Data of Geochemistry

Sixth Edition

Chapter W. Chemistry of the Iron-rich Sedimentary Rocks

GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-W

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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MICHAEL FLEISCHER, *Technical Editor*

Chapter W. Chemistry of the Iron-rich Sedimentary Rocks

By HAROLD L. JAMES

GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-W

Chemical composition and occurrence of
iron-bearing minerals of sedimentary rocks,
and composition, distribution, and
geochemistry of ironstones and iron-formations

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DATA OF GEOCHEMISTRY

CHEMISTRY OF THE IRON-RICH SEDIMENTARY ROCKS

By Harold L. James

ABSTRACT

The iron-rich sedimentary rocks, defined as those containing 15 percent or more iron of depositional or diagenetic origin, have a wide range of physical and chemical properties, in part because of gradations into more common sedimentary types and in part because of the wide variety of iron minerals possible. The iron may be in the form of goethite (limonite), hematite, and magnetite; siderite, with a substantial range in amounts of manganese, magnesium, and calcium in solid solution; chamosite, greenalite, and glauconite (which upon slight metamorphism may be converted into thuringite and other chlorites); minnesotaite, and stilpnomelane; and pyrite and marcasite. Many of these minerals may be preceded by metastable species of uncertain status, such as ferric hydroxide and hydrotroilite. Other minerals, of rare occurrence, are lepidocrocite, maghemite, the tetragonal iron sulfide, greigite, smythite, and pyrrhotite.

By custom, the noncherty and generally oolitic iron-rich rocks, most of which are of post-Precambrian age, are referred to as ironstone (including the "minette type"), whereas the chert-banded rocks, most of which are of Precambrian age, are called iron-formation. Both ironstones and iron-formations may be divided into four major facies—oxide, silicate, carbonate, and sulfide—on the basis of the dominant iron mineral. This facies classification has a theoretical base established by the distribution of stability fields of the iron species, expressed most effectively in terms of redox potential (Eh) and pH. Examples of stability-field diagrams show that at given anion concentrations almost any combination of oxides, silicates, carbonates, and sulfides of iron can exist stably at some geologically reasonable value of Eh and pH. The dominant aspect, however, is one of sequential appearance of stable fields for oxide, carbonate, and sulfide with decrease in Eh. In an idealized restricted basin in which iron sediments are being formed, this corresponds to progressive decrease in available oxygen in the bottom environment. The facies, therefore, are a direct reflection of depositional environments.

Chemical analyses of the iron-rich rocks are organized and presented according to facies and in part according to age (Precambrian and post-Precambrian), and the distribution in space and time is summarized in a series of tables. The major differences in bulk compositions are inherent in the classification—as in the ratio of FeO to Fe_2O_3 and the content of CO_2—the silicate facies being significantly higher in Al_2O_3. The SiO_2 content varies chiefly according to the relative amounts of clastic quartz (in ironstone) or chert (in iron-formation).

Data on minor-element content are relatively scarce. The information available shows the amounts to be generally low in comparison with crustal abundance. Differences between facies are slight, except for higher chromium and vanadium in chamositic rocks, and commonly are submerged by local differences related to the geochemical nature of the terrain adjacent to basins of deposition.

The origin of the iron-rich sedimentary rocks remains a matter of speculation, as no modern-day examples exist. A few deposits, exemplified by the ironstone of the Lahn-Dill district of Germany and the Helen iron-formation of the Michipicoten district of Canada, appear to have a genetic relation to volcanic and igneous activity and may be classed as "exhalative-sedimentary." The more typical and more extensive ironstones and iron-formations, however, are entirely lacking in volcanic and igneous associations; for these the iron seemingly must be derived by weathering of exposed land, although the large chemical and physical differences between ironstone and iron-formation imply some significant difference in the nature of the process. It is suggested, by analogy with bog-iron deposition, that for both types the iron is extracted and transported by ground waters of low pH, and that this process was more effective in Cambrian and pre-Cambrian time, possibly because of a significantly higher content of CO_2 in the earth's atmosphere.

INTRODUCTION

Iron, which is estimated to make up about 4.7 percent of the earth's crust, is present in significant amounts in almost all sedimentary rocks. The average sandstone, including graywacke, contains 1.7 percent Fe_2O_3 and 1.5 percent FeO (Pettijohn, 1963, p. 15); the average shale contains 4.2 percent Fe_2O_3 and 2.45 percent FeO, and the average limestone 0.54 percent combined Fe_2O_3 and FeO (Clarke, 1924, p. 25, 564). Each of these rock types, however, ranges in composition into facies in which the iron content is 20 percent or more. The iron-rich sedimentary rocks, here defined as those containing 15 percent or more Fe of primary origin (depositional or diagenetic), in part therefore can be considered a family of end members of the sedimentary series. These rocks commonly are referred to as ironstone or iron-formation.

The iron-rich rocks have a great range of physical and chemical characteristics. In part this is due to gradations from the common sedimentary rocks—sandstone, shale, limestone, chert—with retention of attributes of the parent stem. In larger part, however, the diversity is due to the extraordinary ability of iron to form different minerals in response to different conditions of the bottom and diagenetic environment. Iron may precipitate as ferric oxide or hydrate (hematite, maghemite, goethite, lepidocrocite), as a ferrous-ferric oxide (magnetite), as a ferric-ferrous silicate (glauconite), as a ferrous-ferric silicate (greenalite, chamosite), as a carbonate (siderite), or as a sulfide (pyrite, marcasite, or less stable precursors). Inasmuch as the classification of the iron-rich rocks is based in large part on the mineralogy of the iron, the character, composition, and occurrence of the iron minerals found in sedimentary rocks are reviewed in the following section. The discussion will deal only with those aspects of importance to the problem at hand; more complete data on the optical, structural, and chemical properties of the pure minerals are available in standard texts and references.

IRON MINERALS OF SEDIMENTARY ROCKS

IRON OXIDES

Goethite (limonite), hematite, and magnetite are found as important constituents of the iron-rich sedimentary rocks; lepidocrocite and maghemite have been observed but are rare.

Hydrogoethite, hydrohematite, turgite, and other reported oxide-hydrates have questionable status as minerals, and have not been identified in mineralogical studies supported by X-ray examination. The "hydrogoethite" of Tula, central Russia, has been shown to be lepidocrocite with adsorbed water (Palache, Berman, and Frondel, 1944, p. 644) and it is likely that more recently described occurrences, such as reported by Tochilin (1952) are of similar material. Hydrohematite and turgite probably represent mixtures of hematite and goethite or hematite with adsorbed water (Posnjak and Merwin, 1919). Akaganeite (β-FeO(OH)), recently described by Mackay (1962), has not yet been recognized in the iron-rich sedimentary rocks, but Mackay states (p. 278–279), "The colloidal properties of β-FeO(OH) are shown to be of considerable complexity and undoubtedly will have a bearing on the formation of deposits of hydrated iron oxides."

Both ferrous and ferric hydroxides can, of course, be readily precipitated in the laboratory, and they may well be transitory species in natural chemical precipitates. The development of stable phases of iron oxides from original hydrates is discussed by Garrels (1959, p. 29–30), who considers the first precipitate to be $Fe_2O_3 \cdot nH_2O$, with a solubility product of 10^{-37} (as compared with 10^{-42} for hematite).

Structural data for the oxides and hydroxides of iron are given by Bernal, Dasgupta, and Mackay (1959, p. 17).

GOETHITE (α-FeO(OH)) AND LIMONITE

Goethite is the principal constituent of the post-Precambrian deposits of such sedimentary iron oxide ores as those of the Jurassic of Europe (Correns and Engelhardt, 1941; Taylor, 1949; Correns, 1952a). The "limonite" of the iron-rich sedimentary rocks consists of goethite intimately mixed with other materials and commonly has appreciable adsorbed additional water. Caillère and Kraut (1953) and others have suggested that goethite, as well as other iron minerals in the sedimentary ores, develop diagenetically from an original iron hydroxide gel, which may well be true, but no direct evidence is available. According to Correns (1952a) the goethite may contain appreciable amounts of alumina with contraction of the unit cell constants a_0 and b_0:

Percent AlO(OH)	Percent FeO(OH)	Cell dimensions, in A		
		a	b	c
1.5	98.5	4.59	9.97	3.02
4.5	95.5	4.53	9.88	2.99
11.2	88.8	4.48	9.82	3.00

Bernal, Dasgupta, and Mackay (1959, p. 17) give the dimensions of (presumably) pure goethite as: $a=4.587$, $b=9.937$, $c=3.015$.

The goethite of the sedimentary ores characteristically occurs in the form of ooliths built of successive shells of the oxide or of alternating shells of iron oxide and chamosite in a matrix that may be chamosite, clay, siderite, or calcite; rarely or never is it a matrix to ooliths of different composition. The compositions of separated limonite (goethite) ooliths from two English ironstones of Mesozoic age are given in table 1. The excess water is characteristic, and the ooliths quite evidently contain admixed silicate, phosphate, and carbonate.

The absence of goethite in the Precambrian sedimentary ores, and the dominance of hematite in most of the lower Paleozoic oolitic ores strongly suggests a progressive development of hematite from original goethite (or a more primitive hydrate). The generalization is not absolute, however, as hematite is present in some of the Mesozoic rocks (see Harder, 1951, for description of Lias-γ hematite oolite), and some lower Paleozoic ironstones are goethitic—the Mayville ore of the Neda Formation of Wisconsin, for example (Hawley and Beavan, 1934). Certainly both hematite and goethite are stable at low temperatures, but according to Smith and Kidd (1949) goethite in neutral solutions decomposes to hematite above 125° ± 15° C.

TABLE 1.—*Analyses of separated limonite (goethite) ooliths from two Mesozoic ironstones*

	A	B		A	B
SiO_2	5.15	5.53	H_2O-	2.07	3.44
Al_2O_3	4.49	4.62	TiO_2	1.05	.71
Fe_2O_3	69.93	69.50	P_2O_5	1.23	.95
FeO	.95	.56	CO_2	.48	.43
MnO	.48	.20	C	.41	.37
MgO	1.05	.68	FeS_2	--------	.20
CaO	.57	.53	(Co, Ni)O	.03	.05
K_2O	.32	.14			
Na_2O	.01	.01		100.11	100.24
H_2O+	11.89	12.32			

A. Frodingham ironstone, England (Hallimond, 1925, p. 79). Ooliths occur in matrix mostly of chamosite and siderite.
B. Claxby ironstone, Lincolnshire, England (Hallimond, 1925, p. 79). Ooliths occur in matrix mostly of clay (altered chamosite?) and carbonate.

LEPIDOCROCITE (γ-FeO(OH))

Lepidocrocite is rare or absent in most sedimentary ironstones, but is reported by Correns (1952a) as a constituent in the oolitic ores of Kladno Nucic, Czechoslovakia.

HEMATITE (α-Fe_2O_3)

Hematite is only locally an important constituent of the Tertiary and Mesozoic ironstones and is virtually absent from many. It is, however, a dominant mineral in some (though not all) of the lower Paleozoic oolitic ironstones such as those in the Clinton Group or Formation of New York (Alling, 1947) and of the Birmingham district, the Wabana ores of Newfoundland (Hayes, 1915), and the Bliss Sandstone of New Mexico (Kelley, 1951). Hematite is the principal mineral in Precambrian iron formations of every continent, in which rocks it is interbedded with quartz ("chert").

MAGHEMITE (γ-Fe_2O_3)

Maghemite, the strongly magnetic isometric dimorph of hematite, is of rare occurrence in the sedimentary ironstones, though it is abundant in some laterites. Crystallographically it is very similar to magnetite, and the cell dimensions a_0 of the two minerals are nearly identical, so that even with X-ray techniques it is difficult to distinguish the two. In polished section the mineral is isotropic, gray to blue with brownish-red internal reflections.

Correns and Engelhardt (1941) describe maghemite and magnetite in the Mesozoic ironstones of Germany, although later work by Harder, reported by Correns (1952a), casts doubt on the determinations of the maghemite. Recently, however, Deudon (1957) used a combination of X-ray, magnetic-separation, and chemical analysis to show that one bed 10 to 20 cm thick in the "Couche Grise" of the Ottange basin of Lorraine and Luxembourg contains about 40 percent maghemite, 20 percent hematite, 20 percent magnetite, and 20 percent geothite plus calcite.

MAGNETITE (Fe_3O_4)

Magnetite is an abundant iron oxide in the Precambrian iron formations, in which it may be either of diagenetic or metamorphic origin. It is not common in the younger ironstones, but is by no means rare. It is a constituent in the Jurassic ores of Lorraine, Luxembourg, and Germany (Berz, 1922; Caillère and Kraut, 1946; Hoehne, 1955). Hoehne describes the magnetite as occurring both as isolated crystals and as a constituent of individual ooliths; the characteristic crystal form is shown by Ramdohr (1955a) to be the cube. Magnetite occurs locally in ooliths in the unmetamorphosed Northampton sand ironstone of England, in places as shells between chamosite and limonite (Taylor, 1949); it is locally abundant in the Jurassic beds of Yorkshire, in sideritic chamosite oolite, where it occurs as octahedra 0.002 mm to 0.012 mm diameter in chamosite ooliths (Rastall and Hemingway, 1949).

In the iron-formations of Precambrian age, magnetite most commonly occurs as impure layers alternating with chert (quartz); magnetite-bearing itabirite of Brazil may contain as much as 20 percent dolomite (Dorr, 1958, p. 62).

SIDERITE

Siderite is one of the most important constituents of sedimentary ironstones, including those of the Precambrian. In Sweden it is the principal mineral in ironstones of the Lias (Lower Jurassic), 12 beds of which have an aggregate thickness of 60 meters in a sequence of clastic and coaly sediments 1,000 meters thick (Hadding, 1933; Palmqvist, 1945); in England it is a dominant mineral in the Cleveland ironstones of equivalent age (Whitehead and others, 1952), and in the slightly younger Northampton ironstone (Taylor, 1949). In these rocks it is typically associated with chamosite, less commonly with limonite (goethite) and calcite; the Swedish rocks are characterized also by the presence of detrital sand and clay. The so-called "blackband ores" are thin layers of massive siderite that are particularly abundant in the Paleozoic coal measures of Europe and the United States; according to Tyler (1950), 75 beds occur in the lower coal measures of Wales. Siderite also is common as concretionary masses in clays and marls, as for example in the Lower Cretaceous beds of the Atlantic coastal plain (Singewald, 1911). Some of the principal Precambrian iron-formations of the Lake Superior region—those of the Mesabi, Gogebic, Marquette, Cuyuna, and Iron River-Crystal Falls districts—are in large part composed of interbedded siderite and chert.

Analyses of six sedimentary siderites are given in table 2.

Most of the siderite in the sedimentary rocks is so very fine grained and intimately mixed with other materials that chemical and optical properties are not easily determined, although in many ironstones more

TABLE 2.—*Analyses of siderite*

	A	B	C	D	E	F
SiO_2	0.9	1.5	1.2	0.65	0.09	0.53
Al_2O_3	1.3	2.6	1.6	---------	---------	---------
Fe_2O_3	.4	1.5	.6	---------	---------	---------
FeO	46.89	47.92	45.83	46.7	46.0	49.0
MnO	.13	.18	.18	8.2	5.0	4.2
MgO	3.37	2.46	3.68	4.2	5.2	4.8
CaO	4.66	3.71	5.10	1.1	3.5	2.2
H_2O+	[1]2.0	[1]2.4	[1]2.1	.09	.12	.10
H_2O-	.25	.43	.33			
TiO_2	---------	---------	---------	.00	.00	.00
P_2O_5	---------	---------	---------	.64	2.4	1.4
CO_2	35.36	33.33	35.20	38.0	36.4	37.4
Insol. residue	4.57	3.06	3.74	---------	---------	---------
C	---------	---------	---------	.20	1.5	.38
S	---------	---------	---------	.06	.02	.03
	99.8	99.4	99.6	99.84	100.23	100.04

[1] Calculated from loss on ignition; includes organic matter.

A. Northamptonshire, England. Sphaerosiderite from Northampton sand ironstone (Taylor, 1949, p. 48). Analyst: C. O. Harvey.

B. As above. From oolitic chamosite-siderite rock, Northampton sand ironstone (Taylor, 1949, p. 48). Anayst: C. O. Harvey. Total includes 0.3 percent CdO.

