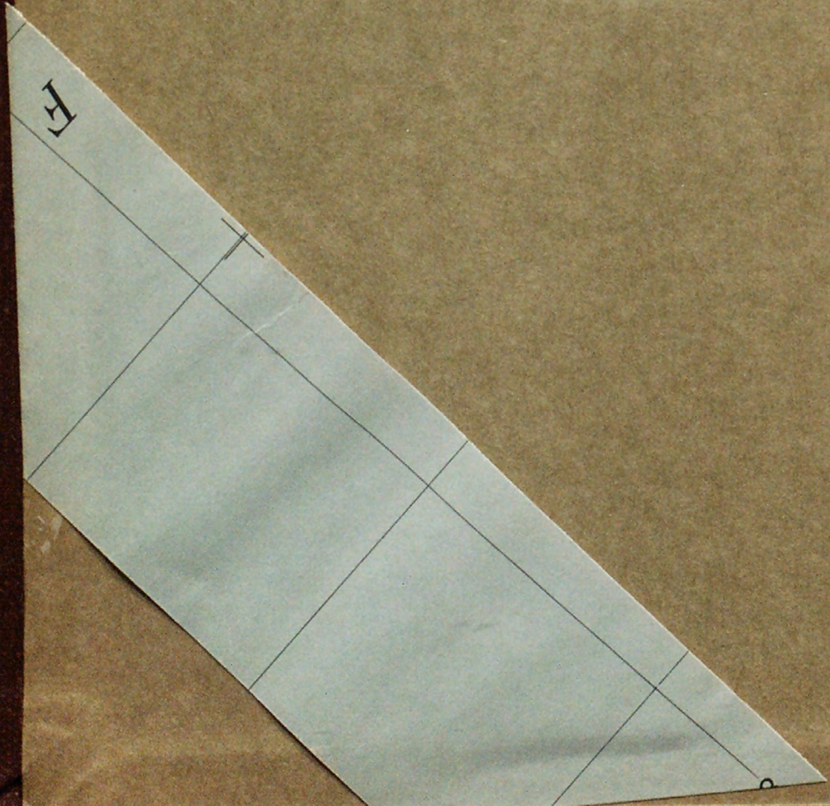
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The Geological Survey is releasing in open files the following maps and reports on the geology of various parts of the United States. Copies are available for consultation at the Geological Survey, Room 1033 (Library), General Services Administration Building, Washington, D. C., and other places as listed.

1. Preliminary report of geology of Lake Mary quadrangle, Iron County, Mich., by R. W. Bayley, 133 p., 7 pls., 37 figs., 4 tables.

   On file at the Geological Survey Office, First National Bank Bldg., Iron Mountain, Mich.

2. Environmental control of sedimentary iron minerals and its relation to origin of Ironwood iron formation, by N. K. Huber, 95 p., 12 figs., 13 tables.

   On file at the same places as item 1 above.

3. Geology and ore deposits of the Whitepine area, Tomichi mining district, Gunnison County, Colo., by C. S. Robinson, 225 p., 14 pls., 3 figs., 15 tables.

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THE ENVIRONMENTAL CONTROL OF SEDIMENTARY IRON MINERALS AND ITS RELATION TO THE ORIGIN OF THE IRONWOOD IRON-FORMATION

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56-57

ABSTRACT

The Ironwood iron-formation of the Gogebic range of Michigan and Wisconsin is made up of several differing rock types each of which is characterized by a different iron-rich mineral: hematite, magnetite, pyrite, iron carbonate, or iron silicate (minnesotaite, stilpnomelane). Where the iron-formation is relatively unaltered the Plymouth, Norrie, and Anvil members consist of irregularly bedded magnetite and silicate rocks whereas the Yale and Pence members consist of even-bedded carbonate, silicate, magnetite, and pyrite rocks. These rock types represent differing primary facies of the iron-formation and were deposited under differing physical and chemical conditions during a period of continuous iron-rich sedimentation.

An Eh-pH stability diagram is developed for hematite, magnetite, siderite, and pyrite, and indicates the relative positions of their stability fields, progressively from oxidizing to reducing conditions, in a normal sea water system. With the exception of the magnetite-siderite relationship, Eh is a much more critical environmental parameter than pH. The relative size and position of the magnetite field suggests that magnetite should be more important as a primary or diagenetic mineral in sedimentary rocks than has been previously recognized. This is in accord with numerous recent suggestions to that effect. The importance of thermodynamic equilibrium is stressed and it is suggested that differences in rates of formation of the various minerals are the commonest causes of lack of equilibrium.

Huronian sedimentation in the Gogebic district began with the deposition of sandstone and dolomitic limestone in a shallow sea

advancing over a low-lying land mass of lower Precambrian granite and greenstone. Continued advance of the sea, with effective separation of clastic material near shore, permitted the dominantly chemical sedimentation of the iron-formation in somewhat deeper water. The development of an off-shore basin with partially restricted circulation would facilitate such deposition. Minor fluctuations in the physical and chemical conditions within the depositional environment are reflected in the differing facies of the iron-formation. Deposition of the iron and silica-rich chemical sediments was terminated by increased orogeny and the deposition of the thick sequence of slates and graywackes of the Tyler formation.

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INTRODUCTION

The Gogebic range of Michigan and Wisconsin (Fig. 1) has long been an important producer of iron ore in the United States. Since ore was first mined in 1883, extensive surface exploration, diamond drilling and mine workings have provided a great deal of information on the geology of the region. The principal reports on the geology are those by Irving and Van Hise (1892)[1], Van Hise and Leith (1911), Hotchkiss (1919), and Aldrich (1929). Aldrich presents an excellent history of the development of the range and a review of the literature up to 1929.

The Ironwood iron-formation of the Gogebic range has long been recognized as being of sedimentary origin and, to a large extent, the result of chemical precipitation. Many differing suggestions have been made, however, as to the source of the materials involved, the mode of transportation, the nature of the original formation, and the chemical and tectonic framework of the sedimentary environment. The present study applies some relatively new concepts of chemical sedimentary environments to the problem of the origin of the Ironwood iron-formation.

The study was begun with the hope that enough unoxidized and relatively unmetamorphosed material could be found in the areas of established stratigraphy to permit determination of the primary lithology of each of the stratigraphic units. This hope has been only partly realized, for although the rocks that make up the iron-formation are only slightly metamorphosed in a large part of the district, the iron-formation has been extensively oxidized to depths in excess of

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[1] The dates or names and dates in parentheses refer to items listed in the bibliography at the end of the paper.

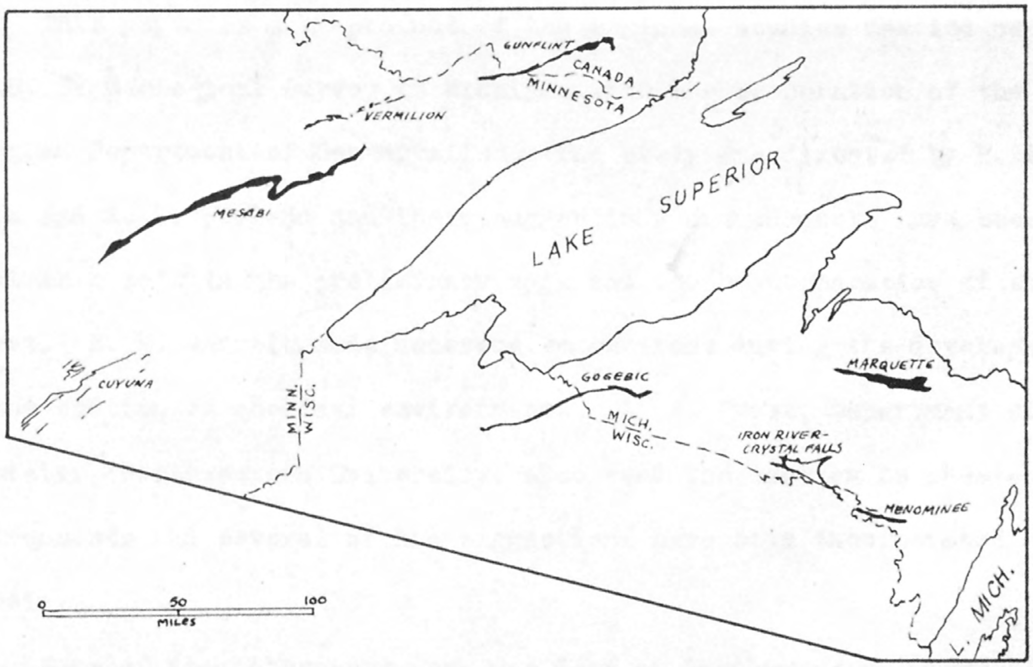

Figure 1. Index map showing location of Gogebic range in relation to other Lake Superior districts

4,000 feet in the area of active mines. It is nevertheless possible in many places to determine the approximate primary mineralogy of various facies of the iron-formation and to postulate physical and chemical sedimentary environments for each type.

Acknowledgments

This paper is a by-product of the regional studies carried out by the U. S. Geological Survey in Michigan with the cooperation of the Michigan Department of Conservation. The study was directed by H. L. James and A. L. Howland and their suggestions and comments have been invaluable both in the preliminary work and in the preparation of this report. R. M. Garrels made numerous suggestions during the development of the section on chemical environments. A. A. Frost, Department of Chemistry, Northwestern University, also read the section on chemical environments and several of his suggestions have been incorporated therein.

Some of the laboratory work was done at Northwestern University where assistance was provided by the S. F. Emmons Memorial Fellowship, which the writer held during the academic year 1953-54.

The writer wishes to acknowledge the complete and generous cooperation of the geologists, engineers and mining companies of the district and to emphasize his indebtedness for aid and information from this source. Companies that have contributed information and material for study include the M. A. Hanna Company; Jones and Laughlin Steel Corporation; Oglebay, Norton and Company; Oliver Iron Mining Company; Pickands, Mather and Company; and the Republic Steel Corporation.

GENERAL GEOLOGY

Regional stratigraphy

The general stratigraphy of the Gogebic range (Table 1) has been fairly well established by Hotchkiss (1919) and by Aldrich (1929). The Huronian formations rest with profound unconformity upon granite and greenstone of lower Precambrian age. Because of pre-middle Huronian erosion, the lower Huronian Sunday quartzite and Bad River limestone are only locally preserved and in most parts of the area the middle Huronian Palms quartzite and Ironwood iron-formation lie directly upon the pre-Huronian basement complex. Atwater (1938) has demonstrated that the iron-formation and the overlying upper Huronian Tyler formation are unconformable and that the Tyler and Copps formations are stratigraphically equivalent. Clastic and extrusive rocks of the Keweenawan series rest unconformably upon the Huronian series.

Post-Huronian intrusives are represented by the Mellen gabbro and related Keweenawan rocks in the western part of the range and by many diabasic dikes cutting the Huronian section throughout the range. The Presque Isle granite of the eastern part of the range has been called post-middle Huronian by Allen and Barrett (1915) and by Atwater (1938), but this age is doubted by James (1955).

Table 1

Generalized stratigraphic succession in the Gogebic district

Upper Precambrian	Keweenawan series		Sandstone, conglomerate, extrusives and intrusives
Middle Precambrian	Huronian series	Upper	Tyler formation (Copps in east)
		Middle	Ironwood iron-formation Palms quartzite
		Lower	Bad River limestone Sunday quartzite
Lower Precambrian			Granite Greenstone

Stratigraphy of the Ironwood iron-formation

General description

The Ironwood iron-formation was divided into five separate mappable units by Hotchkiss (1919). The subdivision into members was based on textural and structural features which to some extent also reflect mineralogical differences. The five members are, from youngest to oldest:

Anvil - ferruginous chert
Pence - ferruginous slate
Norrie - ferruginous chert
Yale - ferruginous slate
Plymouth - ferruginous chert

Two general rock types are described by Hotchkiss. These are: (1) Wavy-bedded "ferruginous chert", which consists of irregular beds and lenses of granular or oolitic chert, a fraction of an inch to several inches thick, that are separated by thin laminae of more evenly bedded iron-rich material. The iron-rich laminae consist largely of iron oxides, silicates, and carbonate, together with some fine-grained interstitial chert. (2) Even-bedded "ferruginous slate", in which the beds are extremely regular and finely laminated. The chert (or jasper) in this rock is generally dense or flinty although locally it is granular or oolitic. The term "slate" as used in the mining district indicates a thin-bedded, fine-grained rock, commonly with good parting parallel to the bedding. Most of the "slaty" material consists of iron-rich carbonate and silicate. The term argillite will be used in this paper to denote fine-grained rocks of clastic origin.

Each individual member of the iron-formation contains both wavy-bedded "ferruginous chert" and even-bedded "ferruginous slate", but in different proportions. Thus the Plymouth member contains both wavy-bedded and even-bedded iron-formation but can be described as dominantly composed of the wavy-bedded, granular chert type of iron-formation. The overlying Yale member consists dominantly of even-bedded iron-formation but does contain some wavy-bedded iron-formation.

The contacts between the various members of the iron-formation are commonly gradational and difficult to define with any degree of exactness, particularly where the formation has been extensively oxidized.

General features of the iron-formation members

Some of the general features of the various members of the iron-formation are summarized here. More detailed descriptions are given by Hotchkiss (1919) and by Aldrich (1929).

The base of the Plymouth member consists of dense granular chert and jasper with numerous clastic quartz grains. The contact is generally sharp and is marked by the presence of the chert and jasper, neither of which appears in the underlying Palms formation. The abundance of clastic quartz grains in the iron-formation diminishes upward so that within several feet above the base clastic quartz is almost completely absent. In general, clastic quartz is scarce throughout the rest of the iron-formation. The zone of clastic quartz in a chert matrix at the base of the Plymouth has been termed the "sweepings bed" (Aldrich, 1929, p. 158). In places the "sweepings bed" contains concentric concretion-like structures as much as 2 or 3 inches in diameter, which are similar to the algal structures described by Gruner (1946, p. 38) on the Mesabi range. When these structures are present this zone is often called the "gnarled conglomerate".

The so-called "footwall-slate" of the Plymouth member lies several feet above the base of the formation and is in general only a few feet thick. It appears to be fairly continuous throughout the range although it cannot be identified in all drill holes or sections.

The remainder of the Plymouth consists of wavy-bedded, granular-cherty iron-formation with a few zones of even-bedded iron-formation.

The Yale member consists dominantly of even-bedded iron-formation with minor granular chert sections. The stratigraphy of the Yale member is somewhat complicated by the "great bedding fault" which can be traced for much of the length of the district and which lies almost wholly within or adjacent to the Yale member (Hotchkiss, 1919, p. 504).

The Norrie member, like the Plymouth, is dominantly wavy-bedded, granular-cherty iron-formation with only minor even-bedded sections.

The base of the Pence member is commonly marked by an extensive fragmental zone in which the fragments are entirely composed of iron-formation. This, plus variations in thickness of the Norrie member, caused Hotchkiss to postulate the presence of a disconformity between the Norrie and the overlying Pence. The Pence member is dominantly even-bedded iron-formation although in some parts of the range a fairly thick granular-cherty zone occurs near the middle of the unit.

The Anvil member consists mostly of wavy-bedded, granular-cherty iron-formation with many fragmental zones. The upper part of this unit, however, does contain a fairly large even-bedded zone.

Lateral continuity of the iron-formation members

Mine workings and drill core information obtained since 1919 have served to confirm Hotchkiss' subdivision of the Ironwood, at least within the main mining district from Iron Belt, Wisconsin, to Wakefield, Michigan (see Figure 2). Beyond the area of active mining, west of Iron Belt and east of Wakefield, both lack of continuous surface outcrops and the scarcity of good core or other exploration data make it difficult to evaluate the continuity of the various members of the iron-formation.

In the eastern part of the mining district an additional complicating factor is presented by the Sunday Lake fault (Hotchkiss, 1919, p. 539). Drill core data are incomplete in the area west of the fault, and it is difficult with the available information to delineate the individual members of the iron-formation, which is badly deformed both by folding and by intrusion of diabasic dikes and sills.

East of the fault, the iron-formation has not undergone appreciable deformation and can easily be divided into units similar to those in the main part of the mining district. In the Sunday Lake mine at Wakefield, Michigan, five distinct units are present which are similar both in general thickness and in textural and structural properties to the five-fold division present west of the fault. The upper granular-chert unit, however, is truncated by the Keweenawan unconformity and the amount of iron-formation which has been removed is unknown. On the basis of the similarity of these units to those to the west it would appear that the Plymouth, Yale, Norrie, Pence and the lower portion of the Anvil are all present in the Sunday Lake area. The total thickness

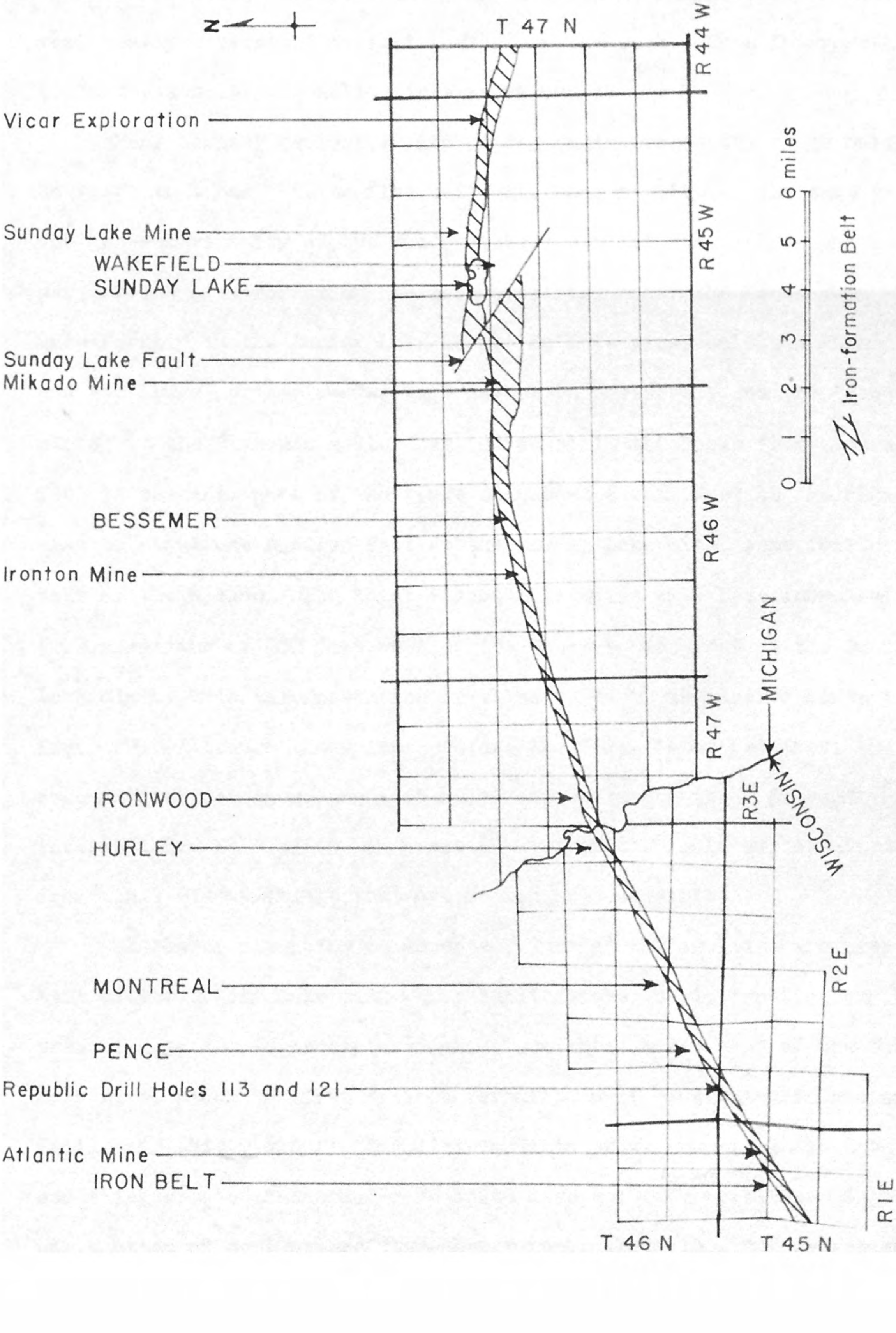

Figure 2. Index map of main part of the Gogebic range showing location of places and features mentioned in text

of iron-formation preserved under the Keweenawan unconformity is also very nearly equivalent to that farther to the west. This interpretation is illustrated by the solid lines in Figure 3.

