

THE ORIGIN OF SEDIMENTARY IRON FORMATIONS: THE
BIWABIK FORMATION OF THE MESABI RANGE

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THE ORIGIN OF SEDIMENTARY IRON FORMATIONS:
THE BIWABIK FORMATION OF THE
MESABI RANGE.

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INTRODUCTION.

Few problems of geology have offered such difficulties as the explanation of the origin of the large sedimentary iron ore deposits—for example, those of the Lake Superior region, especially the Mesabi Range. The source of the iron is as yet uncertain, as are the means by which the iron is dissolved and transported. The most probable hypothesis is that the iron of the iron-bearing formations, such as the Biwabik, may be derived from igneous and sedimentary rocks by ordinary processes of weathering, carried to the sea by rivers rich in organic matter, and deposited by microorganisms.

The writer is indebted to Dr. W. H. Emmons and to Dr. F. F. Grout for many valuable suggestions and criticisms during the progress of the work. Thanks are also due to the officials of many of the operating companies of the Mesabi range, especially to Mr. J. Uno Sebinus, general mining engineer, and to Mr. J. F. Wolff, geologist, of the Oliver Iron Mining Co.

GENERAL GEOLOGY.

Stratigraphy.

In the following description only the central and western part of the Mesabi Range will be treated,¹ but with few minor modi-

¹ For detailed descriptions see:

Winchell, N. H., and Winchell, H. V., "Iron Ores of Minnesota," Geol. Nat. Hist. Surv. Minn. Bull. 6, 1891.

Winchell, N. H., "Some Problems of the Mesabi Iron Ore," Geol. Nat. Hist. Surv. Minn., 21st Ann. Rpt., 1893, p. 134.

Winchell, H. V., "The Mesabi Iron Range," Geol. Nat. History Surv. Minnesota, 20th Ann. Rept., 1891.

Spurr, J. E., "The Iron-bearing Rocks of the Mesabi Range," Geol. and Nat. Hist. Survey of Minn., Bull. 10, 1894.

fications, most of the statements may be applied to the Eastern Mesabi and Gunflint ranges. The total length of these ranges from a point west of Pokegama Lake to the west end of North Lake, Canada, is about 175 miles.² The widths of the ranges vary considerably. The Biwabik formation has been found at a depth of 2,200 to 2,700 feet, 5 miles south of the town of Biwabik. The stratigraphic succession of the Huronian rocks in the Mesabi district is as follows:

	Virginia slate
Upper Huronian	Biwabik formation (iron-bearing)
	Pokegama quartzite.
Unconformity	
	Giants Range granite
Lower-Middle Huronian	Slate-graywacke-conglomerate formation.

The Upper Huronian rocks lie on the truncated older sediments and intrusives.

Biwabik Formation.—The Biwabik formation rests on the Pokegama quartzite practically conformably. A thin conglomerate is at its base. This conglomerate represents hardly more than a very short, if any, erosion interval. A vertical section of the subdivisions of the Biwabik formation is given below. The four larger divisions are essentially those of Wolff's³ classification.

Upper Slaty Division.

Limy carbonate, with greenalite, greenalite slate, and slaty taconite	0 to 25
Slaty, and cherty taconite, greenalite and slate	0 to 145

Upper Cherty Division.

Cherty, banded, slaty, and greenalite taconite with layers of conglomerate and algal structures. Some beds rich in magnetite 95 to 250

Leith, C. K., "The Mesabi Iron-bearing District of Minnesota," U. S. Geol. Survey, Mon. 43, 1903.

Van Hise, C. R., and Leith, C. K., "The Geology of the Lake Superior Region," U. S. Geol. Survey, Mon. 52, 1911.

² If the Animikie district of Ontario is included, this belt is 300 miles long.

³ Wolff, J. F., "Recent Geologic Developments on the Mesabi Iron Range, Minnesota," *Proc. Lake Sup. Min. Inst.*, 1917, p. 229.

Lower Slaty Division.

Slaty taconite, greenalite, greenalite slate, banded and cherty taconite, carbonates and scattered conglomerates. Some rich magnetite beds	0 to 250
"Intermediate Slate." Black slate, greenalite slate and paint rock .	½ to 40

Lower Cherty Division.

Lean member. White cherty and greenalite taconite, greenalite and greenalite slate	12 to 52
Member rich in magnetite. Irregularly banded, mottled and greenalite taconite	90 to 250
Member with iron in ferric state.	
Beds of cherty and banded taconite with slate and slaty taconite on top	8 to 70
Red basal taconite	0 to 40
Basal conglomerate and algal structures	0 to 12
Total	400 to 755

Detailed explanations of the terms used in this table have been given by Grout and Broderick.⁴ Taconite is a word locally applied to almost any phase of rock of the iron-bearing formation. It includes ferruginous, sideritic, calcareous, and amphibolitic cherts, and greenalite rock, all ranging from granular to slaty phases.

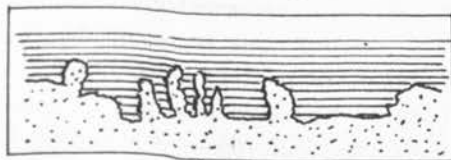


FIG. 42. Stylonitic surface between carbonate and slate in the Biwabik formation. Natural size.

A few new observations are here recorded. Amphiboles which were formerly thought to occur only east of Mountain Iron have been found throughout the whole range in considerable amounts. Siderite, as well as mixed carbonates, occurs abundantly in places. Considerable graphite has been observed by the writer in the cherts.⁵ It occurs in very irregular black films. In cross sec-

⁴ Grout, F. F., and Broderick, T. M., "The Magnetite Deposits of the Eastern Mesabi Range, Minnesota," Minn. Geol. Survey, Bull. 17, 1919, p. 14.

⁵ Steiger reports organic matter from greenalite. Van Hise and Leith, *op. cit.*, p. 167.

tion these layers are typical stylolites.⁶ (See Fig. 42.) They are more abundant in the carbonates of the ferruginous cherts than where carbonates are absent. Recent study⁷ has shown that magnetite is the most abundant iron oxide of the unweathered iron-bearing formation. In amounts sufficiently large to attract an ordinary horseshoe magnet, it is observed as aggregates of the size and shape of greenalite granules, and in dense fine-grained bands between cherty or slaty material. These bands may be straight, or irregular and contorted. Rarely they are two inches wide (on the East Mesabi, as much as 6 inches). Their usual thickness is from about $\frac{1}{2}$ to $\frac{3}{4}$ inch. They consist largely of magnetite with a little siderite. Such bands of magnetite are commonly not directly in contact with chert. Very thin bands of carbonates separate the chert from the magnetite. In many places magnetite seems to have replaced carbonate, and it appears to be least abundant where much siderite is present. This suggests that in places, magnetite is formed by partial oxidation of siderite.

Structures whose significance had escaped notice until recently are the so-called algal structures, of organic origin,⁸ which were described by Grout and Broderick on the East Mesabi and Gunflint ranges, and which have been traced westward by the writer. The structures look like fine, closely spaced, contorted lines resembling the grain of an especially gnarled and knotty piece of wood. The algal layers usually do not exceed a few feet in thickness, and in some places are only a few inches wide. One of the layers which has been traced throughout the Gunflint and

⁶ Gordon, C. H., "On the Nature and Origin of the Stylolitic Structure in Tennessee Marble," *Jour. Geol.*, vol. 26, 1918, pp. 561-567.

⁷ Wolff, J. F., *op. cit.*

Grout and Broderick, *op. cit.*

Broderick, T. M., "Economic Geology and Stratigraphy of the Gunflint Iron District, Minnesota," *ECON. GEOL.*, vol. 15, 1920, p. 422.

Gruner, J. W., "Paragenesis of the Martite Ore Bodies and Magnetites of the Mesabi Range, Minnesota," *ECON. GEOL.*, vol. 17, 1922, pp. 1-14.

⁸ Grout and Broderick, "Organic Structures in the Biwabik Iron-bearing Formation of the Huronian in Minnesota," *Am. Jour. Sci.*, vol. 48, 1919, p. 199.

Broderick, T. M., "Detail Stratigraphy of the Biwabik Iron-bearing Formation, East Mesabi District, Minnesota," *ECON. GEOL.*, vol. 14, 1919, p. 441.

Mesabi ranges is at the bottom of the Biwabik formation, closely associated with the basal conglomerates. Another is in the Upper Cherty division. It was not observed farther west

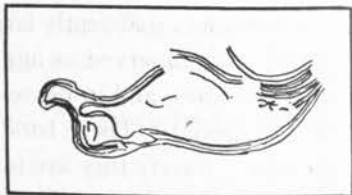


FIG. 43. Tracing of an organic structure from the algal structures of the Upper Cherty in the Gunflint formation. $\times 80$. Slide M. 561. A portion of this organism is shown in Plate VII., B.

than the Hull-Rust mine at Hibbing, but to the east this algal formation is of the same persistence as the basal bed. It is also associated with conglomerates. These conglomerates are as persistent as the algal structures. They have been described in detail by Grout and Broderick.⁹

One excellent horizon-marker is the so-called Intermediate Slate, which on weathering forms the well-known "Intermediate Paint Rock" of the mines. Similar slaty layers can be traced for many miles, though they may not be thicker than a foot or two in places.

Original Extent of the Biwabik Formation.

The area of the Biwabik formation not covered by the slate has been estimated as 135 square miles;¹⁰ that of the Gunflint formation does not exceed 10 square miles. Assuming much erosion and the gradual thinning out of the formations, the total area originally covered by the Biwabik and Gunflint formations may be estimated as 5,000 to 10,000 square miles. The writer examined the cores of over a thousand drill holes in the solid un-

⁹ *Op. cit.*, p. 20.

Also: Grout, F. F., "The Nature and Origin of the Biwabik Iron-bearing Formation of the Mesabi Range, Minnesota," *ECON. GEOL.*, vol. 14, 1919, p. 458.

¹⁰ Van Hise and Leith, *op. cit.*, p. 164.

weathered formation alone, and the greatest thickness of the Biwabik formation found was 750 to 760 feet. At the west end of the range the formation thins out to less than 400 feet. Still more thinning occurs on the east end,¹¹ and an average thickness of 330 feet has been given by Broderick¹² for the Gunflint formation. Probably 550 feet would represent the average thickness of the exposed Biwabik formation. For a sheetlike sediment with an area of 5,000 to 10,000 square miles, an average thickness of 330 feet may be a fair estimate. The explored portion of the iron-bearing formation contains an average of a little more than 25 per cent. iron and has a specific gravity of 3.0 to 3.1. Thus, the total amount of iron in 10,000 square miles of formation 330 feet thick would be about 1,940,000 million metric tons.

Formation of Oölites and Similar Granules.

Link's¹³ experimental work has shown that calcium carbonate, when precipitated as finest mud, will form oölites. Essentially the same thing is reported by Vaughan.¹⁴ Brown¹⁵ comes to the conclusion that oölites are produced either by algæ or similar organisms, or chemically by precipitation. The tendency now is to favor more the organic origin of deposits in cases in which it may be either inorganic or organic, since bacterial and other microörganic action are now being recognized.¹⁶ It is also possible that inorganic and organic formation of oölites can go on side by side, or that organisms cause precipitation of colloids, while the actual shaping of oölites is due to the "tendency of the

¹¹ Grout and Broderick, *op. cit.*, p. 24.

¹² *Op. cit.*

¹³ Link, G., "Die Bildung der Oolithe und Rogensteine," *Neues Jahrb., Beilage Bd. 16, 1903, pp. 495-513.*

¹⁴ Vaughan, T. W., "Remarks on the Geology of the Bahama Islands and on the Formation of the Floridian and Bahaman Oölites," *Jour. Wash. Acad. Sci.*, vol. 3, 1914, pp. 302-304.

¹⁵ Brown, T. C., "Origin of Oölites and the Oölitic Texture in Rocks," *Bull. Geol. Soc. Am.*, vol. 25, 1914, p. 772.

¹⁶ See, for example: Drew, G. H., *Papers from the Tortugas Laboratory, Carnegie Institution, Washington*, vol. 5, 1914, p. 44.

Wethered, E. B., "The Formation of Oölitic," *Quart. Jour. Geol. Soc.*, vol. 51, 1895, p. 205.

droplets forming during the separation of the dispersed phase of an emulsoid to coalesce," as expressed by Bucher.¹⁷

The cause of the formation of concentric layers in oölites has been studied by Schade,¹⁸ who comes to the conclusion that in a deposit consisting mostly of colloidal material (gel), the tendency for the formation of concentric rings is less than in a mixture of crystalloids and colloids. Bucher¹⁹ thinks that the rate of formation of the spherulites is important, those forming rapidly being more or less without definite structure. He also says that "the amount of other substance thrown out simultaneously with, and mechanically enmeshed in, the growing structure" has some effect on the structure. In the Biwabik formation are three kinds of granules:

1. Typical oölites made up of concentric layers. They consist of red jaspery or black graphitic (?) material with a center of the same material or of fine-grained chert. Spurr²⁰ and Leith²¹ have called attention to them. They do not make up one per cent. of all the granules.