C. As above. From siderite mudstone, Northampton sand ironstone (Taylor, 1949, p. 48). Analyst: C. O. Harvey.

D, E, F. Iron River, Michigan. Thin layers of carbonate in Riverton Iron-Formation. Analyses by H. F. Phillips, P. L. D. Elmore, and P. W. Scott, U.S. Geological Survey. Laboratory numbers 138255, 138258, and 138260. All samples contain small amounts of phosphate, free carbon, quartz, and pyrite.

coarsely crystalline siderite occurs as spherulitic aggregates, and as diagenetic replacements particularly of chamosite ooliths. The composition of the siderite can be expressed in terms of four components—$FeCO_3$, $MnCO_3$, $MgCO_3$, and $CaCO_3$—that are in solid solution. For three separated and analyzed siderites (table 2, analyses A, B, C) from the Northampton sand ironstone, Taylor (1949, p. 48–50) gives calculated compositions in weight percent, together with measured properties. The data in table 2, with compositions converted to mol percent (weight percent in parentheses), are given in columns A, B, C, below. For comparison, the composition of siderite of the Lias-γ of Germany as calculated by Harder (1951, p. 458), is shown in column D. Cohen (1952, p. 470–471)—using a microradiographic technique in which the X-ray beam is passed through thin sections to produce a shadow photograph that reveals distribution of iron—finds that at least the larger siderite crystals in Taylor's material are zoned, which accounts for the range of observed indices.

	A	B	C	D
$FeCO_3$	79.1 (82.60)	83.5 (86.18)	77.9 (81.39)	82 (85)
$MnCO_3$	.3 (.26)	.4 (.40)	.4 (.38)	3 (3)
$MgCO_3$	10.2 (7.74)	7.5 (5.66)	10.4 (7.98)	13 (10)
$CaCO_3$	10.4 (9.40)	8.6 (7.76)	11.3 (10.25)	2 (2)
Range of *n*	1.730–1.845	1.775–1.838	1.789–1.837	1.834–1.842
Average *n*	1.813	1.816	1.812	1.84
Specific gravity	3.60	3.62	3.58	------------

The siderite in the Precambrian iron-formations of Lake Superior typically occurs interlayered and to some extent intimately mixed with chert (see James, 1954, for review of occurrence). Analyses of individual layers, less than ½ inch thick, of nearly pure carbonate from the Riverton Iron-Formation of the Iron River district of Michigan are given in table 2, analyses D, E, and F. X-ray examination has shown the carbonate to be a single phase, with calculated molecular proportions as follows (weight percent given in parentheses):

	D	E	F
$FeCO_3$	76.4 (78.5)	77.9 (80.7)	81.2 (83.8)
$MnCO_3$	13.7 (14.0)	8.9 (9.1)	7.2 (7.4)
$MgCO_3$	9.1 (6.8)	11.9 (9.0)	10.7 (8.0)
$CaCO_3$	.8 (.7)	1.3 (1.2)	.9 (.8)

Huber (1959, p. 93) has calculated from rock analyses the composition of carbonate from the Gogebic district of Michigan and other districts of the Lake Superior region. Representative examples are as follows (weight percent in parentheses):

	Ghgebic (Mich.)	Gunflint (Minn.)	Marquette (Mich.)
$FeCO_3$	76.8 (80.9)	75.8 (80.2)	85.7 (89.0)
$MnCO_3$	3.9 (4.1)	.5 (.5)	------------
$MgCO_3$	17.0 (12.9)	16.4 (12.6)	12.5 (9.4)
$CaCO_3$	2.3 (2.1)	7.3 (6.7)	1.8 (1.6)

IRON SILICATES

The only iron silicates definitely of primary origin and of importance in the iron-rich sedimentary rocks are chamosite, glauconite, and greenalite. Thuringite (bavalite), minnesotaite, and stilpnomelane are of common occurrence, however, and are described here. These minerals probably are derived by low-grade metamorphism of preexisting silicates, though a diagenetic origin cannot be ruled out entirely. In any case, the primary sedimentary composition of rock containing them probably has not been significantly altered, as it may be in higher metamorphic zones in which grunerite, garnet, and fayalite are developed.

CHAMOSITE

Chamosite (including "berthierine") is the most abundant primary iron silicate of ironstones other than those of Precambrian age, and is a dominant constituent of many. It typically occurs as ooliths of dark green material in a matrix of siderite or calcite, and often is associated with ooliths of goethite; quite commonly ooliths are constructed of alternating shells of chamosite and goethite, as in the Northampton sand ironstone (Taylor, 1949) and in the ironstones of Lorraine (Cayeux, 1909).

The mineralogical classification of chamosite is still in question. but it seems evident that the term has been—and probably will continue to be—applied to materials that are not mineralogically identical and to some that probably are mineralogically heterogeneous.

Hallimond (1939) and later Engelhardt (1942) showed that differences existed between the structure of the studied chamosites and of accepted chlorite, although Engelhardt computed a formula on the basis of a chlorite structure. Orcel, Hénin, and Caillère (1949) examined a number of chamosites by thermal and X-ray techniques and found distinct differences between the materials from different localities. Brindley (1951) and Brindley and Youell (1953) tentatively concluded that chamosite (in a restricted sense) is closely related to the kaolin-type structure rather than to chlorite; and the critical feature is the presence of a 7A basal reflection in the X-ray diagram, rather than the 14A reflection typical of chlorite.

Caillère and Hénin (1951) also divide the chamositic materials into two main groups on the basis of characteristic 14A and 7A spacings, but relate the 7A variety to an antigorite structure (comparable to greenalite) rather than to a kaolin structure. The silicate of the Lias-gamma beds of Göttingen (Germany) is shown by Harder (1951) to contain both chamosite of 7A structure and chamosite with a 14A chlorite structure; the latter Harder attributes to groundwater alteration of original chamosite. The chamosite of the Saint-Barbe Lias (Lorraine) also has a 7A structure, according to Deudon (1955). Protich (1955) studied the chamosites from 3 localities of Cretaceous strata in Yugoslavia; that from Gledič, with an unusually high Fe_2O_3 content (see table 3, analysis E), and that from Poustenck are of the 7A type, whereas that from Vlakča is of the 14A chlorite type.

TABLE 3.—*Analyses of chamosite*

	A	B	C	C_1	D	E	F
SiO_2	30.07	22.43	22.47	23.81	26.65	21.50	20.62
Al_2O_3	17.26	14.27	21.82	23.12	16.14	20.12	11.96
Fe_2O_3	3.66	11.98	.22	.23	6.69	14.89	5.11
FeO	37.61	37.63	39.79	39.45	34.43	21.90	25.98
MnO	.02	.02	.03			.98	.30
MgO	1.69	3.42	2.82	2.72	4.47	1.92	3.07
CaO		.00	.38			1.18	11.50
Na_2O	.44	.22					.09
K_2O	.16	.04					None
H_2O+	9.01	9.70	10.07	10.67	11.42	11.68	8.36
H_2O-					.08	3.92	2.56
TiO_2	.12	.19	Tr.				.72
P_2O_5			.00				5.11
CO_2			2.04				3.94
	100.04	99.90	99.75	100.00	99.88	99.14	100.34

A. Chamosentze, Switzerland (Déverin, 1945, p. 31); analyst, J. Jakob. From chamosite-calcite bed in Middle Jurassic (Dogger). Indices of refraction $\gamma=\beta=1.63$.

B. Windgalle, Switzerland (Déverin, 1945, p. 89); analyst, J. Jakob. From chamosite-calcite bed in Middle Jurassic.

C. Corby, Northamptonshire (Brindley and Youell, 1953, p. 61); analyst, R. F. Youell. From oolitic chamosite-limonite-siderite rock in Northampton sand ironstone (Middle Jurassic). Total contains 0.11 percent SO_3.

C_1. As above, corrected for calculated impurities (Brindley and Youell, 1953, p. 61).

D. Schmiedefeld, Germany. Analysis by Jung, quoted by Engelhardt (1942, p. 149). From thuringite-bearing ironstone in the Lower Silurian.

E. Gledič, Yugoslavia (Protich, 1955). From chamositic bed of Cretaceous (Aptian) age. Total contains 1.05 percent NiO.

F. Island of Raasay, Scotland (MacGregor, Lee, and Wilson, 1920, p. 197–198). Hand-picked ooliths from bed of Jurassic age. Total includes 0.06 percent (Co,Ni)O, 0.71 percent FeS_2, 0.25 percent C. Total given as 100.35 percent in original.

Nelson and Roy (1954, p. 344) report the important discovery of complete polymorphism between chlorites characterized by 7A and 14A basal spacings; they write (p. 337): "The 7A chlorites formed during sedimentation may be converted into 14A chlorites in one case or remain as 7A chlorites in another as a result of post-depositional history * * *." They propose the term "septechlorite" (and septechamosite) for the 7A mineral, a designation accepted by Deer, Howie, and Zussman (1962, p. 164). It seems evident that chamosite proper, characterized by the 7A spacing and exemplified by the unaltered iron silicate in the Mesozoic ironstones of England and Lorraine, is readily transformed by slight metamorphism to a chlorite (thuringite-bavalite) characterized by the 14A spacing. Hallimond, in printed discussion of the paper by Caillère and Hénin (1951) cites textural evidence that suggests reconstitution of the "chamosite" of Chamoson and states (p. 136) that it would not be surprising if this, the original chamosite, turned out to be bavalite, a view supported by Taylor in the same discussion.

Chamosite, because of its very fine grain size and intimate mixture with other materials, is very difficult to separate for analysis, and even the most carefully prepared materials are impure; furthermore, for many published analyses doubt exists as to the specific mineralogic identity. Of those listed in table 3, only C, D, and E are certainly of the 7A structural type; as previously mentioned, the chamosite of the type locality (analysis A) may actually be a 14A chlorite. The most typical chamosites are essentially ferrous, but the mineral may be oxidized without loss of structure; Brindley and Youell (1953) have prepared ferric varieties by heat treatment of ferrous chamosite, and some natural chamosites have a significant content of ferric iron.

The reported optical properties of chamosite are of course of questionable validity in view of the uncertainty of mineralogic classification of the particular materials. The chamosite ooliths of the unaltered chamositic rocks of the Mesozoic of England (Hallimond, 1925; Taylor, 1949), such as represented by analysis C in table 3, are built of very fine flakes, pale to dark green, arranged tangentially, so that the oolith shows a dark extinction cross under crossed nicols. The flakes have positive elongation, mean indices of refraction that range from 1.62 to 1.66, and birefringence that ranges from zero to about 0.03. Crystalline chamosite in the same rocks occurs as cores to ooliths and as scattered flakes in the chamositic mudstones; this chamosite is uniaxial or nearly so, optically negative, pleochroic in shades of yellow and green, with a prominent fibrous cleavage; mean indices of refraction are as for the oolitic material. The Schmiedefeld chamosite (Engelhardt, 1942—see analysis D, table 3) has higher indices: $\gamma=\beta=1.658$, and those for the Gledic chamosite (analysis E, table 3), according to Protich, are $\gamma=1.679$, $\alpha=1.671$. It is apparent that the increase in index and birefringence is directly related to ferrous-ferric ratio.

Chamosite from most localities has been shown to have a specific gravity of 3.0 to 3.4, but that from the Northampton sand is reported by Taylor (1949, p. 41) to have a specific gravity of 2.7 to 2.9, possibly because of admixture with submicroscopic kaolinite.

Youell (1958) has shown that the degree of disorder of chamosite at different stratigraphic horizons in the Northampton sand ironstone is a distinctive feature of particular beds.

GREENALITE

Greenalite, a common and abundant primary iron silicate in the Mesabi and Gunflint districts of the Lake Superior region, was described and named by Leith (1903, pp. 101–115). The mineral was further described by Jolliffe (1935), and by Gruner (1936), who defined it as a ferrous analogue of antigorite. It has been synthesized by Flaschen and Osborn (1957, p. 926). The mineral, which probably is more closely related structurally to chamosite than to antigorite is classed as a septechlorite by Deer, Howie, and Zussman (1962, p. 167). Steadman and Youell (1958) report the following structural data:

$$a_0=5.54\text{A}$$
$$b_0=9.59\text{A}$$
$$c_0=7.19\text{A}$$
$$\beta=90°$$

A partial chemical analysis by Leith (1903, p. 108), as computed by Gruner (1946, p. 16), is given in table 4 (analysis A); for nearly 60 years this was the only analysis available. Recently, however, Cochrane and Edwards (1960) have described a late Precambrian greenalite-bearing iron-formation from northern Australia. The analysis of separated greenalite is given as analysis B in table 4, and the computed formula is $9(\text{Fe,Mn,Mg})\text{O}.2(\text{Fe,Al})_2\text{O}_3.8\text{SiO}_2.8\text{H}_2\text{O}$ (Cochrane and Edwards, 1960, p. 16). Chemical data on greenalite given by Jolliffe (1935) are of uncertain value because of the probable mixture of the material with minnesotaite, which at that time had not been defined.

Greenalite, in contrast to chamosite and glauconite, occurs in quantity only in rock of Precambrian age, although it has been reported in the Ordovician of southern Scotland (Kennedy, 1936) and in Mesozoic sandstone of Sweden (Hadding, 1929, pp. 235–236). Like glauconite, it occurs as rounded to subangular isotropic light- to dark-green pellets; rarely do the pellets have the concentric structure characteristic of chamosite. It typically is associated with magnetite. The granules have a range in density of 2.85 to 3.15 (Jolliffe, 1935, p. 414), with an aggregate index of refraction of about 1.670.

TABLE 4.—*Analyses of greenalite*

	A	B		A	B
SiO_2	32.02	32.27	Na_2O	--------	.14
Al_2O_3	1.01	3.03	K_2O	--------	.10
Fe_2O_3	22.95	14.83	H_2O+	9.52	8.71
FeO	29.15	36.00	H_2O-		2.37
MnO	--------	.87	TiO_2	--------	.05
MgO	5.34	2.11	P_2O_5	--------	.01
CaO	--------	Tr.		99.99	100.49

A. Greenalite from Biwabik Iron-Formation, Mesabi district, Minnesota. Composition as computed by Gruner (1946, p. 16) from analysis given by Leith (1903, p. 108).

B. Roper Bar, Australia (Cochrane and Edwards, 1960, p. 17). P. J. J. Sinnott, analyst. Greenalite separated from greenalite-magnetite rock. Total given as 100.35 in original.

GLAUCONITE

Glauconite is a common though not especially abundant material in ironstones younger than the Precambrian, and in a few places it forms deposits of considerable thickness. It is rare, but not unknown, in rocks of Precambrian age; glauconite has been identified in strata of the Sinian System of Asia (see, for example, Kazakov and Polevaya, 1958, p. 383–384). Glauconite is an established mineral species, but, as with chamosite, the term is applied to mixtures of minerals of particular form and mass-aggregate properties. It typically occurs as bright-green pellets, which may accumulate as beds tens of feet in thickness containing 75 percent or more glauconite (Mansfield, 1920; Hutton and Seelye, 1941), but it also occurs as intergranular fillings and disseminations, as crustifications, as replacements of other materials, and as canal fillings in organic debris (Cloud, 1955, p. 484), and the color may range from yellow to nearly black. The pellets range in size from about 0.01 in diameter to about 0.5 mm (Burst, 1958b, p. 484).

Burst (1958a, 1958b) divides natural glauconites into four classes:

1. Well-ordered, nonswelling, high-potassium mica-type lattice, with well-defined X-ray reflections at 3.3A and 10A. Closely approaches group 1M of the mica polymorphs.
2. Disordered, nonswelling, low-potassium mica-type lattice. Can be assigned to group 1Md of the mica polymorphs.
3. Extremely disordered, expandable, low-potassium montmorillonite-type lattice.
4. Mixtures of two or more clay minerals, such as kaolinite and illite.

Characteristic X-ray diffraction diagrams of oriented material of these four classes are shown in figure 1.

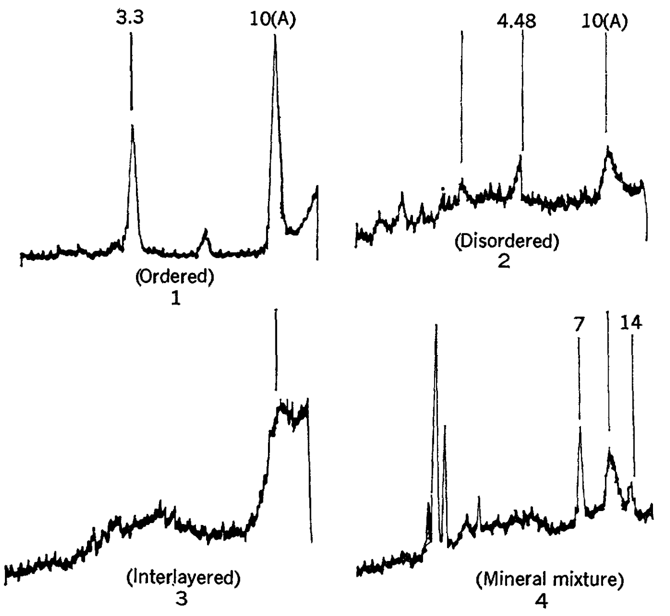

FIGURE 1.—X-ray diffraction patterns of four types of glauconite, according to Burst's classification (Burst, 1958b):

1. Franconia Sandstone, Cambrian, Wisconsin; well-ordered, nonswelling, high-potassium, mica-type lattice;
2. Burditt Marl of Adkins (1933), Cretaceous, Texas; disordered, nonswelling, low-potassium, mica-type lattice;
3. Byram Formation, Oligocene, Mississippi; extremely disordered, expandable, low-potassium, montmorillonite-type lattice;
4. Wilcox Formation, Eocene, Texas; mixtures of two or more clay minerals as normal pellet constituents.

