydrosols are the materials which impart the deep-brown color to streams and lakes in regions of abundant vegetation. By decomposition they change to carbon dioxide and ammonia.

Aschan found that if ferric salts were present within certain narrow limits of concentration, in waters containing humus hydrosols, insoluble ferrihumes were deposited but that above or below this concentration only soluble salts were formed. He found also that if ferrous salts instead of ferric salts were present, no precipitation took place, soluble ferrohumes being formed, which, however, if present in the proper concentration might by oxidation change to insoluble ferrihumes.

The action of humus hydrosols in the formation of lake and bog iron ores is supposed by Aschan to be as follows: When the soluble humus substances are taken into solution by ground waters some of the humic acids in them immediately begin to react chemically on the mineral constituents of the rocks through which the waters percolate and form soluble humates of different bases, among them iron. These humates are supposed to form food for microorganisms and the microorganisms are believed to aid substantially in rock decay. Besides aiding in the decay of rocks humus hydrosols are believed to aid in the precipitation of iron and other substances from solution. When ferric or ferrous salts are in

¹ Van Hise, C. R., op. cit., p. 826.

² Moore, E. J., The occurrence and origin of bog iron deposits in the district of Thunder Bay, Ontario: Econ. Geology, vol. 4, p. 535, 1910.

³ Aschan, Ossian, Die Bedeutung der wasserlöslichen Humusstoffe (Humussole) für die Bildung der See- und Sumpferze: Zeitschr. prakt. Geologie, Jahrg. 15, pp. 56-62, 1907.

solution in water containing humus hydro-sols ferrihumates or ferrohumates are formed. Ferrohumates are soluble, but under certain conditions of concentration and oxygen content insoluble ferrihumates are formed and these are precipitated directly. The soluble ferrihumates and ferrohumates may have their organic portion utilized as food by microorganisms and the ferric hydroxide is then precipitated. Thus insoluble ferrihumates and ferric hydroxide are believed to occur together in lake and bog iron ores, and this is supposed to explain the presence of organic carbon in these ores.

Sjögren¹ believes that the principal agents for the solution of iron in nature are sulphuric acid, carbon dioxide, and organic acids. Sulphuric acid is formed by the decomposition of sulphides, and carbon dioxide and organic acids are formed mainly from decomposing organic matter. The decomposition of organic matter in the absence of oxygen results in the formation of hydrocarbon combinations such as humus, which when acted upon by ammonia or alkalies yield humic acids. This action withdraws oxygen from surrounding mineral compounds, in this matter reducing ferric oxide to ferrous oxide, which then forms soluble double salts with ammonia and humic acids. These double salts may be further changed to ferrous carbonate and this substance may be oxidized to ferric hydroxide by the removal of carbon dioxide in the presence of oxygen. The iron, however, may also be precipitated directly from humic acid solutions. From sulphate solutions iron may be precipitated as basic ferric sulphate, which, according to Sjögren, is changed to ferric hydroxide by the action of ammonium or alkaline carbonates or by humus. From a mixture of humic acid and iron sulphate solutions iron may be precipitated as ferric hydroxide by the action of ammonia.

According to Beck² iron may also be precipitated from iron sulphate solutions by the addition of ammonium humate, which he states is always present in the brown waters

of peaty regions. The precipitate formed is ferric oxide and later ferric hydroxide.

The opinions concerning the precipitation of ferric hydroxide from natural iron-bearing waters have been summarized above. Some of these opinions are largely speculative as to possible reactions which may take place under conditions such as are found in nature, but others are based on well-known chemical phenomena. Though many of the reactions mentioned in connection with the precipitation of insoluble iron compounds from solutions of iron sulphate and organic iron salts probably occur, there is little doubt that far more important than these processes is the direct precipitation from ferrous bicarbonate solutions, whether through simple oxidation and hydrolysis or through the action of iron-depositing bacteria. The nature of the action of the bacteria in the deposition of ferric hydroxide is discussed at length in a subsequent section.

The precipitation of ferric hydroxide from ferrous bicarbonate solutions takes place almost immediately after the iron-bearing waters reach the surface, where they become saturated with oxygen and lose their carbon dioxide. This accounts for the yellowish-brown ochreous scums, which occur around all springs and seepages of iron-bearing waters. However, there is no doubt that iron is also carried in solution by surface streams whose waters are apparently rich in oxygen. In this manner iron in solution reaches lakes, lagoons, and marshes, where it is precipitated and forms bog and lake ores. In what form the iron is carried under these conditions it is difficult to say. Perhaps enough carbon dioxide occurs in these waters to permit the carrying of appreciable amounts of iron as ferrous bicarbonate, or perhaps the iron is carried in the form of organic iron salts. The equilibrium between the solvent carbon dioxide and the ferrous bicarbonate in solution is a subject which requires more thorough investigation.

Besides the iron which is carried in solution by surface streams probably a considerable amount of light flocculent ferric hydroxide, which has been formed where the iron-bearing solutions first reach the surface, is carried in suspension by the current and is deposited when quiet water is reached.

¹ Sjögren, H., Ueber die Entstehung der schwedischen Eisenerzlager: Geol. Fören. Stockholm Förh. 13, p. 373, 1891. Reviewed by R. Scheibe in Zeitschr. prakt. Geologie, 1893, pp. 434-437.

² Beck, R., The nature of ore deposits, vol. 1, pp. 101-103, translated by W. H. Weed, 1905.

The dehydration of iron deposits from their original form as ferric hydroxide to the final form of slightly hydrated ferric oxide is a slow process and results from several conditions.

According to Ruff,¹ as already stated, the red colloidal ferric hydroxide suffers gradual dehydration and becomes anhydrous ferric oxide. The anhydrous oxide, however, in the presence of moisture becomes hydrated again and alters to the stable form, limonite, and remains in this form. Other investigators, however, report that ferric hydroxide left for several years under water at ordinary temperatures became dehydrated and crystalline.²

Spring³ says that ferric hydroxide spontaneously loses its water if the iron is not combined chemically with some other substance. The yellow color would thus indicate the presence of alumina, lime, or magnesia. He believes that limonite is not a stable hydroxide and will give up its water when not in equilibrium with other oxides present.

Pressure has in some places been an important factor in the dehydration of iron-bearing deposits and in other places heat and pressure both have been active. In some deposits the pressure may have been due simply to deep burial, but in other deposits deformational earth movements have been an added factor. It seems reasonable to suppose that long periods of time, aided by pressure due to deep burial, might result in at least a partial dehydration of iron-bearing deposits.

Various impurities besides iron salts are commonly precipitated with ferric hydroxide from solution, such as silica, phosphates, alumina, and manganese oxides. Silicic acid may be carried in solution in the colloidal form or as alkaline silicates.⁴ The alkaline silicates are acted upon by carbon dioxide in solution and silica is thrown down. Colloidal silicic acid is deposited by evaporation. Phosphorus, probably carried in solution in the form of soluble phosphates, may be precipitated either as

calcium phosphate or as iron phosphate. Manganese, which may be present in solution in considerable amount, is thrown down upon oxidation as a mixture of manganese oxides. Some alumina also is probably precipitated with the ferric hydroxide, and, as previously stated, gypsum is thrown down with bog ores by the reaction of ferrous sulphate with calcium carbonate.