2. Typical greenalite granules and their alteration products. No internal structure is visible in these "oölites." Their alteration products are many times as abundant as the unaltered granules, and in many places cannot be distinguished from the alteration product of the kind of structure described under (3).

3. Structures which have the size and outlines of greenalite granules, but whose internal structure is different. They appear to be made up of groups or chains of minute concentric rings which are commonly of chert but may be of a dark graphitic (?) dust or exceedingly minute specks of hematite. Their centers and the matrix in which these rings are imbedded are practically always of the same material, but different from the rings them-

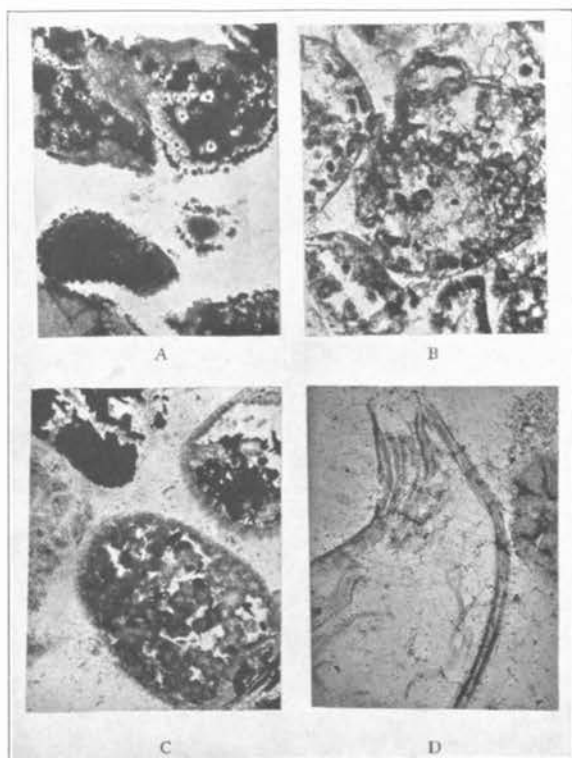
¹⁷ Bucher, W. H., "On Oölites and Spherulites," *Jour. Geol.*, vol. 26, 1918, p. 594.

¹⁸ Schade, H., "Zur Entstehung der Harnsteine und ähnlicher konzentrisch geschichteter Steine organischen und anorganischen Ursprungs," *Zeitschr. Chem. u. Ind. d. Kolloide*, vol. 4, 1909, pp. 175-180, 261-266.

¹⁹ *Op. cit.*, p. 594.

²⁰ *Op. cit.*, Plate VII., Fig. 2.

²¹ *Op. cit.*, Plate XIII., p.

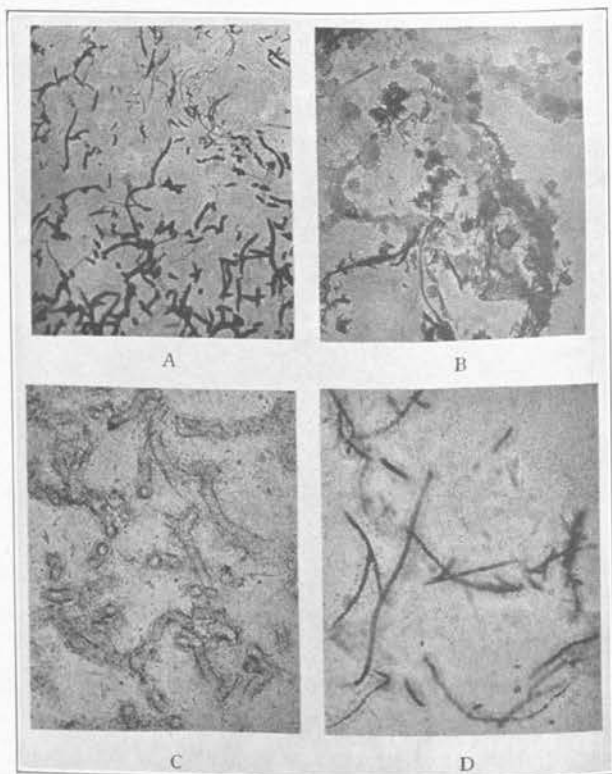


A. Groups and chains of minute concentric rings of chert in granules of greenalite. Matrix of large granules is chert. Nuclei in small rings and surrounding matrix of greenalite-like substance. Some ring structures not visible. $\times 70$.

B. Structures similar to *A*. Chert rings surrounded by "dusty" black rings. Nuclei of same material. Some round dusty black areas without rings. Compare with Pl. VII., *B*. $\times 70$.

C. Large granules (in matrix of chert) with small concentric structures of hematite "dust" and chert. Heavy black areas are magnetite and hematite. Needles of specular hematite cut the concentric structures. Compare with Plate VII., *B*. $\times 130$.

D. Part of structure in Fig. 43. From "algal structure" horizon of Gunflint range. Dark areas in picture are light green. $\times 170$.



A. Iron bacteria and algæ in chert. Most bacteria outlined by heavy sheaths of brown color. $\times 65$.

B. Another view of A. Algæ are prominent. Note resemblance of round structures to those in greenalite structures. (Pl. VI.) Dark colored structures are brown. $\times 70$.

C. Algæ resembling *Microcoleus* (Prof. Josephine Tilden) in chert. Same slide as A. Chert and algæ are practically of the same color. $\times 260$.

D. Iron bacteria resembling *Chlamydothrix* from same specimen as algæ in C. $\times 260$.

selves. For example, Plate VI., *A* shows chert rings with greenalite centers and matrix. Black centers (probably not magnetite) with a white chert ring and another "dusty" black one around it may be seen in Plate VI., *B*. A somewhat similar structure is that of Plate VI., *C*. In it the dark centers are missing. Spurr²² noticed these structures and has an excellent illustration of the greenalite phase of them in his report. He thought that they represented a decomposition phase of "glaucinite." Leith²³ also illustrates them and says that they suggest organic structures. In the Clinton ores in which similar structures occur, they are "clearly due to the replacement of a shell with regular structure," according to Leith. Wethered²⁴ shows some similar structures in oölitic limestone, and attributes them to organisms. These minute structures are of remarkably uniform size (0.03–0.04 mm.). Due to the difference in degree of alteration, they may be composed of different minerals as in the larger greenalite structures. The fact that they are preserved only in fine-grained or almost amorphous material, and not in the more crystallized granules, indicates the primary origin of these structures. It is usual to find them penetrated by magnetite, hematite, or amphibole crystals. In places they may form rings around apparently massive greenalite. When such greenalite granules were examined carefully with strong artificial light, it was sometimes noticed that the apparently homogeneous mass showed faint outlines of these minute structures.

About 200 thin sections from the Biwabik and Gunflint ranges were examined; in many of the less altered ones these structures were seen. In most of them (except those from the East Mesabi) at least traces of the structures were preserved. In the light of the other evidence presented on page 419, they are attributed to the work of microorganisms, and may be called cell structures. Unless all of the greenalite granules are made up of cell structures or some other form of organism, we may con-

²² *Op. cit.*, Plate VI., Figs. 1 and 2.

²³ *Mon.* 43, p. 117 and Plate XIV., *A* and *B*.

²⁴ *Op. cit.*, Figs. 5 and 7.

clude that the following conditions probably would be favorable for the formation of granules without internal structure:

1. Relatively rapid deposition of colloidal precipitates.
2. Lack of strong tendency to crystallize, on account of the colloidal character of silica and ferrous and ferric organic compounds and hydroxides.
3. Absence of fragmental grains which could have formed the nuclei of oölites.

Structures Related to Greenalite Granules.

Many iron ore formations show granular structures similar to greenalite, but most of them differ in one respect—that the majority of their granules are true oölites with concentric ring structures. In most of the formations, however, there occur a relatively small number of granules which have not concentric structures, and therefore resemble typical greenalite structures.

In the Wabana oölites²⁵ other features also are noteworthy. Boring algæ have been found in the oölites, and Hayes thinks it possible that they were active in the production of hematite.

In the Biwabik formation we find hematite and greenalite together. Hematite is commonly taken to be an alteration product of the greenalite. In the Wabana oölites hematite and chamosite occur in alternating concentric rings. It seems fairly certain to the writer that hematite here is not an alteration product of chamosite. It would be difficult to believe that one concentric layer could have remained in one state of oxidation while an adjacent one was changed to some other state, unless there was a conspicuous original difference. There is no reason, then, why hematite (or a ferric hydroxide), where associated with greenalite, could not have been an important primary mineral in the Biwabik formation.

The remarkable similarity in shape of the greenalite and Clinton granules has been emphasized by Leith.²⁶ McCallie²⁷ describes

²⁵ Hayes, A. C., "Wabana Iron Ore of Newfoundland," Canada Geol. Surv. Memoir 78, 1915.

²⁶ Mon. 43, p. 251.

²⁷ McCallie, S. W., "Report on the Fossil Iron Ores of Georgia," Geol. Surv. Georgia, Bull. 17, 1908, p. 174.

Clinton ore granules with a nucleus of a greenish mineral which he thinks is similar to greenalite.

Glaucanite resembles greenalite closely in shape and internal structure. Spurr²⁸ thought that greenalite is a potassium-poor variety of glaucanite. Leith objected²⁹ to this, because aluminum is also absent from the greenalite, and because detrital mud, always associated with glaucanite, is not found with greenalite. It is probable, however, that greenalite granules form by processes similar to those active in the making of glaucanite. According to Clarke,³⁰ this process may be adsorption. So far, however, no generally accepted theory has been advanced for the formation of glaucanite.³¹

Microorganisms in and near the Bixwabik Formation.

Lower organisms were widespread in Upper Huronian time.³² In 1911 Cayeux³³ mentioned organic structures in the Mesabi, Menominee, and Penokee Gogebic ranges, but his work is not clear as to what structures were meant.

In the present investigation, specimens of chert which contain

²⁸ *Op. cit.*, p. 242.

²⁹ *Op. cit.*, pp. 242 and 254.

³⁰ *Op. cit.*, pp. 513-514.

³¹ Murray, J., and Renard, A. F., "Voyage of the Challenger; Deep Sea Deposits," 1891, p. 389.

Murray, J., and Hjort, J., "Depths of the Ocean," London, 1912, p. 189.

Collet, L. W., and Lee, G. W., "Recherches sur la galuconie," *Proc. Roy. Soc. Edinbg.*, vol. 26, 1906, pp. 259-262.

Andree, K., "Über Sedimentbildung am Meeresboden," *Geol. Rundschau*, vol. 8, 1917, pp. 59-61.

³² Walcott, C. D., "Pre-Cambrian Algonkian Algal Flora," *Smiths. Inst. Misc. Coll.*, vol. 64, no. 2, 1914.

Idem., "Notes on Fossils from Limestone of Steeprock Lake, Ontario," *Geol. Survey Canada, Mem.* 28, 1912, p. 16.

Moore, E. S., "The Iron Formation on Belcher Islands, Hudson Bay, etc.," *Jour. Geol.*, vol. 24, 1918, pp. 412-438.

Grount and Broderick, *Am. Jour. Sci.*, vol. 48, 1919, p. 199.

Broderick, T. M., *ECON. GEOL.*, vol. 15, 1920, p. 422.

³³ Cayeux, L., "Existence de restes organiques dans les roches ferrugineuses associees aux mineraux de fer huroniens des Etats-Unis," *Compt. rend.*, vol. 153, 1911, pp. 910-912.

not only algæ, but also iron bacteria and most probably bacilli (Plates VII. and VIII.) were found. The chert was found in the Archean greenstones and the Lower Middle Huronian graywackes northeast of Eveleth. Cherts of gray, greenish, and Jasper-red tints fill joint cracks of varying widths in the greenstone and graywacke. In places the cracks widen out into larger irregular areas. Often these cracks are straight for 6 to 10 feet. They must have been filled after the last severe folding of the area. This folding took place before the laying down of the iron-bearing formation. Glacial erosion has planed off weathered material and has left a smooth, almost fresh, surface of greenstone and graywacke. That the organisms are at least as old as the Upper Huronian rocks seems to be evident from the following observations:

1. The chert is fresh, and indistinguishable, either in the hand specimen or under the microscope, from any of the cherts of the Lake Superior region.

2. Under the microscope it is seen to be finely crystalline and to contain small perfect rhombohedral crystals of carbonate, as in iron carbonate of the iron-bearing rocks.

3. Microscopic needles of an amphibole, probably actinolite, are observed in the chert. These needles are common in the iron-bearing formations, and indicate considerable depth of burial.

4. Minute pyrite cubes replace the chert, and in one place, the algal growths also. Pyrite is abundant throughout the greenstones and graywackes³⁴ in this area. It probably was introduced during or at the end of the last intrusive activity, which, in this area, seems to be represented by a porphyry dike containing pyrite only a few hundred feet away from the place at which the organisms were found. This dike was assigned to the Keweenaw period by the writer.³⁵ In the cherty phases of the Biwabik formation pyrite is almost absent. It seems reasonable to infer, then, that the pyrite associated with the microorganisms was introduced hydrothermally.

³⁴ Van Hise and Leith, *op. cit.*, p. 512.

³⁵ Report in preparation.