The first class corresponds to the mineral glauconite, the structure of which was defined by Gruner (1935), and

> * * * retreating from this end point on gradual steps of diminishing potassium content are materials which less and less resemble glauconites and more and more resemble montmorillonites. (Burst, 1958b, p. 492.)

A somewhat similar scheme by Smulikowski (1954), based on the relations between interlayer cations (K, Na, Ca), Al^4, and Al^6, requires chemical analysis and formula calculation for classification.

Glauconite is a constituent of modern sediments in many parts of the world (Cloud, 1955). It has been found in sandy sediments at depths ranging from that of near-shore shallows to 14,400 feet, but its most common locale is 60 to 2,400 feet. Glauconites are essentially ferric (ferric-ferrous ratio typically about 7 : 1) and the material does not form in strongly reducing environments. Burst (1958b, p. 482) concludes, "Decaying organic material * * * creates a local reducing environment which sufficiently counteracts the over-all oxidizing marine environment * * *." Under such conditions glauconite can form as direct accretions or as replacements of preexisting material. Modern glauconites characteristically are deficient in potassium, which fact has been interpreted by some to indicate lower potassium content of present seawater as compared with that of previous eras. More likely, however, it reflects "immaturity" of the glauconitic material, which after diagenesis will attain a more ordered structure with fixation of additional potassium. Both Burst (1958a, 1958b) and Hower (1961) stress progressive reactions in the development of glauconite.

Glauconite is a very fine-grained material and, by virtue of its mode of origin, may contain considerable admixtures of other material. A large number of analyses have been reported in the literature, but many are of dubious value; many have been made on samples treated with acids or alkalis or separated by use of inorganic liquids such as Thoulet's and Clerici's solutions, with resultant significant ion exchange. The selected analyses listed in table 5, except for A and B, in general typify the mineral glauconite; the material glauconite has a far greater range in composition, as indicated in column I. The only consistent relations between composition and age or type of enclosing rock is the lower content of K_2O in recent glauconites as compared with those of older age, and the higher Al_2O_3 content of glauconite from limestone.

CHLORITE (EXCLUDING CHAMOSITE)

The chlorite of the iron-rich rocks is typified by the iron-rich variety, thuringite, the occurrence and habit of which are described here. Chlorite of similar character but of somewhat lesser iron content is not uncommon; Hunter (p. 26),[1] for example, classes the nonchamositic chlorite of the Clinton as daphnite-brunsvigite.

Thuringite is an abundant mineral of the Lower Silurian ironstone of Thuringia, Germany, where it forms ooliths in a matrix of quartz and magnetite. Engelhardt (1942) established that thuringite has the structure of an orthochlorite, and also established the virtual identity of bavalite with thuringite, and the distinction of both from chamosite. Analyses are given in table 6, E and F. The bavalite studied by Engelhardt was from Devonian strata of Brittany, France, where it occurs in oolitic form in association with magnetite and siderite(?). Thuringite is also reported from the lower Paleozoic oolitic chamositic ironstones of North Wales, where it occurs in association with magnetite and stilpnomelane (Pulfrey, 1933).

Thuringite and bavalite are optically negative; $2V=0°$ or very small; they are pleochroic in shades of green and greenish yellow; and have low birefringence. Indices of refraction for analyzed material listed in table 6 are:

Thuringite (sample E, table 6): $\gamma=\beta=1.672$
Bavalite (sample F, table 6): $\gamma=\beta=1.681$

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[1] Hunter, R. E., 1960, Iron sedimentation of the Clinton Group of the central Appalachian Basin: The Johns Hopkins University [Baltimore], unpublished Ph. D. thesis, 416 pp.

TABLE 5.—*Selected analyses of glauconite*

[Except for A and B, these glauconites probably would belong to Burst's class 1 (ordered mica-lattice) and class 2 (disordered mica-lattice) Burst, 1958b]

	A	B	C	D	E	F	G	H	I
SiO_2	46.90	54.58	52.64	49.89	50.58	49.07	49.13	48.66	41.0–56.0
Al_2O_3	4.06	7.17	5.78	7.52	6.72	10.95	9.96	8.46	1.5–22.2
Fe_2O_3	27.09	18.27	17.88	18.93	19.50	15.86	16.67	18.80	6.2–28.0
FeO	3.60	2.86	3.85	3.00	2.96	1.36	1.29	3.98	1.3– 8.6
MnO			Tr			Tr		.01	
MgO	.70	2.95	3.43	3.75	4.10	4.49	3.01	3.56	.6– 4.8
CaO	.20	1.86	.12	.25	.34	.07	.95	.62	.1– 4.0
Na_2O	1.28	1.23	.18	.11	.04	.13	.49	.00	.0– 3.0
K_2O	6.16	5.34	7.42	7.52	8.26	7.51	8.87	8.31	3.7– 9.3
H_2O+	9.25	6.53	5.86	6.11	7.76	6.63	5.03	4.62	4.8–13.5
H_2O-			2.83	2.34		3.66	4.34	1.94	
TiO_2			.16	.05		.15		.10	
P_2O_5			.18	.22	.27	.19		.12	
	99.24	100.79	100.33	99.69	100.83	100.20	99.74	99.18	
Sp. gr			2.708	2.772		2.687	2.825	2.855	

A, B. Recent sediments:
- A. Recent greensand from Agulhasbank, near Agulhas, South Africa. Analyst Gumbel (Smulikowski, 1954, p. 36).
- B. Recent glauconite from Aomori Bay, Japan. Analyst, Takahashi (Smulikowski, 1954, p. 36).

C–E. Greensand or sandstone:
- C. Glauconite from Tertiary greensand at Makerewau Creek, New Zealand. Analyst, Seelye (Hutton and Seelye, 1941, p. 596).
- D. Glauconite from lower Oligocene sandstone, Tysmienica, Carpathian Mountains. Analyst, Szubartowski (Smulikowski, 1954, table 3, No. 26).
- E. Glauconite from Upper Cretaceous greensand, Sewell, New Jersey, U.S.A. Analyst Bailey (Mansfield, 1920). Total includes CO_2 0.30 percent.

F–H. Limestone:
- F. Glauconite from glauconitic limestone, Milburn Quarry, Otago, New Zealand. Analyst, Seelye (Hutton and Seelye, 1941, p. 596). Analysis total includes Cr_2O_3 0.07 percent and S 0.06 percent.
- G. Glauconite from Lower Ordovician limestone, Berg, Sweden. Analyst, Palmqvist (Hadding, 1932, p. 124).
- H. Glauconite from Upper Cambrian Bonneterre Dolomite. Analyst, Brown (Specific gravity given by Gruner, 1935, p. 708). This is the material for which Gruner developed the structural formula of glauconite as $(OH)_8\ K_2\ (Mg, F^{+2})_3\ (Fe^{+3}, Al)_6\ (Si_{14}\ Al_2)\ O_{40}$.

I. Maximum and minimum of 40 analyses in Hendricks and Ross (1941, p. 692–693).

The structural formula for the thuringite (sample E in table 6) is given by Engelhardt (1942) as:

$$(Si_{4.8}Al_{3.2})(Mg_{1.4}Fe^{+2}_{7.4}Fe^{+3}_{1.5}Al_{1.7})(OH)_{16.0}O_{20.0};$$

that for bavalite (sample F in table 6):

$$(Si_{4.5}Al_{3.5})(Mg_{.7}Fe^{+2}_{9.5}Fe^{+3}_{.1}Al_{1.6})((OH)_{13.9}O_{.2})O_{20.0}$$

Thuringite is very similar in composition to chamosite, and it is likely that it is the product of mild metamorphism of originally chamositic rocks. Probably much of the difficulty in establishing the mineralogical identity of chamosite is due to development of thuringite in varying amounts from the original silicate. According to Hallimond (1925, p. 28), thuringite is distinguished from chamosite in thin section or fine powders by the hexagonal habit of the scales, retention of green color in fine powders (chamosite is grayer), and bluish-green rather than green pleochroism parallel to the base.

TABLE 6.—*Analyses of minnesotaite, stilpnomelane, thuringite, and bavalite*

	A	B	C	D	E	F
SiO_2	51.29	48.03	44.77	42.42	20.82	21.71
Al_2O_3	.61	6.48	5.16	6.71	17.64	21.35
Fe_2O_3	2.00	4.12	16.38	33.24	8.70	.82
FeO	33.66	22.88	15.08	.85	37.96	43.01
MnO	.12	2.67	1.15	2.27		.05
MgO	6.26	4.94	5.88	5.20	4.15	2.33
CaO	.00	.83	.00			.16
Na_2O	.08	.00	.84			.35
K_2O	.03	.83	1.79	.00		
H_2O+	5.54	6.90	7.17	8.33	10.31	10.10
H_2O-	.24	2.64	1.83	1.45	.07	.11
TiO_2	.04	.23	.18		Tr.	.08
	99.87	100.55	100.23	100.47	99.65	100.07

A. Minnesotaite. From Biwabik Iron-Formation, Mesabi district, Minnesota (Gruner, 1944a). R. B. Ellestad, analyst.
B. Stilpnomelane. From Otago Schist, New Zealand. C. O. Hutton, analyst (Hutton, 1938).
C. Stilpnomelane. From Mont Chemin, Wallis, Switzerland. J. Jakob, analyst (Jakob, 1927).
D. Stilpnomelane. Iron County, Michigan (Ayres, 1940). V. L. Ayres and B. Park, analysts.
E. Thuringite. From Schmiedefeld, Thuringia, Germany. (Jung and Köhler, 1930).
F. Bavalite. Bas-Vallon, Brittany, France. (Orcel, 1923).

MINNESOTAITE

Minnesotaite, the iron analogue of talc, is a rock-forming mineral in some Precambrian iron-formations. In 1927, Richarz (1927) recognized that some of the "amphibole" reported in rocks from the Mesabi district of Minnesota could not be an amphibole and suggested the term "crystallized greenalite" for the material. Jolliffe (1935), in a study of greenalite, describes a "mineral x" from the Gunflint Iron-Formation of Ontario and Minnesota and gives a partial chemical analysis and optical properties. The problem was finally resolved by Gruner, who defined the structure of the mineral and named it minnesotaite (Gruner, 1944a). Further data on occurrence in the Lake Superior region are given by Gruner (1946), Tyler (1949), James (1954, 1955), and by Huber (1959), and by Harrison (1952, 1953) for the Quebec-Labrador iron belt of Canada. Because of its characteristic extremely fine grain size, the mineral probably has gone unrecognized in many iron-rich rocks of other parts of the world. It is generally associated with one or more of the following minerals: greenalite, stilpnomelane, siderite, magnetite, and quartz. Gruner (1946, p. 12) believes it to be a primary constitutent of the rocks; Tyler, James, and Harrison believe it to be a low-grade metamorphic product.

Minnesotaite is greenish gray in hand specimen, with a waxy luster. As seen under the microscope it is in aggregates of very fine plates and fibers, colorless or pale green; it strongly resembles talc, sericite, and pyrophyllite, but commonly forms tiny rosettes or sheafs. Optically negative, $2V$ less than 5°, positive elongation, slightly pleochroic ($\gamma=\beta=$pale green; $\alpha=$ colorless or very pale yellow); indices $\gamma=1.615$, $\alpha=1.580$ ($\gamma-\alpha=0.035$). The mineral has been synthesized (Flaschen and Osborn, 1957, p. 926). The formula proposed by Gruner (1944a, p. 370) is:

$$(OH)_{11}(Fe^{+2}, Mg)_{11}(Si, Al, Fe^{+2})_{16}O_{37}.$$

The analysis is given in table 6, A. In simplified form the formula may be written as $(Fe, Mg)_3Si_4O_{10}(OH)_2$.

STILPNOMELANE

Stilpnomelane, a so-called "brittle mica", is a common constituent of many iron-rich rocks. In the iron-formations of the Lake Superior region it is a rock-forming mineral (Gruner, 1944b, 1946; Tyler, 1949; James, 1954); it also occurs as thin veins of coarsely crystalline material cutting stilpnomelane-bearing rock (Grout and Thiel, 1924; Ayres, 1940), and as a metamorphic mineral near dikes and sills (Tyler, 1949). Stilpnomelane occurs in North Wales as a secondary mineral adjacent to dikes in oolitic chamosite rock of Ordovician age (Hallimond and Enos, 1924; Hallimond, 1925, p. 29), and in the iron-rich rocks of the Lahn-Dill district of Germany (Holzner, 1933).

Stilpnomelane is very similar in appearance to biotite and doubtless has gone unrecognized in many rocks as a result. In veins, as in the Cuyuna district of Minnesota, it forms foliae as much as several centimeters in diameter, olive green to nearly black. As a rock-forming mineral in ironstones it occurs as microscopic needles and plates, rarely more than a few tenths of a millimeter in length, with very strong pleochroism and absorption. The color ranges from olive green to dark brown, depending on the ferrous-ferric ratio. Density ranges from about 2.8 to 2.9. It is optically negative, and $2V$ is very small or zero. Indices show large ranges that can be related to ferric-ferrous ratio (Hutton, 1938, 1945, 1956); $\alpha=1.55-1.63$; $\gamma=\beta=1.68-1.74$. On the basis of X-ray studies, Gruner (1937; 1944b, p. 296) concludes that stilpnomelane is fundamentally a talc structure with layers "stacked in such a manner that the hexagonal rings more or less fit on each other as in micas". Al and Mg are essential constituents. The general structural formula developed by Gruner is:

$$(OH)_4(K, Na, Ca)_{0-1}(Fe, Mg, Al)_{7-8}Si_8O_{23-24}\cdot(H_2O)_{2-4}.$$

The three analyses of stilpnomelane given in table 6 (B, C, D) show the range in FeO and Fe_2O_3.

IRON SULFIDES

Pyrite and marcasite. the latter relatively scarce, are the only sulfides of quantitative significance in lithified iron-rich sedimentary rocks. As with the oxides, however, these minerals may have been preceded in certain sedimentary environments by less stable materials of primary origin and transitory existence. The terms *hydrotroilite* and *melnikovite* have been used by many authors to apply to amorphous black sulfides present in unlithified sediments of Recent and Tertiary age, but definition as true mineral species has been lacking. Recently, however, the existence of a tetragonal form of FeS has been established, which Berner (1962, 1964) believes to be the main mineral component of hydrotroilite, and Skinner and his coworkers (1964) have isolated and defined the new mineral greigite (Fe_3S_4) that appears to be the main component of melnikovite. The two pairs hydrotroilite and tetragonal FeS and melnikovite and greigite are therefore discussed separately under these headings below.

Smythite (rhombohedral Fe_3S_4) and pyrrhotite ($Fe_{1-x}S$) occur as authigenic minerals in some sedimentary rocks Erd, (Evans, and Richter, 1957), but both are very rare. Pyrrhotite is also produced by metamorphism of pyrite (see, for example, Neumann, 1950).

PYRITE (FeS_2)

Pyrite, the most common sulfide of the sedimentary ironstones, generally occurs as scattered isolated crystals that clearly are of diagenetic origin. It is a dominant mineral in the Sulphur Bed of the Cleveland ironstone of England and in the middle part of the Dominion Bed of Wabana, Newfoundland; at these places it forms layers as much as a foot thick and is in in the form of pellets, spherules, and replacements of shell fragments. The graphitic Wauseca Pyritic Member of the Dunn Creek Slate, a 50-foot Precambrian unit of the Iron River district, Michigan, contains 35 to 40 percent pyrite as crystals about 0.003 mm diameter (James, 1951). Pyrite of extraordinary occurrence is described by Tyler and Barghoorn (1963) in chert of the Precambrian Gunflint Iron-Formation of Ontario; the crystals appear to have moved bodily in the chert, leaving a marked trail.

The occurrence of microspheres of pyrite in Recent muds as well as ancient rocks has been extensively investigated in recent years. Shales and muds may contain 10,000 or more spheres per cubic millimeter of rock. They are described by Love (1962b, p. 122) as follows:

> The spheres range in diameter between 3 and 30 microns, commonly being 7–10 microns and are composed of large numbers of minute euhedral sulfide crystals, each generally ½–2 microns in size * * *.