FORMATION OF DEPOSITS OF FERROUS CARBONATE.

Ferrous carbonate is known to occur in two forms—the insoluble carbonate (FeCO_3) and the soluble carbonate or bicarbonate (hypothetical formula, $\text{Fe}(\text{HCO}_3)_2$). The insoluble carbonate occurs only in the solid form and is either crystalline or fine grained and amorphous. It is made in the laboratory by precipitating a solution of green vitriol ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with sodium bicarbonate and heating the mixture for 12 to 36 hours at a temperature of 150°C .⁵ In this manner microscopic rhombohedra of ferrous carbonate (FeCO_3) are formed. When a cold solution of pure ferrous sulphate is treated with sodium carbonate, a flocculent white precipitate of ferrous carbonate is formed, which becomes dirty green in color on exposure to air, due to the absorption of oxygen and the evolution of carbon dioxide, and soon changes to ferric hydroxide. If the precipitate is washed in the absence of oxygen it may be obtained pure and colorless, but usually it takes the form of a gray powder, which oxidizes readily to ferric oxide on exposure to air.

Ferrous bicarbonate occurs in many natural waters, being taken into solution by the action of carbon dioxide on ferrous carbonate. It is not known in the dry state, for on precipitation in the absence of oxygen it changes to insoluble ferrous carbonate (FeCO_3) and in the presence of oxygen it is precipitated as ferric hydroxide.

The supposition that iron is carried in solution in natural waters principally as the bicarbonate, or at least as a soluble carbonate, is probably fairly well founded, because abundant iron is found in many places in solution

¹ Ruff, O., op. cit.

² Wittstein, Vierteljahresschrift für Pharmacie, Band 1, p. 277. Cited by Moore, E. J., op. cit., p. 537.

³ Spring, W., Ueber die eisenhaltigen Farbstoffe sedimentären Erdboden und über den wahrscheinlichen Ursprung der rothen Felsen: Neues Jahrb., 1899, Band 1, pp. 47-62.

⁴ Sjögren, H., op. cit.

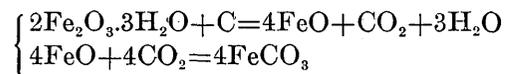
⁵ Roscoe, H. E., and Schorlemmer, C., A treatise on chemistry, vol. 2, p. 1247, 1913.

in waters in which there is no other acid radicle present except the bicarbonate. Ferrous bicarbonate remains in solution for an indefinite length of time, as long as the waters carry an excess of carbon dioxide in the free state. As soon, however, as waters become depleted of free carbon dioxide precipitation in one of the various forms already mentioned will take place, the particular form depending on the conditions under which deposition occurs. When abundant oxygen is present precipitation will occur in the form of ferric hydroxide. When no oxygen is present and at the same time carbon dioxide is removed precipitation occurs in the form of iron carbonate. This form of precipitation takes place in marshes or shallow bodies of water where vegetation and decaying organic matter are abundant. The free carbon dioxide is supposed to be removed in part by diffusion and in part through absorption by plants, and at the same time the waters are depleted of their oxygen by decaying organic matter. Even if part of the iron is precipitated in the first place as ferric hydroxide, that substance would probably be reduced and altered to carbonate on becoming mixed with muds rich in organic matter. The deposition of ferrous carbonate in bogs, therefore, is very similar to that of bog-ore deposits of ferric hydroxide, except that under these conditions the abundance of decaying organic matter results in the precipitate remaining in the ferrous form or being changed to the ferrous form.

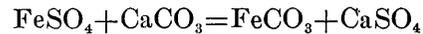
If the iron is thrown down as ferric hydroxide and sinks to the bottom it may become mixed with more or less organic matter as well as fine clastic sediments, and thus a considerable thickness of material may be built up.¹ The reducing action of the organic matter in the muds which changes the ferric hydroxide to ferrous carbonate is due to the removal of oxygen required for the oxidation of carbon compounds. As such places are below the level of ground water the conditions for the oxidation are imperfect, owing to the scarcity of free oxygen. The carbon, therefore, takes part of its oxygen from the ferric hydroxide, reducing it to ferrous hydroxide, which reacts with carbon dioxide to form ferrous carbonate.

¹ Van Hise, C. R., *op. cit.*, p. 827.

The reaction, on the assumption that carbon is the reducing agent, is as follows:

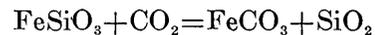


From ferrous sulphate solutions ferrous carbonate may be precipitated by calcium carbonate² according to the reaction:



In the absence of oxygen and free carbon dioxide the ferrous carbonate thus formed will be precipitated along with the calcium sulphate.

According to Van Hise and Leith,³ ferrous silicate which has been precipitated from ferrous sulphate or other iron solutions by alkaline silicates, as explained elsewhere (p. 73), may, in the presence of abundant carbon dioxide, be partly or entirely changed to ferrous carbonate, according to the following reaction:



In the presence of excess carbon dioxide the ferrous carbonate will go into solution but may become deposited by the removal of free carbon dioxide.

Various impurities may be precipitated with ferrous carbonate, such as calcium carbonate, magnesium carbonate, and manganese carbonate.⁴ Of these impurities calcium carbonate, which is almost invariably present in solution in iron-bearing waters, is by far the most important. Magnesium carbonate, however, is commonly present and manganese carbonate may be conspicuous locally. Silica also occurs abundantly in many places with ferrous carbonate. It may be deposited in the form of clastic grains along with clay and other materials, but generally it is in the amorphous form as chert, and in that form it may be either a chemical precipitate or it may be derived from

² Moore, E. J., The occurrence and origin of some bog iron deposits in the district of Thunder Bay, Ontario: *Econ. Geol.*, vol. 5, pp. 528-537, 1910.

³ Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: *U. S. Geol. Survey Mon.* 52, p. 526, 1911.

⁴ Vogt, J. H. L., Marmor und Eisenerze von Dunderland: *Bildung der Eisenerzlager: Dunderlandsdalens jernmalmfelt*, 1894, p. 106. Reviewed in *Zeitschr. prakt. Geologie*, 1895, pp. 37-39.

the casts of minute siliceous organisms living in the water. Phosphorus probably remains in solution under conditions which cause precipitation of iron carbonate.

FORMATION OF DEPOSITS OF IRON SILICATE.

Various iron silicates, such as amphibole, pyroxene, biotite, garnet, epidote, olivine, and chlorite, which occur in igneous and metamorphic rocks have already been mentioned. Most of them are complex silicates containing iron, aluminum, magnesium, calcium, and other elements. Besides these there are a number of secondary hydrous iron silicates which form under ordinary conditions of sedimentation, such as glauconite, greenalite, thuringite, chamosite, berthierine, and bavalite. The occurrence and association of these have also been described.