5. The chert filling the cracks in the greenstone and graywacke is found only within 1,800 feet of the present edge of the Biwabik formation; farther away there is none. If the dip of the Biwabik formation be projected toward the greenstone, it is found that the fossils would be only a very short distance, if any, below the bottom of the former iron-bearing sediments. The Pokegama quartzite is thin in this area, and probably was almost absent in some places. This would mean that the iron-bearing formation practically rested on the Archean or Lower Middle Huronian rocks, as it does in some other places on the range.

6. No chert later than that of the Biwabik formation has ever been reported from the Lake Superior region. On the other hand, the chert is removed in enormous quantities from the ore. Where silica has been redeposited in veins, it has been in the form of quartz. As a matter of fact, in one place small quartz veins were found which cut the chert in the joint cracks. If this chert, however, were really deposited by descending solutions, it would be, so far as the writer knows, the first fossiliferous chert observed in true veins.

7. The chert is embedded in country rock which seems to be practically fresh at the contacts, as if it had not been exposed to weathering. It is probable that the massive, already metamorphosed, rock protected the chert in the joint cracks from deformation and changes experienced by the Biwabik formation proper.

8. According to Grout,³⁶ on the East Mesabi Range fissures in granite are filled with rock of the iron-bearing formation which overlies the granite. Cases are also known in which chert and jasper filling joint cracks in greenstone and basalt are associated with overlying cherts and iron-bearing formations.³⁷

In studying the algæ of Plate VII., *B* and *C* and thin sections of other specimens from the same locality, it was observed that there seems to exist a gradation from the perfect ones (which form a

³⁶ Personal communication.

³⁷ Leith, C. K., "An Algonkian Basin in Hudson Bay—a Comparison with the Lake Superior Basin," *ECON. GEOL.*, vol. 5, 1910, p. 242.

Dewey, H., and Fleet, J. S., "On Some British Pillow-lavas and the Rocks Associated with Them," *Geol. Mag.*, vol. 48, 1911, pp. 202-209, and 241-248.

network) to groups which seem to consist only of concentric rings, or round spots (like some in Plate VII., *B*) without any connecting portions or sheaths between them. These simpler rings or spots usually seem to be a little larger than the cross sections of the algæ in Plate VII., *C*. They resemble the rings in the greenalite structures (Plates VI. and VIII., *A*) very much, and strongly suggest a relation in origin.

New organisms were also found in the cherts of the algal structure horizon of the Gunflint and Biwabik formations. Bacilli (there is little doubt that they are such) of the same kind as those shown in Plate VIII., *B* were found in two specimens from the algal structures of the Upper Cherty Division near Hibbing. They are of the same shape and size as those in Plate VIII., *B*, but are less numerous. According to Professor A. T. Henrici,³⁸ they are probably the same species.

In this connection may be mentioned rods of silica (about 10 to 12 microns long) which were observed by Bleicher³⁹ in oölites of the Minette ores of France. These rods are said to resemble bacteria. In a specimen from the algal structure horizon of the Upper Cherty Division on the Gunflint Range, the algæ shown in Fig. 43 and in Plate VI., *D* were found. There still exists some doubt as to whether these plants belong to a higher class than algæ. Microorganisms, probably fungi and algæ, were also found by the writer in chert pebbles of the basal conglomerate of rock assigned by Leith⁴⁰ to the Pokegama quartzite. Lack of space prevents their being described here. They corroborate, however, the evidence that the algæ and bacteria described in the preceding paragraphs are of at least Upper Huronian age.

The writer wishes to express his thanks to Dr. C. D. Walcott and to Dr. Albert Mann, of the Smithsonian Institute, for examining one of the sections containing fungi-like plants, to Professor Josephine Tilden, Professor C. O. Rosendahl, and Profes-

³⁸ Dept. of Bacteriology, Univ. of Minnesota.

³⁹ Quoted by Van Werweke, L., "Bemerkungen über die Zusammensetzung und die Entstehung der lothringisch-luxemburgischen oolithischen Eisenerze," *Zeitschr. prak. Geol.*, vol. 9, 1901, p. 396.

⁴⁰ *Op. cit.*, Mon. 43, p. 97.

sor F. K. Butters, of the department of Botany of the University of Minnesota, for the identification of algæ and similar structures, and to Professor A. T. Henrici for identification of the bacteria. Professor Charles Schuchert of Yale University also had the kindness to examine the photographs.

SOLUTION OF IRON AND SILICA.

In the following experiments an attempt has been made to show that iron and silica are dissolved by solutions from decaying organic matter. The results have been compared with those obtained in experiments with carbonated water and with other dilute acid solutions.

Amounts of Iron in Natural Waters.

The average river water contains less than one part per million of iron.⁴¹ Sea waters also are very low in iron. This suggests that such waters are an inadequate source for the deposition of a great iron-bearing formation. There are, however, some analyses showing more iron. The rivers of Brazil and other parts of South America carry from 2 to 7 parts of Fe_2O_3 ; this is a relatively large percentage of their total mineral content, which is usually low.⁴²

Swamp waters commonly contain more iron than other surface water.⁴³ Moore⁴⁴ reports three waters with 47 to 61 parts of Fe_2O_3 per million, either from lakes in which iron ores are in the process of formation, or from creeks tributary to such lakes.

⁴¹ Clarke, F. W., "The Data of Geochemistry," U. S. Geol. Survey, Bull. 695, 1920.

⁴² Clarke, F. W., *op. cit.*, pp. 90-92. See also analyses *B* and *E*, p. 77; *G*, p. 93; and *E*, p. 105, which contain unusual amounts of iron and organic matter.

⁴³ Endell, K., "Der Säuregehalt des Moorwassers," *Jour. prakt. Chem.*, vol. 82, pp. 414-422, 1910.

See also Endell, K., "Über die chemische und mineralogische Veränderung basischer Eruptivegesteine bei der Zersetzung unter Mooren," *Neues Jahrb. Min.*, Beilage Bd. 31, 1911, pp. 1-54.

⁴⁴ Moore, E. J., "The Occurrence and Origin of Some Bog Iron Deposits in the District of Thunder Bay, Ontario," *ECON. GEOL.*, vol. 5, 1910, pp. 528-538.

Simpson⁴⁵ mentions a small stream which contains 17 parts per million of iron and much organic matter. It is noteworthy that organic matter seems to be always present in surface waters that contain much iron.

Spring waters often carry iron, but such waters are probably not the sources of the large iron-bearing formations, on account of their limited quantity.

Decaying Organic Matter as Solvent.

From decaying plant life there may be extracted by water a brownish solution which is, for the most part, colloidal in nature.⁴⁶ These solutions are slightly acid, but it is not known yet whether this acidity is due to so-called "humus acid"⁴⁷ (which is an indeterminate substance), or to other organic or inorganic acids, such as carbon dioxide.⁴⁸

With such solutions,⁴⁹ it is thought that iron can form so-called ferrous and ferric humates, which probably are colloidal in nature and, under certain conditions, retain iron persistently. In 1870 Thenard⁵⁰ stated that silica could form "silico-azo humic acids" with humus and nitrogen. Julien⁵¹ based some of his conclu-

⁴⁵ Simpson, E. S., "Notes on Laterites in Western Australia," *Geol. Mag.*, vol. 49, 1912, p. 405.

⁴⁶ Clarke, F. W., *op. cit.*, p. 106.

Odén, Sven, "Die Huminsäuren. Chemische, physikalische und bodenkundliche Forschungen," *Kolloidchemische Beihefte*, vol. II, 1919, p. 104.

Albert, R., "Bemerkungen zu den Abhandlungen von H. Stremme über die 'so-genannten Humussäuren,'" *Zeitschr. prakt. Geol.*, vol. 17, 1909, p. 528.

Stremme, H., "Die so-genannten 'Humussäuren,'" *Zeitschr. prakt. Geol.*, vol. 17, 1909, pp. 353-355.

Gillespie, L. J., and Wise, E., "Action of Normal Salts on Humus and Other Experiments on Soil Acidity," *Jour. Am. Chem. Soc.*, vol. 40, 1918, p. 796.

Aschan, O., "Die Bedeutung der wasserlöslichen Humusstoffe für die Bildung der See und Sumpferze," *Zeitschr. prakt. Geol.*, vol. 15, 1907, p. 57.

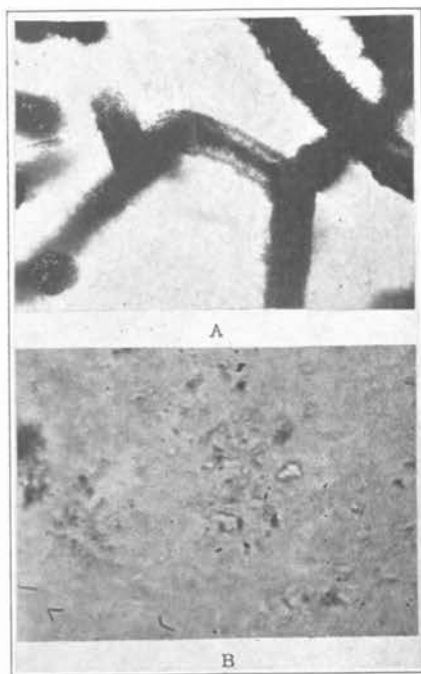
⁴⁷ Odén, Sven, *op. cit.*, pp. 138 and 147.

⁴⁸ Van Hise, C. R., "A Treatise on Metamorphism," U. S. Geol. Survey Mon. 47, 1904, p. 461.

⁴⁹ Odén, S., *op. cit.*, p. 180.

⁵⁰ Thenard, P., *Compt. Rend.*, vol. 70, 1870, p. 1412.

⁵¹ Julien, A. A., "On the Geological Action of the Humus Acids," *Am. Assoc. Adv. Sci.*, vol. 28, 1879, pp. 311-410.



A. Iron bacteria from the same specimen as in Plate VII. Note sheath and cross section of sheath in upper right corner. Black areas brown in specimen. $\times 1300$.

B. Bacilli from the same specimen as *A.* Minute rods rounded at the ends; some are bent; uniform in size and numerous. Only a few can be got into focus at one time. They are white like the chert. $\times 1300$.

sions on the existence of these "acids." Clarke,⁵² however, discredited Thenard's statement. Niklas,⁵³ in the study of soils, has demonstrated the solubility of minerals and rocks in peat solutions. Weiss⁵⁴ has shown that peat solutions will change an impure clay to a residue of almost pure kaolin.

Experiments with Peat Solutions.

Material Used and Methods of Analysis of Solutions.—In all experiments distilled water and the same kind of a lime-deficient peat from William's bog north of Duluth, Minnesota, were used. A partial analysis of the peat (after drying at 110° for 5 hours) gave:

	Per Cent.		Per Cent.
Total ash	7.110	CaO	0.510
SiO ₂	5.660	MgO	0.360
Fe	0.012		

Mineral and rock powders (ground in agate mortar) that passed through 200 mesh were used. Glauconite sand was used without powdering it. In all experiments with a certain mineral or rock, powder from the same crushed sample was taken. Determinations of silica and iron were made of most samples. A list of the minerals and rocks used follows:

1. *Pyrite*—crystals with possibly a little quartz. Washed with dilute HCl.
2. *Hematite*—compact columnar variety. It was used in preference to specular hematite, as the latter seems to be mixed with magnetite, as a rule. The powder in water was cleaned with a magnet. No magnetic particles were found.
3. *Limonite*—reniform. Contains some SiO₂. Treated like hematite. Washed with dilute HCl to free from any carbonate.

⁵² *Op. cit.*, p. 106.

⁵³ Niklas, H., "Untersuchungen über den Einfluss von Humusstoffen auf die Verwitterung der Silikate," *Int. Mitt. f. Bodenkunde*, vol. 2, 1912, pp. 214-244.

⁵⁴ Weiss, F., "Vorkommen und Entstehung der Kaolinerden des ostthüringischen Buntsandsteinbeckens," *Zeitschr. prakt. Geol.*, 1910, p. 365.

4. *Siderite*—massive, crystalline with some quartz. CaO trace; MgO 4.5.
5. *Magnetite*—from Port Henry, N. Y. Massive variety.
6. *Augite*—black massive variety with a little calcite. Powder was cleaned under water with a strong magnet. SiO₂ 38.6; Fe 14.06.
7. *Olivine rock*—granular, from Scott's creek, Jackson County, N. C. Washed and treated magnetically to extract any magnetite. SiO₂ 41.9; Fe 4.99.
8. *Serpentine*—massive yellowish green variety. Apparently contains no other mineral. SiO₂ 41.8; Fe 3.57.
9. *Glaucconite sand*—from New Jersey.
10. *Greenalite rock*—Mesabi Range, Section 19, T. 57 N., R. 21 W. Greenalite granules are conspicuous. SiO₂ 46.40; Fe 16.27; CaO 2.96; MgO 26.20.
11. *Magnetic ferruginous chert*—Mesabi Range, Section 27, T. 56 N., R. 24 W. Contains about 20 per cent. of iron as magnetite and a little carbonate (no calcite). SiO₂ 44.09; Fe 29.39.
12. *Ely greenstone*—spherulitic. Near Ely, Minnesota. SiO₂ 45.3; Fe 10.69.
13. *Duluth gabbro*—dark variety. Near Duluth, Minnesota. SiO₂ 54.93; Fe 10.02.
14. *Sudbury nickel ore*—norite, pyrrhotite, and pentlandite. Pyrrhotite makes up 70 or more per cent. of specimen.