Chemical analysis by Vallentyne (1962) of a 450-mg concentrate from a Recent lake sediment yielded the following results, in weight percent:

Fe	46.59
S	53.16
Si	.13
C	.009

Isolation of pyrite spheres from rocks of early Paleozoic to Recent age and dissolution in acid have yielded organic residues of distinctive aspect; these forms have been named "*Pyritosphaera barbaria*" by Love (1957, 1962a). Vallentyne (1962, p. 145) suggests that the spheres may be "secondarily biogenic"—that is, that the pyrite formed as a result of reactants produced by the organism rather than as accretion around living cells.

In a few areas, notably Meggen, Germany, and Mount Isa, Australia, pyrite of similar habit to the microspheres is a major rock constituent (see Schouten, 1946; Baker, 1960; Love and Zimmerman, 1961). Whether the pyrite in these rocks is of sedimentary or later origin has been debated at length. Baker (1960) suggests that the microsphere form may be the product of either hydrothermal or sedimentary processes.

MARCASITE (FeS_2)

Marcasite, rare or absent in most ironstones, is the characteristic sulfide associated with "black band" siderite ores of coal-bearing strata, where it occurs as nodules, partings, and thin layers. Newhouse (1927) describes marcasite layers—in the Carboniferous of the Appalachians—a few inches thick that cover square miles. Edwards and Baker (1951) consider deposition of marcasite in coaly deposits to be a reflection of an acid environment, in contrast to the neutral or alkaline environment of marine deposits characterized by presence of pyrite.

HYDROTROILITE AND TETRAGONAL FeS

The term hydrotroilite was used by Arkhangelskii (1933) and previous authors to describe the unstable amorphous iron sulfide fraction of bottom sediments of the Black Sea. The material was distinguished by its black color and by generation of H_2S upon treatment with hydrochloric acid. As Berner (1964) has observed, the term pervades the sedimentologic literature, including that of recent date, even though justification as a definite mineral species has been lacking and the composition is uncertain. Although the composition generally is assumed to be $FeS{\cdot}nH_2O$, Volkov (1959, p. 398) concludes that the common ferrous sulfide of Black Sea muds is hydrotroilite with a composition $FeS{\cdot}nH_2S$, and Korolev (1958, p. 460) suggests that there exists a series of transitional phases between hydrotroilite and stable pyrite or marcasite.

Detailed study of natural hydrotroilite has been hampered by its instability and extremely fine grain size. By designing an experiment to simulate to some degree the natural environment Berner (1962) synthesized tetragonal FeS; he also recognized this compound in sediment from the highly contaminated Mystic River of Massachusetts, U.S.A. In a later study (Berner, 1964) the nature and occurrence of tetragonal FeS are more completely discussed; the mineral is shown to be essentially identical with mackinawite, which has been found in sulfide ore deposits (Evans and others, 1964; Kouvo and Vuorelainen, 1963), and with the informally named kansite, a product of steel-pipe corrosion (Myers and others, 1958). Berner shows further that X-ray data published by Volkov (1961) for a sulfide concretion from Black Sea bottom muds are consistent with those of tetragonal FeS plus a lesser amount of greigite (Fe_3S_4, see next section).

The calculated specific gravity of synthetic tetragonal FeS is 4.29. The cell dimensions are $c_0=5.047\pm0.002$A; $a_0=3.679\pm0.002$A. In natural occurrence—that is, as "hydrotroilite"—the mineral may contain "absorbed or nonessential water" (Berner, 1964), so that the formula of $FeS{\cdot}nH_2O$ would apply.

Arkhangelskii (1933) reported that where "hydrotroilite" was present in abundance, it was in part converted to marcasite, and Ostroumov and Shilov (1956) report similar transition in deep-sea deposits of the north Pacific. In most sediments, however, the only positively identified crystalline sulfide is pyrite or marcasite. (See Tageeva and Tikhomirova, 1957, for further data on Black Sea muds; Brodskaya and Martova, 1957, for Sea of Okhotsk; Shepard and Moore, 1955, for Gulf of Mexico.)

A recent study of isotopic compositions of sulfur compounds of bottom sediments in four basins off the southern California coast (Kaplan, Emery, and Rittenberg, 1963) has thrown considerable light on the complex process of sulfide formation. The sulfur is present in five forms: pyrite (dominant), acid-volatile sulfide ("hydrotroilite"), elemental sulfur, organic sulfur, and sulfate sulfur (in interstitial solutions). The bacterial reduction of sulfate results in strong enrichment in the lighter isotope (S^{32}) in precipitated materials. Kaplan, Emery, and Rittenberg (1963, p. 319) state:

> Using the isotope data, a series of diagenetic reactions can be traced beginning with sulphate and ending with pyrite * * * the greatest fractionation in the reduced entities exists in the

> surface sample and that the S^{32} enrichment there is similar for all compounds * * * must mean formation from a large sulphate reservoir. With increase in depth, all reduced components become less enriched in S^{32}, free sulphide showing the greatest change and pyrite the least. The changes become apparent after burial and isolation from the infinite sulphate reservoir. Under such conditions the first sulphide evolved must be the lightest, later sulphide becoming more enriched in S^{34} as the sulphate is depleted. The trends * * * indicate that the earliest formed sulphide is converted first into acid volatile sulphide and then to pyrite. The isotopic variation of elemental sulphur with depth and its δ S^{34} values between those of free and acid volatile sulphide suggest that (a) it is continually being formed and destroyed and (b) its formation probably occurs through oxidation of free sulphide. These findings support earlier hypotheses * * * that pyrite forms by the direct reaction of hydrotroilite and elemental sulphur:
>
> $$FeS + S \rightarrow FeS_2.$$

MELNIKOVITE AND GREIGITE

Doss (1912 and earlier papers) described melnikovite as an amorphous black magnetic iron sulfide, which was found in clays of Miocene age in Samara, Russia. The material was reported to have a hardness of 2 to 3 and a density of 4.2 to 4.3, to be soluble in dilute HCl, and to have the composition Fe_5S_7. Berz (1922), however, concluded that the material was a mixture of magnetite and pyrite, and subsequently the terms melnikovite-pyrite or melnikovite-marcasite were used for fine-grained mixtures of pyrite and marcasite (Ramdohr, 1955b). In 1957 Lepp synthesized a sooty magnetic sulfide (or sulfide hydrate) with a distinctive X-ray pattern and properties similar to the melnikovite of Doss (Lepp, 1957), but his data were not adequate for complete chemical and mineralogical definition. Material also referred to as melnikovite has been produced experimentally by Korolev (1958), but the X-ray properties are significantly different from those given by Lepp. As a mineral species, therefore, the status of melnikovite has remained unclarified.

Iron sulfide similar to the melnikovite of Doss recently has been found in lacustrine sediments of Tertiary age in San Bernadino County, Calif. (Skinner, Erd, and Grimaldi, 1964). The HCl-soluble magnetic iron sulfide has the composition Fe_3S_4 (spinel structure) and has been named greigite, a polymorph of smythite. It is sooty black and occurs with marcasite in grayish black laminae in the sediment. The unit cell dimension is 9.876±0.002A, with a calculated density of 4.079±0.003. Skinner, Erd, and Grimaldi conclude that greigite formed by the action of anaerobic bacteria in bottom sediments of an alkaline lake.

The X-ray properties of "cubic magnetic iron sulfide" synthesized by Berner (1964) are essentially identical with those of natural greigite and conform to the "melnikovite" synthesized by Lepp (1957). As mentioned in the previous section, Berner shows that the X-ray properties of the melnikovite of Volkov (1961; see also Volkov and Ostroumov, 1957), which occurs in hard black concretions at depths of 335–337 cm in Black Sea bottom muds, can be accounted for by a mixture of tetragonal FeS with the cubic iron oxide (greigite). Berner also suggests that Doss' melnikovite was a mixture of elemental sulfur with one or more of the magnetic iron sulfides (pyrrhotite, smythite, greigite).

CLASSIFICATION AND FACIES

MAJOR SUBDIVISIONS

Two major groups of the iron-rich sedimentary rocks are recognized: (1) the "ironstones", which are noncherty and largely of post-Precambrian age, and (2) the "iron-formations", which are typically laminated with chert and largely (but not exclusively) of Precambrian age. Use of the two terms in this manner is entirely the result of custom, not prior definition or logic, but it is continued as it provides ready distinction between dissimilar rocks. "Ironstone" appears to have no synonym, other than the commonly used "iron ore", whereas the rock here referred to as iron-formation is known also as itabirite (Brazil,) banded hematite quartzite (India), iron-bearing formation and taconite (U.S.A.), and quartz-banded ore (Scandinavia). Only in South Africa, where the term "banded ironstone" is used for Precambrian cherty iron-formation is there overlap in usage of the two terms.

With minor exceptions, both ironstone and iron-formation probably have originated as chemically precipitated marine sediments. The younger rocks commonly contain marine fossils—often replaced by iron oxides—and the older iron-formations occur within typically marine sequences of strata. A nonmarine origin for the Precambrian iron-formations has been suggested, however, most explicitly by Hough (1958). Hunter[2] (p. 212, 229) has produced evidence to indicate that the Clinton ores of eastern United States were deposited in marginal marine waters of less-than-normal salinity. The best documented example of a nonmarine sedimentary ironstone appears to be that of Oligocene age in northern Turgai, U.S.S.R., where oolitic ironstone contains fresh-water molluscs (Davidson, 1961).

Three other groups of iron-rich rocks of lesser importance can be defined: (1) the blackband and clayband ores, most of which are diagenetic or postdiagenetic deposits of siderite, often with associated marcasite or pyrite, found in coal measures and in some

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[2] See footnote, p. W7.

clays; (2) the "bog iron ores" found in many bogs and small lakes in higher latitudes; and (3) surficial accumulations, known as canga in Brazil, derived from nearby outcrops of iron-rich rocks. These accumulations, of considerable extent and importance in some areas, have much in common with lateritic deposits and with residual-transported deposits of bauxite and therefore are not discussed in this chapter. The blackband and clayband ores, though not strictly or sedimentary origin, are included here because they occur in sedimentary rocks and because they share common factors in chemistry of origin with the marine deposits.

Still another group consists of iron-rich sedimentary rocks that grade into manganese-rich beds, such as those of the Kazakh region of the U.S.S.R. (Maksimov, 1960). This class of deposits, commonly associated with volcanic rocks, is noted in passing here but is not treated in detail.

FACIES

Of greater significance to problems of genesis and distribution than the groupings given above is a classification according to the nature of the dominant iron mineral—oxide, silicate, carbonate, or sulfide. Geochemical facies based on mineralogy are suggested or established both in relation to the geochemistry of iron (Teodorovich, 1947; Krumbein and Garrels, 1952; Huber and Garrels, 1953; Krauskopf, 1957; Huber, 1958; Garrels, 1960), and to geologic occurrence (Harder, 1919; Tyler, 1950; James, 1954; Borchert, 1952, 1960a, 1960b; Strakhov, 1959).

GEOCHEMICAL ASPECTS

The relations among the various compounds of iron are most effectively illustrated by the showing of stability fields in diagrams of oxidation potential (Eh) versus hydrogen-ion concentration (pH). Stemming in considerable part from the work on corrosion of iron by Pourbaix (1949 and earlier papers), the use of stability-field diagrams in application to geology has developed rapidly in recent years. A series of papers by Garrels with his colleagues and students (Castaño and Garrels, 1950; Krumbein and Garrels, 1952; Garrels, 1953; Huber and Garrels, 1953; Huber, 1958), all of which deal in part or specifically with the problem of iron sedimentation, culminated in the publication of a book (Garrels, 1960) in which the method and the application to iron equilibria are discussed fully. Krauskopf (1957) has used Eh-pH diagrams to analyze the behavior of manganese and iron, and Hem (1960a, 1960b) and Hem and Cropper (1959) have utilized the Eh-pH approach to define the stability fields of iron in solution.

The field boundary between any two molecular species, or between two ionic species in solution, is established from the Nernst equation, expressed as

$$\mathrm{Eh}=E^\circ+\frac{RT}{nF}\ln k, \qquad (1)$$

where

Eh = oxidation potential (redox potential),
E° = potential of the reaction under standard conditions,
R = universal gas constant, 0.00198 kcal/degree mole,
T = temperature, degrees Kelvin,
n = number of electrons involved in the reaction,
F = Faraday constant, 23.06 kcal per volt-gram equivalent,
$\ln k$ = natural logarithm of the equilibrium constant of the reaction;

and from the relation

$$E^\circ=\frac{\Delta F^\circ}{nF}, \qquad (2)$$

where

ΔF° = standard free energy of the reaction.

To establish the Eh-pH relation between a pair of compounds such as hematite and magnetite, write the electrode reaction:

$$2F_3O_4+H_2O=3Fe_2O_3+2H^++2e$$

The standard free-energy change of the reaction is obtained by subtracting the free energy (values in kcal given in table 7) of the reactants from those of the products:

$$\begin{aligned}\Delta F^\circ&=(3\times-177.1)+(2\times0)-(2\times242.4)-(-56.69)\\&=+10.2\text{ kcal}\end{aligned}$$

then from (2)

$$\begin{aligned}E^\circ&=\frac{+10.2}{2\times23.06}\\&=0.221\text{ volt}\end{aligned}$$

Substituting in (1), at 25° C or 298.16° K, and converting to $\log_{10}$,

$$\mathrm{Eh}=0.221+\frac{.00198\times298.16}{2\times23.06}\left(2.303\log\frac{[Fe_2O_3]^3[H^+]^2}{[Fe_3O_4]^2[H_2O]}\right)$$

Noting that the activities of Fe_2O_3, Fe_3O_4, and H_2O are unity by convention, and that $\mathrm{pH}=-\log H^+$, the Eh-pH equation for the reaction is the straight line

$$\mathrm{Eh}=0.221-0.059\text{ pH} \qquad (3)$$

At fixed concentrations of carbonate species in solution (CO_3^{-2}; HCO_3^{-1}; H_2CO_3) or sulfur species (H_2S; S^{-2}; HS^{-1}; HSO_4^{-1}; SO_4^{-2}), similar equations can be derived for equilibrium relations between oxides and siderite, siderite and sulfide, or oxides and sulfide.

Values of free energy of formation, ΔF°, for species of importance to the sedimentary iron system are listed in table 7. Equilibrium constants for significant reactions are given by Latimer (1952), from which source part of the data given in table 7 is derived.

Figure 2 is from Krauskopf (1957, p. 64). On the diagram the field boundaries are based on total carbonate =0.002M, which is the aqueous concentration at pH 8 in equilibrium with the atmosphere; total sulfur =0.1M; and total silica =0.002M, which is the

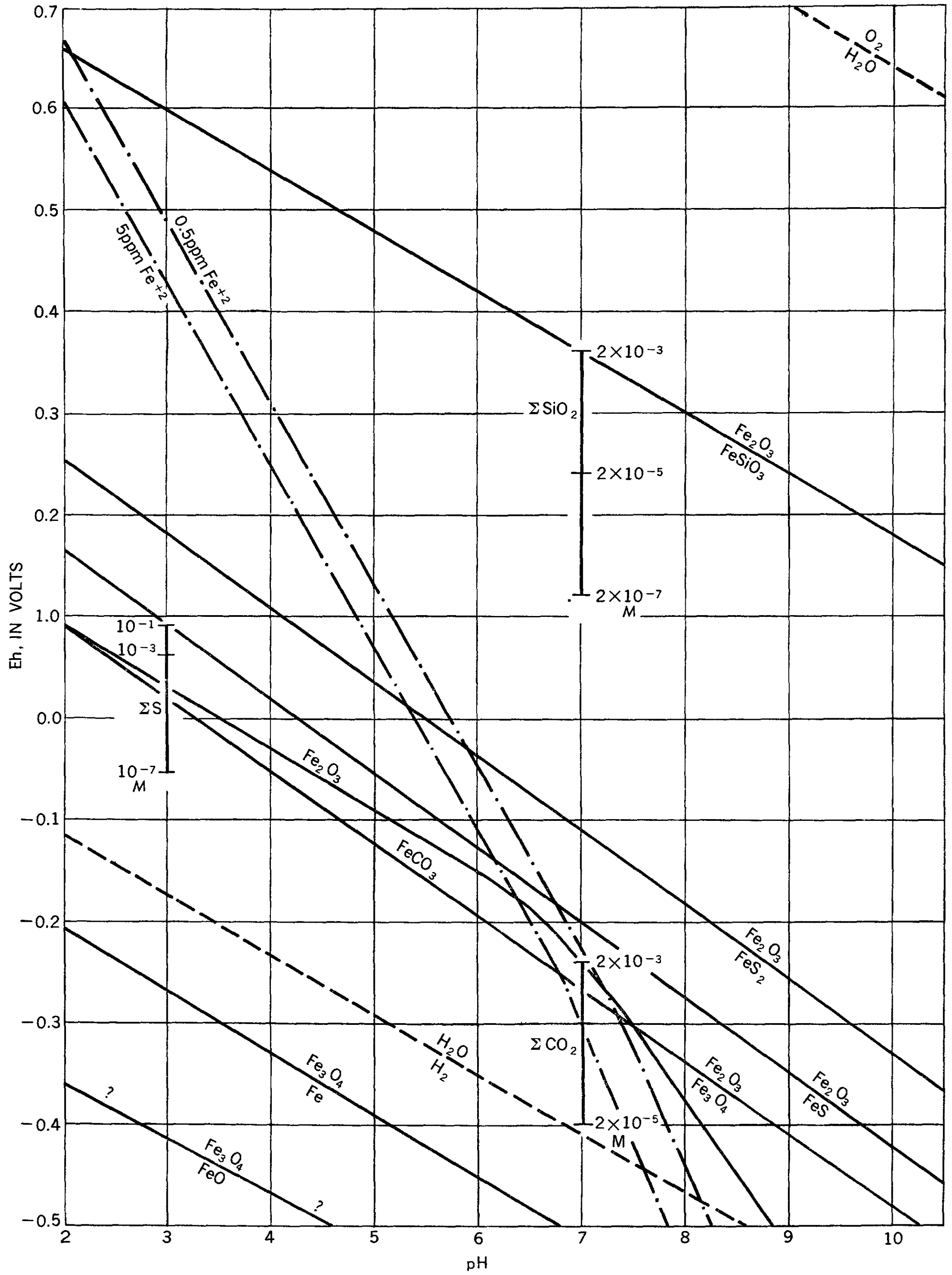

FIGURE 2.—Eh-pH diagram showing relations between anhydrous iron compounds at 25° C, 1 atm pressure (from Krauskopf, 1957, p. 64).