Many company geologists and mining engineers on the range believe, however, that each of the five units thickens rapidly to the east in the general vicinity of the Sunday Lake fault and that only a small part of the iron-formation has been preserved under the Keweenawan unconformity in the Sunday Lake area. In this view, only the Plymouth and the lower portion of the Yale have been preserved, and the "footwall-slate" in the Plymouth member has increased in thickness from several feet in the main part of the range and about twenty feet at the Mikado mine to about one hundred feet at the Sunday Lake mine, some four miles east of the Mikado. The total Plymouth likewise will have increased from a maximum of 200 feet west of the fault to 350 feet at the Sunday Lake mine. This interpretation is illustrated by the dashed lines in Figure 3. Although the writer prefers the first interpretation, the second interpretation cannot be ruled out on the basis of present information. Much of the information west of the fault was obtained from small mine workings that are no longer accessible.

Whichever viewpoint is accepted, further difficulties are presented east of the Sunday Lake mine where duplications due to faulting may be present. At the Vicar exploration, about three miles east of the Sunday Lake mine, about 900 feet of iron-formation were penetrated in a diamond drill hole (Vicar #1201), but division into units comparable in nature and thickness to the normal five units does not seem possible. Only one section of typical granular-cherty rock, about 100-150 feet thick, is located about 300 feet from the base of the formation. If this

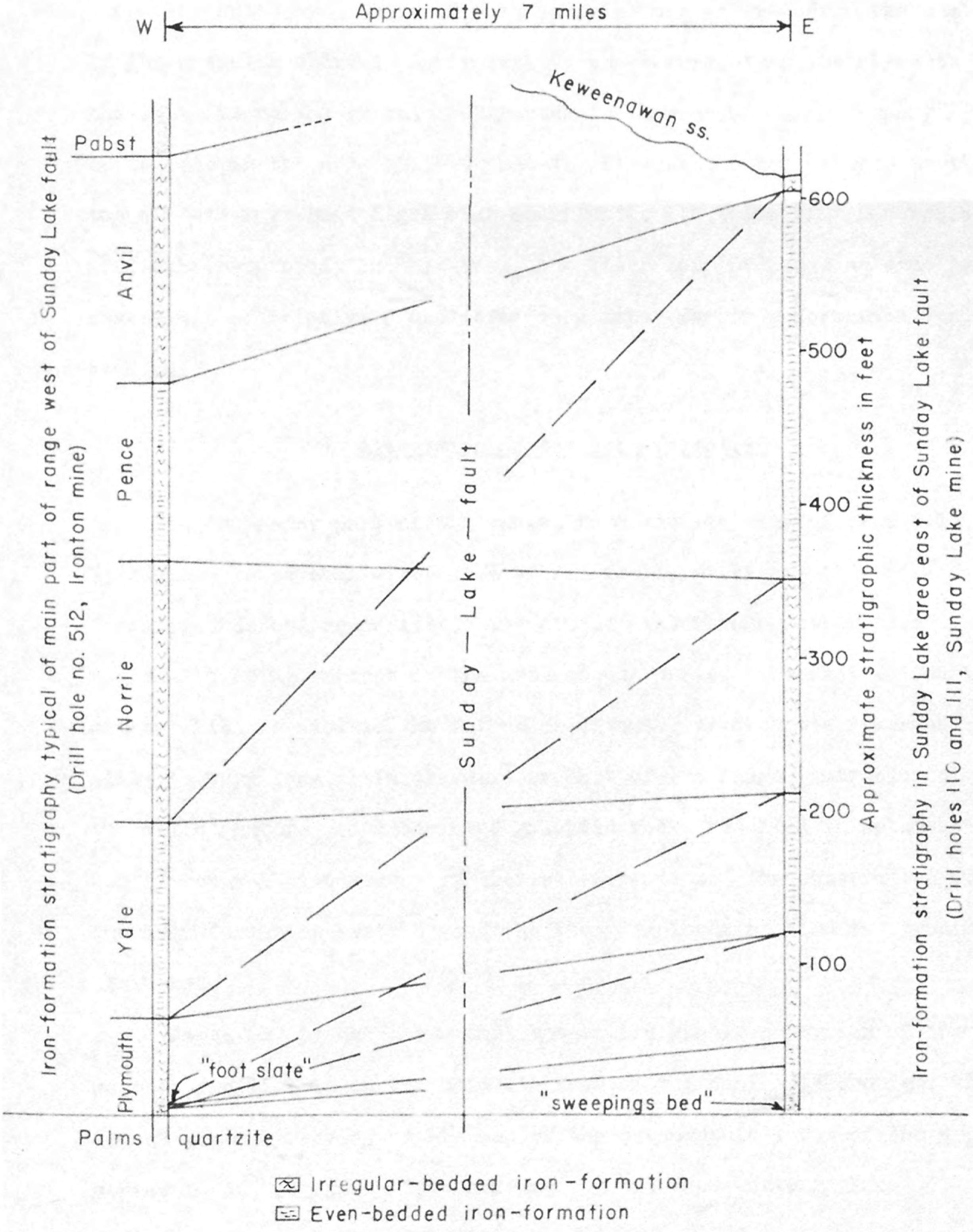

Figure 3. Diagram illustrating alternate interpretations of iron-formation stratigraphy in the Sunday Lake area.

granular chert unit is equivalent to the Plymouth, then either the lower part of the Plymouth in this area consists of a large slaty silicate and carbonate unit, or a wedge of such material has entered from the east. If the granular chert is equivalent to the Norrie, then the Plymouth has lost its normal granular character in this area. Many company geologists in the area believe that the Plymouth member extends to the top of this wavy-bedded granular chert unit. In spite of the correlation difficulties present in this area, the Vicar core presents an excellent assemblage of relatively unaltered rock types for iron-formation facies studies.

Alteration of the iron-formation

In the major part of the range, from the vicinity of Iron Belt, Wisconsin, to several miles east of Wakefield, Michigan, the iron-formation has undergone little structural disturbance, other than regional tilting, except in the area of the Sunday Lake fault. Contact metamorphism related to the intrusion of numerous diabasic dikes and sills is very local. In the western part of the range, intrusion of the Mellen gabbro and associated granitic rocks resulted in metamorphism and structural disturbance of the iron-formation. The eastern end of the iron-formation belt, beyond the Vicar exploration also is structurally disturbed.

James (1955) has shown that the entire Michigan portion of the Gogebic district is in the chlorite zone of regional metamorphism, the lowest grade appearing on his map of the metamorphic zones of the upper peninsula of Michigan. This zone can be extended westward into

Wisconsin to an area between Iron Belt and Tyler Forks creek where evidence of higher metamorphic grade begins to appear.

In addition to regional and contact metamorphism the iron-formation has locally been altered by other processes, chiefly oxidation of iron and leaching or replacement of silica, which have resulted in the formation of the commercial ore bodies of the range. Within the producing part of the range, from just west of Montreal, Wisconsin, to just east of Wakefield, Michigan, the iron-formation has generally been extensively oxidized.

PRIMARY MINERALOGY AND COMPOSITION OF THE IRONWOOD IRON-FORMATION

The term "primary mineralogy", as used here, refers to minerals formed by direct precipitation as well as minerals formed by diagenesis in the bottom sediments after deposition. The diagenetic environment is considered as part of the depositional environment even though great differences in various physical and chemical parameters may be present above and below the depositional interface. The problem arises as to whether the origin of certain minerals can be attributed to diagenesis or metamorphism. Magnetite and some of the iron silicates fall into this category. Although certain criteria will be considered, the two processes grade into each other and an absolute distinction is not always possible.

As this study is essentially an attempt to determine the primary mineralogy of the iron-formation as a key to the environmental conditions existing at the time of deposition of the formation, minerals of recognizable metamorphic origin and other products of secondary alteration, including the iron ores themselves, are excluded from this discussion.

Location of material studied

The areas of iron-formation which have undergone neither high degrees of metamorphism nor other secondary alterations are limited to (1) the area centered around Pence, Wisconsin, located between a zone of high metamorphism to the west and a zone of high oxidization to the east, and (2) the area around the Vicar exploration east of Wakefield, Michigan located between a zone of high oxidation to the west and a zone of structural disturbance to the east. The majority of the specimens examined in this study as representing the "least altered" iron-formation come from these two areas.

Iron-formation minerals and rock types

Introduction

The major minerals that comprise the bulk of the unaltered or weakly metamorphosed iron-formation are few; namely chert (quartz), carbonate, magnetite, hematite, minnesotaite, and stilpnomelane. Chlorite and pyrite are widespread but are of minor importance. With the exception of quartz, they all are iron-rich minerals and reflect varying conditions in a period of continuous iron-rich sedimentation.

Individual parts or samples of iron-formation can be classified according to the dominant minerals present, but there is a great deal of intergradation between rock types and almost all intermediate varieties can be found.

Carbonate-rich rocks

Carbonate-rich rocks form one of the more important lithologic types of iron-formation. The carbonate-rich rocks are almost all even-bedded with individual beds of uniform thickness. The beds are finely laminated, reflecting slight differences in mineralogical composition. Most commonly the carbonate-rich layers are interbedded with thin chert layers that average about a quarter of an inch in thickness. The chert layers now consist of microcrystalline quartz, which occurs also as interstitial material with the carbonate. Megascopically the chert is dense or flinty and usually is gray or greenish. Locally the chert stringers are nodular or irregularly shaped.

Magnetite is common, both disseminated or in clusters throughout the carbonate material and in discrete layers within the carbonate beds.

Silicate material (minnesotaite, stilpnomelane, occasionally chlorite) commonly occurs intimately admixed with carbonate rather than as separate layers. Within a given series of layers the carbonate-silicate ratio will vary considerably between adjacent units. Analysis D, Table 2, represents an example where the average silicate percentage exceeds that of the carbonate; all ratios are not only possible but are commonly found.

Hematite is seldom if ever present in the carbonate-rich rocks unless secondary oxidation has taken place.

Stylolites, parallel or sub-parallel to the bedding and typically of small amplitude, are common in the carbonate-rich rocks, both within carbonate layers and at the contact between carbonate and chert layers.

Table 2 gives four chemical analyses of carbonate-rich iron-formation. Analyses A, B, and C are of chert-carbonate rock. Analysis D is of carbonate-silicate rock that contains slightly more silicate that carbonate; it is included here for comparative purposes and may be considered an intermediate type. The samples analyzed consisted of split diamond drill core of as much as ten feet of stratigraphic section. Each analysis represents the average for a rock which is actually made up of thin beds of vastly different character.

The important minerals present in these samples have been determined in thin-section, so that the approximate mineralogical composition of the

Table 2

Chemical analyses of carbonate-rich iron-formation

	A	B	C	D
SiO_2	39.24	40.09	32.87	29.10
Al_2O_3	2.18	2.23	2.46	.03
Fe_2O_3	1.40	9.96	4.78	4.40
FeO	24.70	25.84	30.84	40.05
MgO	4.63	2.79	3.58	3.79
CaO	4.45	.50	.62	2.12
Na_2O	.00	.03	.00	.03
K_2O	.00	.40	.00	.03
H_2O^-	.04	.56	.28	.05
H_2O^+	1.39	1.80	1.69	2.90
TiO_2	.09	.23	.27	.02
CO_2	20.43	14.38	20.94	16.34
P_2O_5	.13	.13	.09	.17
S	.05	.01	.09	.06
V or	<.002			<.002
V_2O_3		.01	.00	
MnO	1.25	1.25	1.33	1.05
C	.31	.05	.45	.15
TOTAL	100.29	100.26	100.29	100.29
Less O for S	.03	.01	.05	.03
	100.26	100.25	100.24	100.26

A. Chert-carbonate iron-formation. Drill hole #1201, 1224 to 1241 feet, SE¼, SE¼, sec. 12, T. 47 N., R. 45 W., Gogebic County, Michigan. Analyst: Robert N. Eccher, U. S. Geological Survey.

B. Chert-carbonate iron-formation. Drill hole #121, 301 to 313 feet, SE¼, SE¼, sec. 31, T. 47 N., R. 2 E., Iron County, Wisconsin. Analyst: Lucille M. Kehl, U. S. Geological Survey.

C. Chert-carbonate iron-formation. Drill hole #121, 660 to 674 feet, SE¼, SE¼, sec. 31, T. 47 N., R. 2 E., Iron County, Wisconsin. Analyst: Lucille M. Kehl, U. S. Geological Survey.

D. Carbonate-silicate iron-formation. Drill hole #1201, 651 to 665 feet, SE¼, SE¼, sec. 12, T. 47 N., R. 45 W., Gogebic County, Michigan. Analyst: Robert N. Eccher, U. S. Geological Survey.

analyzed rocks can be calculated by the following procedure, in which several arbitrary assumptions are made:

1. In these samples hematite is negligible and all Fe_2O_3 is therefore assigned to magnetite and balanced by an equivalent quantity of FeO.
2. All CaO and MnO are combined as carbonate. The remaining CO_2 is balanced by FeO and MgO in the same ratio as that in the bulk analysis after subtraction of FeO for magnetite.
3. Remaining FeO and MgO are assigned to minnesotaite $[(Fe,Mg)_3Si_4O_{10}(OH)_2]$ in the ratio determined for carbonate. In the samples for which calculations were made, stilpnomelane is minor and other iron or magnesium-rich minerals negligible.
4. Remaining SiO_2 is assigned to quartz.
5. Other oxides—alumina, phosphate, alkalies, etc.—are listed as miscellaneous material. In the samples for which calculations were made this category does not exceed 5 percent of the total and in some is less than 2 percent.

Step two in the procedure, which determines the composition of the carbonate material (and indirectly the silicate material), is the most arbitrary, although the assignment of all CaO and MnO to carbonate is reasonable as no other calcium or manganese-rich minerals are important constituents of the iron-formation. The method of assignment of FeO and MgO to the carbonate may not be entirely valid, but some arbitrary ratio is necessary as both ferrous iron and magnesium are shared by more than one mineral in unknown quantities. The ratio assumed here seems reasonable, although the iron-magnesium partition coefficient would not necessarily be the same in the carbonate as in, for example, the iron-rich silicates. Problems concerning the composition of the silicate minerals are discussed in the section on silicate-rich rocks.

The approximate mineralogical compositions of the analyzed material, as calculated by the above method, are listed in Table 3. Some of the alumina, which has all been placed in the miscellaneous category, may occur in the silicate material if stilpnomelane or chlorite are considered. The rest of the alumina may occur as kaolin although kaolin has not been specifically identified in this study.

Table 4 gives the approximate composition of the carbonate, in mole percent, as calculated from the analyses of the four carbonate-rich samples of iron-formation presented in Table 2. Also included in Table 4 are carbonate compositions calculated for ten other samples of carbonate-rich iron-formation from various sources. Figure 4 illustrates the composition of these samples as plotted on a $CaCO_3$-$MgCO_3$-$FeCO_3$ diagram. Figure 5 illustrates the variation in $MnCO_3$ content as plotted on a plane connecting the $CaCO_3$-$MgCO_3$-$FeCO_3$ face with the $MnCO_3$ apex of the carbonate tetrahedron. In addition to the carbonate compositions from Table 4, Figures 4 and 5 also include compositions calculated from six partial analyses provided by The Cleveland-Cliffs Iron Company[1/] and from six additional analyses provided by H. L. James[2/]. The plot assumes that the carbonate occurs as a single phase although this may not actually be the case. Kulp, Kent, and Kerr (1951) note that complete

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[1/] B. H. Boyum, The Cleveland-Cliffs Iron Company: personal communication, April, 1955.

[2/] H. L. James, U. S. Geological Survey: personal communication, April, 1955.