The solutions, after having been in contact with the mineral matter the required time, were filtered and evaporated in pyrex beakers to 50 c.c., then in platinum dishes; and the organic matter was burned off. The residue was analyzed by standard methods (silica by hydrofluorizing, iron by titration with potassium permanganate). When only approximate results were desired, as in Table III., colorimetric estimates were made. Potassium ferri-cyanide in excess was added to the organic solution, and the color of the latter was compared with another organic acid solution of known iron content, to which the same amount of potas-

sium ferricyanide had been added. Quantitative check analyses showed this to give good results.

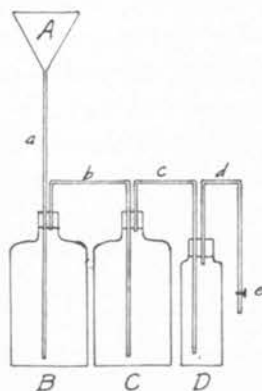


FIG. 44. Apparatus used in the solution of minerals by peat waters.

Action on Powdered Mineral Matter.—The apparatus shown in Fig. 44 was used to assure a large and continuous supply of solution from the different minerals. The stoppers and connections between the glass tubes and funnels were of rubber. 20 grams of the mineral were mixed with as much peat as could be conveniently put into bottle (B) without stopping the circulation of water. 15 grams of the same mineral were put into bottle (C) with distilled water and allowed to settle. Flask (D) was filled with distilled water and was intended to catch any solid particles that might come over from bottle (C). Funnel (A) was filled with peat, and in order to keep the peat from entering tube (a), glass-wool was placed in the bottom of (A). The whole apparatus was then filled by letting the air slowly escape through the stopcock (e) and pouring distilled water into the funnel. Then 500 c.c. of solution were drawn off each week through stopcock (e). For each of the minerals and rocks mentioned, except serpentine, and for a blank, the apparatus and conditions for the experiment were identical.

While it was expected that the peat solution would dissolve all the mineral matter it could hold in bottle (B), the vessel (C)

was introduced in order to have the solution also come into contact with mineral matter in the absence of peat. This would correspond to natural conditions, where the peat solutions percolate through underlying rocks, and, according to some geologists, deposit a part of the salts they contain. Considerable amounts of gas were observed to collect in the bottles about two weeks after they were filled, and continued to form to the end of the experiments. It was probably a mixture of hydrocarbon gases, as some of it was inflammable. The amount of organic matter in different solutions varied greatly. The maximum amount observed was 317 parts of organic matter (dried at 105°) per million.

As the peat solution slowly rose in bottle (C) when the water was drawn off at (e), a relatively sharp line was observed at the contact of the solution with the distilled water. The colloidal solution evidently did not diffuse in the water above it to an appreciable extent. The solutions were clear, though ranging in color from yellow to dark brown. All the peat solutions, unless the contrary is stated, reacted either slightly acid or neutral, with litmus solution or neutral red as indicators.

Not all the minerals gave up iron with the same rapidity. The pyrite, magnetite, siderite, magnetic ferruginous chert, greenstone, augite, olivine, and Sudbury ore solutions contained iron when the peat water first reached the outlet of the apparatus (after 40 days). The solutions from greenalite and Duluth gabbro gave tests for iron 20 days later, while iron did not appear from hematite, limonite, and glauconite until 30 days after the peat water had reached the outlet. This is probably due to the fact that iron is contained in these last three minerals in the ferric state, which requires more time for solution, on account of the necessary reduction to the ferrous condition.

Qualitative tests for iron (which was always in the ferrous state) were made with potassium ferricyanide. Colloidal iron does not react with potassium ferro- and ferricyanide,⁵⁵ for this reaction takes place between the ions. Since tests with the cy-

⁵⁵ Zsigmondy, R., "Kolloidchemie," 1918, p. 270.

nides showed ferrous iron, we know that the iron is present in part in true solution. Dialysis of one of the solutions through a collodion membrane showed that Fe ions were abundant, though colloidal ferro-humates may have been present also. Alumina seemed to be present in traces only, according to qualitative tests. The partial analyses of two samples of 500 c.c. each, taken at intervals of about 80 and 170 days respectively, are given in Table I.

TABLE I.
SOLUBILITY OF MINERALS AND ROCKS IN PEAT SOLUTIONS.
(Parts per Million.)

	After 77 Days.		After 182 Days.			
	SiO ₂ .	Fe.	SiO ₂ .	Fe.	CaO.	MgO.
Blank	1	Trace	6	2	9	Trace
Pyrite	Not det.	23	9	14	7	Trace
Hematite	Some	25	10	27	8	Trace
Limonite	Some	14	15	30	7	Trace
Magnetite	Not det.	31	8	41	10	Trace
Siderite	Some	94	10	48	9	Trace

	After 90 Days.		After 165 Days.			
	SiO ₂ .	Fe.	SiO ₂ .	Fe.	CaO.	MgO.
Augite	40	9	35	8	31	2
Olivine	161	14	106	9.5	8	24
Greenstone	81	20	68	15	16	Trace
Duluth gabbro	78	19	82	15	16	Trace
Greenalite rock	47	17	44	9	8	2
Magnetic ferrug. chert	30	27	33	25	14	2
Glauconite sand	26	15	35	19	29	3
Sudbury ore	25	22	30	16	14	Trace

Some experiments were performed to ascertain the reaction of peat solution on minerals under static conditions. Glass bottles of a volume of 2,500 c.c. were filled with 20 grams of the mineral, about 75 grams of peat, and distilled water. Then they were closed with greased glass stoppers. Occasionally they were shaken. After 120 days, 500 c.c. of each solution were analyzed (Table II.).

go into solution at all; MgO and CaO, on the other hand, while dissolved, are adsorbed by the colloids of the peat,⁵⁸ or precipitated as organic compounds, and appear in the solutions in only small amounts. The amount of silica in the solutions from olivine is greater in the presence of air than in the absence of air.

The following experiments indicate that the efficiency of peat solutions alone is practically as great as that of peat solutions in contact with the peat. The minerals tested in filtered peat solutions were siderite, pyrite, hematite, limonite, and magnetite. One gram of each was put into a large test tube (75 c.c.), and filtered peat solution from the blank sample of the first experiment (Table I.) was added. The full tubes were closed with rubber stoppers. Colorimetric estimations of iron after 45 days gave results similar to those of Table I.

In order to find out whether a mineral such as serpentine, due to its easy solubility and basic character, could influence the solubility of the iron oxides in a marked degree when mixed with them, three experiments were made. To three bottles of 2,500 c.c. capacity each, containing distilled water, 20 grams of peat, and 10 grams of serpentine, were added: (1) 10 grams of siderite, (2) 10 grams of limonite, and (3) 10 grams of magnetite. The water present was sufficient to fill the bottles. They were stoppered and agitated a little about every two days. The analyses after 45 days showed, in parts per million:

	SiO ₂ .	Fe.
(1) Serpentine + siderite	60.5	24.7
(2) " + limonite	68.9	29.0
(3) " + magnetite	83.2	15.7

In the case of siderite and limonite, the amount of iron is a little smaller than in the absence of serpentine. In the case of magnetite, only about half as much iron, on an average, has gone into solution as in the absence of serpentine.

Action on Polished Surfaces and Thin Sections.—Polished pieces of magnetite, pyrite, magnetite and hematite together in one specimen, and magnetite, chert, and carbonate together in

⁵⁸ Clarke, F. W., *op. cit.*, p. 497.

another specimen, were submerged in stoppered bottles that contained peat and water. The bottles were carefully stoppered. After two months all the solutions contained at least traces of iron. The magnetite and hematite had lost some of their luster, while the pyrite was practically unaffected. In the specimen that contained magnetite, chert, and carbonate, the carbonate had been eaten out to appreciable depth, leaving the other minerals unchanged.

Thin sections of Mesabi taconite (chert with granules of hematite), basalt, gabbro, olivine gabbro, hornblende schist, quartz diorite with biotite, and opal were treated as follows: For each slide an apparatus similar to Fig. 44 was used. Half of the cover glass and Canada balsam of each slide was removed, and the slide put into a bottle which would correspond to bottle (C) in Fig. 44. The slide was thus not in contact with peat. About 500 c.c. of solution were drawn off every month. After seven months the slides were examined.

In the taconite the hematite contained in the granules had been partly dissolved. In the olivine gabbro, the olivine in the uncovered portion had been either changed to an almost isotropic substance with an index of 1.552, or had been "eaten out" entirely in a few places. The resemblance of the remaining portions to serpentine is great in index and birefringence. Augite, which was also present in the olivine gabbro, was not altered noticeably. In the other slides only slight clouding was observed.

Combinations of Peat and Salt Solutions.

Colloids or very porous substances, when brought into contact with solutions of neutral salts, commonly adsorb the base-forming element, causing the solutions to become acid.⁵⁹ Many experi-

⁵⁹ Cameron, F. K., and Bell, J. M., "The Mineral Constituents of the Soil Solution," U. S. Dept. Agr. Bur. of Soils, Bull. 30, 1905, p. 39.

Sullivan, E. C., "The Interaction between Minerals and Water Solutions with Special Reference to Geologic Phenomena," U. S. Geol. Survey, Bull. 312, 1907, p. 10.

Harris, J. E., "Some Adsorption Phenomena in Soils and Kaolin," *Jour. Phys. Chem.*, vol. 18, 1914, pp. 355-371.

Bancroft, W. D., "Applied Colloid Chemistry," New York, 1921, pp. 90-128.

Clarke, F. W., *op. cit.*, p. 496.

ments were made by the writer to determine the effect of adsorption by peat solutions. Peat and powdered mineral matter were added to a salt solution. A few of the results are given in Table IV. They clearly indicate that strong acids were liberated in the case of sulphate and chloride solutions. These acids attacked the minerals much more than the ordinary peat solutions (Table I.). In the solutions containing carbonates, on the other hand, only carbonic acid was freed. This was shown by strong effervescence when the bottles were opened. The carbonic acid attacked the minerals relatively feebly. The solutions with the chlorides and sulphates were almost colorless and contained very little organic matter; those with the carbonates were brownish yellow and had much organic matter. The solubility of iron and silica in the presence of air was similar to that in its absence, in these solutions. When mineral matter and a salt were added to a *filtered* peat solution, very similar results were obtained. The uniformity in the amounts of iron in the vessels containing CaCO_3 (Table IV.) seems to indicate that the combination of

TABLE IV.
SOLUBILITY OF IRON AND SILICA FROM MINERALS IN SALT SOLUTIONS IN CONTACT WITH PEAT IN CLOSED BOTTLES FOR 40 DAYS.
(Parts per Million.)

$\frac{1}{2}$ G. of Peat and $\frac{1}{2}$ G. of Mineral in 75 c.c. Sol.	Kind and Concentration of Salt Used in 75 c.c. Distilled Water.					
		$1\frac{1}{2}$ G. Na_2SO_4 .	$1\frac{1}{2}$ G. NaCl .	$1\frac{1}{2}$ G. MgCl_2 .	$\frac{1}{2}$ G. MgCO_3 .	$\frac{1}{2}$ G. CaCO_3 .
Pyrite.....	Fe	333.8				
Magnetite.....	Fe	157.8				
Olivine.....	Fe		22.4*	36.1		8.4
	SiO_2		132.4	121.2		57.1
Greenalite.....	Fe					8.4
	SiO_2					33.1
Magnetic ferruginous chert.....	Fe				5.1	8.7
	SiO_2				12.0	26.6
		Solutions acid†			Sol. alkal.	Sol. neutral

* 224.0 parts MgO in solution.

† Litmus for indicator.

water, peat, and CaCO_2 cannot hold more than 8.5 to 9.0 parts of iron per million in solution.⁶⁰

Artificial sea water⁶¹ was used with peat in two experiments. After 135 days (in closed bottles) the solutions contained, in parts per million:

	From Greenstone.	From Serpentine.
SiO_2	18.0	111.2
Al_2O_3	3.2	—
Fe	124.0	13.0

All iron was in the ferrous state.

Sea water alone and sea water with greenstone after 135 days contained only traces of iron and silica.

This behavior of decaying plant life when acted on by sea water or other chlorides and sulphates is, it seems to the writer, of great geologic importance. Possibly an indication that decaying animal tissue brings about similar reactions is the statement by Murray and Irvine⁶² that putrifying mussel flesh in sea water is able to dissolve 25 parts of silica per million from diatom and globigerina oozes.

Carbonated Water as Solvent.

A few experiments were made with carbonated water, and the results were compared with those of former experiments.⁶³ Flasks (500 c.c.) were filled with distilled water as nearly satu-

⁶⁰ The solutions from augite, which contains calcite (Tables I. and III.), also have not more than 9 parts of iron.