Solid lines are boundaries of stability fields, as labeled. Cross-bars on short vertical lines show the intersection of field boundary at low concentrations of carbonate, sulfide, and silica. Dashed lines are theoretical limits of water stability. Dash-dot lines are isoconcentration lines, drawn through points where concentration of Fe^{+2} in equilibrium with oxides is 0.5 ppm and 5 ppm. Question marks along Fe_3O_4-FeO boundary indicate that FeO is unstable with respect to Fe and Fe_3O_4.

Other conditions are specified in text.

Table 7.—*Values for free energy* ($\Delta F°$) *for species of importance to the iron system, at standard conditions*

State: aq, species in solution; s, solid; l, liquid; c, crystalline

[From compilations by Garrels (1960)]

Species	State	Free energy (kcal)	Species	State	Free energy (kcal)
Fe	c	0.0	HCO_3^-	aq	−140.31
Fe^{+2}	aq	−20.30	H_2CO_3	aq	−149.00
Fe^{+3}	aq	−2.53	CO_2	aq	−92.31
FeO	c	−58.4	H^+	aq	.0
Fe_2O_3 (hematite)	c	−177.1	OH^-	aq	−37.595
Fe_3O_4	c	−242.4	H_2O	l	−56.690
$Fe(OH)^{+2}$	aq	−55.91	H_2O_2	aq	−31.47
$Fe(OH)_2$	c	−115.57	$H_3SiO_4^-$	aq	−286.8
$Fe(OH)_2^+$	aq	−106.2	H_4SiO_4	aq	−300.2
$Fe(OH)_3$	c	−166.0	SiO_2 (quartz)	s	−192.4
FeO_2H^-	aq	−90.6	S^{-2}	aq	22.1
α-FeS	c	−23.32	H_2S	aq	−6.54
FeS_2 (pyrite)	c	−36.00	HS^-	aq	3.01
$FeCO_3$	c	−161.06	HSO_4^-	aq	−179.94
$FeSiO_3$	c	257.0	SO_4^{-2}	aq	−177.34
CO_3^{-2}	aq	−126.22			

amount soluble in water (chiefly as H_4SiO_4) at 25° C. Figure 3, from Huber (1958, p. 134), shows "blocked-out" fields for the compounds; it is based on total carbonate as in "normal sea water" (activities not specified, but from Sverdrup, Johnson, and Fleming, 1942, pp. 195–202); total sulfur as for "average river and lake water"—17.7 ppm SO_4^{-2} and salinity 146 ppm, or about 3.2×10^{-8} M. Figure 4, from Garrels (1960, p. 157), shows field boundaries at relatively low concentration of dissolved sulfur and very high concentration of dissolved carbonate.

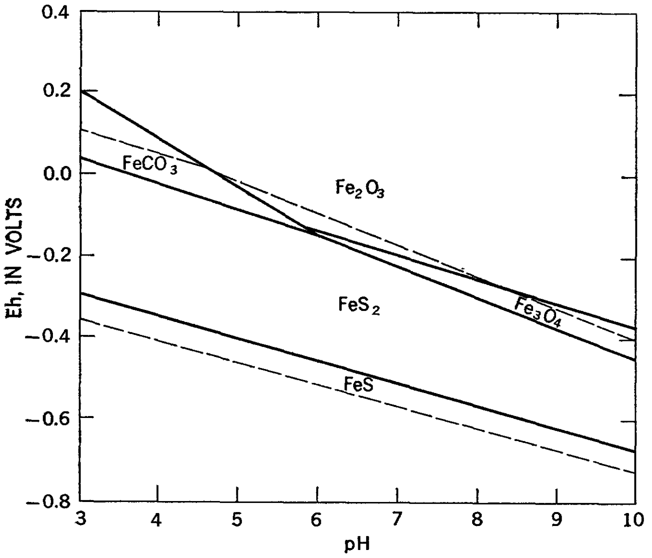

Figure 3.—Eh-pH stability fields for iron minerals with carbonate equilibria as in "normal sea water" and total dissolved sulfur as in "average river and lake water" (about 3.2×10^{-8}M), at 25° C. (From Huber, 1958, p. 134.) Dashed lines indicate field boundaries for sulfur as in normal sea water (about $10^{2.2}$ times concentration of river and lake water).

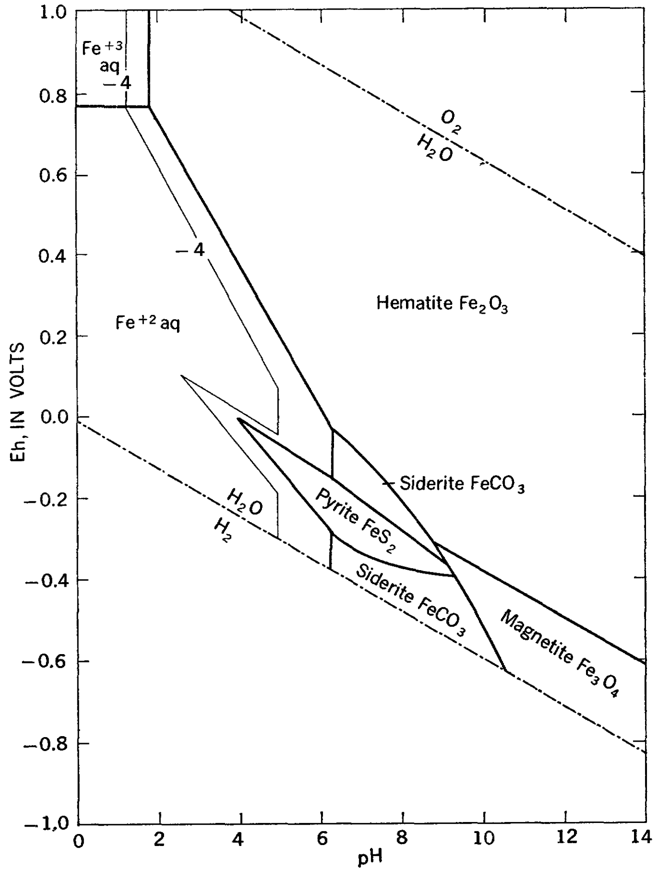

Figure 4.—Eh-pH relations of iron oxides, sulfide, and carbonate with total dissolved sulfur $=10^{-6}$M and total dissolved carbonate $=1$M, at 25° C. (From Garrels, 1960, p. 157.) Heavy lines are field boundaries. Light line shows position of isoconcentrations of Fe in solution, at activity of 10^{-4}. Dot-dash lines indicate theoretical limit of water stability.

The three diagrams illustrate the wide range of thermodynamically stable associations possible; virtually any combination of oxides, silicate, carbonate, and sulfide is stable at standard temperature and pressure under some geologically reasonable values of Eh, pH, and ionic concentrations. Notable, however, is the restricted field of siderite at all but very high carbonate concentration, and the remarkable persistence of the pyrite field at very low sulfur concentration (fig. 4). The stability realm of magnetite shown on figures 3 and 4 is wiped out by assuming an appreciable amount of silica in solution, as indicated on figure 2 by the Fe_2O_3-$FeSiO_3$ field boundary. The formation of the sedimentary ores, in all their variety, clearly requires a variety of special conditions; as stated by Garrels (1960, p. 162), "* * * it is obvious that a siderite facies can be obtained by having a high dissolved CO_2 and by removing sulfide sulfur from the system; a silicate facies by removing sulfur and a high CO_2 content, while preserving enough silica to yield chert; a magnetite facies by reducing sulfur, CO_2, and maintaining silica at a value undersaturated with respect to amorphous silica."

The Eh-pH diagrams are extremely helpful in appraising the significance of natural assemblages, but a number of factors seriously restrict the direct application to the geologic problems. Chief among these are that the compounds used in the thermodynamic calculations do not correspond exactly to the natural phases and that metastable phases are not accounted for. Natural siderite in the sedimentary ores is not $FeCO_3$; it is a complex (Fe, Mn, Mg, and Ca)-bearing carbonate. The silicate is not $FeSiO_3$; it is the far more complex chamosite, greenalite, or glauconite. The original oxide is not Fe_2O_3; it is limonite or some more primitive hydrate. The primary sulfide may not be pyrite, but a metastable phase such as tetragonal FeS. The natural occurrence of these phases indicates that they have larger stability (or metastability) fields than do the compounds being considered. Furthermore, the thermodynamic analysis indicates only theoretical phases; whether or not a particular phase will form may depend on other factors—the presence of a catalyst, for example. In spite of the difficulties involved in their application, however, Eh–pH diagrams do indicate equilibrium associations under specified condition. Much more rigorous analysis of natural associations will be possible with the gradual accumulation of free-energy values for the more complex materials, coupled with greater understanding of the role of metastable phases and with more specific data on the natural environmental ranges of Eh, pH, and ionic concentrations.

NATURAL ASSOCIATIONS

That the iron-rich sedimentary rocks fall into natural groups based on the dominance of oxide, silicate, carbonate, or sulfide has long been recognized (for example, see Harder, 1919). The concept of sedimentary or geochemical facies based on mineralogy and reflecting sedimentary environments has been given explicit definition by Teodorovich (1947) and particularly by Borchert (1960a, 1960b) for the younger ironstones, and by James (1954) for the Precambrian iron-formations. The general relations as visualized by Borchert are shown unequivocally in figure 5. Strakhov (1959, p. 765) presents a somewhat similar generalization, with two important differences: (1) all the iron minerals except the oxides are considered of diagenetic origin, and (2) the relative positions of siderite and chamosite are reversed—that is, the shore-to-depth sequence is oxide-silicate-carbonate-sulfide. This sequence also is proposed for the Precambrian iron-formations (James, 1954), with the addition of a magnetite-bearing facies and substitution of greenalite (plus stilpnomelane and minnesotaite) for chamosite.

No example is known of a complete array of major facies grading laterally one into the other as indicated diagrammatically in figure 5. The main reason for this is that the shore-to-depth profile is merely a device for indicating a range in environmental conditions, particularly oxygen availability. Nevertheless, to quote from an earlier paper (James, 1954, p. 242),

> Although it is doubtful if the pattern of precipitation indicated is ever actually obtained in nature because of complicated relationships between depth of basin, height of barrier, and details of circulation, the facies relationships between the various mineralogies are valid.

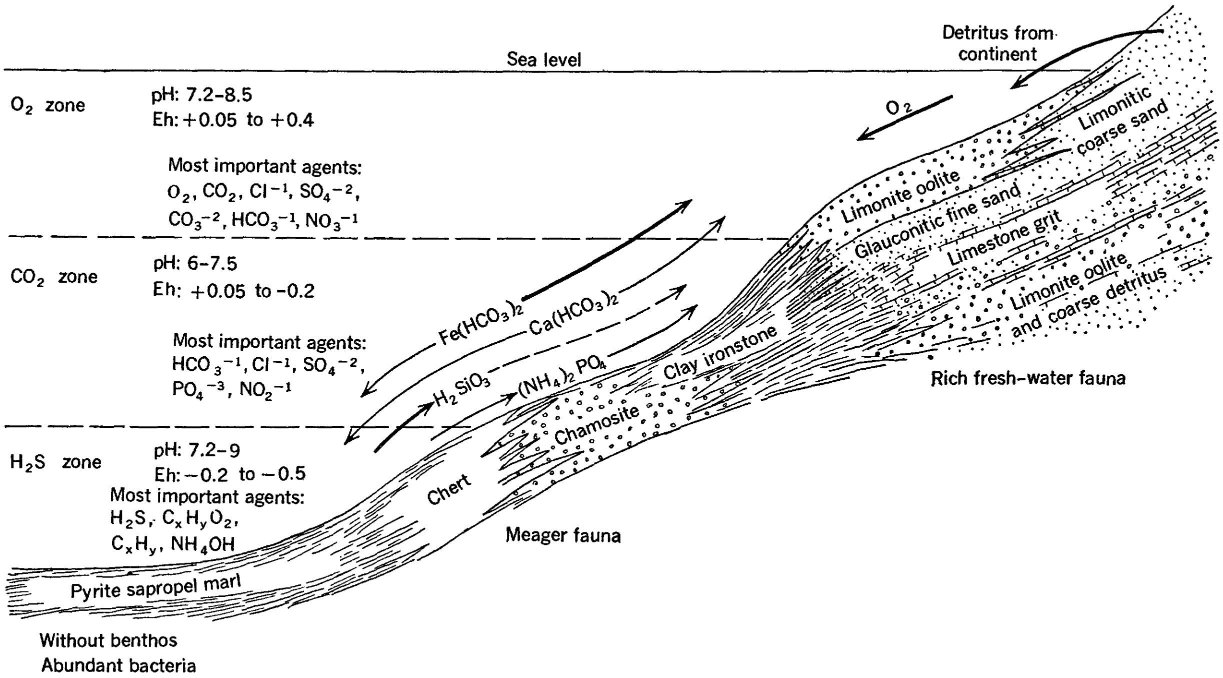

FIGURE 5.—Schematic section showing relations between ironstone facies and physico-chemical conditions. (From Borchert, 1960b, p. 34.)

Partial facies arrays—that is, time-equivalent gradations from one facies into adjoining ones—have been described for many areas: oxide to chamosite in the Clinton (Hunter,[3] figs. 66, 69); chamosite to siderite in the Northampton sand ironstone (Taylor, 1949, fig. 1); magnetite-greenalite to carbonate in the Gunflint (Goodwin, 1956, figs. 3 and 6); hematite to magnetite to silicate and carbonate in the Labrador trough (Gastil and Knowles, 1960, p. 1249).

A valuable analysis of relations within the oxide facies is provided by Plaksenko (1959), in his study of relations between hematitic and magnetitic phases of iron-formation in the Kursk district, U.S.S.R. From west to east, dominantly hematitic iron-formation gives way to rocks in which magnetite is dominant, and this transition is accompanied by a considerable increase in the amount of interbedded metashale. In a typical vertical section (thicknesses range from 120 m to nearly 500 m), metashale is succeeded first by magnetite iron-formation and then by hematite iron-formation, and this sequence is repeated several times. Plaksenko relates the cyclic aspect to transgression and regression, and concludes that the normal shore-to-depth sequence is shale, magnetite, hematite. This reversal of the idealized relative position of hematite and magnetite is to be expected if a significant amount of clastic material is being contributed from the land, especially if the clastic material is clayey, with an organic component; it is particularly to be expected during regressive cycles. White (1954) shows that in the Mesabi district of Minnesota the initial transgression produced a normal pattern, with hematite grading into clean sand (Pokegama Quartzite) on the shoreward side, and into magnetite in the deeper part of the basin; during regression sideritic and even pyritic rock accumulated in near shore positions and these graded seaward into magnetite and silicate facies.