In ordinary sedimentary iron-bearing deposits, such as bog ores, ferrous silicates are stated by Van Hise to be formed by reaction between colloidal silica and ferrous compounds.¹ When ferric hydroxide is precipitated in the presence of abundant organic matter and becomes mixed with it in the mud it is reduced to ferrous oxide, as already explained. Van Hise says that if under these circumstances abundant colloidal silica is present it may unite with the ferrous oxide and form ferrous silicate, generally more or less hydrated. The formation of hydrous ferrous silicate under these conditions, rather than ferrous carbonate, is said to be probably dependent on the law of mass action.¹ It seems to be extremely questionable, however, whether ferrous silicate is ever formed in this manner.

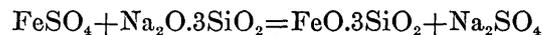
Van Hise and Leith² give a discussion of the formation of iron silicate from iron solutions by the action of alkaline silicates on ferrous salts. The iron silicate greenalite ($\text{Fe}(\text{Mg})\text{O} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$), of the Lake Superior iron-bearing formations, is supposed to have been thus precipitated.

Various laboratory experiments were performed to show the reactions between silicic acid or alkaline silicates and iron salts. The

silicic acid used was produced from alkaline silicates by treatment with hydrochloric acid, so that the solutions contained sodium chloride as well. They thus resembled sea water, in which the deposition of greenalite is believed to have taken place. Van Hise and Leith come to substantially the following conclusions concerning the formation of iron silicates:³

1. A solution of ferrous salt when boiled with silicic acid prepared as above stated [by neutralizing sodium silicate or water glass ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$) with hydrochloric acid] produces (in the absence of air) no precipitate, showing that silicic acid and a ferrous salt do not react to form ferrous silicate.

2. Ferrous sulphate reacts directly with solutions of silicates of the alkalis, producing a granular precipitate corresponding in composition to the water glass used in the precipitation. Thus:



The precipitate formed in this manner is composed of ferrous silicate and free silica. When the relative proportions of alkali and silica are varied in the water glass the amount of silica precipitated with the ferrous silicate also varies. If a soluble magnesium salt is present it will be precipitated with the iron as magnesium silicate. The ferrous silicates produced were as follows: (1) $\text{FeO} \cdot 3\text{SiO}_2$, formed from hot or cold solutions with ferrous salt in excess, (2) $\text{FeO} \cdot 5\text{SiO}_2$, formed from cold solutions with water glass in excess, and (3) $\text{FeO} \cdot 10\text{SiO}_2$, formed from hot solutions with water glass in excess. When $\text{FeO} \cdot 3\text{SiO}_2$ is boiled with water silica is taken into solution and the precipitate which remains approaches $\text{FeO} \cdot \text{SiO}_2$ in composition. However, this composition is not reached, for the iron oxidizes, rendering the remaining silica soluble. If allowed to stand and dry, out of contact with the air, the hydrous ferrous silicates also gradually lose water.

3. The ferrous silicates require neutral or slightly alkaline conditions for precipitation. They are soluble in acids or strong alkalis.

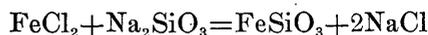
4. In the presence of oxygen varying amounts of ferric oxide form with the ferrous silicate.

¹ Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, p. 827, 1904.

² Van Hise, C. R., and Leith, C. K., op. cit., pp. 521-526.

³ Idem, p. 521.

5. Ferrous silicates may be precipitated by alkaline silicates from various ferrous salts, such as ferrous sulphate, ferrous bicarbonate, and ferrous chloride. The reaction for ferrous chloride would be



6. In the presence of an excess of carbon dioxide ferrous silicate may be changed to ferrous carbonate.

The precipitates of hydrous ferrous silicates formed as described above are flocculent and of a green color. According to Van Hise and Leith they develop on settling a granular texture similar to the greenalite occurring in the Lake Superior iron formation. This phenomenon is stated to be due probably to the surface tension between the precipitate and the liquid.

The commonly quoted hypothesis of the formation of the iron silicate glauconite is that of Murray and Renard which has already been mentioned.¹ According to this hypothesis the iron silicate is not precipitated as such but is formed by secondary processes. Shells of dead organisms, mainly Foraminifera, drop to the bottom and become filled with fine mud containing iron. This mud is acted upon by the organic matter of the organism in the presence of sulphates in the sea water resulting in the reduction of the iron present in the mud to sulphide. This sulphide later oxidizes to ferric hydroxide setting free sulphuric acid, which removes the alumina in solution and sets free colloidal silica. The colloidal silica in turn reacts upon the hydroxide, and in the presence of potassium salts, derived from other minerals, forms glauconite.

FORMATION OF DEPOSITS OF IRON SULPHIDE.

Sulphides of iron may be precipitated from either organic or inorganic solutions of iron salts by simple chemical reaction with other constituents in solution or with materials in contact with the solutions. Precipitation may also take place by the reduction of iron sulphate in solution through the action of organic matter, bacteria, or other reducing agent,

or by the action of hydrogen sulphide, liberated from decaying organic matter, on iron carbonate or other iron salts in solution.

The following are the principal sulphides of iron:²

	Formula.
Ferrous sulphide, troilite.....	FeS
Magnetic iron sulphide, pyrrhotite.....	Fe ₁₁ S ₁₂
Ferric sulphide	Fe ₂ S ₃
Iron disulphide, pyrite, marcasite, and melnikowite.....	FeS ₂

Ferrous sulphide, or iron monosulphide, occurs in nature as a constituent of certain sediments containing abundant organic matter and laid down under strongly reducing conditions. Such deposits occur in the Black Sea and elsewhere and have already been described. Ferrous sulphide is also found as the mineral troilite, a constituent of some meteorites. It is easily formed in the laboratory² by the direct union of the elements iron and sulphur, (1) by burning iron in sulphur vapor, (2) by heating iron filings and sulphur together in a red hot crucible, or (3) by stirring a white-hot iron rod in molten sulphur. In this manner ferrous sulphide forms as a yellowish crystalline metallic substance. When iron filings and sulphur are mixed with water and rubbed to a paste, black ferrous sulphide is produced with the evolution of heat. It is also formed as a black amorphous mass by the action of ammonium sulphide on solutions of ferrous salts or by the reduction of ferric oxide or its salts in the presence of sulphates and decomposing organic matter. Ferrous sulphide may also be formed by action of hydrogen sulphide, liberated from decaying organic matter, on iron carbonate or other iron salts in solution.

Magnetic iron sulphide is a mixture of the monosulphide and the sesquisulphide of iron. It occurs abundantly in metalliferous veins as the mineral pyrrhotite. It does not form under ordinary conditions of sedimentation but is a product of hot magmatic solutions.

Ferric sulphide is not known to occur in nature. In the laboratory² it is produced by the action of ammonium sulphide on solutions of ferric salts in an excess of alkali. When the ferric salt is in excess a mixture of ferrous sulphide and sulphur is formed. Ferric sul-

¹ Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, p. 383, 1891.

Clarke, F. W., *The data of geochemistry*, 3d ed.: U. S. Geol. Survey Bull. 616, p. 516, 1916.