⁶¹ The solutions contained per liter:

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	8.00 grams	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	3.30 grams
NaCl	27.20 "	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.50 "

⁶² Murray, J., and Irvine, R., "On Silica and Siliceous Remains of Organisms in Modern Seas," *Proc. Roy. Soc. Edinburgh*, vol. 18, 1891, p. 248.

⁶³ Müller, R., "Untersuchungen über die Einwirkung des kohlensäurehaltigen Wassers auf einige Mineralien und Gesteine," *Thermaks Min. Mitteil.*, 1877, pp. 25-48.

Henrich, F., "Über die Einwirkung von kohlensäurehaltigem Wasser auf Gesteine und über den Ursprung und den Mechanismus der kohlensäureführenden Thermen," *Zeitschr. prakt. Geol.*, vol. 18, 1910, pp. 85-94.

Leitmeier, H., "Zur Kenntniss der Karbonate," *Neues Jahrb.*, Beil. Bd. 40, 1916, pp. 681-684.

rated with CO_2 as possible, and 5 grams of the mineral matter were added. The flasks were quickly stoppered and sealed. After seven weeks the solutions were analyzed, with the following results:

TABLE V.

MATERIAL DISSOLVED IN WATER SATURATED WITH CARBON DIOXIDE IN 7 WEEKS.
(Parts per Million.)

From	SiO_2 .	Fe.	CaO.	MgO.
Siderite*.....		19.1	Trace	46.0
Magnetite.....		28.0		
Olivine.....	44.7	28.9		105.0

* Siderite contains 3.3 per cent. MgO and traces of CaO and SiO_2 .

In order to ascertain whether a continuous stream of carbon dioxide would be more effective, 5 grams of each mineral were put into bottles and washed CO_2 was bubbled through the bottles for 2 and 4 weeks respectively.

Special precautions were taken to avoid contamination by air. 50 c.c. of each solution were analyzed each time. The results are given below:

TABLE VI.

MATERIAL DISSOLVED IN WATER THROUGH WHICH CO_2 WAS PASSED
CONTINUOUSLY.
(Parts per Million.)

From	After 2 Weeks.				After 4 Weeks.			
	SiO_2 .	Fe.	CaO.	MgO.	SiO_2 .	Fe.	CaO.	MgO.
Siderite*.....		29.4		21.0		37.3		89.0
Olivine.....	61.0	49.7	Trace	235.0	92.0	34.3	Trace	229.0
Duluth Gabbro.....	14.0	14.0			23.0	26.1	149.0	64.4

* Siderite contains 3.3 per cent. MgO and traces of CaO and SiO_2 .

These experiments show that siderite containing some MgO does not go into solution in carbonated water more readily than the silicates or magnetite. The experiments, furthermore, show that more silica and magnesia and less iron was dissolved from olivine

than in similar experiments by Müller and Leitmeier.⁶⁴ A continuous stream of carbon dioxide was more effective in attacking magnesia, as might have been expected, but it also dissolved more silica.

Conclusions.

From these experiments⁶⁵ the following conclusions may be reached:

1. Solutions from decaying plants dissolve all oxides and carbonates of iron, and most of the silicates, but do not seem to attack pyrite appreciably.

2. The strength of such solutions is similar to that of carbonic acid. It is possible that carbonic acid is the chief acid of the so-called "natural organic acids," but the organic colloids in such solutions give special properties to them.

3. One of the differences between natural organic solutions and carbonic acid is that the organic solutions reduce ferric iron compounds to soluble ferrous salts, while carbonic acid does not.

4. When a solution of a neutral salt with a strong acid radical comes into contact with natural organic colloids, acid is set free which dissolves much iron and silica.

5. The presence of carbonates impedes the solution of silica and iron in natural organic solutions.

6. Ordinarily the ratio of iron to silica in peat solutions in the absence of air (Table I.) is very similar to the ratio of iron to silica in the undecomposed minerals.

The following conclusions, which are of particular value in the study of lateritic deposits, apply to all dilute acid solutions:

7. As a general rule, the less silica a silicate contains, the greater will be the amount of silica dissolved by a given amount of dilute acid.

8. Magnesium salts, in general, accelerate the solution of silica, but impede that of iron.

9. For a similar reason an acid will not extract as much iron

⁶⁴ *Op. cit.*

⁶⁵ Other experiments by the writer not included in this paper corroborate the conclusions.

from a mixture of a basic silicate (serpentine) and an iron oxide, as from the iron oxide alone.

PRECIPITATION OF IRON AND SILICA.

Precipitation of Iron.

Harder⁶⁶ has summarized the precipitation of iron. He says that iron may be precipitated as some form of ferric hydroxide, as basic sulphate, as normal carbonate, as sulphide, or as silicate.

The following observation was made on the solutions which contained iron bicarbonate in the experiments recorded on pages 433 and 434. Three days after the bottles had been opened, all the iron was precipitated as hydroxide, though there had been no agitation of the solutions. This throws doubt on the assumption that iron is carried largely as bicarbonate in surface waters. Spring waters containing much CO₂, however, do carry considerable iron as bicarbonate.

Experiments with Filtered Peat Solutions.—Peat solutions which had taken up iron, after they had been filtered, held the iron in solution in the absence of air without any tendency to precipitation. Even if air had access to the solutions, the precipitation of iron did not begin immediately and did not become complete during one year. Bubbling air through a solution for twenty-four hours had no visible effect on the solution, and did not oxidize the iron. Drying up of a solution produced dark brown, shiny, brittle solids. A large part of this solid could be dissolved again in distilled water. Iron, probably a ferric colloidal compound, was present in the material redissolved. The addition of clean sand or finely-powdered chalcedony or orthoclase did not accelerate precipitation of iron from any of the solutions.

The following experiments show the influence of the addition of carbonates and sulphates: Large test tubes were filled with solutions containing iron which had been drawn off from the large apparatus shown in Fig. 44. Small amounts of the salts

⁶⁶ Harder, E. C., "Iron-depositing Bacteria and their Geologic Relations." U. S. Geol. Survey, Prof. P. 113, 1919, pp. 64-84.

TABLE VII.

EFFECT OF CARBONATES AND SULPHATES ON PEAT SOLUTIONS CONTAINING IRON IN STOPPERED BOTTLES.

Minerals from which Peat Solutions Had Dissolved Iron.	Salts Added to 75 c.c. of Solution to Precipitate the Iron.														
	0.1 g. MgCO ₃ .			0.1 g. CaCO ₃ .			0.2 g. MgSO ₄ .			0.2 g. CaSO ₄ .			0.2 g. Na ₂ SO ₄ .		
	Days.	Kind of Pppte.	Amount of Pppte.	Days.	Kind of Pppte.	Amount of Pppte.	Days.	Kind of Pppte.	Amount of Pppte.	Days.	Kind of Pppte.	Amount of Pppte.	Days.	Kind of Pppte.	Amount of Pppte.
Pyrite.....	8	FeS	Trace*	60	FeS	Trace*	30	Fe ox.	Incompl.				8	FeS	Trace*
	30	FeS	Complete	200	FeS	Complete	180	FeS	Complete				30	FeS	Complete
Hematite.....	8	FeS	Trace				30	FeS	Trace*						
	30	FeS	Complete				200	FeS	Complete						
Magnetite.....	10±	FeS	Trace	36	FeS	Trace	60	FeS	Trace	4	FeS	Trace*	5	FeS	Trace
	30	FeS	Complete	200	FeS	Complete	200	FeS	Complete	30	FeS	Complete	30	FeS	Complete
Siderite.....	14	Fe ox.	Small				40	Fe ox.	Small	14	Fe ox.	Large	30	Fe ox.	None
	30	Fe ox.	Incompl.				180	FeS	Complete	30	Fe ox.	Incompl.	200	Fe ox.	Very small
Augite.....	8	Fe ox.	Small				8	White	Small						
	30	FeS	Complete				200	FeS	Complete						
Olivine.....	8	Fe ox.	Small				60	None	None						
	30	FeS	Complete				200	FeS	Complete						
Greenalite.....	8	Fe ox.	Small												
	30	FeS	Complete												
Glauconite.....	8	Fe ox.	Small	40	FeS	Trace	8	White	Small	30	Fe ox.	Incompl.	30		None
	30	FeS	Complete	200	FeS	Complete	200	Fe ox.	Very small				200	Fe ox.	Very small

* "Trace" means that precipitation is just started. "Incompl." means that precipitation of iron is incomplete. In every case FeS gave tests for Fe and S.

were added, and half of the tubes were stoppered, the other half being left open except for cotton plugs to keep out dust. A large number of such experiments were performed, those in stoppered tubes being recorded in Table VII. In the table the smaller number under "days" indicates the time required for a precipitate to become noticeable. The second figure shows the number of days before the sample was analyzed. "FeS" means that a black precipitate, containing iron and sulphur, formed. "Fe ox." stands for a brown precipitate containing iron.

In the open tubes most solutions, on addition of salts, lost most of their iron in less than thirty days, but a few parts per million remained in solution. In some open tubes the iron was precipitated first as black sulphide, which changed to brown a little later. In those cases only was precipitation complete. Magnesium carbonate, in the presence of air, precipitated the iron incompletely in a few days (see Precipitation diagram, Fig. 45). From

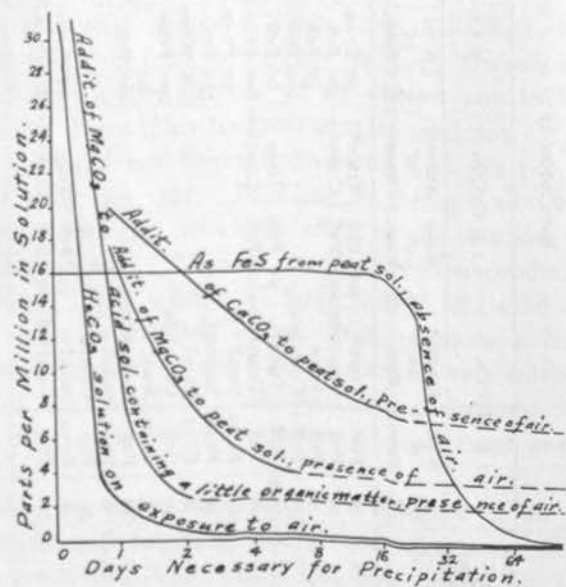


FIG. 45. Precipitation diagram showing approximate stability of iron in solutions with and without organic matter. Broken lines indicate that iron remaining in solution was probably in the colloidal state.

3 to 5 parts of iron stayed in solution for a long time. This iron will not pass through the collodion or parchment dialyser and, therefore, is most probably colloidal. It cannot be detected in the solutions except after addition of hydrochloric or some other highly ionized acid. Calcium carbonate precipitates iron from peat solutions as hydroxide more slowly, and from 4 to 8 parts of iron may stay in such solutions for many months (see Fig. 45).

When $MgCO_3$ or $CaCO_3$ was added to a solution (in a stoppered bottle) which had obtained its iron through the action of acid set free by adsorption (p. 432), iron sulphide was never precipitated, but iron hydroxide was precipitated incompletely (see Fig. 45). Two to five parts of iron per million stayed in solution. Since these solutions contained very little organic matter, it seems that very minute amounts of it are sufficient to hold some iron in solution. The fact that no iron sulphide formed in these solutions may be due to the presence of too little organic matter and the relatively great acidity of the solutions before the carbonate was added. It seems improbable that sulphide-producing bacteria existed in these acid solutions, for they are supposed to live in neutral or alkaline solutions.⁶⁷

Probability of the Presence of Sulphide-producing Bacteria.—Certain bacteria⁶⁸ produce hydrogen sulphide directly from decaying organic matter. Others take oxygen away from sulphates, producing sulphides which may react with iron salts to produce iron sulphides. It is stated that organic matter reduces sulphates to sulphides directly, but this probably does not take place except at high temperature, as experiments by Allen⁶⁹ and others⁷⁰ have shown.

In the experiments recorded here, no hydrogen sulphide was

⁶⁷ See culture media cited by Harder, *op. cit.*, pp. 41-43.

⁶⁸ Harder, E. C., *op. cit.*, pp. 40-44.

⁶⁹ Allen, E. T., Crenshaw, J. L., and Johnston, J., "The Mineral Sulphides of Iron," *Am. Jour. Sci.*, 4th ser., vol. 33, 1912, p. 171.

⁷⁰ Siebenthal, C. E., "Origin of the Zinc and Lead Deposits of the Joplin Region, Missouri, Kansas, and Oklahoma," U. S. Geol. Survey, Bull. 606, 1915, p. 62.

produced or iron sulphide precipitated in any peat solution, unless some salt was added, although such solutions (Table I.), after having been filtered, stood over a year in the absence of air. Other experiments were made bearing on this point. Ferric sulphate (0.1 gram) was added to peat solutions in sealed bottles (500 c.c.). No iron sulphide formed within 5 months. When a little solid peat was added to the solutions, no precipitate of sulphide formed. Similar results were obtained with ferrous sulphate.

If we assume that in the experiments of Table VII. chemical reactions took place without the aid of microorganisms, it is difficult to understand why many weeks should be necessary in one case and only a few days in another to produce the same result in similar solutions.