Mixed assemblages and small-scale alternations between facies are common. These multiphase rocks owe their character to one or any combination of several factors:

1. Clastic accumulation of iron minerals that were formed initially in separated environments. This process is typified by many oolitic ironstones, which may contain chemically heterogeneous assemblages of limonite ooliths, chamosite ooliths, ooliths of alternating chamosite and limonite, partly replaced fossil fragments and clastic grains, and phosphate pellets.
2. Precipitation of iron minerals at boundary conditions between facies, so that the minerals of each facies are in equilibrium.
3. Precipitation in overlapping stability fields. Little is known of the true stability field of chamosite, for example, but its occurrence is controlled in part by available alumina and the stability field may overlap that of other iron minerals.
4. Periodic changes in bottom environment, due to seasonal effects or longer-range shifts in water currents, which result in small-scale interlamination of dissimilar facies.
5. Incomplete mineralogic response to changes in environment because of slow reaction rates or inadequate capacity of the system. This effect is particularly to be expected in diagenesis: the commonly observed partial replacements of chamosite and limonite ooliths by siderite, for example, doubtless are due to reactions below the depositional interface, and these reactions may be halted by depletion of CO_2 in the burial environment.
6. Post-diagenesis metamorphism, again with incomplete reactions due to low capacity of the system or to sluggish reaction. The development of hematite in Paleozoic and Precambrian rocks is probably a metamorphic process, one which has gone to completion in many rocks whereas in others (the Mayville ore of Wisconsin, for example) both goethite and hematite are present. The partial development of thuringite from chamosite is another example.

Textural relations provide the most significant guides as to which factor or combination of factors is to be invoked to explain a specific assemblage, particularly if considered in the light of theoretical possibilities set up by Eh–pH diagrams and known differences in natural environments. It is to be expected, however, that diagenetic modifications will be in the direction of decreasing state of oxidation; studies of recent bottom sediments show that the Eh below the water-sediment interface is generally lower than that of the depositional environment (Zobell, 1946; Bruevich, 1938a, 1938b).

The interrelationships between ooliths and matrix, arising principally from physical mixing of materials deposited in separated environments plus diagenetic modifications, have led Braun (1964) to define, for minette-type ironstone, 14 classes within the framework of the 4 main facies. Each is illustrated by chemical and modal analyses.

ROLE OF ORGANIC ACTIVITY

A number of organisms are known to cause the precipitation of iron (see Harder, 1919, for a thorough review), but the true importance to the accumulation

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[3] See footnote, p. W7.

of iron-rich rocks is difficult to assess. The subject will be only briefly surveyed here, as actual data significant to the question are few.

Three general situations may be considered;

1. The organism acts essentially as a catalyst—that is, it causes or speeds up precipitation of a compound that is thermodynamically appropriate to the environment. The well-known abundance of bacterial populations in natural precipitates of iron oxides, as in emerging ground waters, is an example; in effect, the organism derives energy for growth from the oxidation of metastable ferrous iron. The products of biochemical precipitation will be mixed with inorganic precipitates of the same character. In a sense, the organism is of only incidental importance; it flourishes by taking advantage of the slow rate at which equilibrium is reached by wholly inorganic processes.
2. The organism selectively accretes a compound as part of its cell wall or skeletal structure, as in the familiar example of silica secretion by radiolaria. This accretion may or may not be in harmony with the inorganic aspects of the system; a diatom, for example, can secrete and maintain a silica test in an environment greatly undersaturated with respect to silica. However, with the possible exception of *Pyritosphaera barbaria* (see under "Pyrite"), no organism is known to secrete an iron compound as a principal constituent of its hard parts.

   Foraminifera, and possibly some other organisms, are known to extract particulate iron oxide from sea water; foraminiferal tests are reported by Correns (1937) to contain 0.16–0.65 percent Fe_2O_3. As has previously been mentioned, this concentration, followed by death of the organism and return of $CaCO_3$ to solution, probably is the main reason for the high content of iron in deep-sea sediments (Wakeel and Riley, 1961). A somewhat similar process is suggested by Strong (1956), who has isolated iron bacteria in rock salt of Devonian and younger age; he suggests (p. 585) that bacterially precipitated iron "* * * provide[s] material for certain deposits of iron oxide by solution of salt and aqueous redeposition of haematite."
3. The organism significantly modifies the physicochemical nature of the environment through its life processes. Reducing conditions—that is, low Eh—are created by bacterial action on included organic detritus in sediments, which results in consumption or displacement of oxygen, reduction of sulfate to produce H_2S or to directly precipitate iron sulfide, and liberation of H_2S by destruction of proteins. Berner (1963) has shown that direct measurements on black muds show a good fit to the theoretical curve $Eh=0.4850+.0295\ pS^{-2}$. In such an environment, the iron is the main poising element in the system (Zobell, 1946).

Whether by precipitating material directly or by creating the appropriate environment, microorganisms almost surely play a dominant role in the formation of many sulfide-rich sediments. They also may create reducing microenvironments in the vicinity of organic particles in an otherwise oxidizing regime. Glauconite probably is formed in such localized environments, in which the Eh is appreciably lower than in the surrounding medium.

In general, however, it seems fair to conclude that, except for the sulfide-rich rocks, organisms have not been of first-order importance in the concentration of iron to form the ironstones and iron-formations, even though they may have been involved with the actual process of precipitation.

CHEMISTRY OF IRON-RICH ROCKS, ACCORDING TO GROUPS AND FACIES

Tables 8 to 19 present selected analyses of iron-rich rocks, grouped according to facies and to some extent according to age, and some of the more significant aspects of each group are given in summary fashion below. The separation according to age is to permit isolation of differences between the Precambrian iron-formations and the younger ironstones; these differences are discussed in a later section.

Except where otherwise stated, the analyses are known or believed to be of representative samples of particular rock types—in general of hand specimen size or somewhat larger.

OXIDE FACIES

The oxide facies of the normal iron-rich sedimentary rocks comprises the oolitic limonitic and hematitic ironstones of post-Precambrian age, banded hematitic iron-formation of Precambrian age, and magnetite-rich rocks of both Precambrian and younger age. In the tables these are grouped according to subfacies—for example, limonitic ironstone—and according to age (Precambrian and post-Precambrian).

OOLITIC LIMONITE IRONSTONE

The oolitic limonites are very largely restricted to ironstones of Tertiary and Mesozoic age. An exception is that of the Mayville ore of Ordovician age (table 8, analyses Q–R).

The rocks typically consist of oolitic or pelletal grains of limonite, many with cores of clastic material, in a matrix of chamosite or calcite. Some consist of mixtures of chamosite and limonite ooliths, with the chamosite either partly altered to limonite or containing limonite in alternating layers with chamosite. The rocks are chemically heterogeneous and doubtless are the products of a primary chemical precipitation followed by mechanical transport and sorting of the ooliths. Siderite, present in quantities of as much as 10 percent or more, is of diagenetic origin.

Chemically the rocks are marked by a wide range in composition that is related in considerable part to the rudely inverse relation between quartz and calcite content, and to the amounts of chamosite and of secondary siderite. The P_2O_5 content is generally high, reflecting the presence of pelletal collophane.

HEMATITIC ROCKS OF MESOZOIC AND PALEOZOIC AGE

Most of the hematitic ironstones listed in table 9 are oolitic rocks similar in physical character to the oolitic limonites and with similar associations and origin. As in the limonites, an inverse relation between CaO and SiO_2 reflects the dominance of either clastic quartz or clastic or interstitial calcite. Chemically the chief difference is in the lesser H_2O content, represented mineralogically in the dominance of hematite.

Two analyses, L and M, are of ironstone of the "Lahn-Dill" type, as contrasted to the "minette" type. The Lahn-Dill ironstone is a type example of the so-called exhalative-sedimentary class (Borchert, 1960b, p. 25; Oftedahl, 1958), produced by sedimentary deposition of materials derived from submarine volcanic and fumarolic activity. The Lahn-Dill ironstone, which includes both quartz-rich and calcite-rich varieties, has a distinctly lesser content of P_2O_5, Al_2O_3, and MgO than do ironstones of the normal minette type.

Two analyses, Q and R, are quartz-banded ores of the Dunderland belt of Norway. These rocks, which consist chiefly of interlayered quartz and crystalline iron oxides, are of early Paleozoic age and have been metamorphosed. Physically and mineralogically they are very similar to many of the Precambrian iron-formation rocks.

HEMATITIC IRON-FORMATION OF PRECAMBRIAN AGE

The hematitic variety (or subfacies) of the oxide facies (table 10) is one of the more common types of Precambrian iron-formation, though in some places there is some question as to the primary nature of the hematite. Edwards (1936) and Miles (1941), in discussing the now dominantly hematitic rocks of South and Western Australia, for example, note that much of the hematite is secondary after magnetite; according to Johnson (1962, p. 31), residual magnetite is present

TABLE 8.—*Analyses of oolitic limonite (goethite) ironstone*

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
SiO_2	8.60	17.75	25.03	5.39	8.64	8.44	7.83	10.40	6.55	3.45	10.45	23.85	14.32	3.90	9.25	13.77	6.90	5.12
Al_2O_3	3.72	3.38	4.60	4.32	4.89	5.27	4.62	7.89	6.91	3.56	5.28	7.57	5.20	3.34	4.6	4.77	4.72	3.25
Fe_2O_3	35.82	47.36	41.61	40.45	35.07	36.78	43.14	50.48	62.88	36.40	39.00	39.46	43.22	19.4	24.86	38.71	60.50	72.34
FeO	9.57	7.37	7.46	8.72	12.02	14.27	8.23	.93	.18	.18	.28	8.78	1.31	11.31	10.66	6.56	.604	.44
MnO	.39	.45	.39	.36	.33	.26	.34	.16	.38	.31	.33	.29	.36	1.58	1.4	.167	.20	-------
MgO	2.10	1.72	2.10	1.63	1.95	1.94	2.10	1.47	1.10	.58	.41	1.95	1.03	1.3	1.83	2.92	2.97	.61
CaO	15.90	5.25	4.85	15.13	14.05	11.30	12.75	7.67	6.06	27.08	20.07	4.91	14.66	26.3	21.1	11.18	6.70	5.98
H_2O+	6.84	8.23	7.68	7.20	7.16	7.78	7.94	11.64	10.24	6.56	7.59	8.23	7.99	--------	--------	([1])	7.06	4.90
H_2O-								1.66	[2]1.44	[2]1.60	[2]1.72	[2]1.85	[2]1.64	--------	--------	--------	.95	.32
TiO_2	--------	--------	--------	.17	--------	--------	--------	.19	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
P_2O_5	1.67	2.20	1.88	1.67	1.86	2.06	1.95	2.35	1.83	1.05	1.10	.96	1.35	.77	.85	.917	3.33	3.73
CO_2	15.10	6.08	4.67	15.00	13.84	12.04	12.00	2.52	3.33	20.64	15.11	3.26	10.32	--------	--------	[3]20.13	5.86	3.60
S	.18	.04	.07	.04	.07	.05	.07	--------	.004	.009	.045	.25	.032	.41	.27	.055	.048	-------
Subtotal	99.89	99.83	100.34	[4]100.18	99.88	100.19	100.97	[5]99.82	99.46	99.82	99.67	99.51	99.79	--------	--------	99.18	99.84	100.29
Less O for S	.09	.02	.03	.02	.03	.02	.03	--------	--------	--------	.02	.12	.02	--------	--------	.03	.02	-------
Total	99.80	99.81	100.31	[4]100.16	99.85	100.17	100.94	[5]99.82	99.46	99.82	99.65	99.39	99.77	--------	--------	99.15	99.82	100.92

[1] Included under CO_2.
[2] Not included in total. Reported as "hydration grad" in original reference.
[3] Includes H_2O.
[4] Total includes 0.08 percent V_2O_5, 0.02 percent As.
[5] Total includes 2.24 percent SO_3, 0.13 percent V_2O_5, 0.01 percent NiO, 0.08 percent C.

A–G. Minette ores of the "Grise," "Noire," and "Verte" horizons of Landres-Amermont basin, Lorraine: A–C from Coche and others, 1954; D–G from Cocke and others, 1955, analyses credited to Ecole de Mines, Nancy. Calculated modes as follows:

	A (Couche Grise)	B (Couche Noire)	C (Couche Verte)	D (Couche Grise)	E (Couche Grise)	F (Couche Grise)	G (Couche Grise)
Goethite	40.9	54.1	47.6	43 76	39.8	37.0	45.4
Siderite	10.3	9.2	5.5	13.17	9.2	10.3	8.7
Ankerite	2.1	--------	1.0	--------	--------	--------	--------
Chamosite	14.9	9.9	19.5	14.22	20.9	29.1	19.4
Calcite	23.2	5.9	4.5	22.71	23.4	17.5	19.1
Quartz	4.0	15.2	17.6	1.45	2.0	.7	2.9
Phosphate	3.7	5.0	4.1	5.67	4.4	4.8	4.3
Other	.9	.6	.5	1.40	.1	.3	1.1

H. Ore from the Lias-γ horizon, north Göttingen, Germany, between Harz and Solling (Harder, 1951, p. 465). H. Harder, analyst. Calculated mode· calcite, 4.9 percent, gypsum 4 8 percent, apatite 5.5 percent, goethite (with minor chamosite and siderite) 84 percent.

I–M. Minette ores of Luxembourg, stratigraphically assigned as follows: I, Rotes Haupt Lager 3; J, Gelbes Neben Lager 2a; K, Gelbes Haupt Lager 2; L, Braunes Lager I; M, Rotes Lager I. Separate values given in original reference for quartz and combined SiO_2. Quartz content of samples as follows: I, 0.05 percent; J, 0.11 percent; K, 6.46 percent; L, 11.46 percent; M, 8.90 percent. From Lucius (1945, table B); analyses by technical laboratory of Konzerns A.R.B.E.D.

N–O. Partial analyses of unweathered "* * * chamosite-siderite mudstone * * * crowded with limonite ooliths"; from Frodingham ironstone, North Lincolnshire, England. N is from "Appleby bore 2"; O is from Yarborough Pit. Analysis of separated limonite ooliths from this bed given in table 1, this report. Hallimond (1925, p 78); analyses by Frodingham Iron Co., Ltd.

P. Limonite oolite of Jurassic age (Corallian Beds), from East Kent, England (Lamplugh, Wedd, and Pringle, 1920, p. 225). Sample from drill core; analysis credited to E. O. Forster Brown.

Q–R. Mayville ironstone from the Neda Formation of Ordovician age, Mayville, Wisconsin (Hawley and Beavan, 1934, p. 505). Q is composite analysis of run-of-mine ore, made in 1925 by E. J. Wechter and Mayville Iron Co; R, by E. J. Beavan, analyst. Ore chiefly goethite and calcite, with a wide variety of other minerals in minor quantity.

TABLE 9.—*Analyses of hematite-rich sedimentary rocks of Paleozoic and Mesozoic age*

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
SiO_2	11.51	13.36	10.94	4.21	11.98	12.59	9.85	4.66	15.29	8.90	--------	2.59	46.79	13.60	30.82	19.08	34.35	36.32
Al_2O_3	6.85	7.89	3.72	4.38	5.13	5.71	3.23	3.05	9.63	2.79	--------	.75	.25	5.17	10.33	4.45	3.73	4.58
Fe_2O_3	29.90	29.62	42.88	37.72	75.90	75.12	67.79	52.08	44.17	66.55	52.83	52.56	50.80	55.56	43.13	55.48	50.41	43.47
FeO	12.08	2.69	7.67	7.27	(1)	(1)	10.03	21.17	19.38	1.13	--------	.88	.40	.23	.45	.18	1.17	2.35
MnO	.058	.33	.29	.18	.23	.06	--------	.78	.26	1.13	.81	.11	.01	.14	.21	.15	.39	.35
MgO	1.82	.93	5.90	1.68	.21	.42	0.37	1.14	1.45	1.39	5.70	.21	.02	1.49	1.01	2.05	.20	2.66
CaO	16.97	21.90	10.80	22.49	2.71	1.49	2.42	2.88	1.54	9.40	14.61	22.40	.80	10.26	2.16	7.14	3.85	4.25
Na_2O	.019	.014	.05	.01	--------	--------	--------	--------	.46	.15	--------	.05	.05	.07	.07	.07	1.1	1.7
K_2O	.30	.50	.02	.00	--------	--------	--------	--------	.08	.43	--------	.03	.04	1.22	2.36	1.05		
H_2O+	4.15	1.85	1.76	1.98	[2]1.86	[2]2.17	2.35	1.72	5.80	2.12	4.75	1.12	.27	1.88	4.78	1.87	.50	.64
H_2O-	.30	1.48	.12	.21	--------	.52	.32	.27	.83			.21	.08	.80	2.05	.67		
TiO_2	.39	.45	.14	.12	--------	.27	.40	.28	--------	--------	--------	.1	.05	.22	.34	.20	.23	.32
P_2O_5	1.27	2.35	.71	1.00	2.02	1.63	2.26	2.11	1.07	1.02	.32	.084	.12	1.80	1.34	1.41	.46	.55
CO_2	11.97	14.59	14.98	18.62	--------	--------	1.05	10.78	.43	5.73	18.14	18.50	.06	7.36	.10	6.02	2.9	2.8
S	.10	.32	--------	.00	.03	.00	--------	--------	--------	--------	--------	.31	.028	.03	.02	.03	.04	.19
SO_3	1.90	1.05	.00	.00	--------	--------	--------	--------	--------	1.31	.32	.009	.17	.00	.00	.00	--------	--------
C	.38	.33	--------	--------	--------	--------	--------	--------	--------	[3].38	[3]1.30	.08	.09	--------	--------	--------	--------	--------
Subtotal	[4]100.13	[5]99.93	[6]100.03	99.87	100.07	99.98	100.07	100.92	100.39	102.43	98.78	100.12	[8]100.14	99.83	99.17	99.85	99.33	100.18
Less O	.05	.16	.03	--------	.02	--------	--------	--------	--------	--------	--------	.15	.01	.02	.01	.02	.02	.10
Total	[4]100.08	[5]99.77	[6]100.00	99.87	100.05	99.98	100.07	100.92	100.39	102.43	98.78	[7]99.97	[8]100.13	99.81	99.16	99.83	99.31	100.08

[1] All iron reported as Fe_2O_3.