Table 3

Approximate mineralogical compositions, in weight percent, of carbonate-rich iron-formation as calculated from analyses in Table 2

	A	B	C	D
Carbonate	49.6	35.9	52.4	41.4
Quartz	32.6	34.7	29.5	4.6
Silicate[1]	12.3	10.2	6.5	46.8
Magnetite	2.0	14.4	6.9	6.4
Excess constituents[2]	3.7	5.0	5.0	1.6

[1] Calculated as minnesotaite

[2] Includes minor elements

Table 4

Approximate composition of carbonate, in mole percent, from carbonate-rich iron-formation

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
$FeCO_3$	58.8	74.6	76.8	72.8	81.2	75.0	84.2	84.8	77.5	78.9	71.4	75.8	85.7	89.5
$MgCO_3$	20.4	17.3	17.0	13.0	14.1	14.9	12.3	12.0	12.6	12.5	8.4	16.4	12.5	7.8
$CaCO_3$	17.1	2.7	2.3	10.2	2.3	2.7	2.1	1.8	5.1	3.4	4.4	7.3	1.8	2.0
$MnCO_3$	3.7	5.4	3.9	4.0	2.4	7.4	1.4	1.4	4.8	5.2	15.8	0.5	—	0.7
Weight percent of carbonate in total sample														
	49.6	35.9	52.4	41.4	63.6	44.6	48.9	56.9	70.0	77.1	67.7	49.7	55.3	67.2

A. Chert-carbonate iron-formation, Gogebic range, Mich. (Analysis A, this paper)
B. Chert-carbonate iron-formation, Gogebic range, Mich. (Analysis B, this paper)
C. Chert-carbonate iron-formation, Gogebic range, Mich. (Analysis C, this paper)
D. Silicate-carbonate iron-formation, Gogebic range, Mich. (Analysis D, this paper)
E. Carbonate iron-formation, Gogebic range, Mich. (Analysis II, Irving and Van Hise, 1892, p. 192)
F. Carbonate iron-formation, Gogebic range, Mich. (Analysis III, Irving and Van Hise, 1892, p. 192)
G. Carbonate iron-formation, Gogebic range, Mich. (Analysis IV, Irving and Van Hise, 1892, p. 192)
H. Carbonate iron-formation, Gogebic range, Mich. (Analysis V, Irving and Van Hise, 1892, p. 192)
I. Chert-carbonate iron-formation, Iron River district, Mich. (Analysis A, James, 1951, p. 257)
J. Carbonate-rich layer from iron-formation, Iron River district, Mich. (Analysis C, James, 1951, p. 257)
K. Carbonate-rich layer from iron-formation, Iron River district, Mich. (Analysis D, James, 1951, p. 257)
L. Carbonate iron-formation, Gunflint district, Minn. (Analysis VIII, Irving and Van Hise, 1892, p. 192)
M. Carbonate iron-formation, Marquette district, Mich. (Analysis I, Van Hise and Bayley, 1897, p. 337)
N. Carbonate iron-formation, Marquette district, Mich. (Analysis II, Van Hise and Bayley, 1897, p. 337)

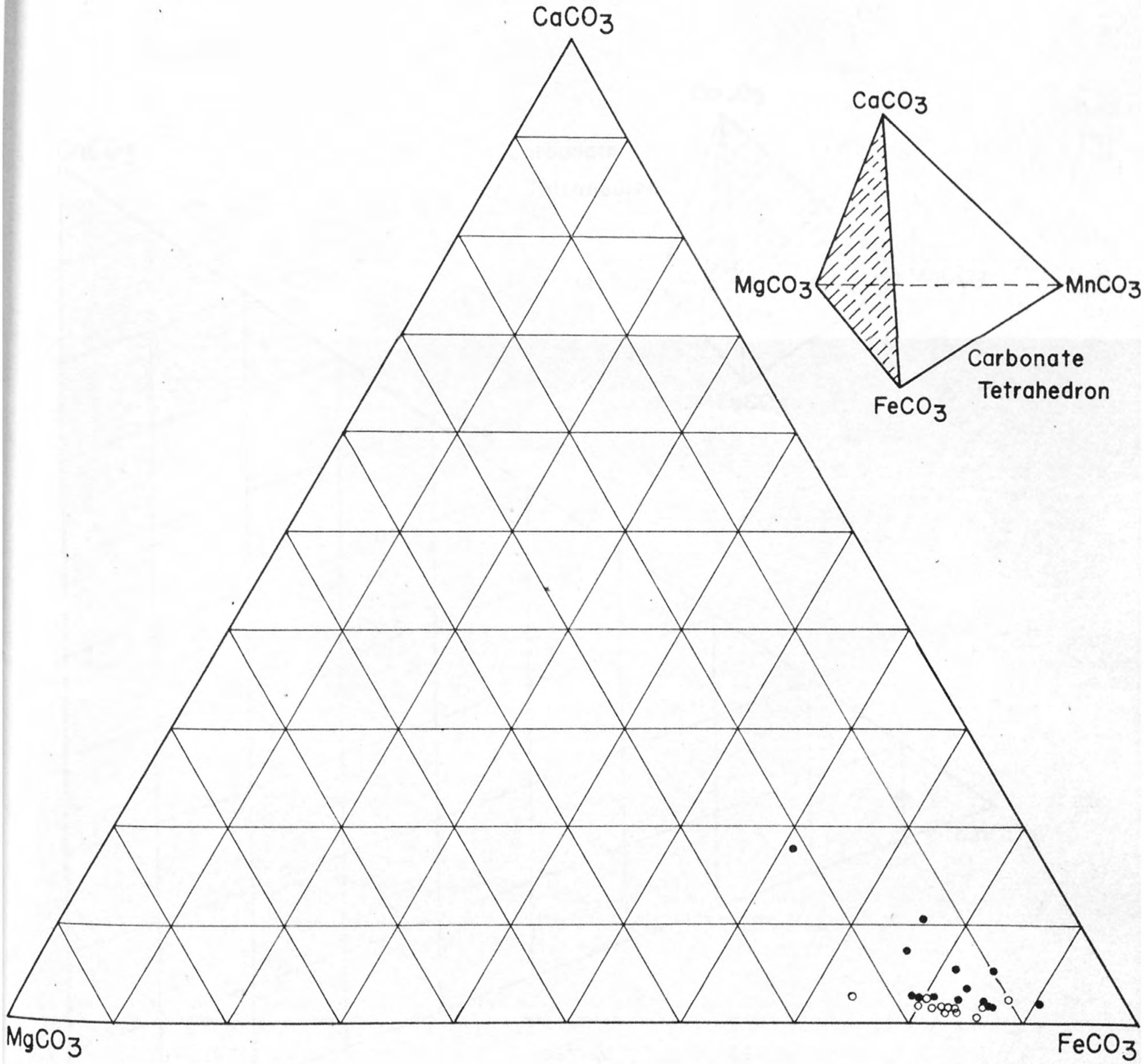

Figure 4. Approximate composition of iron-formation carbonate as projected on $CaCO_3$-$MgCO_3$-$FeCO_3$ face of carbonate tetrahedron. Dots indicate samples listed in Table 3. Circles indicate compositions calculated from partial analyses.

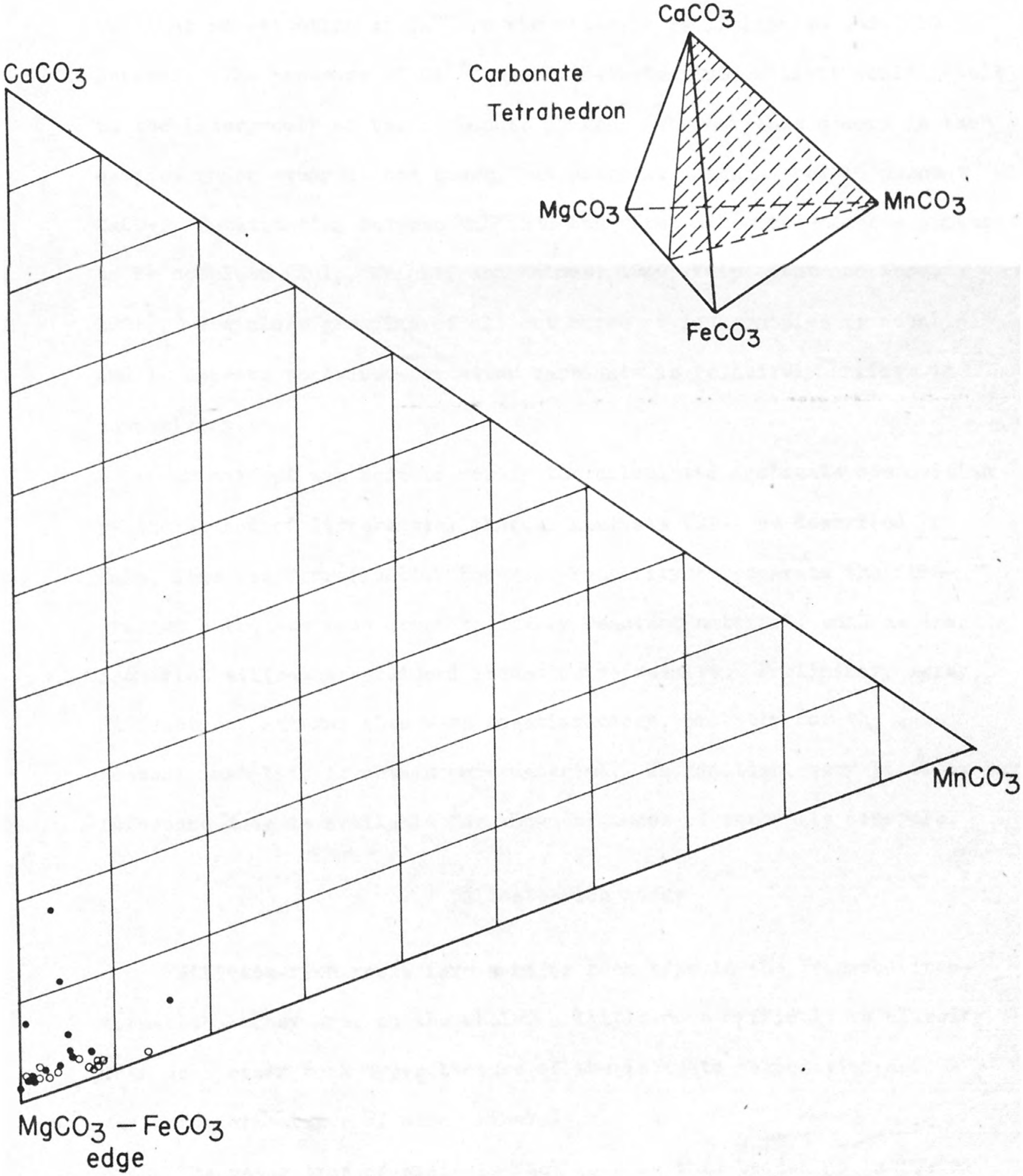

Figure 5. Approximate composition of iron-formation carbonate plotted to indicate variation in $MnCO_3$. Dots indicate samples listed in Table 3. Circles indicate compositions calculated from partial analyses.

substitution is observed between Fe^{++} and Mg^{++} in the carbonate lattice but that substitution of Ca^{++} in the siderite is limited to about 10 percent. The presence of Ca^{++} beyond the substitution limit would result in the intergrowth of two carbonate phases. Whether this occurs in the samples under study is not known, but only two contain over 10 percent $CaCO_3$. Substitution between Mn^{++} and the three other end-members appears to be complete (Kulp, Wright, and Holmes, 1949; Kulp, Kent and Kerr, 1951). The close grouping of all but three or four samples is notable and it appears that iron-formation carbonate is relatively uniform in composition.

An attempt was made to verify the calculated carbonate composition by the method of differential thermal analysis (DTA) as described by Kulp, Kent and Kerr (1951). However, inability to separate the fine-grained carbonate from other thermally reactant material, such as the iron-rich silicates, produced inconclusive results. Preliminary x-ray diffraction patterns also were unsatisfactory, probably for the same reason: inability to obtain pure material. In addition, very little x-ray reference data is available for known mixtures of carbonate minerals.

Silicate-rich rocks

Silicate-rich rocks form a major rock type in the Ironwood iron-formation. They are, on the whole, a little more difficult to classify than some other rock types because of the intimate association and variable percentages of other minerals.

The major type of silicate-rich rock is thin-bedded or laminated and contains carbonate and magnetite in addition to silicate. Typically it is light to dark green but may be dark gray if a high percentage of magnetite is present. The chemical composition of such a rock is shown in Table 2, sample D, and its approximate mineralogical composition in Table 3, sample D. The silicate-rich rocks grade with all mineralogical proportions into rocks in which carbonate or magnetite is the dominant iron mineral. Magnetite occurs both as disseminated material and as discrete layers. Granule-bearing silicate rocks, which are abundant on the Mesabi and Gunflint ranges (Leith, 1903; Gruner, 1946; James, 1954; White, 1954), do not seem to be common on the Gogebic range, although some of the wavy-bedded iron-formation discussed under magnetite-rich rocks contains silicate granules and some iron-formation beds near Tyler Forks contain stilpnomelane aggregates that might have been granules before metamorphism (James, 1954, p. 268).

Minnesotaite and stilpnomelane are the two most important silicate minerals in the iron-formation. Because minnesotaite was not established as a mineral species until 1944 (Gruner 1944b), studies of the Ironwood prior to that date have identified this iron silicate as another mineral, usually an amphibole. In the so-called actinolitic slates of Irving and Van Hise (1892), minnesotaite or stilpnomelane is the dominant silicate, at least in the relatively unmetamorphosed rocks. Stilpnomelane also has only recently been recognized as an important constituent of various iron-formation rocks of the Lake Superior district (Gruner, 1937, 1944a, 1946; James, 1954; White, 1954).

Minnesotaite is essentially a ferrous iron analogue of talc (Gruner, 1944b; Winchell, 1951, p. 365). Pure iron minnesotaite $[Fe_3Si_4O_{10}(OH)_2]$ has been synthesized by Flaschen and Osborn (1952) but in natural occurrences magnesium substitutes for some of the ferrous iron. In the chemical analysis of natural minnesotaite given by Gruner (1944b) the Fe^{++}/Mg ratio is about 5.4. In a partial analysis by D. W. Scott (presented by Gruner, 1946) the Fe^{++}/Mg ratio is 10.5. This may indicate that the Fe^{++}/Mg ratio in minnesotaite is variable and that a complete or partly complete solid-solution series exists between minnesotaite and talc. In the analyses presented in this paper (A, B, C, D, Table 2) the calculated Fe^{++}/Mg ratio in minnesotaite ranges from 2.9 to 5.6. How closely this calculated ratio agrees with the actual ratio is not known.

In the rocks of the Gogebic district, the minnesotaite occurs as colorless to pale green or yellowish needles or flakes that commonly are arranged as rosettes. Often there is a slightly noticeable pleochroism with Z and Y = pale green, X = pale yellow or colorless. Indices measured on a sample in the present study (see Table 5) are similar to those determined by Gruner (1944b) and by Flaschen and Osborn (1952).

Table 5

Optical indices for minnesotaite

	N_x	$N_y \simeq N_z$
Gruner (1944b)	1.580	1.615
Flaschen and Osborn (1952)	1.586	1.618
This study	1.585	1.616

Stilpnomelane is present in much of the silicate-rich iron-formation, typically as a minor mineral associated with minnesotaite. Like minnesotaite, stilpnomelane occurs as needles, and though it has a darker color, higher birefringence, and stronger pleochroism, the two minerals are often difficult to differentiate in very fine-grained rocks. The optical properties of stilpnomelane vary greatly with the ratio of iron to magnesium and of ferrous iron to ferric iron (Hutton, 1938).

Greenalite was not identified in the present study although it was previously reported as being present in subordinate amounts by Van Hise and Leith (1911, p. 231).

Chlorite is an important constituent only in iron-formation in which there is evidence of some clastic material. The chlorite has not been specifically identified, but James (1951, p. 256) has recognized the variety aphrosiderite and possibly thuringite in the Iron River district and Mann (1953, p. 261) has identified aphrosiderite in the Ironwood iron-formation. The parts of the iron-formation containing appreciable chlorite typically analyze much higher in alumina than the rest of the formation.

Although greenalite has generally been accepted as being of primary origin (Gruner, 1936; Tyler, 1949; James, 1954; White, 1954; and others) there is some doubt as to the primary origin of minnesotaite and stilpnomelane. Gruner (1946, p. 12) considers minnesotaite and stilpnomelane to be original constituents of the iron-formation and suggests that they crystallized from a colloidal gel. White (1954, p. 37), after careful consideration of the mineralogical relationships of the Biwabik iron-formation, concludes that most of the minnesotaite and stilpnomelane in the Biwabik is of primary origin, largely formed during the diagenetic period.

James (1954, pp. 266-267) cites evidence to suggest that minnesotaite and stilpnomelane may be derived by metamorphism from pre-existing silicate material of similar composition. Tyler (1949), Tyler and Twenhofel (1952), and Mann (1953) regard all minnesotaite and stilpnomelane as being metamorphic in origin. Tyler (1949, p. 1105) notes that "...greenalite which contains about 39 per cent iron may be observed in thin sections in all stages of alteration to minnesotaite".

The lines of evidence cited by White (1954, pp. 35-38) as opposing the contact metamorphic origin of the major portion of the iron silicates in the Biwabik iron-formation apply equally well to the Ironwood iron-formation. Most notable of these are the stratigraphically controlled distribution of the iron-silicates and the lack of correlation with local metamorphic effects due to dikes or veins. The role of low-grade regional metamorphism is more difficult to assess and it is probable that much of the present minnesotaite and stilpnomelane has been formed by this means, possibly from some pre-existing silicate material such as greenalite.

Magnetite-rich rocks

Several varieties of magnetite-rich rocks are found in the Ironwood iron-formation. The most common of these makes up much of what has been called "wavy-bedded" iron-formation by Hotchkiss (1919) and Aldrich (1929), and is the dominant rock type of the Plymouth and Norrie members. This rock type corresponds in all respects to the "irregularly banded taconite" as described from the Mesabi range by Gruner (1946) and White (1954).

Typically this rock is made up of irregular beds and lenses of chert separated by lamina of dark material that consists dominantly of magnetite, carbonate, and silicates. The cherty layers range in thickness from a fraction of an inch to several inches and are on the average somewhat thicker than the interbedded slaty layers. The cherty layers pinch and swell, often terminating rather abruptly, while the slaty layers are generally finely laminated and of more constant thickness.

The chert is dark gray to red. The red chert typically is granular or oolitic. Some of the ooliths are made up of concentrically arranged hematite and chert. The good preservation of the concentric structure suggests a primary origin for the hematite. Fine clastic quartz grains form nuclei for some of the ooliths. Granules or ooliths composed dominantly of chert are either structureless (granules) or contain ghost-like rings of dusty hematite, magnetite, or other material. In ooliths or granules in which magnetite is dominant, the magnetite is generally coarse-grained and euhedral, suggesting replacement of hematite in the oolith. Silicate granules or interstitial silicate material is present in many of these cherts. The carbonate occurs both as scattered grains showing rhombic outline and as fine-grained interstitial material.

The slaty material which separates the granular cherty beds and lenses is composed dominantly of magnetite, carbonate, and silicates, with interstitial chert. The magnetite is usually euhedral; it occurs both as disseminated material and clustered in preferred layers. The other minerals also show some preferential layering. In many thin sections probable granule structure may be observed in the silicate material, although the outlines are obscure; stilpnomelane appears to be slightly dominant over minnesotaite in this rock type.