When peat solutions which had been in contact with magnetite were treated with different concentrations of the same sulphate, it was found that $\frac{1}{2}$ gram of a sulphate added to 75 c.c. of solution in a stoppered test tube usually caused the precipitation of black colloidal FeS in about 15 to 30 days. One gram precipitated FeS at the beginning, but after some time the iron came down as brown hydroxide. Two grams seemed to be without any effect whatever on the iron of the solution. The writer can find no explanation for such behavior due to the concentration, except that greater concentration of sulphates may make solutions toxic for organisms. It seems, then, that microorganisms played an important part in the precipitation of the sulphide of iron.

The black sulphides, if the solutions are exposed to air, are oxidized extremely rapidly.

Experiments on Replacement of Calcite and Silica by Iron.—A number of experiments were made with peat solutions to find out, if possible, the speed of replacement of calcite and silica by iron oxide. Microscopic slides of oölitic limestone, opal, and siliceous oölite were put into bottles containing peat solutions which had been in contact with iron oxides, and contained over 20 parts of iron. The solutions were renewed once a month. All bottles were kept stoppered.

With oölitic limestone, it was found that the calcite would go into solution slowly and would be replaced by a soft dark brown mass in which the oölitic structure was still visible. On being dried in the air, the mass cracked in many places. Small recent shells of calcium carbonate were introduced in the same manner. In them only the surface was coated or replaced by the brown mass. In every case the brown mass consisted of iron and organic compounds.

In one experiment a mixture containing about 200 parts per million of iron, and made up half of peat solution and half of $N/50$ H_2SO_4 , was used. The shell in this solution was completely replaced by a very soft dark brown mass which contained iron.

A small piece of soft crumbling oölitic limestone was treated like the microscopic slides. After a few months, black iron sulphide with organic matter had formed a thin coating on it. In the experiments with slides of opal and siliceous oölite, no changes could be detected, even after one year.

Protective Colloids.—The sulphates and chlorides are strong electrolytes and would be expected to precipitate the colloidal organic matter, but such precipitation occurred only to a very minor degree, even after many months of standing.

The humus colloids, therefore, seem to belong to the group called emulsoids or reversible colloids, which are coagulated only very slowly, and whose precipitation is reversible.⁷¹ Such emulsoids have the property of exercising protective action for suspended colloids, even when present in minute amounts. That such protection is afforded by humus colloids is suggested by the fact that in the majority of experiments in which black FeS was formed as the end-product of the reaction, this sulphide appeared as colloidal suspension and was not precipitated for many days or weeks, even in the presence of electrolytes. It is also probable that the same protective action is responsible for the large amounts of silica that can be held in suspension by such humus solutions, as well as the small amounts of iron that could not be precipitated.

⁷¹ Bancroft, W. D., *op. cit.*, p. 170.

Precipitation of Silica.

It was formerly believed that silica was carried in solution as alkaline silicate and that on separation from the alkali the silica was precipitated,⁷² but it is now held that silicates are hydrolyzed and that silica is carried as colloid in dilute natural solutions.⁷³

As a colloid, silica usually carries a negative charge,⁷⁴ but under certain conditions the charge is positive. According to Zsigmondy,⁷⁵ silica in solutions with less than one per cent. of SiO_2 is sometimes stable for years, and is coagulated immediately by relatively few electrolytes. Taylor⁷⁶ states that colloidal silica is positively charged in acid solutions, and negatively in alkaline or very feebly acid solutions. A definite concentration of an electrolyte is necessary for precipitation. An excess or insufficient amount of the electrolyte is usually ineffective, or causes only partial precipitation.

Dean,⁷⁷ in recent experiments, found that dialyzed silica would not be precipitated from a solution containing only CaCO_3 , but that it would coagulate quickly if CO_2 was bubbled through to form the bicarbonate of calcium. W. A. Tarr⁷⁸ observed that silica as sodium silicate in dilute solutions was precipitated by sea water. Lovering⁷⁹ treated a dialyzed solution of silica with carbon dioxide and obtained a precipitate of silica. The writer took one of his own solutions in which $N/50$ sulphuric acid had acted

⁷² Dienert, M. F., "Etude de la dissolution des elements constituant les sables alluvionnaires par les eaux souterraines," *Bull. Soc. Chem.*, 4th ser., vol. 13, 1913, pp. 381-394.

⁷³ Kahlenberg, L., and Lincoln, A. T., "Solutions of Silicates of the Alkalies," *Jour. Phys. Chem.*, vol. 2, 1898, p. 90.

For other references see:

Leuher, V., and Merrill, H. B., "The Solubility of Silica," *Jour. Am. Chem. Soc.*, vol. 39, 1917, p. 2630.

⁷⁴ Zsigmondy, R., *op. cit.*, p. 211.

⁷⁵ *Op. cit.*, p. 211.

⁷⁶ Taylor, W. W., "The Chemistry of Colloids and Some Technical Applications," New York, 1915.

⁷⁷ Dean, R. S., "Formation of Missouri Cherts," *Am. Jour. Sci.*, vol. 45, 1918, p. 413.

⁷⁸ Tarr, W. A., "Origin of Chert," *Am. Jour. Sci.*, vol. 44, 1917, p. 409.

⁷⁹ Unpublished thesis, Univ. of Minnesota.

on serpentine and which contained 120 parts of SiO_2 per million, and added just enough sodium carbonate to make the solution slightly alkaline. All the silica coagulated immediately. If no carbonates were added to these sulphuric acid solutions, silica was not observed to coagulate during the time of observation (nine months). If a number of these acid solutions with silica derived from various minerals were poured into one container, no silica was precipitated, though the solutions differed widely in composition. They had one point in common, however—all were acid.

It seems, then, that silica in dilute solutions is precipitated only when its charge is neutralized, or changed to the charge opposite to that which it had. It would not be likely, therefore, that an acid solution would lose its silica on meeting another slightly acid solution.

Experiments with Filtered Peat Solutions.—To a peat solution (500 c.c.) that had been in contact with greenstone and contained 68.0 parts of SiO_2 and 15.3 of Fe per million was added $\frac{1}{2}$ gram of MgCO_3 . The solution was kept out of contact with air. After one month 52.0 parts of SiO_2 and 8.1 of Fe had been precipitated. A sample of the original solution without MgCO_3 remained unchanged.

The same procedure was followed with a solution from olivine containing 106.0 parts of SiO_2 and 9.2 of Fe (ratio 11:1). After one month, 45.0 parts of SiO_2 and 3.4 of Fe (ratio 13:1) were still in solution.

In a similar experiment with a solution from serpentine containing 83.0 parts of SiO_2 and 4.0 of Fe (ratio 21:1), after 30 days 59.0 parts of SiO_2 and 2.5 parts of iron (ratio 24:1) remained in solution. The slowness and incompleteness of the precipitation of silica, as well as that of iron in these three experiments, is significant.

The following experiments show that silica is not precipitated by electrolytes of sea water nor some of the other common electrolytes, even if iron contained in the same solution is precipitated as sulphide.

To 1,000 c.c. of a solution of artificial sea water which had been in contact with peat and greenstone (p. 433) were added 1,000 c.c. of peat solution from olivine (Table I.). The mixed solution, which was kept in a stoppered vessel, contained 124 parts of SiO_2 and 133 of Fe per million. Within a day the solution became turbid and a black colloidal iron sulphide slowly formed. It did not coagulate entirely within forty days. After that time the solution was filtered. The precipitate contained only black FeS and organic material. After 2 more months the solution had become clear. An analysis showed that no silica whatever had been precipitated.

When 250 c.c. of peat solution from olivine (106.0 SiO_2 , 9.0 Fe) were mixed with 250 c.c. of "artificial" sea water (p. 433), no precipitate was produced within several months.

In the following four experiments, the filtered solutions were from the peat solution in contact with serpentine, and contained 83.0 parts of SiO_2 and 4.0 of Fe per million.

1. 250 c.c. of solution were mixed with 250 c.c. of artificial sea water. No precipitate occurred in 4 months. For the first two months the vessel was stoppered.

2. To 400 c.c. of solution 1 c.c. of concentrated H_2SO_4 was added. After two weeks the solution still contained all its silica. Hydrochloric acid acted the same way.

3. Carbon dioxide was bubbled through the solution for 30 minutes. No precipitate formed during two weeks, the time of observation.

4. Three grams of pure white kaolinite were added to 300 c.c. of solution in a closed bottle, which was agitated a few times. After 16 days most of the iron had been precipitated. Of 83 parts of SiO_2 13.5 were still in solution.

Conclusions.

Precipitation of Iron from Organic Solutions:

1. In the presence of air, iron is precipitated exceedingly slowly, if at all.

2. The addition of sand, crushed chalcedony, or orthoclase does not accelerate precipitation noticeably.

3. The addition of carbonates of alkalis and alkaline earth metals to a solution exposed to air causes *incomplete* precipitation of iron as hydroxide. In the absence of air, similar reactions occur, but often iron sulphide is precipitated instead.

4. Sulphates of alkalis and alkaline earth metals added to a solution in the presence of air may first cause precipitation of a sulphide which changes to a hydroxide, or may precipitate the hydroxide directly. In the absence of air, the iron is precipitated by these sulphates, either as a sulphide when precipitation of iron is complete, or as hydroxide when precipitation is incomplete. When the amount of sulphate exceeds a certain limit, no precipitation as sulphide occurs.

5. At low temperature organic matter alone does not reduce ferrous or ferric salts to iron sulphide. Bacteria seem to be necessary.

6. From natural organic solutions iron is usually *not completely* precipitated as hydroxide. From 2 to 8 parts per million remain in solution (see diagram, Fig. 45).

These amounts are in agreement with those found in river waters containing organic matter. As iron, with the possible exception of a fraction of one part per million, is precipitated from surface waters unless organic matter is present, it is highly probable that larger amounts are *carried as organic colloids* or *adsorbed by organic colloids*, and *not as bicarbonate*.

Precipitation of Silica.—Colloidal silica in inorganic solutions and natural organic solutions behaves differently.

In inorganic solutions silica is relatively unstable and therefore easily precipitated by certain electrolytes and colloids with an opposite charge. Carbonic acid, carbonates of the alkalis, and bicarbonates of the alkaline earth metals seem to be among the most efficient precipitants. It depends on the initial charge of the colloids of silica which electrolyte will act. Silica with a positive charge is easily precipitated by an electrolyte which neutralizes the charge or gives the colloid a negative charge, provided

that the solution is of the proper concentration. The reverse also takes place.

In natural organic solutions which contain protective colloids, silica follows the same laws, but on account of the protection afforded by the organic colloids, it is precipitated much more slowly, and apparently incompletely, in some cases. Electrolytes, such as the salts of sea water, seem to be ineffective as precipitants. The formation of colloidal iron sulphide does not cause precipitation of silica.

ORIGIN OF THE BIWABIK FORMATION.

*Previous Views on the Origin.*⁸⁰

H. V. Winchell⁸¹ in 1892 concluded that the iron formation consists of chemical and mechanical oceanic deposits. N. H. Winchell⁸² in 1899 accepted Spurr's⁸³ hypothesis that the iron formation was a glauconite-like formation, but later he⁸⁴ proposed that the greenalite resulted from a volcanic sand. Leith⁸⁵ objects to Spurr's glauconite hypothesis (see p. 417) and thinks that colloidal silica may have combined with ferrous iron to form greenalite. He concludes: ". . . that the greenalite granules may possibly have developed directly from the abstraction, through the agency of organisms of iron from solution in sea water, whence it was contributed from adjacent land areas. . . ."

Van Hise and Leith⁸⁶ in 1911 concluded that all the important Lake Superior iron-bearing formations are very similar in origin. They believe that a very large part of the iron and silica was contributed to the ocean directly, either by magmatic emanations from igneous rocks (probably poured out on the ocean floor), or

⁸⁰ For older literature see Leith, C. K., *op. cit.*, p. 31.

⁸¹ *Op. cit.*, pp. 138-146.

⁸² Winchell, N. H., "The Geology of Minnesota," Geol. Nat. Hist. Surv. Minn., Final Rept., vol. 4, 1899, p. 359.

⁸³ *Op. cit.*, p. 242.

⁸⁴ Winchell, N. H., "Structural and Petrographic Geology of Minnesota," Geol. Nat. Hist. Surv. Minn., Final Rept., vol. 5, 1900, pp. 990 and 997.

⁸⁵ *Op. cit.*, pp. 242, 254, and 257.

⁸⁶ Van Hise, C. R., and Leith, C. K., "The Geology of the Lake Superior Region," U. S. Geol. Survey, Mon. 52, 1911, p. 499.

by rapid decomposition of basic igneous rocks, due to their contact, while hot with sea water. Van Hise and Leith, however, think that considerable portions of the iron and silica may have been derived from the land by processes of ordinary weathering.

Wolff⁸⁷ believes that the bulk of the iron oxides in the Biwabik formation are in the same "chemical state" now as that in which they were laid down, and that greenalite was relatively unimportant as original mineral. Grout and Broderick⁸⁸ advocate the hypothesis of the deposition of the ferruginous cherts, "with more or less siderite, ferric oxide, and greenalite" in shallow water, mainly by organic agencies.