[2] Reported as "loss on igition"; includes CO_2.

[3] "Organic matter".

[4] Total includes 0.116 percent V_2O_5, 0.001 CoO, 0.05 NiO.

[5] Total includes 0.28 percent V_2O_5.

[6] Total includes 0.05 percent F.

[7] Total includes 0.05 percent V_2O_5, 0.08 percent B_2O_3.

[8] Total includes 0.015 percent V_2O_5, 0.1 percent B_2O_3.

A–B. Oolitic hematite in chamosite-siderite matrix, from the Lias (Lower Jurassic) of north Göttingen (Harder, 1951, p. 463–464); analyses by H. Harder. Calculated modes as follows, in percent:

	A	B
Hematite	46	54
Calcite	24.83	32.09
Chamosite	15	4
Siderite	12.52	1.25
Apatite	3.00	5.53
Gypsum	4.09	2.27
Pyrite	.17	.60
Humus	.65	.56

C. Oolitic hematite of Westmoreland bed of the Clinton Group (Silurian), Kirkland, N.Y. Rock is dominantly hematite and calcite. Analysis by Paula M. Buschman, U.S. Geological Survey. Sample F-2640, collected by R. P. Sheldon.

D. Hematitic ironstone, from base of Keefer Sandstone of Clinton Group (Silurian) age. Sample F-2635, collected by R. P. Sheldon from road cut 1 mile south of Allenwood, Pennsylvania; analysis by Paula M. Buschman, U.S. Geological Survey. Sample consists of hematite, calcite, dolomite, minor quartz.

E–F. Dominion bed (Lower Ordovician), Wabana, Newfoundland. Analysis E by Nova Scotia Steel and Iron Co.; analysis F by T. G. McFarlane. Reported as analyses C and D in Hayes (1915, p. 45), from "average" samples of Zone 2. Specific gravity of No. F is 4.10. Average mode for analyses E and F in percent: hematite 65.5 percent; chamosite 23.9 percent; phosphate (shell fragments) 4.4 percent; quartz 6.0 percent (Hayes, 1915, p. 47).

G–H. Ore bed of zone 4, Wabana, Newfoundland. Analysis G of lower part of ore zone 4, specific gravity 4.23; analysis H is of upper part of ore zone 4. A. V. Seaborn, analyst, as reported by Hayes (1915, p. 52–53).

I. Ore bed of zone 4 (lower part), Wabana, Newfoundland. C. O. Hayes (1915, p. 53), analyst. Oolitic hematite and chamosite.

J. Rhubina hematite (Carboniferous), South Wales. Analysis made in laboratories of Geological Survey of Great Britain; quoted by Hallimond (1925, p. 85). Oolitic hematite with abundant shell fragments. As given by Hallimond, analysis is divided into two parts. The first is of the "soluble part," with 10.36 percent reported as insoluble residue; the second is of the ignited insoluble residue. The total for the first (including 10.36 percent insoluble) is 101.72 percent; the total for the second is 11.07 percent.

K. Cheadle hematite (Carboniferous), Froghall, North Staffordshire, England. Massive hematite with calcite and dolomite. Partial analysis made in laboratory of Geological Survey of Great Britain; reported by Hallimond (1925, p. 86). Total includes 0.04 percent insoluble.

L. Hematite-calcite ore (Devonian), Koenigszug mine, Lahn-Dill region, Germany (Harder, 1954, p. 60). H. Harder, analyst. Sample contains about 0.001 percent NiO, and less than 0.0005 percent CoO.

M. Hematite-quartz ore (Devonian), Constanze mine, Lahn-Dill region, Germany (Harder, 1954, p. 61). H. Harder, analyst. Sample contains about 0.005 percent NiO, less than 0.0005 percent CoO.

N. Oolitic hematite with chamosite, calcite, dolomite, and quartz. From the Martin Formation of Devonian age, Gila County, Ariz. (Willden, 1961). Sample F-2726, analysis by Paula M. Buschman, U.S. Geological Survey. Sample represents the upper 6 feet of the bed (see also Willden, 1960, p. B21–B23).

O. As above. Sample G-2892; represents lower foot of the ore bed; may be slightly oxidized.

P. As above. Sample F-2727, representing 6.2 feet of beds.

Q. Quartz-banded hematite ore, Ørtrann mine, Dunderland, Norway (Bugge, 1948, table 1, borehole sample 115/II). Late Cambrian or Early Ordovician age. Rock contains 48.6 percent hematite, 3 percent magnetite. Analysis made in laboratories of Rana Gruber A/S (Company).

R. Quartz-banded hematite ore, same locality, reference, and analyst as for Q, borehole sample 122/III. Rock contains 38.8 percent hematite, 7 percent magnetite.

in some of the dominantly hematitic rocks of the Cauê Itabirite of Brazil.

The hematitic iron-formation consists of thin layers or laminae of hematite alternating with those of recrystallized chert. In the Lake Superior region, at least, the layers pinch and swell to give rise to "wavy bedded" iron-formation. Oolitic textures are typical of such rock (James, 1954) and are preserved even in areas of moderate to strong metamorphism (James and others, 1961, p. 44–45).

Chemically, the rock is remarkable in its simplicity; SiO_2 and Fe_2O_3 generally account for all but a small percentage of the total. In contrast to hematitic and limonitic rocks of younger age, the phosphorus content is very low—rarely as much as 0.1 percent.

MAGNETITE-RICH ROCKS OF MESOZOIC AND PALEOZOIC AGE

Magnetite-bearing facies are not common in rocks of post-Precambrian age, but they have been described as minor rock types in several unmetamorphosed ironstones. The characteristic occurrence of magnetite in ironstones of the minette type (table 11, analyses A to G) is as fine granules or small crystals of diagenetic origin, clustered within limonite or chamosite ooliths. As Taylor (1949, p. 83) states with respect to magnetite in the Northampton sand ironstone (analysis G):

> Clearly it was not formed normally as a result of the alternation between oxidizing and reducing conditions. This is shown by its complete absence between concentric skins of chamosite and limonite in the ooliths.

Magnetite in the chloritic ironstones of early Paleozoic age in Brittany, Normandy, and Wales (represented by analysis H) may be a metamorphic mineral, the by-product of conversion of an original iron-rich chlorite to chlorite of lower iron content (Pulfrey, 1933).

Analyses I and J are from the same district as analyses Q and R (table 9), the Dunderland belt of Norway. As in the hematitic rocks of that area, the

TABLE 10.—*Analyses of hematite-rich rocks of sedimentary origin, Precambrian age*

[All rocks have been moderately metamorphosed]

	A	B	C	D	E[1]	F[1]	G	H	I	J	K
SiO_2	44.80	39.72	46.81	37.54	40.1	28.30	46.94	51.56	56.23	39.3	51.4
Al_2O_3	.37	.45	.49	.80	.8	3.86	.00	Tr	.45	<.5	<.5
Fe_2O_3	53.08	58.58	46.91	50.41	50.1	63.39	51.00	47.48	34.96	60.1	47.8
FeO	.71	1.03	5.03	10.17	1.6	2.57	1.41	.90	5.67	.3	.4
MnO	Tr	.00	Tr	.00	.2	.00	.02	---	.07	---	---
MgO	.07	.07	.36	.19	2.0	.56	.00	.00	1.13	<.1	<.1
CaO	.28	.03	.14	Tr	1.4	.86	Tr	.00	.81	<.1	<.1
Na_2O	.12	.07	.13	.03	---	---	.00	---	.15	---	---
K_2O			.03					---	.12	---	---
H_2O+	.04	.28	.28	.26	---	.72	.68	---	.49	.3	.1
H_2O-	.03	.02	.04	.02	---	---	---	---	.03	---	---
TiO_2	.07	Tr	Tr	Tr	---	.00	.00	---	.02	---	---
P_2O_5	---	.02	---	.03	.07	.085	.39	---	05	.03	.12
CO_2	---	.40	---	.58	2.6	---	---	---	.06	---	---
S	---	---	---	---	.009	---	---	---	---	---	---
SO_3	---	.03	---	.02	---	---	---	---	---	---	---
Total	99.57	[2]100.70	[3]100.22	100.05	98.9	100.34	100.44	99.94	100.24	---	---

[1] Samples dried at 100° C. before analysis.
[2] Given as 100.60 in original reference.
[3] Given as 100.19 in original reference.

A–B. Banded specularite iron-formation, Krivoi Rog Series, Ukraine, U.S.S.R. (Semenenko and others, 1956, p. 95). Analysis A by S. A. Panchenko; analysis B made in laboratories of Ukranian Geologic Administration.

C–D. Hematite-magnetite iron-formation, Krivoi Rog Series, Ukraine, U.S.S.R. (Semenenko and others, 1956, p. 101). Analysis C by P. P. Makhovka; analysis D made in laboratories of Ukranian Geologic Administration.

E. Hematite iron-formation, Menominee district, Michigan. Composition as recast by James (1954, p. 260; error in P_2O_5 content corrected) from commercial analysis. Representative of shipment of 13,417 tons. Sample dried at 100° C. before analysis. Approximately 47 percent hematite, 40 percent quartz, 5 percent dolomite, 5 percent magnetite, 3 percent kaolin and chlorite.

F. Banded ironstone ("calico rock") of the Swaziland System, Umhlatuzi Valley Zululand, South Africa (Wagner, 1928, p. 71). Name of analyst not given.

G. "Hematite quartzite", Camel Hill, Middleback Ranges, Australia (Edwards, 1953, p. 468). Edwards(?), analyst.

H. Banded ironstone of the Hospital Hill Slate Zone, Witswatersrand System. Johannesburg, South Africa (Wagner, 1928, p. 73). Name of analyst not given.

I. Specularite-magnetite iron-formation, Atlantic City district, Wyoming (Bayley, 1963, p. 10). Chip sample taken from about 200 feet of outcrop. Dorothy F. Powers, analyst, U.S. Geological Survey.

J–K. Banded chert-specularite, Cauê Itabirite, Minas Gerais, Brazil. (J. V. N. Dorr II, written communication of December 12, 1963). Samples are composites of 25–75 chip samples; dried at 110° C. before analysis. Selected from 10 analyses, which show SiO_2 range of 36.3 to 51.4 percent (average 44.2), Fe_2O_3 range of 47.8 to 63.6 percent (average 54.9). M. B. J. Fernandes, analyst.

TABLE 11.—*Analyses of magnetite-rich sedimentary rocks of Mesozoic and Paleozoic age*

	A	B	C	D	E	F	G	H	I	J
SiO_2	3.2	3.4	4.8	7.03	8.20	15.63	6.2	[1]12.90	35.6	35.94
Al_2O_3	2.2	3.2	4.7	7.13	4.77	7.92	5.9	3.66	4.76	4.49
Fe_2O_3	30.3	20.9	44.1	32.56	14.90	16.21	18.2	34.14	32.73	34.46
FeO	38.3	18.8	24.9	25.92	33.69	32.82	34.8	32.90	14.84	14.99
MnO	.19	.31	.21	.22	.32	---	.3	---	.26	.31
MgO	2.1	1.0	1.2	1.82	1.80	.25	2.4	1.00	2.17	3.04
CaO	4.6	28.2	6.4	2.84	12.45	2.62	4.6	5.00	4.84	3.55
Na_2O	Tr	---	---	---	---	---	---	---	1.2	1.6
K_2O		---	---	---	---	---	---	---		
H_2O+	3.1	3.1	9.4	4.88	5.60	7.82	4.6	[2]7.90	.50	.3
H_2O-				6.20		---	1.3			
TiO_2	Tr	---	---	---	---	1.55	---	---	.38	.32
P_2O_5	1.14	1.4	2.1	1.57	1.72	6.33	1.8	2.25	.44	.55
CO_2	13.0	19.2	1.0	9.38	15.80	8.33	19.0	---	1.86	1.12
S	.55	---	---	.02	.42	.17	.10	.25	.08	.23
SO_3	---	---	---	---	---	---	.04	---	---	---
C	1.1	---	---	.56	---	---	---	---	---	---
Subtotal	99.91	99.51	98.81	100.13	99.67	99.65	99.24	100.00	99.66	100.90
Less O	.28	---	---	.01	.21	.09	.05	.13	.04	.12
Total	[3]99.63	99.5	98.8	100.12	99.46	99.56	99.2	99.87	99.62	100.78

[1] Reported as "clay and silica."
[2] Reported as "Loss on ignition (carbonic acid, organic matter, etc.)."
[3] Total includes 0.05 percent As, 0.05 percent Zn, 0.03 percent V.

A–C. Magnetite oolite in minette ores of Jurassic age of the Lorraine basin, France (Hoehne, 1955). Sample A from Angevillers; samples B and C from Amermont.

D. Magnetite ironstone of Jurassic age (Upper Lias, Dogger Seam), West Rosedale, Cleveland district. England. Quoted by Lamplugh and others (1920, p. 60) as an average of many analyses of the Dogger, or Top, Seam.

E. Magnetite-siderite ironstone, Couche Grise, of Aalenien (Jurassic) age, Lorraine, France. Mode: Quartz <1 percent, siderite 25.1 percent, magnetite 21.6 percent, phosphate 3.8 percent, calcite 14.3 percent (Deudon, 1955, p. 478). Analysis made in mineralogical laboratory, Facultés des Sciences de Toulouse.

F. Calcitic chamosite-magnetite-siderite ironstone of Dogger (Middle Jurassic) age. Analysis by C. Schmidt. Erzegg-Planplatte region, Switzerland (Deverin, 1945, p. 42). Specific gravity 3.24.

G. Siderite-magnetite-chamosite, Northampton sand ironstone, Middle Jurassic age. Easton Neston, England (Taylor, 1949, p. 60). Calculated mode: Sideritic carbonate 48.5 percent, magnetite 26.4 percent, chamosite 18.9 percent, phosphate 4.0 percent (Taylor, 1949, p. 63). Analyst, C. O. Harvey, Geological Survey of Great Britain.

H. Oolitic magnetite ironstone of Cambrian age. Gareg-fawr mine, Carnarvonshire, Wales (Strahan and others, 1920, p. 24): analysis made by "Dr. Price of Newport."

I. Banded magnetite-quartz rock, Late Cambrian or Early Ordovician age, Ørtvann mine, Dunderland, Norway (Bugge, 1948, table 1, borehole sample 131/II). Rock contains 47 percent magnetite, 0.6 percent hematite. Analysis represents 2.5 m of core. Analyst not specified; analysis presumably made in laboratories of Rana Gruber A/S (Company).

J Banded magnetite-quartz rock, same locality as sample I (Bugge, 1948, table 1, borehole 123). Rock contains 48 percent magnetite, 1.5 percent hematite. Analysis represents 9 m of core. Analyst not specified; analysis presumably made in laboratories of Rana Gruber A/S (Company).

magnetite-rich rocks are interlayered with quartz and are more like Precambrian iron-formation than they are like the normal minette type.

Except for the quartz-banded ores (analyses I and J), the rocks are not different chemically in any significant respect from the hematitic ironstones, other than in ferrous-ferric ratio.