² Roscoe, H. E., and Schorlemmer, C., *Treatise on chemistry*, vol. 2, pp. 1232-1236, 1913.

phide is formed also by the action of hydrogen sulphide on ferric hydroxide in the presence of traces of ammonia. It may be formed dry by gently heating sulphur and iron together or by the action of hydrogen sulphide on ferric oxide at a temperature not above 100° C. When thus formed the material is a yellow nonmagnetic mass.

Disulphide of iron occurs abundantly in nature as the minerals pyrite and marcasite and locally as melnikowite.¹ Pyrite forms beds and lenses interlayered with sedimentary and metamorphic rocks and occurs disseminated or as concretions in sedimentary rocks, such as shale, limestone, and quartzite. It is also abundantly disseminated through igneous rocks and occurs in association with metalliferous ore deposits, both in those of magmatic origin and those of meteoric origin. In general it is one of the most widespread iron minerals and occurs in rocks of various kinds. Marcasite occurs in metalliferous veins. It is not as common as pyrite.

Iron disulphide is said to be formed in nature by the action of organic matter on water which contains iron sulphate in solution and generally occurs as spherical, botryoidal, or stalactitic masses. It also is common in peat and coal, replacing organic matter and taking the form of roots, wood, etc.²

In the laboratory iron disulphide is formed by heating ferrous sulphide with sulphur or by passing hydrogen sulphide over oxides or chlorides of iron heated to redness. It is formed also as yellow crystalline pyrites when carbon bisulphide vapor acts upon heated ferric oxide; when a mixture of ferric oxide, sulphur, and salammoniac is heated slowly above the volatilization temperature of salammoniac; or when ferric chloride is heated with phosphorus pentasulphide.

Van Hise³ says that iron disulphide may be formed in sedimentary iron-bearing deposits by the reduction of basic ferric sulphate, which, as has been explained, results from the oxidation of ferrous sulphate solutions and may be deposited together with ferric hydroxide in the bottoms of lagoons. The reduction is due to decaying organic matter, which re-

quires abundant oxygen and takes part of it from the basic ferric sulphate, which is thus reduced to disulphide of iron. As there is more iron present than is required for combination with the sulphur, it is believed that the excess iron may combine with carbon dioxide or perhaps with silica and form ferrous carbonate or ferrous silicate.

Much of the iron sulphide occurring in sedimentary rocks has doubtless been formed by chemical processes, but the chemical action is for the most part the result of the decomposition of organic matter by bacteria. Decomposing organic matter may cause the formation of iron sulphide (1) by the direct reduction of iron sulphate in solution, owing to the removal of oxygen by the oxidation of carbon, or (2) by the action of hydrogen sulphide, produced during the decomposition, on various iron salts in solution. Much of the iron sulphide also is deposited directly by the bacteria which have the power of reducing iron sulphates to sulphide and which have already been described.

As bacteria are largely responsible for the deposition of iron sulphide in nature, the discussion of this subject is therefore taken up in connection with the biologic deposition of iron.

DEPOSITION OF IRON BY BIOLOGIC AGENCIES.

FORMATION OF DEPOSITS OF FERRIC HYDROXIDE.

As bacterial processes are becoming better understood their relations to various phenomena in geology are found to be of increasing importance. Not only do they aid in the decomposition of rocks, as has already been shown, but they are important factors in the formation of certain rock and mineral deposits, notably those of calcium carbonate, calcium phosphate,⁴ ferric hydroxide, and iron sulphide.

Drew,⁵ Kellerman, Vaughan, and others who have recently investigated modern calcium carbonate deposits of the sea bottom have come

⁴ Blackwelder, Elliot, The geologic rôle of phosphorus: *Am. Jour. Sci.*, 4th ser., vol. 42, pp. 285-298, 1916.

⁵ Drew, G. H., On the precipitation of calcium carbonate by marine bacteria and on the action of denitrifying bacteria in tropical and temperate seas: *Carnegie Inst. Washington, Dept. Marine Biology, Papers from Tortugas Laboratory*, vol. 5, pp. 7-45, 1914.

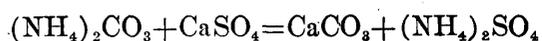
¹ Doss, Bruno, *Zeitschr. prakt. Geologie*, Jahrg. 20, pp. 453-483, 1912.

² Roscoe, H. E., and Schorlemmer, C., *op. cit.*, p. 1234.

³ Van Hise, C. R., *op. cit.*, p. 828.

to the conclusion that bacterial processes have played an important part in the formation of the vast beds of marine, nonfossiliferous limestone of various geologic ages.

The generally accepted hypothesis for the formation of nonfossiliferous limestones has been that they were formed as chemical precipitates, the precipitation being ascribed to the action of ammonium carbonate, an end product of the decomposition of nitrogenous organic matter, on calcium sulphate present in sea water, according to the following equation:¹



Decay-producing bacteria are of great importance in this process, for it is due largely to their activity that ammonia is produced, and this unites with carbon dioxide in solution to form ammonium carbonate.

Drew in his recent work has shown that widely distributed marine denitrifying bacteria are also of great importance in the precipitation of calcium carbonate. He claims that these bacteria have largely caused the extensive accumulations of chalky mud in the vicinity of the Bahamas and the Florida Keys which are being formed at the present time, and that they also play an important part in the cementation of fragments of coral and shells into coralline rock. He suggests that bacterial action has been an important factor in the past in the formation of chalks and limestones of different geologic ages.

The principal denitrifying bacterium active in this precipitation is a minute, actively motile bacillus with rounded ends, named *Bacterium calcis* by Drew but found by Kellerman to have a single polar flagellum and to belong to the genus *Pseudomonas*.² It is a facultative anaerobe and has the power of reducing nitrates to nitrites. The nitrites thus formed gradually disappear with the formation of some ammonia but without the perceptible formation of free nitrogen.

¹ Murray, J., and Hjort, J., *The depth of the ocean*, 1912.
Murray, J., and Irvine, R., *On coral reefs and other carbonate of lime formations in modern seas*: Roy. Soc. Edinburgh Proc., vol. 17, 1889.

² Vaughan, T. W., *Geological investigations in the Bahamas and southern Florida*: Carnegie Inst. Washington, Ann. Rept. Dept. Marine Biology, Yearbook 13, pp. 227-233, 1915.

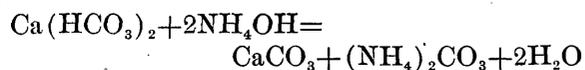
The principal culture medium used by Drew in the laboratory for preparing cultures of this organism consisted of calcium malate (or calcium acetate), potassium nitrate, sodium phosphate, and sea water. Agar and gelatin were used in conjunction with these salts in the preparation of solid media. In these artificial media the reduction of the nitrates begins in a very short time and is accompanied by the precipitation of calcium carbonate.

Drew states that the precipitation of calcium carbonate by these bacteria is in part caused by the greater alkalinity of the solution which results from the breaking down of nitrates and setting free of the bases during the process of denitrification but is probably due in part also to the direct breaking up of calcium salts (chiefly of organic acids), the calcium then uniting with carbon dioxide to form calcium carbonate.