Some magnetite-rich rock is evenly bedded, commonly with magnetite in layers up to half an inch thick interbedded with impure layers of silicate, carbonate, and chert. Carbonate is the most important accessory in the magnetite layers although some silicate is usually present.

Another even-bedded, magnetite-rich variety consists of interbedded chert and magnetite with little or no silicates or carbonate. Commonly the chert is a brilliant red jasper that is in striking contrast to the black magnetite layers. Most of the jasper layers are non-oolitic; the hematite that is the coloring matter occurs as a fine dust scattered throughout the chert. The jasper layers often fray out laterally into magnetite-rich layers. Chert layers that are oolitic are more irregular in thickness than the non-oolitic type. The ooliths contain hematite with well-preserved concentric structures, but commonly the hematite is nearly or completely replaced by coarse euhedral magnetite or carbonate or silicate. James (1954, p. 262) has interpreted this as indicating at least partial instability of the primary hematite in the diagenetic environment with the resultant alteration to ferrous compounds.

A chemical analysis of the jasper-magnetite type of iron-formation is given in Table 6. As with the other iron-formation analyses presented in this paper, this analysis represents the average for several feet of stratigraphic section and does not reflect the vastly different character of individual beds. The approximate mineralogical composition of the analyzed material is given in Table 7. FeO and MgO have been partitioned according to the procedure described in the section on the carbonate-rich rocks. All Fe_2O_3 was assigned to magnetite, but the relatively low iron

Table 6

Chemical analysis of jasper-magnetite iron-formation

SiO_2	34.68
Al_2O_3	.45
Fe_2O_3	30.43
FeO	22.20
MgO	2.32
CaO	1.80
Na_2O	.04
K_2O	.12
H_2O^-	.11
H_2O^+	.53
TiO_2	.05
CO_2	7.08
P_2O_5	.08
S	.02
V	$<.002$
MnO	.21
C	.06
TOTAL	100.18
Less O for S	.01
	100.17

Locality: Drill hole #1201, 499 to 510 feet, SE¼, SE¼, sec. 12, T. 47 N., R. 45 W., Gogebic County, Michigan

Analyst: Robert N. Eccher, U. S. Geological Survey

Table 7

Approximate mineralogical compositions, in weight percent, of magnetite-jasper iron-formation as calculated from analysis in Table 6

Magnetite	44.1
Chert	30.7
Carbonate	16.9
Silicate[1]	7.4
Excess constituents[2]	1.2
	100.3

[1] Calculated as minnesotaite

[2] Includes minor elements

content calculated for the carbonate suggests that some allowance should be made for hematite with a resulting slight decrease in magnetite percentage and increase in carbonate and silicate percentages. Magnetite and chert are by far the dominant minerals with carbonate and silicate as important constituents.

Hematite-rich rocks

Hematite-rich iron-formation, although of local importance in some of the Lake Superior districts, seem to be rare as a primary rock type on the Gogebic range. The wavy-bedded iron-formation previously described often contains appreciable hematite, but magnetite generally is the dominant oxide.

Pyrite-rich rocks

Pyrite-rich rocks are of minor importance in the Ironwood iron-formation and are represented by pyritic carbonaceous slates. These slates are black, fine-grained, and have a well-developed parting parallel to the bedding. The pyrite is usually concentrated in discrete layers. Some later mobility of the pyrite is indicated by occasional cross-cutting veinlets but the restriction of the pyrite to specific stratigraphic units attests to its primary or diagenetic origin.

The pyrite occurs as irregular blebs or aggregates of fine-grained material in which individual crystal outlines are not generally discernible; the matrix consists of chert, chlorite, and carbonate, with minor carbonaceous material. The non-pyritic beds consist of an intimate mixture of chert, carbonate, chlorite, and undetermined argillaceous and carbonaceous material. Quartz is present also as scattered very fine clastic grains.

A chemical analysis of pyritic slate is presented in Table 8. The analysis shows a pyrite content of approximately 3.6 percent, but the analyzed sample represents about 12 feet of stratigraphic section and as the pyrite is not uniformly distributed, some layers of the rock contain much more than the above percentage.

The sample contains 2.54 percent carbon. X-ray study of similar material from the Iron River district has shown that the free carbon occurs as "poorly crystalline carbon" rather than as true graphite (James, 1954, p. 251). In areas of higher metamorphic grade, true graphite may be present (James, 1955).

Carbonate content is about 10 percent, but the calculation of molecular composition is inexact because of the uncertainty of the mineralogical distribution of FeO, MgO, CaO, and MnO in this rock type.

Miscellaneous rock types

Fragmental or conglomeratic rocks--Fragmental or conglomeratic zones occur at many places within the iron-formation. The principal occurrences of breccia or conglomerate are at the base of the Plymouth member, near the top of the Plymouth member, and at the base of the Pence member (Hotchkiss, 1919; Aldrich, 1929). The latter, which is the most persistent, is known in the district as the "Middle Conglomerate". These zones have been interpreted by Hotchkiss as indicating disconformities within the iron-formation sequence. Fragmental zones are not confined to specific horizons, however, and can be found at many places throughout the section.

Table 8

Chemical analysis of pyritic slate

SiO_2	51.81
Al_2O_3	6.78
Fe_2O_3	3.44
FeO	19.83*
MgO	3.46
CaO	.37
Na_2O	.00
K_2O	.00
H_2O^-	.33
H_2O^+	4.32
TiO_2	.93
CO_2	4.30
P_2O_5	.16
S	1.94
V_2O_3	.04
MnO	.49
C	2.54
TOTAL	100.74
Less O for S	.49
	100.25

Locality: Drill hole #121, 715 to 736 feet, SE¼, SE¼, sec. 31, T. 47 N., R. 2 E., Iron County, Wisconsin

Analyst: Lucille M. Kehl, U. S. Geological Survey

* The acids used to dissolve the sample do not attack pyrite. Therefore, a calculated correction, based on the sulfur present, was made on the FeO to take care of the Fe in the pyrite. In making this correction it was assumed that all sulfur is present as pyrite.

The fragments in the breccias are entirely composed of iron-formation, and most fragments are similar to the rocks of the underlying strata. The angularity of most fragments indicates that the eroded or disturbed material was at least partly indurated and the distance of transportation small. The matrix of the rock consists of chert, hematite, siderite, silicate and magnetite in various combinations. The chert is commonly reddish, with granular or oolitic structure. The evidence suggests that most of the fragmental zones represent periods of strong wave or current action on the ocean bottom rather than extensive erosion and redeposition. The formation of the Middle Conglomerate and other more widespread zones may call for shallowing of the water with elevation of extensive parts of the depositional basin above the normal wave base.

"Sweepings bed"--The so-called "sweepings bed", which occurs at the base of the iron-formation, is a transition phase between the iron-formation and the underlying Palms quartzite. It marks the beginning of the period of chemical sedimentation, typified by the iron-formation, with the gradual exclusion of clastic material.

The "sweepings bed" is commonly several feet thick and rarely is as much as ten feet thick. The lower part is a quartzite with a chert matrix. The percentage of clastic quartz decreases upward in the unit so that near the top it consists of chert with only scattered quartz grains. The chert is granular and oolitic, commonly reddish, and similar to the cherts described elsewhere in this paper.

Argillite--Argillite, a fine-grained rock of clastic origin as distinguished from the fine-grained, even-bedded "slates" largely of chemical origin, is of importance within the iron-formation only on the eastern end of the range. At the Sunday Lake mine at Wakefield, Michigan, about 100 feet of argillite occurs in the lower part of the iron-formation. Drilling at the Vicar exploration, about three miles east of the Sunday Lake mine indicates about 165 feet of argillite occurring just above the base of the formation.

The argillite is quite uniform in appearance, generally being finely laminated and dark greenish-gray in color. Most of it possesses good parting parallel to the bedding, with locally a true slaty cleavage developed at an angle to the bedding.

Two chemical analyses of this argillite are given in Table 9. Also included in Table 9 for comparison is an average analysis for Precambrian lutites (mostly of Huronian age) as compiled by Nanz (1953, p. 57).

It can readily be seen that the iron content of these argillites is approximately twice that of Nanz's average. With the exception of two Keweenawan samples, the only other samples among the 36 analyses listed by Nanz (1953, p. 53-54) which approach this iron content are those closely associated with iron-formation, such as the "footwall" and "hangingwall" strata of the Iron River district and a "magnetic clay slate" from the base of the Tyler formation.

The complete absence of carbonate is notable when compared with the presence of this material in all the iron-formation analyses presented in previous sections of this paper.

Table 9

Chemical analyses of argillite from iron-formation and average composition of Precambrian lutites

	A	B	C Average Precambrian lutite
SiO_2	56.64	55.73	58.32
Al_2O_3	10.18	14.82	18.44
Fe_2O_3	4.66	1.37	3.75
FeO	16.07	14.21	4.13
MgO	4.09	4.17	2.21
CaO	.19	.04	.78
Na_2O	.04	.06	.96
K_2O	1.97	3.38	4.42
H_2O^-	.19	.11	.43
H_2O^+	5.39	5.22	3.43
TiO_2	.47	.53	.78
CO_2	.00	.00	.74
P_2O_5	.09	.04	.13
S	.01	.12	.03
V_2O_3	.01	.01	trace
MnO	.03	.06	.08
C	.00	.46	.69
SO_3			.14
FeS_2			.54
TOTAL	100.03	100.33	100.00
Less O for S	.01	.06	
	100.02	100.27	

A. Argillite from drill hole #131, 352 to 355 feet, Sunday Lake mine, sec. 10, T. 47 N., R. 45 W., Gogebic County, Michigan. Analyst: Lucille M. Kehl, U. S. Geological Survey

B. Argillite from drill hole #1201, 1461 to 1482 feet, Vicar exploration, SE$\frac{1}{4}$, SE$\frac{1}{4}$, sec. 12, T. 47 N., R. 45 W., Gogebic County, Michigan. Analyst: Lucille M. Kehl, U. S. Geological Survey

C. Weighted average of 36 analyses of Precambrian lutites from the Lake Superior region (Analysis 2, Table 2, Nanz, 1953, p. 57)

In thin-section the argillite is seen to consist largely of fine-grained clastic quartz, chlorite, and sericite (?) with minor magnetite and carbonaceous material. Occasional beds of coarser fragmental material and of granular chert are present within the argillite. Carbonate does not appear to occur as a primary constituent although minor vein carbonate can be seen in some specimens.

Distribution of rock types

Granular, cherty, magnetite-rich rock makes up most of the irregular-bedded iron-formation typical of the Plymouth, Norrie and Anvil members. This rock locally grades into material in which carbonate, silicate, or hematite predominates among the iron minerals. The irregular-bedded parts of the Yale and Pence members are similar.

Carbonate and silicate rocks make up the greater part of the even-bedded iron-formation. These rocks intergrade both vertically and laterally, and may be interbedded with or gradational into even-bedded magnetite-silicate rocks. Chert-magnetite and jasper-magnetite rocks occur most commonly in the upper part of the Pence member and are especially well developed on the eastern end of the range. Even-bedded, pyritic, carbonaceous rock appears to be confined to the Yale member, usually in the lower part.

As examples of the distribution of rock types in the iron-formation, descriptions are presented of the rocks encountered in two drill holes just west of the town of Pence, Wisconsin. Parts of the formation in this area have been extensively oxidized, with resultant mineral alteration and destruction of primary textures, but many sections of the core show only minor alteration and serve as excellent examples of various rock types occuring in the iron-formation (Tables 10 and 11).

On the generalized cross section (Figure 6) corrections have been made for the angle between the bedding planes and the direction of penetration, but the stratigraphic thicknesses indicated are only approximate.

The stratigraphic descriptions show that the granular-cherty rocks in this area have been extensively oxidized as they have been throughout the remainder of the range to the east. This is illustrative of the fact that this rock type is more susceptible to oxidation than the even-bedded types of iron-formation, as noted by Hotchkiss (1919, p. 579) and by Aldrich (1929, p. 140). A specimen of virtually unoxidized, irregular-bedded, granular-cherty rock was obtained from drilling at the Atlantic property, about one mile west of the described holes near Pence. This rock, as described in the section on magnetite-rich rocks, consists of irregular beds of granular chert separated by laminae of carbonate-silicate material. Considerable magnetite is present, both in the granular chert and in the carbonate-silicate laminae.

An example of lateral gradation of rock types is also present in the Pence area. The Pence member as described in drill holes #113 and #121 consists largely of even-bedded chert-carbonate rock. About one mile to the east of these holes the Pence member is represented by an even-bedded chert-magnetite rock with considerable jasper and minor silicate material. Unfortunately, information concerning the details of gradation in the intervening area are lacking.

Table 10

Generalized stratigraphic description of iron-formation from drill hole #121, Pence, Wisconsin

D.D.H. #121, SE¼, SE¼, sec. 31, T. 46 N., R. 2 E., Wisconsin. This hole was drilled from the surface just northwest of the town of Pence and encountered the Pabst member of the Tyler formation at ledge. Approximate stratigraphic thicknesses are given.

Pabst member of Tyler formation:

5.5 ft.	(Core lost[1]) Conglomerate. Red and gray chert pebbles in a matrix of granular chert. Occasional layers of even-bedded, carbonate-rich rock.
11 ft.	(Core lost) Even-bedded, chert-carbonate rock.
2.5 ft.	Conglomerate with fragments of red and gray chert in a granular chert matrix. Minor magnetite and carbonate present. Partly oxidized.

Ironwood iron-formation:
Anvil member:

17 ft.	Even-bedded, chert-carbonate rock with considerable magnetite. In some layers carbonate is minor and magnetite is dominant iron mineral. Partly oxidized.
25 ft.	(Core lost) Even-bedded, chert-carbonate rock with considerable magnetite.
11 ft.	(Core lost) Even-bedded, chert-carbonate rock with some dense flinty chert layers and irregular layers of granular chert.

53 ft. Total Anvil.

(Note: In this part of the range much of the Anvil has been removed by erosion prior to the deposition of the Pabst (Atwater, 1938, p. 163).

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[1] The notation "core lost" indicates that for a particular section of drilling the core has been lost or misplaced and was therefore unavailable for re-examination. For those sections, descriptive information was obtained from core logs written by Theodore Roy and used with the permission of the Republic Steel Corporation.

Table 10 (cont.)

Pence member:

26 ft.	(Core lost) Even-bedded, chert-carbonate rock with minor magnetite. Partly oxidized.
61 ft.	Even-bedded, chert-carbonate-silicate rock with considerable magnetite. The chert occurs chiefly as interstitial material although scattered layers of granular chert are present. Carbonate is usually dominant over silicate although the ratio varies greatly from layer to layer. Magnetite occurs disseminated throughout individual layers but varies greatly in percentage from layer to layer. Carbonaceous material is often present as thin irregular laminae. Analysis B, Table 2, gives the average chemical composition of about 6.5 feet of the lower part of this section and Table 3 gives the approximate mineralogical composition.
15.5 ft.	(Core lost) Even-bedded, chert-carbonate rock with occasional beds of conglomeratic, granular chert.
14 ft.	Even-bedded, chert-carbonate-silicate rock similar to above.
6.5 ft.	Conglomerate. Angular fragments of green to gray chert in a granular and oolitic chert matrix. Also contains fragments of what appears to have been partly indurated even-bedded material.

122 ft Total Pence.

Norrie member:

117 ft.	Irregular-bedded, granular-cherty rock. The entire Norrie has been extensively oxidized and the iron occurs mostly as soft red hematite. Core recovery is poor except for scattered pieces of chert. Chert shows relict granule structures.

Yale member:

15 ft.	Even-bedded, chert-carbonate rock with minor silicate and magnetite. Partly oxidized.
6.5 ft.	Irregular-bedded, granular chert, somewhat conglomeratic. Oxidized.

Table 10 (cont.)

34 ft. Even-bedded, chert-carbonate rock with minor silicate and magnetite. Rock is similar to much of the Pence above except for greater percentage of carbonate and smaller percentage of silicate and magnetite. The chert occurs both as disseminated material in the carbonate-rich layers and as thin beds, often irregular or nodular. Carbonaceous material is present along stylolite seams, both within carbonate layers and at the contact between carbonate and chert layers. The stylolite seams range in size from microscopic structures with extremely small amplitude to megascopic structures with an amplitude of several millimeters. Analysis C, Table 2, gives the average chemical composition of about 7.5 feet of the carbonate rock type, located about 5.5 feet from the top of this section. Table 3 gives the approximate mineralogical composition.

12 ft. Finely laminated, black, carbonaceous, pyritic slate. The average chemical composition of this rock is given in Table 8.

67.5 ft. Total Yale.

Plymouth member:

100 ft. Irregular-bedded, granular-cherty rock. The entire Plymouth has been extensively oxidized and the iron occurs largely as soft red hematite. Core recovery poor except for pieces of granular chert. Chert layers occasionally conglomeratic.

48 ft. (Core lost) Similar to above.

6 ft. (Core lost) "Sweepings bed". Conglomeratic and granular chert with clastic quartz.

154 ft. Total Plymouth.

513.5 Total Ironwood.

Palms formation:

Quartzite.

Table 11

Generalized stratigraphic description of iron-formation from drill hole #113, Pence, Wisconsin

D.D.H. #113, NW$\frac{1}{4}$, NE$\frac{1}{4}$, sec. 6, T. 45 N., R. 2 E., Wisconsin. This hole was drilled from the surface just west of the town of Pence and encountered the Tyler formation at ledge. Approximate stratigraphic thicknesses are given.

Tyler formation:

11 ft.	Black magnetic slate and dark green, even-bedded rock containing carbonate, chlorite, magnetite, and minor quartz.

Pabst member of Tyler formation:

11.5 ft.	Conglomerate with angular jasper and chert fragments in a granular chert matrix. Minor zones of even-bedded chert-carbonate rock.
8 ft.	Even-bedded, carbonate-silicate-magnetite rock similar to even-bedded rock in Tyler above and in iron-formation below.
10.5 ft.	Conglomerate. Jasper and chert pebbles in matrix of granular and oolitic chert. Considerable magnetite.

30 ft. Total Pabst.

Ironwood iron-formation:
Anvil member:

8 ft.	Even-bedded, carbonate-silicate rock with considerable magnetite. Carbonate, silicate, and magnetite percentages vary greatly from layer to layer. Silicate material largely chlorite.
14.5 ft.	Irregular-bedded, granular-cherty rock. This section is extensively oxidized and the iron occurs largely as soft red hematite.