*Possibility of Direct Contribution of Silica and
Iron from Magma.*

Association of Lavas with Chert.—Van Hise and Leith⁸⁹ based their argument, that probably the greater part of the silica and iron of the iron-bearing formations had been contributed directly from the magma or from hot lavas poured out on the ocean floor, on the frequent association of basic igneous flows with chert and jasper. Their best evidence seems to be the discovery, near Hudson Bay, of chert and jasper grading into basalts of Algonkian age. Leith⁹⁰ says that this jasper must have been deposited "under conditions differing radically" from those observed today.

In California radiolarian cherts are associated with basalts, some of which are spheroidal and ellipsoidal.⁹¹ Geikie⁹² mentions a number of occurrences of pillow lavas and interstratified cherts. Of the cherts of the Lower Silurian (Arenig group) of Scotland he says:⁹³

⁸⁷ *Op. cit.*, pp. 233-235.

⁸⁸ *Op. cit.*, p. 46.

⁸⁹ *Op. cit.*, p. 499.

⁹⁰ *Op. cit.*, ECON. GEOL., vol. 5, 1910, p. 242.

⁹¹ Ransome, F. L., "The Eruptive Rocks of Point Bonita," Bull. Dept. Geol. Univ. California, vol. 1, 1893, p. 109.

Lawson, A. C., "Sketch of the Geology of the San Francisco Peninsula," 15th Ann. Rept. U. S. Geol. Surv., 1895, p. 420.

⁹² Geikie, A., "The Ancient Volcanoes of Great Britain," London, 1897, vols. 1 and 2.

⁹³ *Op. cit.*, vol. 1, p. 198.

It thus appears that during the volcanic activity there must have been intervals of such quiescence, and such slow, tranquil sedimentation in clear, perhaps moderately deep water, that a true radiolarian ooze gathered over the seabottom. . . . Thus the great depth of strata which elsewhere constitute the Upper Arenig and Lower and Middle Llandeilo subdivisions is here represented by only some 60 or 70 feet of radiolarian cherts.

It has recently been pointed out by Davis⁹⁴ that pillow lavas are also intrusive, and not necessarily submarine flows. Davis presents many arguments in favor of and against the direct contribution theory of silica. Dewey and Fleet⁹⁵ believe that pillow lavas are usually accompanied by radiolarian cherts, and that the silica of the cherts was derived directly from the magma.

Scrivenor,⁹⁶ on the other hand, does not think that this hypothesis is applicable to many East Indian cherts which are probably algal cherts, but lays stress on the removal of silica by tropical weathering.

Magmatic Springs or Submarine Lava Flows Possible Source of Silica.—If direct contribution of silica from the magma is assumed, the present writer favors the hypothesis of the derivation of silica from hot submarine lava flows rather than from magmatic springs, for two reasons:

1. If we assume a siliceous water with 1,000 parts of SiO_2 per million (a much more concentrated solution than those of geysers), over 524,000 cubic miles of solution would have been necessary to transport the silica of the Biwabik formation (of 10,000 square miles area and 330 feet thickness). Such a quantity would cover an area of the size of the United States to a depth of 900 feet. The magma which could furnish so much aqueous solution would probably have to be 20 to 40 times 524,000 cubic miles in volume,⁹⁷ the equivalent of a cone with an

⁹⁴ *Op. cit.*, p. 404.

⁹⁵ *Op. cit.*, p. 244.

⁹⁶ Scrivenor, J. B., "Radiolaria-bearing Rocks of the East Indies," *Geol. Mag.*, vol. 49, 1912, p. 247.

⁹⁷ Gautier's figures for the amount of combined water in granite are about 2.5 to 3.0 per cent. in "The Genesis of Thermal Waters and Their Connection with Volcanism," abstract by F. L. Ransome in *ECON. GEOL.*, vol. 1, 1906, p. 691.

altitude equal to the radius of the earth, and a base 10,000 square miles in area.

2. On the other hand, if we imagine hot lavas poured out on the ocean floor, there must have been tremendous chemical reaction and physical disintegration. Disintegration would not contribute colloidal silica directly to the water; but diatoms (and probably other organisms), as has been shown by Murray and Irvine,⁹⁸ can abstract silica from detrital material.

The chief objection to the theory of contribution of silica to the sea by hot lavas, in the case of the Biwabik and Gunflint formations, is that contemporaneous igneous rocks have not been found within a considerable distance. Van Hise and Leith⁹⁹ noted this, and thought that the remarkable uniform character of the Biwabik and Gunflint formations was possibly due to their distance from contemporaneous igneous activity. Nevertheless, the iron-bearing formation of the Gogebic Range,¹⁰⁰ which was in or near the area of igneous activity, is much like that of the Biwabik. The iron-bearing formation of Hudson Bay¹⁰¹ and the Belcher Islands,¹⁰² in which basalts occur with the sediments, is also very similar to the Biwabik formation.

Contribution of Iron from Hot Springs.—The evidence seems to show that iron and silica in the ratio found in the Biwabik formation cannot be carried in any but very weak solutions. Clarke¹⁰³ cites many analyses of spring waters high in silica and others high in iron, but no water high in both. As a matter of fact, these two elements seem to be mutually exclusive except in weak solutions. In acid waters which are high in iron, aluminum seems to be equally or more abundant, but this element is only sparingly present in the iron formation. Silica is present to only a very minor degree in the more acid waters, as would be expected

⁹⁸ *Op. cit.*, p. 245.

⁹⁹ *Op. cit.*, p. 517.

¹⁰⁰ Hotchkiss, W. O., "Geology of the Gogebic Range and its Relation to Recent Mining Developments," *Eng. and Min. Jour.*, vol. 108, 1919, p. 501.

¹⁰¹ Leith, C. K., "An Algonkian Basin in Hudson Bay," *ECON. GEOL.*, vol. 5, 1910, p. 227.

¹⁰² Moore, E. S., *op. cit.*

¹⁰³ *Op. cit.*, pp. 174-195.

and as has been demonstrated by many experiments.¹⁰⁴ It is difficult to conceive of an acid ocean or even of an acid large inland sea. The acidity would quickly be reduced by the presence of many base-forming elements in the rocks, and unless the acidity were reduced temporarily or periodically, no iron could be precipitated. Of course, we could imagine acidity around the submarine hot springs and neutralizing conditions at some distance, where deposition occurred. Even then the probable presence of much aluminum and other metals in the solutions and the small amounts of silica would probably preclude the precipitation of ferruginous chert.

Solutions charged with carbonic acid can carry iron and silica (p. 433). Iron as bicarbonate could be present in such cold solutions to the extent of 100–150 parts per million,¹⁰⁵ if other salts were absent. Their presence as bicarbonates necessarily would repress the solubility of iron.¹⁰⁶ In hot solutions bicarbonates can exist only when pressure prevents the escape of carbon dioxide. It is obvious that this gas would have been expelled as soon as the solutions reached an open, probably shallow basin. Iron would have been precipitated immediately. Even if only a part of the carbon dioxide had escaped, from either hot or cold solutions, it would have resulted in the formation of normal carbonates like those of sodium¹⁰⁷ and magnesium. These are alkaline toward litmus, and precipitate iron from solution. It probably would have necessitated special currents in the sea to carry these precipitates a hundred or more miles.

Assuming that a bicarbonate solution with 100 parts of iron per million (which would require 300 parts of SiO_2 to be in the ratio of iron to silica in the cherts—more silica than probably can be held in such solution except under great pressure), we find that it would take about 630,000 cubic miles of solution to

¹⁰⁴ Leuhner, V., and Merrill, H. B., "The Solubility of Silica," *Jour. Am. Chem. Soc.*, vol. 39, 1907, p. 2630.

¹⁰⁵ Smith, H. J., "On the Equilibrium in the System: 'Ferrous Carbonate, Carbon Dioxide and Water,'" *Jour. Am. Chem. Soc.*, vol. 40, 1918, pp. 879–885.

¹⁰⁶ Repression of solubility by a common ion.

¹⁰⁷ Smith, Alex., "General Chemistry for Colleges," New York, 1920, p. 462.

furnish as much iron as is assumed to be in the Biwabik formation. An area the size of the United States could be covered with this volume to a depth of over 1,000 feet. It does not appear probable that so much aqueous solution could come from a limited area.

Derivation of Iron from Hot Lavas.—Van Hise and Leith¹⁰⁸ heated fresh basalt to 1,200° C. and then plunged the mass into salt water. The violent reaction ensuing produced principally sodium silicate, but relatively little iron. They say that "the experiment does not seem to suggest an adequate source for the iron in this reaction." Igneous rocks in hot or cold water react alkaline,¹⁰⁹ for potassium and sodium silicates (water-glass) are strongly alkaline. Therefore, it seems improbable that much iron will go into solution when hot lavas come into contact with sea water, even if some hydrochloric acid should be formed in the reaction of hot lava with sea water. A little iron may have been in the colloidal state, or adsorbed by the colloidal silica formed in such a reaction. It is probable that colloidal or adsorbed iron gives to jasper the red or brown color, but this coloring, if due to colloids, could also be formed in other ways.

Attention is called by Van Hise and Leith¹¹⁰ to the association of basalts and iron-stone in Great Britain. These clay-iron-stone ores are usually associated with coal beds or vegetable remains.¹¹¹ Some of them show that molluscan life flourished on the spot at the time of formation. Geologists generally have not hesitated to connect the origin of these iron ores with the decomposition of rocks by weathering. It is probable, however, that porous, fresh basalts and tuffs on land furnished a considerable portion of the iron by their rapid decomposition, especially in the presence of abundant plant life. Chert does not occur to any extent with clay-iron-stone and associated basalt.

¹⁰⁸ *Op. cit.*, p. 516.

¹⁰⁹ Clarke, F. W., *op. cit.*, p. 475.

Cushman, A. S., "The Effect of Water on Rock Powders," U. S. Dept. Agr., Bur. Chemistry, Bull. 92, 1905, p. 9.

¹¹⁰ *Op. cit.*, pp. 508-509.

¹¹¹ Geikie, A., *op. cit.*, vol. 2, p. 204; vol. 1, p. 181.

Combination of Iron with Silica.—A greenalite-like substance has been produced in the laboratory by Van Hise and Leith.¹¹² They state that silicic acid and a ferrous salt in the absence of air produce no precipitate, but that "ferrous sulphate reacts directly with solutions of silicates of the alkalis," forming a precipitate of silicate similar to greenalite.

In dilute solutions silica probably does not exist as alkali silicate, but as colloidal silica.¹¹³ Therefore it should not react with ferrous salts in the absence of air to form a ferrous silicate. Soluble magnesium salts, which are plentiful in the ocean, should also be expected to form insoluble silicates with alkali silicates if iron salts did.¹¹⁴ Yet only 3 to 5 per cent. of magnesia are combined with the greenalite. It is probable, therefore, that in dilute solutions the reactions are more complicated than those of simple double decomposition, possibly similar to adsorption.

Weathering Suggested as the Source of Iron.

Warm and Humid Climate Necessary.—Under certain conditions, on weathering of igneous rocks, iron oxides remain in place as some of the most stable residual constituents. Under other conditions part of the iron is carried away, though this removal may not keep pace with the abstraction of the more soluble constituents of the rocks.¹¹⁵ Van Hise¹¹⁶ gives a table on rock decomposition in which the loss of Fe_2O_3 compared with Al_2O_3 as zero varies between 8.78 per cent. and 88.84 per cent. In humid regions the loss of iron is much greater than in arid ones.

In tropical countries decomposition of rocks is extremely rapid and extends to great depth, sometimes as deep as 200 to 300

¹¹² *Op. cit.*, p. 521.

¹¹³ Kahlenberg, L., and Lincoln, A. T., *op. cit.*, p. 89.

¹¹⁴ Van Hise and Leith, *op. cit.*, p. 521.

¹¹⁵ Merrill, G. P., "Rocks, Rock-weathering and Soils," New York, 1913, pp. 197-211.

Leith, C. K., and Mead, W. F., "Metamorphic Geology," New York, 1915, pp. 1-24.

¹¹⁶ Van Hise, C. R., "A Treatise on Metamorphism," U. S. Geol. Surv. Monograph, 1904, p. 515.

fect.¹¹⁷ Branner¹¹⁸ states that in the forest-covered portions of Brazil decay is greater than in the parts devoid of dense vegetation. Decomposition, however, is not limited to any particular region. Organic acids are important factors in the decomposition, according to Branner. Under such circumstances, iron is either carried away or is accumulated as laterite deposits. In many places the laterites probably represent only a small part of the iron from the decomposed rocks. Many analyses show that, under the same conditions of laterization, titanium oxide and alumina are much more stable than iron oxide. These conditions have been described as follows:¹¹⁹

1. Alternating wet and dry seasons.
2. Tropical heat with concomitant abundant vegetation.

As to the importance of abundant vegetation there has been some disagreement. Holmes¹²⁰ states that organic growth is usually absent where lateritic deposits occur, and implies that organic matter may be unfavorable to their formation. Campbell,¹²¹ who probably expresses the opinion of the majority of the investigators, however, thinks that sterility of the soil is caused by the formation of a hard crust of iron oxide at the surface. This oxide is deposited there during the dry seasons when iron-bearing solutions are drawn to the surface by capillarity. Changes in water table are also a factor. Simpson¹²² also is of this opinion and remarks that "Primary laterite is a true efflorescence" brought to the surface by capillarity.