Kellerman and Smith,³ who have recently further studied the activity of the microorganisms that precipitate calcium carbonate, believe that the precipitation may take place in any of the following ways:

1. The reduction of nitrates results in the formation of nitrites and finally of ammonia, which unites with the carbon dioxide present to form ammonium carbonate, and this reacts upon calcium sulphate to form calcium carbonate according to the equation already given. Ammonia may also be formed by the decomposition of protein.

2. Ammonia itself may react on calcium bicarbonate present in the sea water and precipitate calcium carbonate according to the following equation:



3. The bacteria feed on organic acids and as far as calcium salts of organic acids are present in sea water these are broken up and the calcium unites with free carbon dioxide and is precipitated as calcium carbonate. For this process denitrifying organisms also may be necessary.

³ Kellerman, K. F., and Smith, N. R., *Bacterial precipitation of calcium carbonate*: Washington Acad. Sci. Jour., vol. 4, No. 14, pp. 400-402, 1914.

Vaughan¹ states that the deposits of calcareous oolite in Florida and the Bahamas have probably resulted from bacterial activity. The calcium carbonate, which is precipitated in a finely divided state, largely as aragonite, forms spherulites, which by accretion or by accumulation around various nuclei build up oolitic grains, and these gradually accumulate to form beds.

The formation of the deposits of calcium carbonate thus outlined shows considerable analogy to the precipitation of iron compounds by bacterial action, which is briefly summarized in the following paragraphs.

Of the various accumulations of iron compounds in nature due to processes of sedimentation, biologic agencies are known to be important only in the deposition of those of ferric hydroxide and ferrous sulphide. Indirectly, however, microorganisms may be of importance in the deposition of ferrous carbonate and ferrous silicate as well.

That biologic processes are important in the formation of iron-ore deposits is no new idea. It was first advanced by Ehrenberg eighty years ago and since then it has been reiterated at various times by observers who have had occasion to study the so-called iron bacteria. The facts regarding the activity of these organisms in the precipitation of ferric hydroxide, however, have been treated in geologic literature only in a very general way and in many reports only vague references are made to them.

It is now well known that not only iron-precipitating bacteria but various other iron-precipitating organisms exist, some belonging to the algae and fungi and others belonging to the protozoa. Whether the term "iron-precipitating organisms" is really applicable to many of the forms is still an open question. It is not definitely known whether certain of the organisms actually aid in the precipitation of iron compounds or whether they simply act as gatherers of iron compounds precipitated by chemical processes. It is certain, however, that many of the forms do aid in the precipi-

tation, among them being certain of the iron thread bacteria which precipitate ferric hydroxide from ferrous bicarbonate solutions, the various microorganisms which precipitate ferric hydroxide and basic ferric salts from solutions of certain organic iron salts, and the sulphate-reducing and hydrogen sulphide forming microorganisms, which precipitate ferrous sulphide from iron-bearing solutions.

In the formation of ferrous carbonate and ferrous silicate deposits organic material is of importance to the extent that its decay results in the reduction to the ferrous form or the retention in the ferrous form of any iron compounds present. In promoting this decomposition bacteria are of importance. The precipitation of such ferrous compounds in the form of ferrous carbonate or ferrous silicate may take place by the absorption of solvent carbon dioxide by plants, by rapid diffusion of carbon dioxide, or by reaction of the ferrous compounds with alkaline silicates.

The activities of bacteria in depositing ferric hydroxide have been described quite fully in the foregoing pages, so that only a general statement concerning them is necessary. According to present knowledge it may be said that, as regards physiologic activities, three principal varieties of these bacteria exist—(1) those which precipitate ferric hydroxide from solutions of ferrous bicarbonate and use the carbon dioxide liberated and the energy produced during oxidation for their life processes, (2) those which do not require ferrous bicarbonate for their life processes but which cause the deposition of ferric hydroxide when either inorganic or organic iron salts are present, and (3) those which attack organic iron salts, using the organic acid radicle as food and precipitating ferric hydroxide, or basic ferric salts, which are gradually changed to ferric hydroxide. These organisms can not utilize inorganic iron salts.

The first group has at least one representative and this is a very common and very important form—*Spirophyllum ferrugineum*. It is probable, however, that *Gallionella ferruginea*, which is a near relative of *Spirophyllum*, also belongs to this group, as well as other so-called iron bacteria whose physiology

¹ Vaughan, T. W., Preliminary remarks on the geology of the Bahamas, with special reference to the origin of the Bahaman and Floridian oolites: Carnegie Inst. Washington, Dept. Marine Biology, Papers from Tortugas Laboratory, vol. 5, pp. 49-54, 1914.

has not yet been studied in detail. Lieske¹ has shown that *Spirophyllum ferrugineum* will not grow in media in which ferrous bicarbonate is not present, and that other iron salts can not take the place of ferrous bicarbonate in culture media for *Spirophyllum*. He found also that the smaller the amount of organic material present in the solutions the better is its growth. In solutions containing an abundance of carbon dioxide but in which organic matter was entirely absent, *Spirophyllum ferrugineum* was found to grow profusely. The culture solutions for *Spirophyllum* which Lieske used contained metallic iron and carbon dioxide for the formation of ferrous bicarbonate, and small amounts of ammonium and magnesium sulphates, potassium chloride, calcium nitrate, and potassium phosphate to supply other elements required by the organisms for growth.

In his experiments Lieske substituted other metals, such as manganese, lead, zinc, tungsten, copper, etc., for iron, but found that with none of these metals did growth take place. He attempted also to substitute ferric salts as well as other ferrous salts for ferrous bicarbonate but found that these did not induce any growth of *Spirophyllum*. However, he found that if ferrous bicarbonate were present in addition to some other iron salts the latter did not impair the growth. Atmospheric oxygen was found to be absolutely necessary for the growth of *Spirophyllum*, and when oxygen was absent no growth took place. The optimum temperature was found to be 5° to 6° C., no growth taking place in solutions above 27° C.

From these results it was concluded that *Spirophyllum ferrugineum* will grow in entirely inorganic media, that it does not require organic carbon for food but will take its carbon from ferrous bicarbonate, and that besides carbon it requires iron and oxygen. It is difficult to see why the organism finds it necessary to take carbon from the ferrous bicarbonate rather than utilize the carbon dioxide in solution in the water, unless, as is probable, the oxidation of ferrous carbonate is necessary as a source of energy.

¹ Lieske, R., Beiträge zur Kenntnis der Physiologie von *Spirophyllum ferrugineum* (Ellis): Jahrb. wiss. Botanik, Band 49, 91-127, 1911; also Centralbl. Bakteriologie, Abt. 2, Band 31, pp. 296-298, 1911.

The physiology of *Crenothrix polyspora*, *Clonothrix fusca*, and *Siderocapsa treubii* has not been thoroughly studied, and the exact conditions under which these organisms thrive are not known. *Crenothrix polyspora* grows abundantly in pure well waters, which, besides calcium and magnesium carbonates and a small amount of iron, contain few impurities. These conditions are very similar to those under which *Spirophyllum* and *Gallionella* thrive and would seem to indicate that *Crenothrix* requires very little if any organic matter. *Crenothrix polyspora* apparently does not grow profusely in marsh waters, where abundant organic matter is present. *Clonothrix fusca* resembles *Crenothrix* in its occurrence. *Siderocapsa*, on the other hand, more nearly resembles *Leptothrix* in its habits, occurring in marshes attached to living or dead vegetable matter and, like *Leptothrix*, probably requires organic matter for growth.