22.5 ft. Total Anvil.
Note: In this part of the range much of the Anvil has been removed by erosion prior to the deposition of the Pabst (Atwater, 1938, p. 163).

Table 11 (cont.)

Pence member:

27.5 ft.	Even-bedded, chert-carbonate rock with considerable silicate and magnetite. Numerous thin layers of irregular-bedded, granular chert.
74.5 ft.	Even-bedded, chert-hematite rock, extensively oxidized.

102 ft. **Total Pence.**

Norrie member:

115 ft.	Irregular-bedded, granular-cherty rock. Entire Norrie extensively oxidized. Iron occurs as soft red hematite. Core recovery poor except for scattered pieces of chert. Chert shows relict granule structures.

Yale member:

35.5 ft.	Even-bedded, chert-carbonate rock with minor silicate and magnetite. Chert in dark flinty layers and as disseminated material. Few granular chert zones present. Minor carbonaceous material present. Carbonate and silicate material partly oxidized.
13 ft.	Finely laminated, black, carbonaceous, pyritic slate.

48.5 ft. **Total Yale**

Plymouth member:

125 ft.	Irregular-bedded, granular-cherty rock. Entire Plymouth extensively oxidized as is Norrie above. Iron occurs largely as soft red hematite. Chert has relict granule structures as evidenced by distribution of powdery hematite and by differences in grain size of the crystallized chert (quartz).
3 ft.	Thinly and evenly bedded hematitic rock, well oxidized.
5 ft.	"Sweepings bed". Conglomeratic and granular chert and jasper with clastic quartz grains near base.

133 ft. **Total Plymouth**

421 ft. **Total Ironwood.**

Palms fortmation: Quartzite.

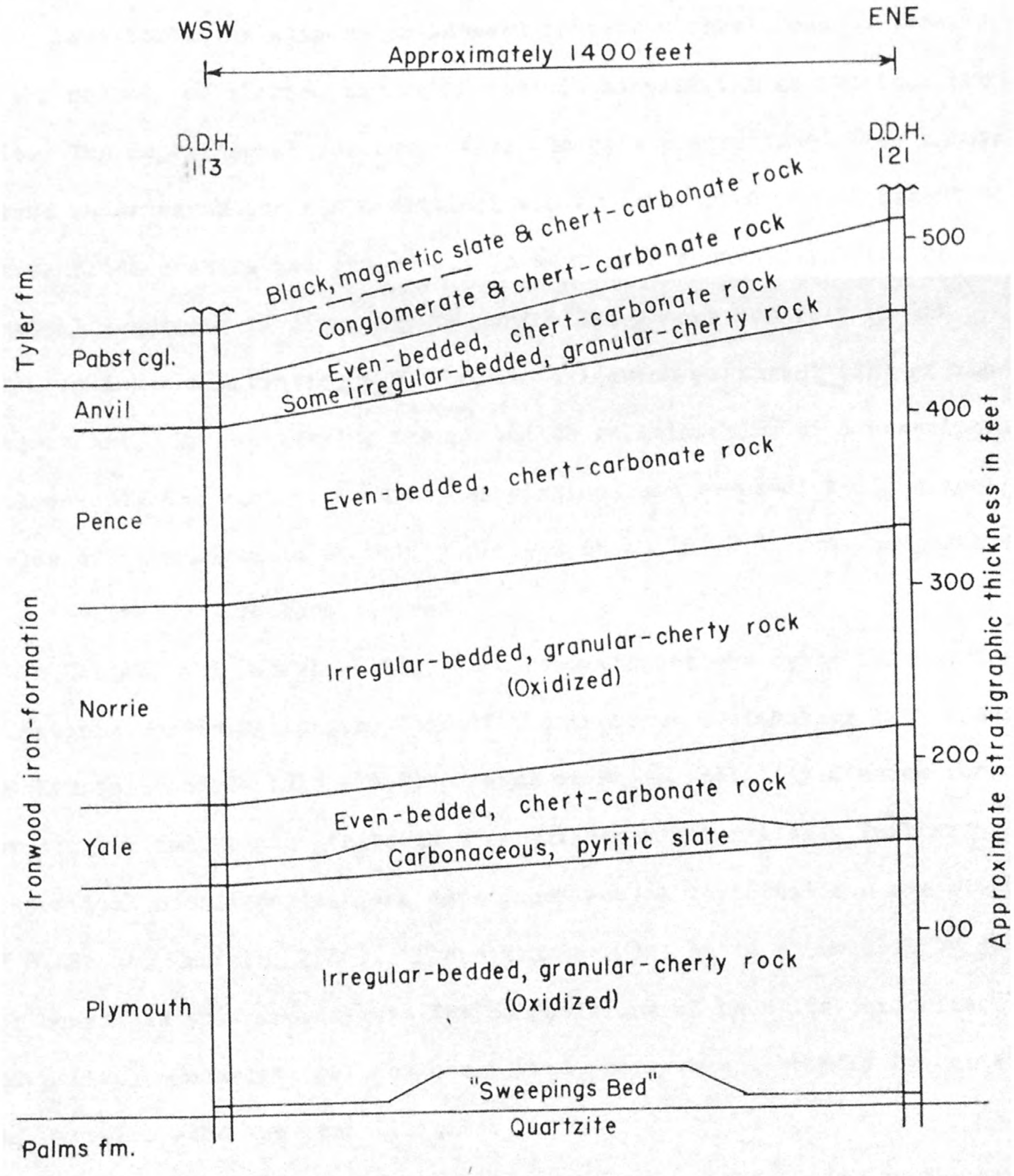

Figure 6. Generalized stratigraphic section of Ironwood iron-formation near Pence, Wisconsin

ENVIRONMENTAL CONTROL OF SEDIMENTARY IRON MINERAL FORMATION

Equilibrium relationships between various minerals can be treated by the methods of thermodynamics if certain simplifying assumptions are made. The depositional environment of minerals precipitated from natural waters under earth surface conditions can be considered one of essentially constant temperature and pressure. In many such natural systems the chemical reactions involved may be controlled almost entirely by the hydrogen-ion concentration (pH) and the oxidation potential (Eh) of the environment. By considering the pH and Eh relationships of a postulated environment, the various mineral associations can be predicted and their fields of thermodynamic stability plotted on an Eh-pH diagram comparable to a temperature-pressure diagram.

Castaño and Garrels (1950) make some suggestions as to the chemical conditions necessary for the formation of various sedimentary iron minerals and Krumbein and Garrels (1952) present an Eh-pH stability diagram for hematite, siderite and pyrite in a normal sea water system. Further theoretical considerations and some experimental verifications are given by Huber and Garrels (1953). These studies were based on solubility data for compounds that approximate the compositions of hematite, siderite, and pyrite. Magnetite was not considered, nor, except briefly by Castaño and Garrels, were the iron silicates.

Since that time, the writer's attention has been called to the work of Pourbaix (1949) who has calculated Eh-pH stability fields for hematite, magnetite and elemental iron in a study of the "corrosion domains" of iron. The methods used by Pourbaix for the determination of phase relationships are based upon free energy data rather than solubility data, allowing application to mineral species for which solubility data are not known. With this information it is now possible to place magnetite in the Eh-pH diagram.

Determination of mineral equilibrium relations

Magnetite-hematite equilibrium

The boundary between the magnetite and hematite stability fields is established by determination of Eh and pH values at which magnetite and hematite can coexist in thermodynamic equilibrium.

The relation between magnetite and hematite in an aqueous system can be written as

$$3Fe_2O_3 + 2H^+ + 2e^- = 2Fe_3O_4 + H_2O; \qquad \text{or}$$

$$3Fe_2O_3 - 2Fe_3O_4 - H_2O + 2H^+ + 2e^- = 0 \tag{1}$$

with all symbols collected on the same side of the equation and where e^- represents the electron. If this is considered a reaction of the type

$$aA + bB + cH_2O + mH^+ + ne^- = 0 \tag{2}$$

(Pourbaix, 1949, p. 9) then the standard potential for the reaction is given by

$$E^\circ = \frac{a\,\Delta F^\circ_A + b\,\Delta F^\circ_B + c\,\Delta F^\circ_{H_2O} + m\,\Delta F^\circ_{H^+}}{23{,}060\ n} \tag{3}$$

(Pourbaix, 1949, p. 9) where ΔF°_X is the standard free energy (standard chemical potential of Pourbaix) for each of the components in the reaction.

The equilibrium potential, Eh (E of Pourbaix), for such a reaction is given by

$$Eh = E^{o} + \frac{RT}{nF} \ln K \qquad (4)$$

where $K = (a_A)^{a}(a_B)^{b}(a_{H_2O})^{c}(a_{H^+})^{m}$ or the product of the activities (expressed in moles/liter) of the various components raised to the power of their coefficients. After substituting the proper constants at 25° C., changing to logarithms of base ten and replacing $-\log a_{H^+}$ with pH the equation becomes

$$Eh = E^{o} - \frac{0.0591\ m}{n}\, pH + \frac{0.0591}{n}\left[a \log(a_A) + b \log(a_B)\right] \qquad (5)$$

Values for the standard free energies of various components used in the calculation of the stability fields are listed in Table 12.

Table 12

Standard free energies @ 25° C.
(calories)

H^+aq.	0	$FeCO_3$	-161,060
H_2O	- 56,690	FeS	- 23,320
Fe^{++}aq.	- 20,300	FeS_2	- 39,840
Fe^{+++}aq.	- 2,530	S^{--}aq.	- 22,100
Fe_2O_3	-176,100*	CO_3^{--} aq.	-126,220
Fe_3O_4	-241,820*		

* starred values from Pourbaix (1949), all others from Latimer (1952).

For the magnetite-hematite relationship given in equation (1), a value for E^o may be obtained from equation (3) by proper substitution of standard free energies from Table 12. For this system, then, equation (5) becomes

$$Eh = 0.941 - 0.059\ pH \qquad (6)$$

the activity of all solids being taken as unity. Equation (6) represents the locus of points lying on the hematite-magnetite boundary (i.e. hematite and magnetite coexisting in thermodynamic equilibrium). If a series of pH values is assumed, corresponding Eh values can be calculated and the hematite-magnetite boundary plotted on an Eh-pH diagram.

The exact position of the hematite-magnetite boundary as calculated by this method depends upon the values used for the free energy of formation of the various minerals. If it were to be assumed that hematite forms by a series of changes from ferric hydroxide through various forms of hydrated ferric oxide, then the free energy for $Fe(OH)_3$ should possibly be used to determine conditions of initial precipitation of the ferric compound. However, since we are primarily interested in the equilibrium relations between the stable anhydrous forms, and furthermore since virtually nothing is known of the mechanism involved in the formation of magnetite, the free energies of the anhydrous forms have been used in the calculations.

Magnetite-siderite equilibrium

The activity product constant for siderite is given by Latimer (1952, p. 222) as

$$({}^{a}Fe^{++})({}^{a}CO_3^{--}) = 10^{-10.68} \qquad (7)$$

It is apparent from the above relation that the solubility of siderite (and thermodynamic stability ?) is dependent upon the activity of carbonate ions in the aqueous system under consideration. The activity of carbonate ions in sea water is dependent upon the pH of the system through the carbon dioxide equilibria

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{--} + 2H^+ \qquad (8)$$

It is also dependent to a lesser degree upon the salinity and chlorinity of the system. Sverdrup, Johnson and Fleming (1942, pp. 195-202) and Harvey (1945, pp. 59-69) give details for calculation of the carbon dioxide components in sea water systems.

Table 13 indicates the concentration and activity of carbonate ions in "normal" sea water (salinity = 35 °/oo, chlorinity = 19 °/oo, partial pressure of CO_2 in equilibrium with the atmosphere at one atmosphere total pressure and 25° C.). The activity coefficient of carbonate ions in water of this salinity is taken as 0.019 (Sverdrup et. al., 1942, p. 205).

Table 13

Concentration and activity of carbonate ions
in normal sea water

(moles/liter)

pH	4	5	6	7	8	9
$C_{CO_3^{--}}$	$10^{-7.6}$	$10^{-6.6}$	$10^{-5.6}$	$10^{-4.6}$	$10^{-3.6}$	$10^{-2.6}$
$a_{CO_3^{--}}$	$10^{-9.3}$	$10^{-8.3}$	$10^{-7.3}$	$10^{-6.3}$	$10^{-5.3}$	$10^{-4.3}$

Figure 7 illustrates the relation between pH and carbonate ion concentration and activity.

The relation between magnetite, siderite and carbonate ion activity can be written as

$$Fe_3O_4 - 3Fe(CO_3) - 4H_2O + 3CO_3^{--} + 8H^+ + 2e^- = 0 \qquad (9)$$

where the equilibrium potential for the reaction is

$$Eh = 1.935 - 0.236pH + 0.089 \log (a_{CO_3^{--}}) \qquad (10)$$

as calculated by the methods of Pourbaix. By substitution in equation (10) of the activity of carbonate ions at various pH values, a series of Eh values can be calculated for magnetite-siderite equilibrium and the boundary between the respective fields can be defined.

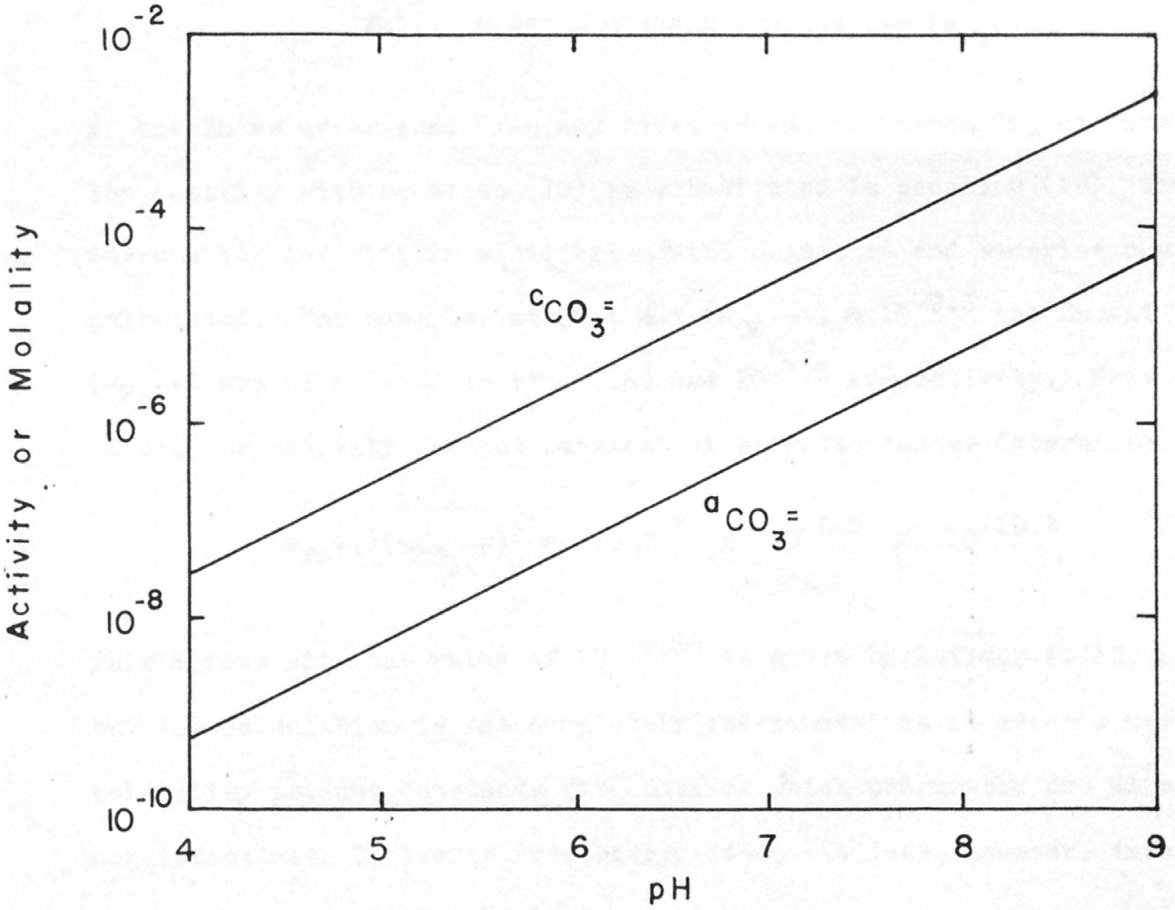

Figure 7. Concentration and activity of carbonate ions in normal sea water. Salinity = 35 °/oo, Chlorinity = 19 °/oo, $\gamma_{CO_3^{--}}$ = 0.019.

As a check, the ferrous ion activity in equilibrium with magnetite can be determined from the following relations:

$$Fe_3O_4 - 3Fe^{++} - 4H_2O + 8H^+ + 2e^- = 0 \qquad (11)$$

$$Eh = 0.983 - 0.236pH - 0.089 \log (a_{Fe^{++}}) \qquad (12)$$

If the Eh as determined from any given pH and corresponding carbonate ion activity with equation (10) is substituted in equation (12), the ferrous ion activity in equilibrium with magnetite and siderite can be calculated. For example, at pH 4 and $(a_{CO_3^{--}}) = 10^{-9.3}$ the Eh and $(a_{Fe^{++}})$ are calculated to be -0.164 and $10^{-1.3}$ respectively. From these values the activity product constant of siderite can be determined.

$$(a_{Fe^{++}})(a_{CO_3^{--}}) = 10^{-1.3} \times 10^{-9.3} = 10^{-10.6}$$

This agrees with the value of $10^{-10.68}$ as given by Latimer (1952, p. 222), but the calculation is not completely independent as it depends upon solubility product constants from Latimer which presumably are already consistent with Latimer's free energy data. It does, however, involve a different method of calculation.

Magnetite-pyrite equilibrium

Like hematite and magnetite, pyrite (or marcasite) formed in an aqueous medium probably passes through an intermediate hydrous stage in which hydrotroilite ($FeS \cdot nH_2O$) is formed (Emery and Rittenberg, 1952, p. 791). Again as with hematite and magnetite, the equilibrium relations between the stable anhydrous forms are of primary interest in this discussion and free energy and solubility data for FeS_2 should be used in the equilibrium calculations. Although both Pourbaix (1949, p. 122) and Latimer (1952, p. 221) list free energy data for FeS_2, neither give solubility data. As it is desirable in the present discussion to relate the stability of iron sulfide to the activity of sulfide ions in equilibrium with the dissociation constants of H_2S and the activity of sulfate ions in normal sea water, solubility data are necessary. Because the free energy values for FeS and FeS_2 differ considerably, the substitution of solubility data available for FeS may be a poor approximation for that of true pyrite. In the absence of additional information, however, the solubility product constant for FeS is assumed to be similar to that of pyrite in the following calculations. It may represent a maximum value for the solubility of true pyrite as suggested by Krumbein and Garrels (1952, p. 10).