¹¹⁷ Derby, O. A., "Note on the Decay of Rocks in Brazil," *Am. Jour. Sci.*, vol. 27, 1884, p. 138.

¹¹⁸ Branner, J. C., "Decomposition of Rocks in Brazil," *Bull. Geol. Soc. Am.*, vol. 7, 1896, pp. 255-314.

¹¹⁹ Maclaren, M., "On the Origin of Certain Laterites," *Geol. Mag.*, vol. 43, 1906, pp. 536-547.

Simpson, E. S., "Notes on Laterite in Western Australia," *Geol. Mag.*, vol. 49, 1912, p. 402.

¹²⁰ Holmes, A., "The Lateritic Deposits of Mozambique," *Geol. Mag.*, vol. 51, 1914, pp. 532-533.

¹²¹ Campbell, J. M., "Laterite, its Origin, Structure and Minerals," *Mining Mag.*, vol. 17, 1917, p. 178.

¹²² *Op. cit.*, p. 400.

It seems to the present writer, then, that no hard iron oxide crust could form near the surface, if really dry seasons do not exist. This seems to be borne out by the fact that areas which are relatively small, compared with the great basins of many tropical rivers, are only covered by lateritic deposits. Most of the iron must, therefore, be removed in some form or other by the surface and ground-waters, probably with the aid of organic solutions.

Iron and Silica Carried by Waters Rich in Organic Matter.

Attention was called to the large amount of silica and iron carried by rivers rich in organic matter (p. 421). The following analyses of the waters of the Amazon River and its tributaries have been taken from Katzer¹²³ and recalculated to parts per million:

TABLE VIII.
ANALYSES OF WATER FROM AMAZON RIVER AND TRIBUTARIES.
(Parts per Million.)

	Amazon, ¹²⁴	Amazon, ¹²⁵	Paraná- mirim.	Mæcuru.	Xingu.	Tapajos.	Itapacurá- mirim.
SiO ₂	9.4	12.2	8.8	19.2	9.6	9.2	9.0
Al ₂ O ₃ + Fe ₂ O ₃	3.6	6.2	9.5	6.6	3.9	2.8	6.8
Organic matter.....	5.7	8.9	6.3	5.8	11.8	12.2	11.6
Total solids at 110°.....	39.0	54.5	59.7	52.6	57.2	50.5	64.1
Suspended organic matter.....	37.2	61.4	100.8	96.7	56.3	62.8	103.2
Suspended inorganic matter.....	63.2	135.2	111.2	99.6	31.2	28.4	188.4

Figures for CaO, MgO, K₂O, and Na₂O have been omitted. Lime is the only constituent which is abundant besides silica and iron. Al₂O₃ and Fe₂O₃ were not separated in the analyses, but there is little doubt that most of the "Al₂O₃ + Fe₂O₃" is iron oxide. This appears very probable when these analyses are

¹²³ Katzer, F., "Grundzüge der Geologie des unteren Amazonasgebietes," Leipzig, 1903, p. 45.

¹²⁴ Amazon River at Obidos at a depth of 26 m.

¹²⁵ Amazon River at Obidos at a depth of 0.5 m.

compared with those of other South American and tropical streams in which iron is almost always greatly in excess over aluminum. These analyses seem to be in accord with experimental evidence of the writer (p. 445), in which it was shown that iron up to 8.5 parts per million was exceedingly stable in organic solutions. A similar agreement is found between the amount of silica held by the tropical rivers, and that contained in the organic peat solutions of the laboratory.

According to Katzer,¹²⁶ the Amazon River normally has a flow of 120,000 cubic meters per second, 200 miles from its mouth. During flood time this volume may increase several fold. If an average of three parts of iron per million is assumed for the water (which would be in keeping with the analyses), the Amazon River in 176,000 years could carry 1,940,000 million metric tons of iron to the sea—the amount assumed for the Biwabik formation (p. 413). The amount of silica carried would be correspondingly large.

In a basin the size of that of the Amazon River, the iron from rock of a thickness of only a few feet would be needed to furnish the stated amount. We may postulate conditions assumed by others¹²⁷—many fresh basalt flows and tuffs on land, possibly with much pyrite like that in the greenstone of the Lake Superior region. Under such conditions enough iron could be dissolved from a much smaller area than the Amazon Basin without there being decomposition to a greater depth than is common.

The following additional reasons favor the hypothesis that iron and silica were derived from land and transported by rivers rich in organic matter:

1. A steady supply of material over a long period would be assured by such a source.
2. No abnormally acid or basic solutions would have been necessary to carry the salts of iron and silica to their places of deposition without suffering premature precipitation.
3. Carbon dioxide, derived from the oxidation of organic mat-

¹²⁶ *Op. cit.*, p. 38.

¹²⁷ Van Hise and Leith, *op. cit.*, pp. 512 and 514.

ter on the sea floor, could prevent the deposition of calcium and magnesium carbonate to a certain extent by the formation of soluble bicarbonates.

4. The average sedimentary rock contains less magnesia and more lime than the igneous rock from which it is derived.¹²⁸ The Biwabik formation contains more magnesia than lime. Experiments dealing with adsorption by organic and inorganic matter seem to show that magnesia is adsorbed more rapidly than and probably in preference to lime. Moreover, the great abundance of ferromagnesian minerals, whether igneous or metamorphic, suggests a closer relationship between iron and magnesium than between iron and calcium.

5. If we consider rivers rich in organic matter as the transporting agency, it does not seem necessary to account for anything except the lack of lime in the iron formation. There is no reason why calcium and the larger part of magnesium carried to the sea by such rivers could not have been deposited in a different, probably a deeper, part of the ocean. The occurrence of almost pure limestone certainly proves that there has been separation of the constituents of river waters. Moreover, there exists a gradation between iron-bearing formation and carbonate rocks on the Gunflint Range and the east end of the Gogebic Range.¹²⁹

6. The Biwabik and Gunflint formations show no signs of volcanic disturbance, either sudden uplift or sinking of the sea floor during sedimentation. A slow steady subsidence probably took place. If great volcanic activity had occurred within a hundred miles, some indications might be expected in the structure of the sediments.

7. Lavas were extruded during Keewatin time in greater quantities than during any succeeding period, yet the greatest development of iron-bearing formations occurred during the Upper Huronian. This suggests, at least, that these lavas were the source of iron-bearing sediments not so much during the time of their extrusion, as during their exposure to weathering much later.

¹²⁸ Leith and Mead, *op. cit.*, p. 84.

¹²⁹ Van Hise and Leith, *op. cit.*, p. 515.

8. There exist large iron-bearing formations which are not associated with larger masses of contemporaneous basic igneous rocks. The pre-Cambrian (?) Itabira formation of Minas Geraes, Brazil, is such a primary sediment.¹³⁰ Harder and Chamberlin express the opinion that bacteria may have caused the precipitation of the iron oxide in it.

Organic and Chemical Precipitation.

The existence of iron bacteria and algæ at the time of deposition of and in the Biwabik formation makes organic precipitation highly probable. Drew¹³¹ has shown the importance of bacilli in organic precipitation of limestone. Algæ, radiolaria, and diatoms cause the deposition of silica.¹³² Iron bacteria, as shown by Harder, are some of the most efficient precipitating agents of iron. According to him¹³³ and to Ellis,¹³⁴ all traces of iron bacteria may easily become altered beyond recognition. Mumford¹³⁵ believes that a certain type of bacillus can precipitate iron under anaerobic conditions, when some of the precipitate will become partially reduced to the ferrous state (not sulphide). If this is the case, it might offer an explanation for the occurrence of a part of the ferrous iron. Though iron bacteria of the higher type have not been found in sea water, this does not preclude their existence there. Neither are we sure that the Biwabik formation was deposited in sea water.

Bacterial action, however, does not mean that inorganic processes did not take part in the precipitation of iron and silica. Temporary conditions may be imagined under which algæ and

¹³⁰ Leith, C. K., and Harder, E. C., "The Hematite Ores of Brazil and a Comparison with the Hematite Ores of Lake Superior," *ECON. GEOL.*, vol. 6, 1911, p. 670.

Harder, E. C., and Chamberlin, R. T., "The Geology of Central Minas Geraes, Brazil," *Jour. Geol.*, vol. 23, 1915, p. 403.

¹³¹ *Op. cit.*

¹³² Murray, J., and Irvine, R., *op. cit.*, p. 245.

¹³³ *Op. cit.*, p. 80.

¹³⁴ Ellis, D., "Iron Bacteria," London, 1919, p. 169.

¹³⁵ Mumford, E. M., "A New Iron Bacterium," *Chem. Soc. Jour.*, vol. 103, 1913, p. 650.

bacteria could not thrive. For example, it is probable that certain algae become extinct with the disappearance of clear water, as is indicated by the vanishing of the algal structures in the Upper Cherty division west of Hibbing, where they enter horizons with abundant slate layers interstratified with the cherts.

Special conditions are required for the separation of mechanical sediments from chemically dissolved or colloidal matter. This separation must depend on physiographic conditions similar to those for the formation of glauconite of which Murray and Renard¹³⁶ say that it is found "most characteristically on the continental slopes of high and bold coasts where currents from different sources alternate with the season."

Alterations of Original Sediments.

Grout and Broderick¹³⁷ have emphasized certain changes of oxidation and re-solution which probably took place during deposition. The writer observed similar phenomena. In Fig. 46



FIG. 46. Sketch showing deformation and breaking of a dense slate-like layer. Natural size.

one is illustrated. A hard slaty layer has buckled and broken in several places. Such breaking may have given rise to intraformational conglomerate. Fig. 42 seems to prove that solution went on at the surface of carbonate precipitates, producing the stylolitic surface upon which slate was laid down. Probably most of the organic matter in the precipitates, while still at or near the surface, was oxidized to carbon dioxide. This could have caused local resolution of iron which was then re-deposited under different conditions. Such a process may have led to the formation of irregular bands of iron oxides and carbonate (page 411), which do not

¹³⁶ *Op. cit.*, p. 234.

¹³⁷ *Op. cit.*, Bull. 17, p. 42.

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seem at all related to original sedimentation. Many other reactions probably occurred at that time.

Amphiboles and magnetite were formed, on deep burial of the formation. The ferruginous cherts are the result of this metamorphism.¹³⁸

CONCLUSIONS.

From the foregoing discussions, the following conclusions may be reached: During Upper Huronian time there existed large land areas in North America which were covered largely with greenstone and basalts. It is probable that fresh extrusive rocks and volcanic tuff and ash were deposited on parts of the land, as well as in the sea basins then existing. The climate of the continent was humid and probably tropical or sub-tropical. Vegetation of a low form was abundant, and aided in the rapid decay of the rocks. Under these conditions iron, which usually is one of the most stable elements in weathering, went into solution to a large extent, but only in waters with organic colloids was it stable for any length of time in the zone of oxidation. Silica was also dissolved on a large scale. Both iron and silica were carried to the sea by rivers rich in organic matter.

Whether this was a large inland sea or the ocean is a matter of speculation. There is little to indicate that the iron-bearing cherts could not have been precipitated in fresh water. The suspended material carried by the rivers was deposited probably in deltas, while the stable colloids of iron and silica were carried by currents to places of shallow and clear water. Only under exceptional conditions did mechanically suspended material reach these places and become deposited as slate. Such exceptional conditions may have been unusually large floods, and temporary changes in the coast lines.

The precipitation of silica, iron, and part of the organic colloids was caused chiefly by algæ and bacteria, which used the organic matter for their life processes and the inorganic silica or iron for the building of their cells or sheaths. It is also probable that inorganic reactions caused much colloidal silica, iron, and

¹³⁸ Gruner, J. W., *op. cit.*, p. 13.

organic matter to be precipitated. By adsorption some of these colloids partly united to form indefinite amorphous iron silicates. These may have been ferrous silicates from the beginning, or may have been ferric at first. Iron hydroxides and silica probably did not form silicates at many places. One reason may have been that the iron was not of the proper valence or condition to make a silicate.

A large part of the colloidal precipitates assumed the shapes of oölites, differing, however, from typical ones in their internal structure. In many places the granules thus formed seem to be made up of groups of cells; this suggests algæ or similar plants. It is thought improbable that all of the granules showing oölitic shape were deposited originally as ferrous silicate. A large portion of them probably consisted of iron oxides, cherts, or carbonates.

A part of the silica contained in the taconite may have been contributed to the sea directly by magnetic springs or hot submarine lava flows. We do not believe, however, that much iron had this origin.

Before a freshly precipitated layer of iron-bearing formation could be buried to any depth, there was considerable alteration of the amorphous material. Re-solution and diffusion in one place and redeposition in another were accompanied by reduction and oxidation of portions of the iron. Most of the organic matter was oxidized to carbon dioxide at this time. On deeper burial, ferruginous chert (taconite) originated by the formation of magnetite, amphiboles, and coarse-grained carbonates from the amorphous minerals and substances. During later elevation above the sea, some of the ferruginous chert was changed to ore under favorable conditions of weathering.

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