Of the second group of iron-precipitating bacteria the principal forms are *Leptothrix ochracea* (*Chlamydothrix ochracea*), and *Cladothrix dichotoma*. *Leptothrix ochracea* occurs abundantly in iron-bearing waters of iron springs and marshes, and *Cladothrix dichotoma* is a common soil organism, apparently being but little influenced in its distribution by the presence of iron compounds.

While the occurrence of *Leptothrix ochracea* in nature is undoubtedly controlled to a large extent by the presence of iron salts, it has been shown by Molisch² that in the laboratory *Leptothrix* will thrive abundantly on iron-free culture media consisting of distilled water with 1 to 2 per cent peptone. If iron is present in the culture solutions, however, *Leptothrix* will show better development and will deposit ferric hydroxide in its sheath. It has a great affinity for manganese compounds as well, and if manganese salts are present it will deposit hydrated manganese oxide in its sheath.

The form in which the iron or manganese occurs apparently makes little difference in the development of *Leptothrix*. In the natural waters in which *Leptothrix* grows the iron is probably largely in solution as ferrous bicarbonate with perhaps subordinate amounts as ferrous sulphate and organic iron salts. In the laboratory Molisch used mainly organic salts

² Molisch, Hans, Die Eisenbakterien, p. 45, 1910.

of iron and manganese, such as iron ammonium citrate, iron ammonium tartrate, and manganpeptone, and obtained profuse growth.

Like *Spirophyllum ferrugineum*, *Leptothrix ochracea* is an aerobic organism, but unlike *Spirophyllum* it requires organic matter as a source of carbon. Molisch states that he has never been able to cultivate it in a medium free from organic matter. The optimum temperature for the growth of *Leptothrix ochracea* is 23° to 25° C., and the temperature limits are 5° to 40° C.

Cladothrix dichotoma is a widespread soil organism, occurring in association with *Streptothrix*, *Actinomycetes*, and other thread bacteria. It grows abundantly on most of the ordinary culture media used for soil bacteria, and if iron is present in them it will deposit ferric hydroxide on its sheath.

The third group of organisms probably includes numerous species, nearly all of which are lower bacterial forms. These bacteria use the acid radicle of organic iron salts as a source of food, and this results in the precipitation of ferric hydroxide or basic ferric salts. Many of the forms probably attack only one or two organic salts, perhaps iron citrate, iron tartrate, or iron malate, but others may be able to use a large number of organic iron salts, including salts of soil acids, such as humates. At present very little definite information is at hand concerning the importance of this process in nature, and even in the laboratory this phenomenon has been studied only in a very general way. It is quite possible that many of the already well-known soil bacteria have the power of thus precipitating insoluble ferric compounds from solution from one or more organic iron salts. I have isolated several forms which actively precipitate insoluble ferric salts from solutions of ferric ammonium citrate and have cultivated them on solid media. I have also succeeded in causing precipitation of insoluble ferric salts by microorganisms from iron oxalate, iron lactate, and other organic iron salts but have not yet been successful in growing any of the precipitants of these organic iron salts on solid media.

It seems probable that the insoluble ferric compounds precipitated as a result of this activity are mixtures of ferric hydroxides and

various basic organic iron salts. After precipitation, however, bacterial activity probably continues, and as a result more and more of the organic acid radicle is doubtless removed from the precipitate until finally only ferric hydroxide is left.

The importance of this group of organisms in the formation of iron-ore deposits of course depends entirely upon the extent to which organic compounds of iron, such as humates, are carried in solution in natural waters. Some investigators believe that large amounts are carried in this way, but others believe that the amounts thus carried are insignificant and that practically all the iron in solution in natural waters is in the form of ferrous bicarbonate. From observations regarding the conditions under which iron is retained in solution in natural waters, notably the fact that surface waters, which are apparently saturated with oxygen and carry little carbon dioxide, commonly contain appreciable quantities of iron, it seems reasonable to believe that iron is carried in other forms besides that of bicarbonate. What these forms are will have to be determined by further work including careful analyses of iron-bearing waters. It is extremely difficult to detect organic iron salts when present in such small quantities as would occur in natural waters.

As both chemical and biologic processes of various kinds are admittedly active in the precipitation of ferric hydroxide, the question as to which process is predominant in the formation of sedimentary iron-ore deposits and iron-bearing formations must be solved largely by field evidence. As many of the present deposits of iron carbonate were probably originally laid down as ferric hydroxide and were subsequently reduced, this question not only concerns the present deposits of ferric oxide but many of the deposits of ferrous carbonate and perhaps of ferrous silicate as well.

From the geologist's point of view, the important things to be considered with reference to bacteria that deposit ferric hydroxide are as follows: (1) Their distribution, whether widespread or limited; (2) the importance of their activity in natural iron-bearing waters, as compared with simple oxidation; (3) the conditions under which they are active; (4)

the part which they have played in the formation of iron-ore deposits in the past.

It has been repeatedly mentioned that iron thread bacteria are found practically wherever iron-bearing waters occur, whether stagnant or flowing. Some varieties are more abundant in iron springs, wells, and mines, where the water is relatively pure, but others are common in marshes and lagoons where organic matter is abundant. I have examined ocherous scums deposited from iron-bearing waters from many different localities and have almost invariably found that they consisted mainly of sheaths of iron thread bacteria associated locally with granular and colloidal ferric hydroxide. In fact, I have examined only one specimen of ocherous scum in which I did not find bacterial remains. This was obtained from the hot springs near Ainsworth, British Columbia, and was sent to me by Mr. A. D. Wheeler, who says that the temperature of the spring is 112° F. The material is yellowish brown in color and in the dry state is a fine powder. Under the microscope it is seen to consist of minute rounded granules, some spherical, some elongated, and some irregular in shape. The granules are light-colored, semi-transparent, but with a dark border as though they might be hollow casts.

One of the most common forms found, and one which occurs in relatively pure surface as well as underground waters, is *Spirophyllum*. I have found this form in nearly all the iron springs which I have examined and also in the waters of several mines and in iron-bearing well waters. It may occur in pure culture or it may be associated with any of the other forms of iron thread bacteria. *Gallionella* is not so common as *Spirophyllum*, and I have found it only in mines, where it is commonly associated with *Spirophyllum* and *Leptothrix*.

Leptothrix is almost as widespread as *Spirophyllum* and usually is the predominant form where it is found. It is common in iron springs and marshes, where in many places it forms large yellowish-brown gelatinous masses. At one locality I found it in a mine occurring in gelatinous masses on the sides and bottoms of drifts near openings where iron-bearing waters issued. With it occurred also *Gallionella* and *Spirophyllum*. This occurrence of

iron thread bacteria in mine drifts at depths as great as 300 feet and probably much deeper is extremely interesting and to my knowledge has not been mentioned in the literature. It opens the interesting possibility that not only may these bacteria be instrumental in the formation of surface bog ores, but they may play a part in the formation of certain underground deposits of limonite such as those which occur in the Appalachian region.