The activity product constant for FeS is given by Latimer (1952, p. 222) as

$$(a_{Fe^{++}})(a_{S^{--}}) = 10^{-18.4} \qquad (13)$$

The relation for sulfide ion activity in equilibrium with magnetite is given by

$$Fe_3O_4 - 3FeS + 3S^{--} - 4H_2O + 8H^+ + 2e^- = 0 \qquad (14)$$

$$Eh = 2.70 - 0.236pH + 0.089 \log (a_{S^{--}}) \qquad (15)$$

The activity of the sulfide ion must also be in equilibrium with the sulfate ion activity through the relations

$$SO_4^{--} - S^{--} - 4H_2O + 8H^+ + 8e^- = 0 \qquad (16)$$

$$Eh = 0.14 - 0.060pH + 0.0075 \log \frac{(a_{SO_4^{--}})}{(a_{S^{--}})} \qquad (17)$$

Furthermore, the sulfide ion must be in equilibrium with the dissociation constants of H_2S as well as with the total sulfur in the system.

The concentration of total sulfide plus sulfate in normal sea water is approximately $10^{-1.5}$ moles/liter (Sverdrup et al, 1942, p. 173). The activity of the sulfide ion will be determined by the dissociation constants of H_2S at any given pH. Under the equilibrium conditions with which we are concerned, $a_{S^{--}}$ will be negligible compared with $a_{SO_4^{--}}$ and therefore the value of $a_{SO_4^{--}}$ may be taken as equal to that for the concentration of total sulfide plus sulfate after the activity coefficients have been taken into consideration. Using this data, a series of Eh-pH values can be obtained from the equilibrium relationships given by equations (15) and (17). These Eh-pH values define the boundary between the magnetite and pyrite stability fields.

Siderite-pyrite equilibrium

The activity product constants for siderite and pyrite and the relations between carbonate and sulfide ion activities and a normal sea water system have been indicated in the preceding sections.

At any assumed pH the carbonate ion activity is fixed and the sulfide ion activity necessary to form pyrite in equilibrium with siderite can be determined by simultaneous solution of equations (7) and (13). Taking cognizance of the sulfide-sulfate relations previously mentioned, an equilibrium Eh may be calculated from equation (17). The Eh-pH values thus obtained will define the boundary between the siderite and pyrite stability fields.

A check on the activity product constant of FeS can be made through the equilibrium relations between FeS and $FeCO_3$:

$$FeCO_3 + S^{--} - FeS - CO_3^{--} = 0 \qquad (18)$$

The equilibrium constant for the reaction is given by

$$\log \frac{(a_{FeCO_3})(a_{S^{--}})}{(a_{FeS})(a_{CO_3^{--}})} = \log K = -\frac{\Delta F^\circ_{FeCO_3} + \Delta F^\circ_{S^{--}} - \Delta F^\circ_{FeS} - \Delta F^\circ_{CO_3^{--}}}{1363} \qquad (19)$$

(see Pourbaix, 1949, p. 8, eq. 6). Upon substitution of standard free energy values from Table 12 we obtain

$$\frac{(a_{S^{--}})}{(a_{CO_3^{--}})} = K = 10^{-7.8} \qquad (20)$$

At a pH of 4, for example, the activity of carbonate ions would be $10^{-9.3}$ and from equation (20) the activity of sulfide ions in equilibrium with $FeCO_3$ and FeS would be

$$(a_{S^{--}}) = K(a_{CO_3^{--}}) = 10^{-7.8} \times 10^{-9.3} = 10^{-17.1}$$

The activity of ferrous ions in equilibrium with siderite at this pH would be $10^{-1.4}$ (from equation (7)) and the solubility product constant of FeS would be

$$(a_{Fe^{++}})(a_{S^{--}}) = 10^{-1.4} \times 10^{-17.1} = 10^{-18.5}$$

This value agrees with the value of $10^{-18.4}$ given by Latimer (1952, p. 222). As in a previous section this check is implicit in the data used but does illustrate a different method of calculation.

Hematite-siderite equilibrium

The equilibrium relations between hematite and siderite can be written as

$$Fe_2O_3 - 2Fe(CO_3) - 3H_2O + 2CO_3^{--} + 6H^+ + 2e^- = 0 \qquad (21)$$

$$Eh = 1.380 - 0.177pH + 0.0591 \log (a_{CO_3^{--}}) \qquad (22)$$

As noted in the previous sections, at any assumed pH, the carbonate ion activity is fixed and the equilibrium Eh can be calculated from equation (22). A series of such calculations will serve to define the boundary between the hematite and siderite stability fields.

Iron Mineral Stability Diagram

The methods for calculating boundaries between stability fields for the various mineral pairs under consideration have been discussed in the preceeding section. Such a series of boundaries are shown in Figure 8 for a normal sea water system. Upon elimination of the mutually exclusive segments of these boundaries a diagram showing the Eh-pH stability fields for hematite, magnetite, siderite, and pyrite (actually FeS) is obtained (Figure 9).

An environmental position within one of the stability fields indicates that that mineral would form in preference to the other minerals on the diagram, assuming of course, that the concentration of iron was sufficient. A position on any of the field boundaries would indicate that the adjacent minerals were in equilibrium with each other and could exist together. At the intersection of any three field boundaries, the three adjacent minerals would be in equilibrium with each other. Actually, because of probable lack of complete thermodynamic equilibrium, it is likely that a zone of apparent stability of adjacent minerals would exist rather than a single boundary line along which they could occur together.

The introduction of magnetite into the diagram and the use of thermodynamic constants of Fe_2O_3rather than those for $Fe(OH)_3$ produces some major changes in the original hematite-siderite-pyrite diagram of Krumbein and Garrels (1952, p. 12), which is shown with some modifications in Figure 10 for comparison.

The hematite field is extended to lower Eh ranges because of the use of constants for Fe_2O_3 rather than $Fe(OH)_3$. At higher pH values

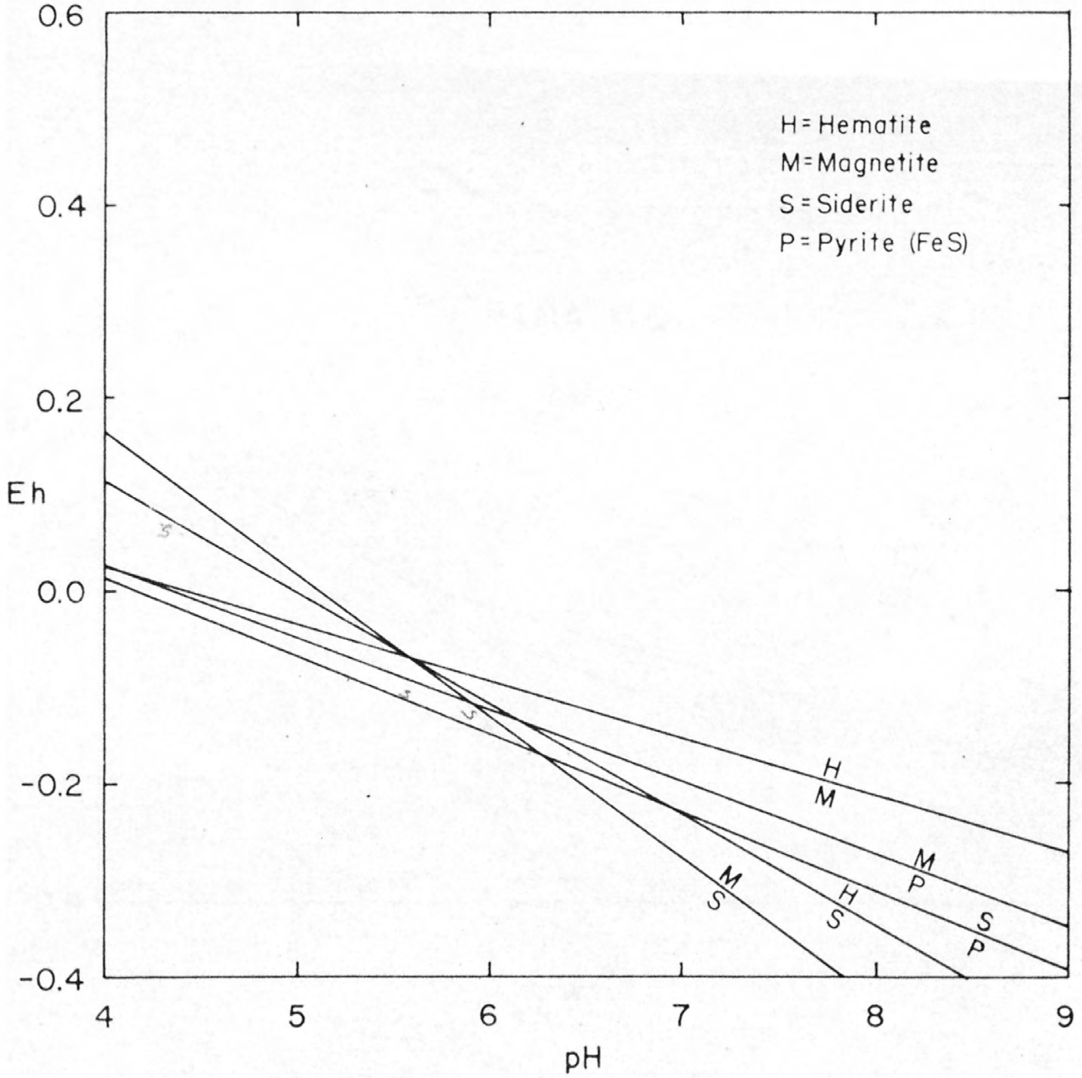

Figure 8. Boundaries between Eh-pH stability fields for mineral pairs

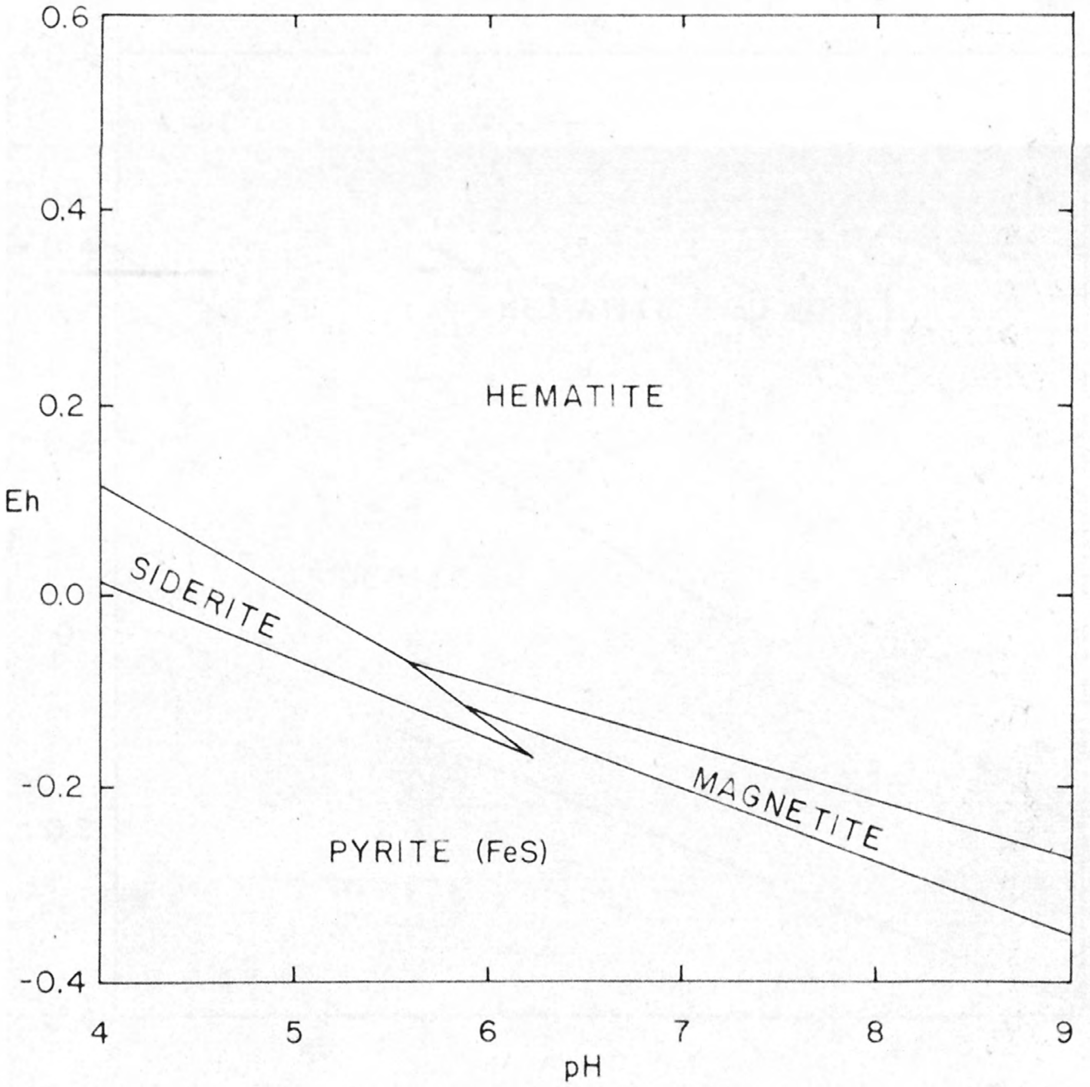

Figure 9. Eh-pH stability fields for hematite, magnetite, siderite, and pyrite (actually FeS) in normal sea water system.

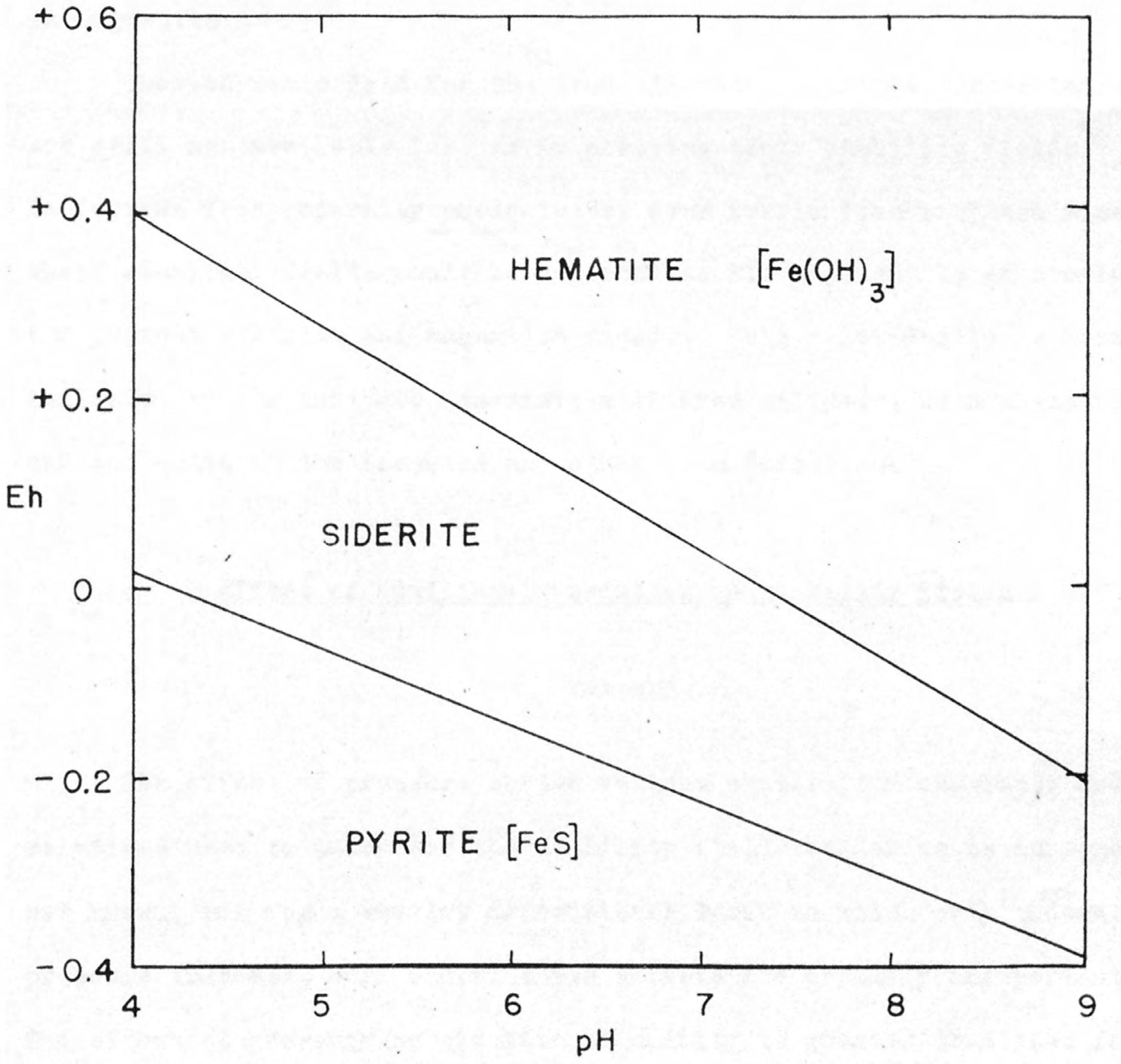

Figure 10. Eh-pH stability fields for hematite (actually $Fe(OH)_3$), siderite, and pyrite (actually FeS) in normal sea water system with magnetite excluded (modified from Krumbein and Garrels, 1952).

the magnetite field occupies a portion of the area previously included in the siderite field. The siderite-pyrite boundary remains in the same position but the pyrite boundary is moved to slightly higher Eh values adjacent to the magnetite field because of the presence of ferric iron in magnetite.

Thermodynamic data for the iron silicates, such as minnesotaite, are still not available for use in plotting their stability fields. As ferrous iron generally predominates over ferric iron in these minerals, their stability fields would be expected to lie adjacent to or overlapping the present siderite and magnetite fields. This relationship is also indicated by the intimate association of iron silicates with magnetite and carbonate in the Ironwood and other iron-formations.

Effect of additional variables on stability fields

Pressure

The effect of pressure on the various equilibrium constants and relations used to calculate the stability field boundaries is in general not known, but for a shallow depositional basin in which only moderate pressure increases will occur, these effects are probably unimportant. The effect of pressure on siderite solubility is greater than that for the other minerals under consideration because of the carbon dioxide relations. Garrels and Dreyer (1952, p. 340), however, note a very small increase in the solubility of calcite within the pressure range to be expected in a moderately shallow basin and the effect of pressure on siderite solubility is probably similarly small.