Crenothrix and *Clonothrix* occur more rarely than the other iron thread bacteria. I have found *Crenothrix* only in well water that has passed through city distributing pipes. Molisch, however, states that in Europe it has been found also in surface waters that contain iron. *Clonothrix* is said to live under the same conditions as *Crenothrix*. I know of its occurrence only on the walls of certain underground aqueducts that conduct water from lakes to city reservoirs.

Though the work concerning the distribution of iron thread bacteria has perhaps not yet been as extensive as might be wished, it has been sufficient to indicate that wherever accumulations of ferric hydroxide occur at the present time under normal conditions they are largely due to the action of iron thread bacteria.

To what extent the lower iron-precipitating bacteria present in soil and natural waters are instrumental in the formation of deposits of ferric hydroxide it is as yet impossible to say. These organisms do not leave residues that are readily identifiable, as are those left by thread bacteria, and besides it is not known to what extent iron is carried in solution in forms that could be utilized by them. In many of the iron scums much granular and colloidal ferric hydroxide is associated with the casts of iron thread bacteria, and it is possible that this material may in part have resulted from the action of the lower bacterial types. At any rate it is of considerable interest to note that these organisms are almost universally present in soil and natural water.

The abundant occurrence of iron thread bacteria on articles of metallic iron that are rusting under water is also interesting. It shows that these organisms are readily distributed in nature and are not confined to certain places where iron-bearing waters are constantly

present. I have seen *Spirophyllum* attached to iron articles that were rusting in small temporary pools of water in localities where it was very difficult to account for its presence unless it had been carried by non iron-bearing waters for long distances. Generally when such pools of water dry up porous tubercles of iron rust are formed on the surface of the metallic iron. These tubercles may be several inches in diameter at the base and consist largely of dried casts of iron thread bacteria. See fig. 13 and Pl. IX, B.)

The question as to the relative importance of microorganisms and simple oxidation in the precipitation of ferric hydroxide under natural conditions is a difficult one to answer. I have allowed samples of water that contain natural ferrous bicarbonate in solution to stand in vessels so that the iron present was precipitated and formed a deposit at the bottom. Upon examination this deposit was found to consist of a mixture of casts of iron thread bacteria and granular ferric hydroxide, the granular ferric hydroxide being somewhat more abundant. The granular material probably resulted from direct oxidation, although there is a possibility that lower forms of iron-precipitating bacteria assisted. However, even though simple oxidation may be more effective in the precipitation of ferric hydroxide from ferrous bicarbonate solutions, the fact that deposits of the precipitate found in nature are made up largely of bacterial remains indicates the importance of microorganisms in the accumulation if not in the precipitation of the ferric hydroxide.

Other questions which arise are what percentage of the iron is carried in other forms besides that of ferrous bicarbonate, and what is the relative importance of organisms and simple oxidation in the precipitation of ferric hydroxide from such iron solutions. By present analytical methods it is practically impossible to tell ordinarily in what form the bases are carried in solution. It has been the common practice to combine certain bases with certain acid radicles without reference to the most probable combinations of salts present. Not only is it difficult, however, to determine in what manner different bases and acid radicles are combined, but also to determine the presence of small quantities of certain acid radicles,

especially those of organic salts, in solution. Iron may not all be present in solution as ferrous bicarbonate or ferrous sulphate but may occur in forms which resist oxidation for a long time or may even require special conditions for any precipitation at all to take place.

The conditions under which iron bacteria are active in nature seem to be extremely varied. They thrive in surface as well as in underground waters and in stagnant as well as in running waters. Temperature also, within moderate limits, seems to have little effect on the growth of iron-depositing bacteria, although most of them seem to prefer cold waters to warm waters. In the hot spring near Ainsworth, British Columbia, having a temperature of 112° F., there are apparently no remains of iron-depositing bacteria present in the ocherous deposits, but in ordinary iron springs both *Leptothrix* and *Spirophyllum* thrive during the winter as well as during the summer, and *Crenothrix* is present in city water pipes throughout the year. Lieske states that the optimum temperature for *Spirophyllum* is 5° to 6° C.¹ I have found 9° to 10° C. to be a common temperature in iron springs containing growths of iron-depositing bacteria.

The amount of iron required in solution for most iron-depositing bacteria seems to be extremely small. *Crenothrix* is abundant in the water of the city supply of Madison, Wis., which contains only 1.8 parts of ferric oxide (Fe_2O_3) per million, and *Leptothrix* was found to grow profusely in iron spring water containing 5.2 parts of ferric oxide (Fe_2O_3) per million. The latter amount of iron imparts a strong iron taste to the water, but I have found both *Leptothrix* and *Spirophyllum* in water in which the iron present was hardly noticeable to the taste.

The amount of organic matter in solution is somewhat of a limiting factor in the growth of iron-depositing bacteria. Some forms, like *Leptothrix*, require a certain amount of organic carbon present, but other forms, such as *Spirophyllum*, thrive best in water containing little or no organic carbon. It is probable, also, that other materials in solution, such as certain inorganic salts, affect the growth of iron-depositing bacteria. Iron-depositing thread bacteria have never been found in sea water and

¹ Lieske, R., op. cit.

probably do not occur there on account of the high percentage of certain inorganic salts present.

The question as to what part iron-depositing bacteria have played in the formation of iron-ore deposits in the past can not be settled by direct field evidence, for bacterial remains are comparatively short-lived in ochreous accumulations of iron oxide, and the slightest metamorphism will completely obliterate all traces of them. Schorler¹ has shown that even in the ferric hydroxide crusts forming inside of water pipes in cities which use iron-bearing waters, the form of the bacterial remains composing them is preserved only for a comparatively short time in the outer layers of the crust and the inside layers consist of compact limonite from which all traces of bacterial forms have vanished.

In some of the recent bog iron ore deposits, however, casts of the organisms are still to be seen, although there are many in which not a trace of them remains. Thus out of 61 specimens of bog ore examined by Molisch² he found only four which showed abundant remains of iron thread bacteria. It is probable that much of the granular ferric hydroxide which composes bog iron ore was originally in the form of casts of thread bacteria, but doubtless also much of it is chemically precipitated material, which has perhaps formed in quiet waters or which has had a chance to accumulate because of becoming attached to bacterial threads or other objects. Perhaps a part of this granular material may have been precipitated by lower bacteria as well, such as *Siderocapsa* and other forms already described, and thus would probably be indistinguishable from the chemically precipitated material.

Both chemical and biologic processes seem to have been important in the formation of iron-ore deposits in the past, and the question as to which has predominated in the formation of any particular deposit must be solved by a study of the conditions at the time of deposition. The method of attack involves a study not only of the sedimentation, but of climate, depth of water, relation to land areas, nature

of currents, nature of materials carried in solution, and many other factors. It is only through a complete study of all the conditions involved that a conclusion may be arrived at as to the most probable manner of deposition of any individual deposit.

FORMATION OF DEPOSITS OF FERROUS SULPHIDE.

The deposition of ferrous sulphide usually takes place in inclosed or partly inclosed bodies of water in which decaying organic matter is abundant. The organic matter is decomposed largely by the action of microorganisms, and during the decomposition hydrogen sulphide, ammonia, hydrogen, methane, and other gases are liberated. Iron salts are probably brought in by streams from surrounding regions. Under strongly reducing conditions and in the presence of hydrogen sulphide these become converted to hydrous ferrous sulphide and are precipitated.

In the formation of deposits of ferrous sulphide, under ordinary conditions of sedimentation, the ferrous sulphide may be precipitated from iron-bearing solutions directly by the reduction of iron sulphates, sulphites, or thio-sulphates by microorganisms, or it may be precipitated by the action of hydrogen sulphide on ferrous salts in solution, the hydrogen sulphide being formed by bacterial action either from decaying sulphur-bearing organic matter, from salts of sulphurous or sulphuric acid by reduction, or from free sulphur by reduction.³ The precipitation of ferrous sulphide occurs under reducing conditions and usually in the presence of abundant decaying organic matter. The action is therefore largely dependent on the presence of various reducing and decay-producing organisms.

Besides forming as a direct precipitate from ferrous solutions, ferrous sulphide may be formed by the reduction of originally precipitated ferric hydroxide under the action of decaying organic matter in the presence of sulphates.

I have already discussed the precipitation of ferrous sulphide in some detail, so that it will not be necessary to state more than the essentials of the process here. Probably the most

¹ Schorler B., Die Rostbildungen in den Wasserleitungsröhren: Centralbl. Bakteriologie, Abt. 2, Band 15, pp. 564-568, 1906.

² Molisch, Hans. Die Eisenbakterien, pp. 59-65, Jena, 1910.

³ Omelianski, W., Der Kreislauf des Schwefels, in F. Lafar's Handbuch der technischen Mycologie, Band 3, pp. 214-220, 1904-5.

interesting of the microorganisms concerned in this activity are those which reduce various salts of sulphurous and sulphuric acid and which are known to be widely distributed in nature. They live under anaerobic conditions and obtain oxygen, which they require for the oxidation of carbon within their cells, from sulphates, sulphites, and thiosulphates, with the result that these compounds are reduced to sulphides. Ferrous sulphide may thus be directly formed by the reduction of iron sulphate.

When sulphides of other metals, such as calcium or magnesium, are formed in an analogous manner, they may be further acted upon by carbon dioxide in the presence of water and changed to carbonates and hydrogen sulphide. The hydrogen sulphide may then react on ferrous salts present in the water, especially ferrous bicarbonate, and precipitate ferrous sulphide. The equation for this reaction has already been given.

Hydrogen sulphide is abundantly produced by the decay of sulphur-bearing proteins. The power to form hydrogen sulphide from proteins during decomposition is common to all putrefying bacteria, of which there are innumerable varieties and which are abundant everywhere. The precipitation of ferrous sulphide (FeS) through the activity of these organisms becomes merely a question of the presence of dead organic matter and of iron salts in solution.

The reduction of sulphur to hydrogen sulphide takes place in the presence of decomposing organic matter. It is probably due to secondary processes that result from various reactions which take place under these conditions. The hydrogen sulphide thus formed will precipitate ferrous sulphide from ferrous solutions which may be present.

The production of hydrogen sulphide through the action of bacteria is important and widespread.¹ In the presence of abundant hydrogen sulphide in the water and the resultant decrease of oxygen the higher organisms frequently disappear entirely and the organisms which thrive in abundance are infusoria, radiolaria, oscillaria, diatoms, *Chroococcus*, and abundant bacteria such as sulphur bacteria and various anaerobes. Of these the sulphur bacteria are especially interesting, as they

oxidize hydrogen sulphide to free sulphur and sulphates and in this manner obtain energy for their life processes. This action is analogous to the oxidation of ferrous carbonate to ferric hydroxide by some iron thread bacteria.

In the Weissowo salt sea in the Charkow government, Russia, Nadson found the following content of hydrogen sulphide per liter of water:¹

Content of hydrogen sulphide, in cubic centimeters per liter of water, from Weissowo salt sea, Russia.

Depth of 16 meters.....	5.91
Depth of 18 meters.....	88.31
Depth of 18.7 meters.....	184.96

According to Lebedinzeff the Russian deep-sea expedition of 1891 found throughout the Black Sea at depths below 200 to 400 meters an increasing amount of hydrogen sulphide in solution.²

Content of hydrogen sulphide, in cubic centimeters per liter, of water from the Black Sea.

Depth of 213 meters.....	0.33
Depth of 427 meters.....	2.22
Depth of 2,026 meters.....	5.55
Depth of 2,528 meters (bottom).....	6.55

This high content of hydrogen sulphide is typical of the Black Sea and does not extend into the Sea of Marmora or the Mediterranean. Its presence is due to the action of anaerobic bacteria on organic matter in the presence of sulphates of the sea water. Sulphate and thio-sulphate reducers have also been found in Black Sea muds. According to Andrussow,³ the presence of hydrogen sulphide in the water of the Black Sea is due to the fact that on account of the rapidly increasing density of the water with depth only the upper 170 meters have circulating currents, the rest being stationary. This is not true of other seas where oxygen is carried to depths and the hydrogen sulphide formed is soon oxidized by sulphur bacteria to sulphates or reacts with iron salts present, causing the precipitation of ferrous sulphide.

The precipitated ferrous sulphide usually does not form pure deposits but becomes more

¹ Omelianski, W., op. cit., pp. 220-224, 1904-1906.

² Lebedinzeff, A., Soc. naturalistes Odessa Travaux, Band 16, 1891. Cited by Omelianski, W., op. cit.

³ Andrussow, N., Acad. sci. St.-Petersbourg Mém., Band 1, p. 1, 1894. Cited by Omelianski, W., op. cit.

or less mixed with fine clastic material and organic matter and forms a black mud. The black mud of the limans that occur along the shores of the Black Sea and elsewhere in southeastern Russia upon exposure to oxygen turns gray, due to the oxidation of ferrous sulphide, but upon being again covered with brine black spots appear and soon the whole mass becomes black, being again reduced to ferrous sulphide through the activity of organisms which are able to live in concentrated salt solutions. These organisms liberate hydrogen sulphide and also ammonia and amino bases. Under the influence of hydrogen sulphide in alkaline solution ferrous sulphide is precipitated from the iron salts present as a black, colloidal, plastic, hydrous deposit, which impregnates the muddy mass of organic and clastic material.

The gray oxidized liman mud when sterilized keeps indefinitely. However, upon being covered with water and reinoculated with fresh mud, with stream water, or with pure cultures of sulphate-reducing bacteria it again takes on a black color. This shows that living organisms are responsible for the reduction.

It has been shown also that at the same time that hydrated ferrous sulphide gel separates out in muds silica gel frequently separates out and forms thin films (less than 4 micra in thickness) around finely divided particles of hydrated ferrous sulphide gel, thus producing minute grains.¹ The granular texture thus produced is often characteristic of ferrous sulphide deposits.

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