By affecting the carbon dioxide equilibrium, increased pressure will have some effect on pH, causing a decrease of only 0.02 - 0.03 pH units for 1000 meters of depth (Buch and Gripenberg, 1932; quoted by Harvey, 1945, p. 53).

Temperature

The solubility of CO_2 in sea water as well as the dissociation constants of carbonic acid are affected slightly by changes in temperature. The net effect of these changes is to cause a pH drop of approximately 0.01 pH unit for a rise of 1° C. over the intermediate pH range and in the temperature range from 0° C. to 25° C. (Harvey, 1945, p. 54). The temperature range which is to be expected in normal marine environments probably is not more than 10° C., so that the effect is slight.

Temperature, as well as pressure, can cause changes in the ΔF^0 values of Table 17used in the calculations. Within the temperature and pressure ranges under consideration these changes will be small.

Total CO_2 components

The pH of most natural waters is chiefly determined by the concentration of carbonic acid and to a lesser degree boric acid, as these are the only weak acids present in sufficient quantity to affect the hydrogen ion equilibria. Under anaerobic conditions the pH is also affected by H_2S. Figure 11 (after Rubey, 1951, p. 1127) illustrates the relation between pH and the partial pressure of CO_2. The carbonate-ion concentration depends upon the dissociation of carbonic acid through the equilibria given in equation (8). Once the hydrogen ion concentration

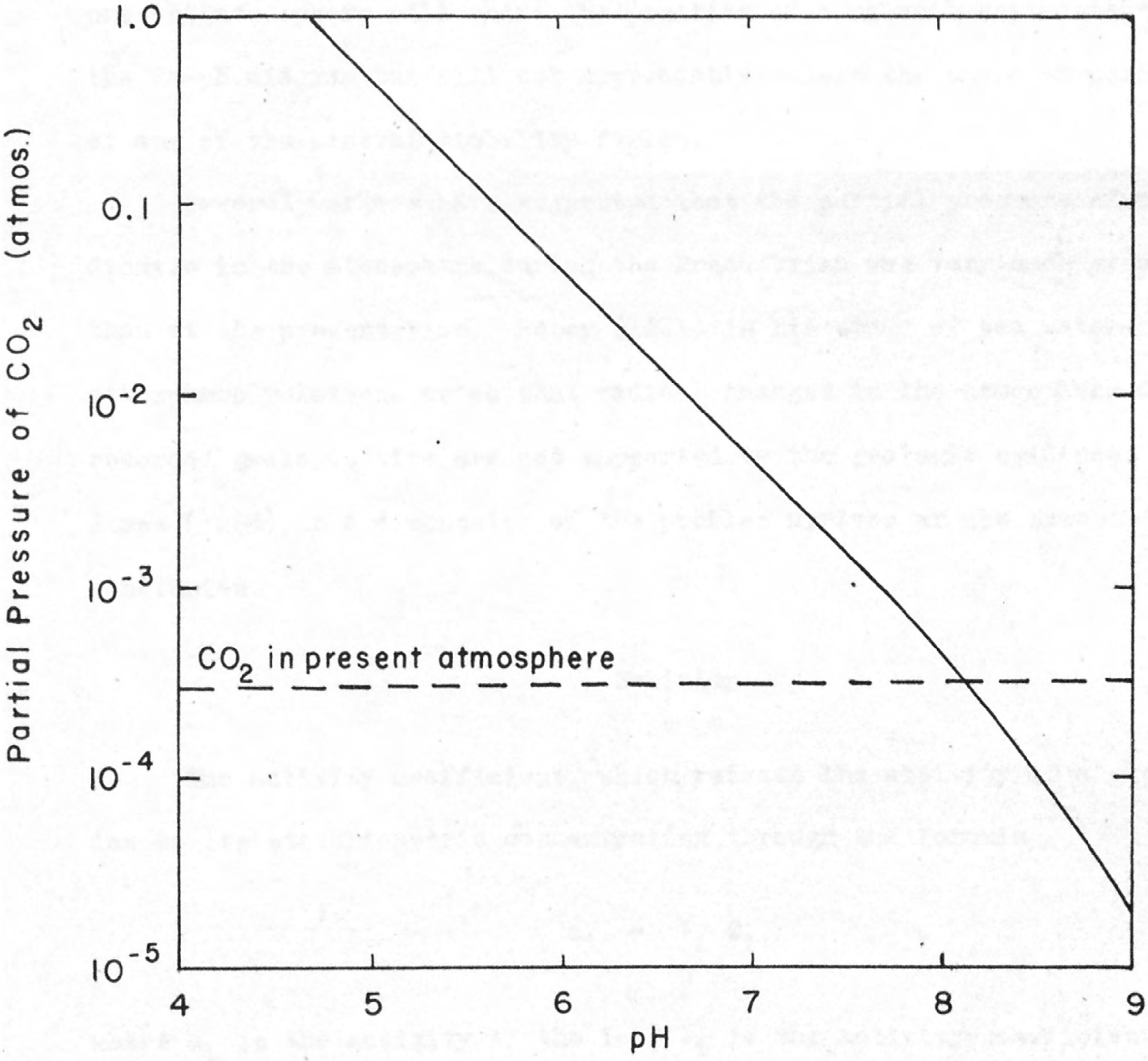

Figure 11. pH as a function of partial pressure of CO_2 (after Rubey, 1951).

has been established by the value of the CO_2 partial pressure, the carbonate-ion concentration follows directly. Thus a change in the partial pressure of CO_2 from that normally in equilibrium with the present atmosphere will shift the position of a natural environment in the Eh-pH diagram but will not appreciably change the shape or position of any of the mineral stability fields.

Several workers have suggested that the partial pressure of carbon dioxide in the atmosphere during the Precambrian was very much greater than at the present time. Rubey (1951) in his study of sea water-atmosphere relations notes that radical changes in the atmosphere during recorded geologic time are not supported by the geologic evidence. James (1954) in a discussion of the problem arrives at the same conclusion.

Salinity

The activity coefficient, which relates the activity of a given ion to its stoichiometric concentration through the formula

$$a_i = \gamma_i C_i,$$

where a_i is the activity of the ion, γ_i is the activity coefficient, and C_i is the stoichiometric concentration, is chiefly dependent upon the valence of the ion and the ionic strength of the solution. The ionic strength is in turn dependent upon the salinity (or chlorinity) of the sea water system. In a sea water system of 19 $^{o}/_{oo}$ chlorinity the ionic strength is about 0.7 and the activity coefficient of the carbonate ion, for example, is 0.019 (Sverdrup et al, 1942, p. 205; Garrels and

Dreyer, 1952, p. 334). Figure 12, after Garrels and Dreyer, shows the relation between the activity coefficient of the carbonate ion and the ionic strength of the system. As stoichiometric concentrations were used only in the calculation of the activity of the carbonate and the sulfide ions, only those boundaries concerned with these ions will be affected by changes in ionic strength.

Changes in activity coefficients over the intermediate salinity range will be small. As salinity increases over that of normal sea water, the activity coefficients change very little, having reached nearly constant values under conditions of normal salinity (see Figure 12). As salinity decreases below that of normal sea water, the activity coefficients increase very slowly down to the range of very low ionic strengths. In any system that has any appreciable quantity of dissolved salts, the activity coefficients are relatively constant and the positions of the various mineral stability fields will not be changed by small variations in these coefficients. The relations between salinity and the activity coefficients of sulfide and other ions will be similar to that for the carbonate ion.

Application of the iron mineral stability diagram

Limitations of the diagram

Before considering the application of the Eh-pH diagram to environmental relationships it seems appropriate to review some of the assumptions used in the development of the diagram and to point out some of its limitations.

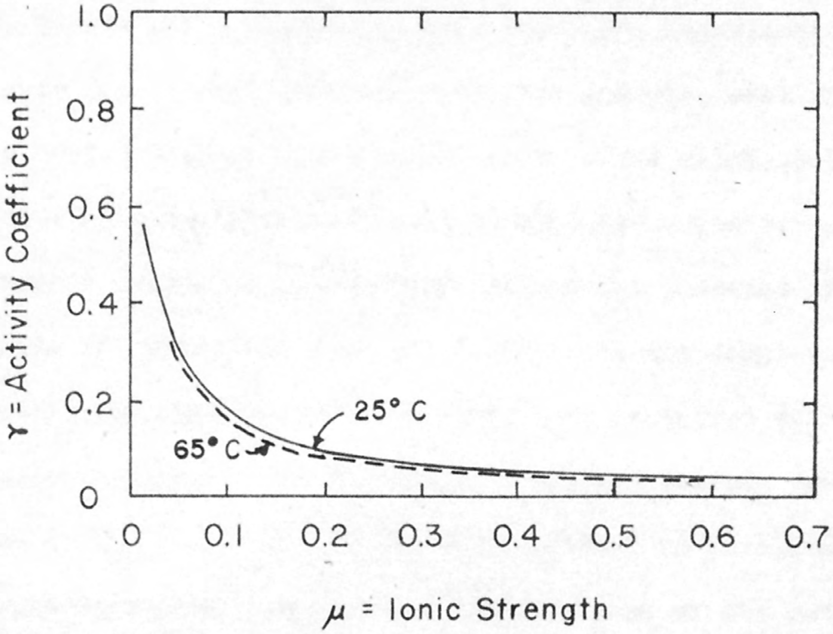

Figure 12. Activity coefficient of the carbonate ion as a function of ionic strength (after Garrels and Dreyer, 1952).

Some of the free energy values used in the calculations must be considered only approximate. This is especially true for Fe_2O_3, Fe_3O_4, and FeS, for each of which several ΔF^0 values may be found in the recent literature. The effect of having used the free energy for FeS rather than that for FeS_2 in the calculation of the position of the pyrite stability field may be considerable. Any change in the free energy values used in the calculations will cause the field boundaries to shift, but remain parallel, thus causing an increase or decrease in the size of the various fields and a modification of the field intersections. The use of a lower free energy for magnetite, for example, will shift the magnetite-siderite boundary toward higher pH values which would extend the siderite stability field into part of that now occupied by magnetite.

The entire system of calculation assumes the presence of an aqueous medium of relatively constant composition and complete thermodynamic equilibrium between the solids and ions contained therein. Thermodynamics considers only the energy relations between reactants and the products of the reactions and makes no attempt to indicate the stages through which the reactants may have to pass or the rate at which equilibrium is attained. It is not possible to assess quantitatively the effect of kinetics on the equilibrium systems. The relative rates of formation of the various minerals will exert some control over the primary deposition and this factor will be overcome only if sufficient time (and ionic mobility) is available for attainment of thermodynamic equilibrium.

Assuming that the free energy values used are approximately correct, the Eh-pH diagram as presented in Figure 9 indicates the stability relations between the various minerals under a given set of conditions: equilibrium with a normal sea water system. Because of the variability of some of these conditions, the value of the diagram lies in its indication of the relative positions of the various stability fields rather than in their exact numerical limits on the Eh and pH scales.

Equilibrium mineral relations

As indicated by the Eh-pH diagram, hematite is stable under oxidizing conditions, siderite and magnetite under intermediate to mildly reducing conditions, and pyrite under moderate to strongly reducing conditions. Only hematite and pyrite are mutually exclusive. Magnetite, although stable under approximately the same Eh conditions as siderite, will form in preference to siderite under intermediate or slightly alkaline pH conditions.

The inclusion of a magnetite field in the iron mineral stability diagram is in accord with numerous recent suggestions that magnetite is probably much more important as a primary or diagenetic mineral in sedimentary rocks than has generally been assumed.

Brown (1943) discusses several occurrences of low-temperature magnetite and possible chemical reactions involved, and concludes that magnetite can be formed by "natural supergene or superficial low-temperature processes". James (1954) reviews additional occurrences and the general problem of magnetite as a primary mineral in sedimentary iron-formations and reaches the same conclusion. White (1954) in an examination of the mineralogy of the Biwabik iron-formation of the Mesabi range concludes that much of the magnetite in that formation is of primary or diagenetic origin.

Most of the evidence upon which Brown, James, White and others have reached their conclusions in regard to low-temperature magentite has been based upon mineral associations and petrographic features in the rocks as observed in the field and under the microscope. The Eh-pH iron mineral stability diagram supplements the field evidence by indicating within approximate limits the Eh-pH conditions under which magnetite can form in a chemical sedimentary environment and its stability relationships relative to other important sedimentary iron minerals.

It has been demonstrated that magnetite can be precipitated from aqueous systems at low temperature and pressure. If alkali is added to a solution containing equivilant amounts of ferrous and ferric salts, a precipitate is obtained that is brownish-black, magnetic, and has an x-ray diffraction pattern identical with that for magnetite from other sources (Weiser, 1953, p. 88; Spiroff, 1938, p. 818). Hydrous Fe_3O_4 rather than hydrous Fe_2O_3 can be obtained by oxidation of ferrous hydroxide in an alkaline medium provided the rate of supply of oxygen is slow (Weiser, 1953, p. 88). However, Weiser notes that with a large supply of oxygen (high Eh) the rate of oxidation to ferric oxide is so high that little or no Fe_3O_4 is formed.

Effects of lack of equilibrium

The failure of a chemical system to maintain equilibrium may permit a thermodynamically unstable mineral to form in preference to a stable one, with resultant anomalous mineral associations.

If magnetite were to be excluded from the Eh-pH mineral stability diagram, the siderite field would be extended into much of what is now the magnetite field. Thus if magnetite were to be retarded from forming because of differences in the relative rates of formation of magnetite and siderite, siderite may first precipitate as a thermodynamically unstable phase under conditions where magnetite is the stable phase. Presumably, as the system approached equilibrium, magnetite would form at the expense of siderite. Lack of the attainment of complete equilibrium might allow considerable siderite to remain although it would be thermodynamically unstable. This would not only permit the original precipitation of much more siderite than would be predicted from the Eh-pH diagram, but would also expand greatly the range of conditions under which siderite and magnetite might occur together.

Lack of equilibrium may also result from the failure of a system to respond to environmental changes. If, for example, siderite should form under conditions of siderite stability, and the environmental conditions then be changed to those appropriate for the formation of magnetite, magnetite should tend to completely replace the siderite. The failure of this reaction to proceed to completion because of insufficient time or restriction of ionic mobility would result in lack of equilibrium and a mixture of siderite and magnetite rather than magnetite alone.

The sulfide-sulfate relationship provides an example in which a biologic catalyst plays an important part in the kinetics of the system. As noted by James (1954, p. 272) the source of sulfide for the formation of pyrite is twofold; bacterial reduction of sulfates in sea water, and of less importance, sulfur derived by bacterial action on organic material. The presence of bacteria for the reduction of sulfate is necessitated by the apparent inability of a natural inorganic system to reduce sulfate to sulfide at ordinary temperatures (Bastin, 1926; ZoBell and Rittenberg, 1948; Emery and Rittenberg, 1952). Therefore, in the absence of sulfide of organic origin or of sulfate-reducing bacteria, pyrite may fail to form even though it is thermodynamically stable and the Eh is low enough to permit reduction of available sulfate.

Seemingly anomalous mineral associations may be produced as a result of extremely local environments, such as in a zone of low Eh surrounding a fragment of organic material in an otherwise oxidizing environment. Under such conditions pyrite might be formed locally in a sediment in which hematite is the stable mineral elsewhere.

In spite of the difficulties involved in its application, the Eh-pH iron mineral diagram does indicate equilibrium relationships under the specified conditions and will only change slightly with minor changes in these conditions. In addition to predicting the mineral associations to be expected under equilibrium conditions it will to some extent indicate the degree of lack of equilibrium in natural mineral occurrences.

ORIGIN OF THE IRONWOOD IRON-FORMATION

Sedimentary facies of iron-formation

James (1954, p. 239) has defined iron-formation as "a chemical sediment, typically thin-bedded or laminated, containing 15 percent or more iron of sedimentary origin, commonly but not necessarily containing layers of chert". This definition makes no attempt to state the chemical or mineralogical form in which the iron and other material occurs. It has been noted that rocks which make up the iron-formation are of widely differing character and that these differences must to some extent reflect differences in the sedimentary environments in which they were formed. Through recognition of these differences and their environmental implications the concept of sedimentary facies of iron-formation was developed.

On the basis of the dominant original iron mineral present, James (1951, 1954) has divided the sedimentary rocks of iron-formations into several lithologic facies. These are the sulfide, carbonate, oxide (both magnetite and hematite), and silicate facies. Each facies has its own chemical and mineralogical characteristics as well as environmental implications. White (1954) in his recent description of the rock types of the Biwabik iron-formation of the Mesabi range develops the same general classification although using a more detailed breakdown and slightly different nomenclature.

Until relatively recently, the carbonate type of iron-formation had been thought to represent the only primary facies in the Ironwood iron-formation; all other iron-formation rocks were thought to have been derived from the chert-carbonate rock by metamorphism or other secondary processes. Thus Irving and Van Hise (1892, p. 247) in the first major work on the Ironwood iron-formation state that "... the cherty carbonates ... were the original rocks of the member." Van Hise and Leith (1911, p. 231) reaffirm this view with respect to the Ironwood: "The cherty iron-bearing carbonate was the original rock of the iron-formation." Aldrich (1929, p. 136) states: "The Ironwood, in its original state, comprised two distinct types of rock. Both types were chemically precipitated silica minerals and iron carbonate. They differ compositionally in ratio of silica to carbonate ...".

One of the few exceptions to this viewpoint was expressed by Hotchkiss (1919, p. 446) who suggested that in the case of the irregular-bedded iron-formation the water was shallow enough and contained enough oxygen for iron to be precipitated as the oxide.

Although there is little doubt as to the primary nature of most of the carbonate present in the iron-formation and as to the importance of carbonate iron-formation as a primary facies of the Ironwood, the diversity of rock types in the relatively unaltered iron-formation indicates that other primary facies are also of importance.

Environmental implications of facies concept

James (1954) and White (1954) have discussed the principal features and origins of the various facies of iron-formation and only a brief summary of some of the environmental implications of the facies concept will be given here.

It has been noted that different primary iron minerals reflect different environmental conditions and it has been suggested that the chief controlling factor involved in their formation is the oxidation potential of the depositional or diagenetic environment. Hematite forms under oxidizing conditions, magnetite and siderite under intermediate to moderately reducing conditions, and pyrite under strongly reducing conditions. Iron silicates probably form under intermediate to moderately reducing conditions. The main factors controlling the oxidation potential are the degree of aeration and the presence of organic material. The latter is reflected by the large amount of carbonaceous material present in the pyritic slates and by the common presence of carbonaceous material in the carbonate rocks.

Hotchkiss (1919, p. 446) was the first to recognize the implication of these environmental factors with respect to the origin of the Ironwood iron-formation and stated:

> "... it is believed that the wavy-bedded members of the iron formation are relatively shallow water deposits in which the bottom was within reach of the action of waves that disturbed the bottom and produced the wavy-bedded structure, and the water contained abundant oxygen to oxidize the iron as it was deposited. The even-bedded portions of the formation are believed to have been deposited in deeper water where the bottom was below the reach of wave action and contained so little oxygen that the iron could persist as carbonate."

In support of this belief is the fact that the irregular-bedded cherts typically show granular or oolitic structures, suggestive of shallow water conditions. What Hotchkiss did not recognize was that under intermediate or reducing conditions, magnetite, iron silicates, and pyrite might form as primary minerals as well as siderite.

Complete separation of the physical-chemical aspects of the depositional and the diagenetic environments is not possible. One of the few generalizations that can be made is that in fine-grained sediments the oxidation potential generally decreases with depth (ZoBell, 1946, p. 503; Emery and Rittenberg, 1952, p. 773). Shepard and Moore (1955, p. 1589) have indicated exceptions to this generalization, however, and such things as content of organic material and water content probably have a notable effect upon the oxidation potential of the burial environment.

James (1954, p. 275) has pointed out that the modifications of iron-formation that might be attributed to diagenesis typically reflect a lowering of the oxidation potential with burial. These include the replacement of hematite ooliths by magnetite, some replacement of primary oxides and silicate by carbonate, and replacement of carbonate by pyrite. All are features that may be observed in the rocks of the Ironwood iron-formation.

Relation of chemical environments to physical parameters

The various chemical environments which determine the form in which the iron is deposited are in turn determined by various physical parameters such as shape and bottom configuration of the basin, depth of water, nearness to shore, degree of circulation, content of organic material, and so on. The effects of some of these parameters are reflected in the sedimentary structures retained in the rocks and others may be deduced from the supposed primary mineralogy.

Granules and ooliths, numerous intraformational conglomerates, and other shallow-water structures throughout the iron-formation suggest shallow-water deposition for at least a large part of the iron-formation. Restricted conditions and lack of aeration are suggested by the parts of the iron-formation requiring low oxidation potentials for their development, although rapid burial with included organic material might also provide these conditions. Elongate basins marginal to a land mass of low relief (James 1954, p. 279) or a shallow, relatively tideless, epicontinental sea (White, 1954, p. 52) best seem to fit these requirements.

Tyler and Twenhofel (1952), James (1954) and White (1954) have all pointed out that vastly different chemical as well as clastic sediments may be deposited simultaneously in a single depositional basin or shelf area. The type of sediment which is deposited at any locality is determined by various factors, of which the most important is probably the distance from shore with its resultant effect upon water depth, aeration, and removal of clastic material.

In his analysis of the sedimentary environment in which the Biwabik formation was deposited, White (1954, p. 45) states that "the contemporaneous deposits being formed, in order of increasing distance from shore, were (1) clean sand; (2) silt and clay (missing at many places); (3) lean chert with algal structures; (4) hematitic rocks; (5) minor chert-siderite rocks; (6) chert and magnetite, with more iron silicates seaward; and (7) iron silicates with some siderite." With the superposition of a transgressing (or regressing) shore line upon this sequence of differing environments, a stratigraphic sequence of lithic units will be built up which will not be time parallel in a section perpendicular to the shore line. Parallel to the shore line the lithic units will be more nearly time parallel but some lateral lithologic gradation may result from local environmental differences. As noted by White (1954, p. 41) "The aspect of sediments formed simultaneously at a given distance from shore ... is characterized by an over-all uniformity which at most places outweighs the changes produced by lateral gradation." Repetition of similar strata would indicate a series of transgressions and regressions.

In the main part of the Mesabi range, the iron-formation stratigraphy is relatively uniform throughout the present outcrop belt. White (1954, p. 47) interprets this as an indication that the present exposure of the range is roughly parallel to the old shore line. He assumes that the closest shore line was to the north of the range because of correlation of rocks of the Animikie group to the south in the Emily district. The increased proportion of argillite and its intertonguing relationship with non-clastic iron-formation on the western Mesabi has been interpreted by White (1954, p. 43) as indicating a southward bend in the shore line, across the present trend of the range.

Marine versus non-marine environment

In the development of the Eh-pH environmental diagram it was assumed that the iron-formation was deposited under "normal" marine conditions. It was realized that conditions may vary appreciably from the assumed "normal", especially in regard to ionic concentrations existing under conditions of restricted circulation. "Normal" marine concentrations only entered into the calculations involving sulfide equilibria, however, as the carbonate system was assumed to be in equilibrium with the partial pressure of carbon dioxide in the atmosphere, which presumably would be the same regardless of the nature of the aqueous sedimentary environment. It is possible that the carbon dioxide content of the Precambrian atmosphere was somewhat different than at present, but the work of Rubey (1951) suggests that radical changes in the atmosphere during recorded geologic time are not supported by the geologic evidence.

Tyler and Twenhofel (1951, p. 137) believe that "the iron and silica deposits are of fresh water and not of marine origin." Their chief argument is based upon the relatively low percentage of calcium and magnesium present in the carbonate of the iron-formations. As noted by both James (1954, pp. 243, 253-255) and White (1954, p. 49), however, and as shown by the carbonate compositions presented in this paper, the amount of calcium and magnesium contained in the iron-formation, is far from insignificant. It is possible that the high iron content merely "masks" the other ions in the carbonate, as might be expected during a period of iron-rich sedimentation. Further evidence in favor of a marine origin for the iron-formations is presented by James (1954, p. 243-244), including the fact that the iron-formations occur within a typically marine sequence.

The source of the iron and silica

In the discussion regarding the deposition of the iron-rich sediments, a source of iron and silica was assumed but not specifically identified. Aldrich, in his study of the Ironwood iron-formation, discounts the adequacy of surficial weathering as a source for the iron and the silica and states that "... these materials (iron and silica) were created in solution by a subsurface environment, a magma" (1929, p. 143). He thus follows the lead of Van Hise and Leith (1911, p. 516) who, however, suggested that some of the iron might have been derived by subaerial weathering.

The only volcanism associated with the Ironwood iron-formation is that which produced the greenstone extrusives that reportedly occur within the upper part of the iron-formation at the eastern end of the range (Allen and Barrett, 1915, p. 48). This volcanism occurred long after iron-rich chemical sedimentation began, however, and the relationship between the volcanism and the iron-formation appears to be spatial or structural rather than genetic.

In a recent analysis of the problem, James (1954, p. 277) concludes "... that volcanism, though not uncommon during the deposition of the major iron-formations, does not have a close enough correlation in space and time with the iron-rich sediments to be genetically related to those sediments", and "... that the relationship between volcanism and iron-formation deposition is structural, not chemical" (1954, p. 279). White (1954, p. 50) suggests "... that volcanism contemporaneous with Animkie sedimentation was detrimental rather than conductive to iron concentration" due to dilution by clastic material of volcanic origin.

James (1954, p. 276) points out that "... under certain tropical or subtropical conditions the iron and silica content of stream water may be very high and entirely adequate to account for iron-formation deposition." Gruner (1922), Gill (1927), Moore and Maynard (1929), and

Sakamoto (1950), among others, have reached much the same conclusions. The present writer favors the weathering source over the volcanic source and supports the view that the iron and silica have been derived from a land mass of low relief undergoing deep chemical weathering, probably under humid tropical conditions, and have been transported to the depositional environment partly in solution and partly in colloidal form.

Recent work by Alexander, Heston, and Iler (1954); White, Banneck, and Murata (1956); and Krauskopf (1956) indicates that silica is a great deal more soluble than suggested by the work of Moore and Maynard (1929) and others. Krauskopf states that the solubility of amorphous silica ranges from 100 to 140 parts per million in fresh water at 25° C. and from 80 to 110 parts per million in sea water at 25° C. Contrary to the conclusions of Correns (1941; 1950) and others, the new work also indicates that the solubility of silica is independent of pH within the range of normal environments (below pH of 9), and furthermore, that silica in true solution ".. is not precipitated by the electrolytes of sea water, by other colloids, or by suspended solids like calcite, kaolinite, or montmorillonite" (Krauskopf, 1956). Thus, according to Krauskopf, while both dissolved and colloidal silica may be expected in natural waters, the former is by far the more common. The transportation of iron in any appreciable amounts, on the other hand, requires a low oxidation potential so as to remain in solution in the ferrous state, or stabilization in the ferric state by protective agents such as organic colloids. Iron and silica in true solution could be separated from clastics near shore and be transported well out into a depositional basin where they would not be precipitated, inorganically at least, until saturation was reached. Upon precipitation, the iron would tend to form minerals in equilibrium with the depositional and diagenetic environments to which it is subjected.

The increase in the known solubility of silica helps to solve the problem of its transportation to the basin of deposition. It does, however, pose new problems regarding the precipitation of silica, as a much higher concentration of silica than hitherto anticipated will be necessary before saturation of the water will occur. Krauskopf (1956) believes that the very great undersaturation of the ocean at the present time may be ascribed to the role played by organisms, particularly diatoms, radiolaria, and siliceous sponges. For example, Jørgensen (1953) demonstrated that two species of diatoms were able to reduce silica concentrations from initial values of 0.65-125 parts per million to the range 0.065-0.085 parts per million. Upon the death of the organisms the silica can either return into solution if enough time is available or collect at the bottom. The presence of silica-secreting organisms in Huronian time cannot be demonstrated, unless the aegal structures in cherts described by Grout and Broderick (1919), Gruner (1946), and Tyler and Barghoorn (1954) represent this type of an organism. There is no reason to believe that silica secreting or depositing organisms did not exist at that time, however, and the ability of such organisms to remove silica from sea water, even though silica concentration is far below saturation, suggests that their role in the formation of siliceous sediments, such as iron-formation, has been greater than has been generally recognized.

The role of sulfate-reducing bacteria in the formation of pyrite has already been mentioned. Harder (1919) discusses in great detail the role of bacteria in the deposition of other iron minerals and it would appear that organisms are as important in the precipitation of iron as they are of silica.

The present writer has no ready explanation for the alternate layering of iron and silica in the iron-formation. It is suggested, however, that a cyclical variation in the activity of organisms might be a possible explanation. For example, variations in the amount of iron in solution in sea water in the English Channel have been related to seasonal variations in the activity of marine plankton by Cooper (1935). Thompson and Bremner (1935) have recorded a reduction in the quantity of iron in sea water coincident with heavy diatom production.

Origin of the chert

Chert is one of the dominant minerals of all facies of iron-formation and occurs both as individual beds or lenses and as interstitial material. The chert is now in the form of microcrystalline quartz and ranges in color from white or gray to green, black, or red (jasper) and is commonly granular or oolitic.

It seems fairly well established that the major part of the chert is primary in origin, having been formed as an original constituent of the iron-formation rather than as a later replacement. Two lines of evidence listed by James (1954, p. 273) in support of this tenet are the fact that the amount of chert in a given bed of iron-formation remains almost constant over wide areas, and that slump structures, intraformational conglomerates, and other primary sedimentary structures suggest at least partial solidification of the chert prior to the formation of these features. White (1954, p. 34) cites similar evidence in regard to the primary nature of the chert in the Biwabik iron-formation of the Mesabi range and these features are also common in the Ironwood iron-formation. Examples are not rare of stylolites cutting chert or forming the boundary between adjacent chert and carbonate layers. These factors all indicate that chert was present and in such a condition as to be able to take part in the formation of various primary sedimentary structures, and therefore must in a large part be considered of primary origin itself.

Tectonic framework of sedimentation and depositional history

By the beginning of the Huronian sedimentation, the pre-Huronian land mass, composed of greenstone schists and granitic rocks had been reduced to one of low relief. The lower Huronian Sunday quartzite and Bad River limestone were deposited in a transgressive sea migrating over this relatively stable, low-lying area. The Sunday quartzite is present only on the eastern end of the range, where it contains a basal conglomerate and is gradational into the overlying Bad River limestone. The limestone is generally dolomitic and contains a high percentage of chert. Where the limestone lies unconformably on the pre-Huronian granites and schists there is frequently a well developed conglomerate at the contact (Hotchkiss, 1919, p. 444). These lithologies represent stable shelf associations. Mild uplift and deformation accompanied by regression of the sea caused the major part of the lower Huronian deposits to be removed by erosion in the present area of the Gogebic district.

The middle Huronian Palms "quartz slate" and quartzite were deposited, still under relatively stable shelf conditions during a second transgression. The basal part of this formation consists of a conglomerate which contains fragments of the immediately underlying rocks, whether Bad River limestone or pre-Huronian granite or greenstone. The main part of the formation, the "quartz slate", is generally a thin-bedded rock that ranges in composition from a fairly clean quartzite to feldspathic quartzite and graywacke. The upper 50-75 feet of the formation consists of a highly indurated, clean, vitreous quartzite with crossbedding and ripple marks. The Palms formation, averaging about 450 feet in thickness, is co-extensive with the range and rather uniform throughout.

The Palms formation grades upward rather abruptly into the Ironwood iron-formation, clastic sedimentation having given way to iron and silica-rich chemical sedimentation. James (1954, p. 279) suggests that this might coincide with the "critical period" in the development of a geosyncline, the formation of a "low, offshore buckle or swell" with the resultant formation of a restricted basin environment appropriate to chemical sedimentation. Of equal importance, however, is the suppression of clastic material previously being deposited.

If it is assumed that the land mass adjacent to the sea or basin was extremely stable the small amount of clastic material supplied could be effectively removed close to shore. Under such conditions, chemical sedimentation could have begun in deeper water while clastic deposition continued near shore. The relations between iron-formation and clastic sediments (graphitic argillite and quartz-mica argillite) on the Mesabi range, as described by White (1954), suggest that a series of transgressions and regressions produced an alternating series of lithic units which were time parallel only in a section parallel with the shore line. It is difficult to demonstrate an analogous situation with respect to the Ironwood iron-formation because the field relations between the iron-formation and associated clastic sediments, such as the argillite on the eastern end of the range, are not clear.

The alternating lithic units of the Ironwood iron-formation do represent changes in the physical-chemical environment and these may be considered regardless of whether produced by migrating shore lines, or by other fluctuations in basin configurement. In the Pence area, where the most complete section of the iron-formation has been preserved, the deposition of the Plymouth member began in a rather shallow water environment, as suggested by the granular and oolitic chert and numerous intraformational conglomerates. Deposition of the even-bedded parts of the member suggests, however, that the bottom must have been below wave base at least part of the time. A period of stagnation then ensued with resultant incomplete oxidation of the organic material present; this period is now represented by the carbonaceous, pyritic slates of the lower part of the Yale member. Gradually circulation and aeration increased to the extent that nearly all organic material introduced into the environment was oxidized, the oxidation potential increased somewhat, and the even-bedded, chert-carbonate rocks of the Yale were deposited. That the environment was a fluctuating one is indicated by the minor beds of granular chert which occur in the Yale member. Return of an environment characteristic of the Plymouth is indicated by the irregular bedded granular cherts of the Norrie member.

The chert-carbonate of the Pence member was deposited under conditions similar to those pertaining during the formation of the Yale member. Local differences in environments are indicated by lateral variations in iron-formation members such the gradation from chert-carbonate to chert-magnetite rock in the Pence member near the town of Pence, Wisconsin.

The depth of water in the depositional basin appears to be extremely critical. The close alternation of irregular and even-bedded material suggests that the depth of water was somewhat greater than "normal" wave base so that only in occasional storms was the bottom disturbed by processes other than ordinary low-angle slumping. The formation of some of the more persistant conglomeratic zones, such as that at the base of the Pence member, suggests more extensive wave action, although still under submarine conditions. The deposition of iron and silica-rich chemical sediments continued under varying environmental conditions until upwards of 500 feet of this material had accumulated.

The relation of the presently exposed part of the Ironwood iron-formation to the shore line of the depositional basin is uncertain. The relative continuity of the five members of the iron-formation on the main part of the Gogebic range suggests that the shore line was parallel with the present outcrop belt. White (1954, p. 49) has suggested that the Gogebic range might bear "a relation to the southern shore line of the Animikie (Huronian) sea similar to the relation of the Mesabi range to the northern shore line." If this interpretation is correct, the shore line would have been to the south of the present outcrop belt of the Ironwood iron-formation and the near-shore clastic equivalent of the iron-formation would have been removed by erosion. A major bend in the shore line, swinging northward at the eastern end of the Gogebic range, would produce a near-shore environment accounting for the argillite associated with the iron-formation and the changes in iron-formation stratigraphy in that area. This northward swing of the shore line would also place a land mass between the Gogebic depositional area and the Marquette area, supporting James' (1954, p. 280) view that "dissimilarities in iron-formation stratigraphy (in the Gogebic and Marquette ranges) indicate deposition in separate basins."

Increased orogenic activity brought to a close the dominantly chemical sedimentation typical of the iron-formation and minor and irregular uplift permitted erosion of parts of the iron-formation. With renewed subsidence the upper Huronian clastic formations were deposited, beginning with the basal Pabst conglomerate (Copps in the east). At first dominantly composed of iron-formation fragments, this formation shows a gradual increase in clastic quartz and argillaceous material supplied by the newly activated adjacent land mass. In the east part of the district, the Copps conglomerate contains feldspar, mica, and even boulders derived from the pre-Huronian granites of that area (Atwater, 1938, p. 172). Chemical sedimentation of iron-rich rocks recurred periodically during the deposition of the Pabst conglomerate and the lower part of the Tyler formation. Ferruginous slates and carbonate with interbedded chert identical to lithologic types within the Ironwood iron-formation are found as much as 800 feet above the base of the Pabst conglomerate (Atwater, 1938, p. 162). With increased tectonism chemical sedimentation finally gives way entirely to the deposition of thick graywacke and slate sequences typical of unstable orogenic conditions.

The end of Huronian deposition is brought about by structural deformation, especially of the far western and eastern parts of the range and reflected in the main part of the range by the Sunday Lake fault and other minor faults. Uplift accompanying this increased orogeny brought about the erosion of vast quantities of material with the removal of the entire upper Huronian sequence in the vicinity of Sunday Lake. The Huronian sequence is overlain unconformably by clastics and extrusive rocks of the Keweenawan series.

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