MAGNETITE-RICH IRON-FORMATION OF PRECAMBRIAN AGE

The magnetite-banded rocks, as represented by analyses A, B, D, E, F, G, and L in table 12, are one of the major types of Precambrian iron-formation. They consist of layers alternately quartz-rich and magnetite-rich. Both chemically and mineralogically the magnetite facies is more complex than the hematite facies with which it commonly is associated. The rock generally contains appreciable quantities of siderite and an iron silicate (greenalite, minnesotaite, stilpnomelane, chlorite), reflected chemically in the significant content of CO_2, MgO, and to a lesser degree, Al_2O_3. The rocks are notably lower in Al_2O_3, CaO, and P_2O_5 than magnetite-bearing rocks of younger age (table 11).

Analyses H to K are of South African rocks from stratigraphically widely separated positions in the Precambrian. Of interest and importance is the occurrence of chamositic rocks (particularly analyses J and K), physically and chemically more closely allied to the post-Precambrian magnetite facies than to the more typical cherty rocks of the Precambrian. The age of the Pretoria Series of the Transvaal System, in which chamositic rocks occur, is believed to be about 2,000 million years (Nicolaysen, 1962, p. 580, 582).

SILICATE FACIES

The silicate facies comprises those rocks in which the primary silicates chamosite, greenalite, and glauconite are dominant, plus those in which minnesotaite, iron-rich chlorite, or stilpnomelane—probably metamorphic in origin—are major constituents.

CHAMOSITIC IRONSTONE

The chamositic rocks are one of the most characteristic facies of the post-Precambrian ironstones (table 13). In some districts they grade into or are interbedded with limonite (or hematite) oolite; in others they grade into or are interbedded with sideritic rocks.

The rocks typically are oolitic, but most do not exhibit chemical heterogeneity to the degree shown by

TABLE 12.—*Analyses of magnetite-rich ironstones of Precambrian age*

	A	B	C	D[1]	E[1]	F[1]	G[1]	H	I	J	K	L
SiO_2	34.44	35.86	2.56	51.52	45.66	39.50	22.70	42.10	50.90	19.05	5.84	47.2
Al_2O_3	.85	1.57	6.20	.08	.28	.44	.31	4.65	6.25	6.60	4.40	1.6
Fe_2O_3	30.54	38.56	21.54	35.37	19.16	29.21	22.07	22.15	20.00	41.30	42.03	38.5
FeO	22.06	20.26	26.57	10.24	21.28	18.51	23.20	17.83	14.40	22.70	34.35	10.1
MnO	.21	.16	.04	----	----	.12	1.06	3.35	.85	.25	.90	----
MgO	2.30	1.74	6.95	.20	2.73	2.00	3.88	2.25	2.00	1.25	.90	1.3
CaO	1.72	.51	1.85	.02	1.04	2.71	4.49	1.00	.85	1.25	1.50	.8
Na_2O	.00	.02	.60	----	----	----	----	----	----	----	----	----
K_2O	.13		1.10	----	----	----	----	----	----	----	----	----
H_2O+	.44	.60	5.66	1.48	1.54	----	----	.75	1.30	5.50	2.90	----
H_2O-	.17	.06	.53	(1)	(1)	(1)	(1)			.65	.28	----
TiO_2	.02	.04	.27	----	----	.040	.014	.15	.30	.15	.26	----
P_2O_5	.07	.14	----	.060	.085	----	----	.05	.05	.20	1.19	[2] .22
CO_2	7.36	.60	3.99	1.06	7.54	6.22	21.18	4.90	1.10	.60	4.75	----
S	.01	----	----	----	----	.129	.005	.10	.15	.25	.08	.007
SO_3	.00	.17	----	----	----	----	----	----	----	----	----	----
C	.04	----	----	.00	.12	[3] .017	[3] .016	----	----	----	----	----
Subtotal	100.36	100.29	99.86	100.03	99.44	[4] 98.90	98.92	[5] 99.28	[6] 98.15	99.75	99.38	99.7
Less O	.01	----	----	----	----	.06	----	.05	.08	.13	.04	----
Total	100.35	100.29	99.86	100.03	99.44	98.84	98.92	99.23	98.07	99.62	99.34	99.7

[1] Samples dried at 100° C. before analysis.
[2] Calculated from 0.088 P.
[3] "Organic C."
[4] Given as 99.90 in original reference.
[5] Given as 99.30 in original reference.
[6] Given as 97.85 in original reference.

A. Banded magnetite iron-formation, Ironwood Iron-Formation, Gogebic district, Michigan (Huber, 1959, p. 100); Lucile N. Tarrant, U.S. Geological Survey, analyst. Calculated mode: Magnetite 44.3 percent, quartz 31.3 percent, sideritic carbonate 17.5 percent, minnesotaite 6.0 percent, excess constituents 1.3 percent. Sample represents 11 feet of drill core.

B. Banded magnetite-quartz rock with minor chlorite, siderite, and cummingtonite. Saksagan (Krivoi Rog) Series, Ukraine, U.S.S.R. (Semenenko and others, 1956, p. 105); O. I. Dokhlenko, analyst.

C. Magnetite-stilpnomelane rock, with minor cummingtonite and carbonate, middle suite of Krivoi Rog Series. From northern part of Saksagan band, U.S.S.R. (Aleksandrov and Zmeenkova, 1958, p. 79); A. V. Zmeenkova, analyst.

D–E. Banded magnetite chert from the Lower Cherty division of Biwabik Iron-Formation, Mesabi district, Minnesota (Gruner, 1946, p. 58–59); analyses by Mines Experiment Station, University of Minnesota; W. E. Apuli, chief chemist. Analysis D is one of 5 given by Gruner of magnetite-rich rock cut by drill hole near Aurora; sample represents 30 feet of core. Analysis E is one of 6 given by Gruner for magnetite-rich rock cut by drill hole near Hibbing; sample represents 20 feet of core. Rocks mostly magnetite and quartz, with siderite and iron silicates (greenalite, minnesotaite, stilpnomelane) in lesser amounts.

F–G. Magnetite chert member of Temiscamie Iron-Formation, Lake Albanel district, Quebec, Canada (Quirke, 1961, p. 312; see also Quirke, Goldich, and Krueger, 1960). Each sample represents 58 feet of core from drill hole. Analysis of major elements by Cleveland-Cliffs Iron Co; CO_2 and C by Mines Experiment Station, University of Minnesota.

H. Magnetite-siderite slate, South Africa. From uppermost part of Pongola beds, Swaziland System (Wagner, 1928, p. 69); analyzed in the Government Chemical Laboratory, Johannesburg. Sample is composite of 37 taken across 40-foot bed in southeastern Transvaal. Reported to contain some chamosite. Specific gravity 3.41.

I. Shaly magnetite ironstone, same locality as H but stratigraphically 40 feet higher (Wagner, 1928, p. 69). Analysis is of a composite sample representing a 20-foot thickness. Analyzed in the Government Chemical Laboratory, Johannesburg.

J. Arenaceous oolitic magnetite-chamosite ironstone (Wagner, 1928, p. 85). From "Magnetic Quartzite Iron Horizon," Pretoria Series. Sample from core of hole drilled near Pretoria, S. Africa; H. G. Weall, analyst. Calculated mode (main constituents): quartz 11.2 percent, magnetite 35.2 percent, hematite 17.0 percent, chamosite 28.6 percent, calcite 1.4 percent (Wagner, 1928, p. 86).

K. Oolitic magnetite-chamosite-siderite ironstone (Wagner, 1938, p.92). From "Clayband Horizon," Pretoria Series. Sample from core of hole drilled near Pretoria, S. Africa. Calculated mode (main constitutents): magnetite 60.9 percent, chamosite 22.0 percent, siderite 12.5 percent, phosphate 0.6 percent (Wagner, 1928, p. 93). Major elements determined in "laboratory of the Gutehoffnungshutte"; CO_2 and H_2O determined by Government Chemical Laboratory, Johannesburg.

L. Magnetite-quartz rock (Krishnan, 1952, p. 524), average of "large number of samples." From Kanjamalai deposit, Madras State, India.

TABLE 13.—*Analyses of chamositic ironstones*

[See also chamositic siderites]

	A	B	C	D	E	F	G	H	I	J	K	L	M
SiO_2	21.78	16.24	49.64	42.76	13.4	13.70	6.60	26.00	26.20	41.80	16.22	15.60	32.04
Al_2O_3	10.67	8.09	8.82	7.82	7.4	9.04	5.27	14.50	15.71	16.18	7.65	6.96	13.24
Fe_2O_3	6.20	5.10	8.71	12.47	8.5	15.15	24.76	2.03	3.70	4.28	2.99	2.24	2.01
FeO	22.70	15.12	16.70	16.29	31.9	36.47	23.34	29.03	28.45	24.28	35.38	18.25	24.32
MnO	.08	.26	.23	.091	-----	-----	-----	-----	1.67	1.86	3.12	.56	.13
MgO	3.61	2.41	3.19	.61	2.5	2.26	.97	3.67	1.36	.43	1.84	8.83	2.78
CaO	12.25	24.15	2.10	1.44	6.1	6.48	19.60	7.30	6.50	1.00	4.01	17.64	8.26
Na_2O	.08	.32	-----	.12	-----	-----	.52	-----	-----	-----	-----	.01	.05
K_2O	.09	.024	-----	.63	-----	-----		-----	-----	-----	-----	.02	.23
H_2O+	8.36	6.00	5.09	7.23	4.9	6.31	4.27	9.68	7.90	8.44	2.61	3.38	5.60
H_2O-	1.01	.51	(1)	5.66	3.6	(1)	(1)	(1)			.78	.14	.37
TiO_2	.53	.75	-----	.50	-----	.62	.31	.87	.10	.05	.61	.18	.70
P_2O_5	1.62	1.53	.91	.30	2.8	1.75	1.21	1.34	3.93	1.12	4.91	.80	.97
CO_2	8.45	18.04	5.15	3.37	17.4	8.95	13.32	4.85	3.00	.00	16.64	24.99	8.42
S	.22	.59	.72	[2] .043	.5	-----	-----	-----	[3] 1.39	[3] .56	-----	-----	-----
SO_3	1.47	.01	-----	-----	-----	-----	-----	-----	-----	-----	-----	.00	.00
C	.50	.63	-----	.98	-----	-----	-----	-----	-----	-----	-----	-----	-----
Subtotal	[4] 99.96	[5] 99.99	101.36	100.31	99.0	100.73	100.17	99.27	99.91	100.00	96.76	[6] 99.96	[7] 99.56
Less O	.11	.30	.36	.02	.3	-----	-----	-----	-----	-----	-----	.15	.19
Total	[4] 99.85	[5] 99.69	101.00	100.29	98.7	100.73	100.17	99.27	99.91	100.00	96.76	99.81	99.37

[1] Samples apparently dried before analysis.

[2] Reported as S_2.

[3] FeS_2.

[4] Total includes 0.23 percent V_2O_5, 0.05 percent B_2O_3, 0.06 percent NiO.

[5] Total includes 0.17 percent V_2O_5, 0.04 percent NiO, 0.004 percent CoO.

[6] Includes 0.36 percent F.

[7] Includes 0.44 percent F.

A. Chamosite ironstone from the Lias (Lower Jurassic) of north Göttingen, Germany (Harder, 1951, p. 460–462). Rock contains about 72 percent chamosite, 16 percent calcite.

B. Calcitic chamosite ironstone, same locality and reference as above. H. Harder, analyst. Rock contains about 53 percent chamosite, 39 percent calcite.

C. Arenaceous chamosite ironstone of the "Couche Noire" of Middle Jurassic (Aalenian) age, Landres-Amermont basin, Lorraine, France (Coche and others, 1954). Analysis by laboratory of Ecole des Mines, Nancy. Rock contains about 38 percent chamosite ("chlorite"), 37 percent clastic quartz, 10 percent siderite, 10 percent limonite.

D. Arenaceous green chamosite oolite of Early Jurassic (Lias) age, Rödingeberg, Sweden (Palmqvist, 1935, p. 69). Sven Palmqvist, analyst. SiO_2 value divided into "sand" 28.79, percent, "SiO_2 (sol.)" 12.38 percent, "SiO_2" 1.59 percent; Al_2O_3 value divided into "Al_2O_3" 6.46 percent, "Al_2O_3 (clay)" 1.36 percent.

E. Chamosite oolite, Northampton sand ironstone, of Middle Jurassic (Inferior Oolite) age, (Taylor, 1949, p. 60). G. A. Sergeant, analyst, Geological Survey of Great Britain. From Lodge Pit, near Irchester, Northamptonshire, England. Rock contains about 36 percent chamosite, 10 percent goethite, remainder mostly sideritic carbonate.

F–H. Chamosite oolite, Chamosentze, Switzerland, of Middle Jurassic (Dogger) age (Déverin, 1945, p. 24). C. Schmidt, analyst. Average mode for 3 analyses includes chamosite 40 percent, magnetite 14 percent, quartz 13 percent, siderite 11 percent, calcite 10 percent.

I. Oolitic ironstone, quarry near Llangoed, Anglesey, Wales (Strahan and others, 1920, p. 14; see also Pulfrey, 1933, for mineralogic descriptions). E. J. Morris and W. E. Williams, analysts. Ordovician.

J. Oolitic ironstone, Bonw, Mynydd-y-Garn, Anglesey, Wales (same analysts as samples F–H; Strahan and others, 1920, p. 15). Ordovician.

K. Oolitic chamosite, Zone 4, Scotia bed, Wabana, Newfoundland (Hayes, 1915, p. 58). A. O. Hayes, analyst. Ordovician. Specific gravity of rock 3.50.

L. Oolitic chamosite, uppermost 6 inches of Westmoreland bed of Clinton Group (Silurian), Westmoreland, New York. Sample F 2639, collected by R. P. Sheldon; analysis by Paula M. Buschman, U.S. Geological Survey. Modal analysis given in Hunter, 1960, p. 104 (see footnote, p. W7) as follows: Hematite and masked chamosite—9.9 percent; chamosite—36.8 percent; calcite, dolomite, siderite—45.9 percent; pyrite—1 percent; quartz—6.0 percent; collophane—0.4 percent.

M. Oolitic chamosite, uppermost 6 inches of Keefer Sandstone of Clinton (Silurian) age, Piato, Allegheny County, Maryland. Sample F 2642, collected by R. P. Sheldon; analysis by Paula M. Buschman, U.S. Geological Survey. Modal analysis given in Hunter, 1960, p. 104 (see footnote, p. W7), as follows: Chamosite—48.4 percent; Calcite, dolomite, siderite—22.8 percent; pyrite—0.2 percent; quartz—11.6 percent; argillaceous matrix—17.0 percent.

the limonitic and hematitic oolitic ironstones. Nevertheless, they have a wide range in mineralogic and chemical makeup, attributable in part to the amount of clastic material—mostly quartz, calcite, or dolomite—and in part to extensive diagenetic modifications such as development of siderite and magnetite. The rocks are dominantly ferrous, but the chamosite ooliths themselves often contain concentric skins of oxidized material that represent interludes of higher Eh of the bottom environment during accumulation. As is to be expected, the Al_2O_3 content is higher than in most other types of ironstone, and to a considerable degree the chamosite can be considered a product of sea-bottom reactions between ferrous iron in solution with detrital clay particles. The replacement of clastic material by chamosite indicates, however, that the process of formation was not simply that of clay diagenesis. In the Northampton sand ironstone the process of iron enrichment of clay to produce chamosite was locally reversed, with the production of kaolinite that partly retains the oolitic form of chamosite (Taylor, 1949, p. 32).

SILICATE IRON-FORMATION OF PRECAMBRIAN AGE

Most of the analyses listed in table 14 are of rocks that have been metamorphosed to some degree. Of the Precambrian rocks, only that from the Roper River (analysis H) can be considered to be essentially in unaltered form; those from the Mesabi district (analyses A-C) are weakly metamorphosed, with the partial conversion of greenalite to minnesotaite and stilpnomelane; that from the Gogebic district (analysis F) is slightly more metamorphosed, with complete loss of original greenalite. Grunerite- and garnet-bearing rocks, representing a higher degree of metamorphism, are arbitrarily excluded in the tabulations.

Most of the rocks consist of quartz (recrystallized chert) in layers alternating with silicate-rich layers that generally contain significant amounts of magnetite and siderite. An exception is represented by analyses D and E, in which quartz, chlorite, siderite, and magnetite occur as fine-grained intergrowths in a laminated rock. The rock, though rich in iron, does not resemble normal iron-formation, and the bulk chemistry can be matched by that of some of the younger chamositic ironstones.

Aside from analyses D and E, the Precambrian silicate rocks are strikingly different in chemical composition from the chamositic ironstones of younger age. Most notable is the much higher content of SiO_2 (original chert) and much lower contents of Al_2O_3 and P_2O_5.

Also included in the tabulation is the analysis of an unusual greenalite-chert rock of Ordovician age (analysis L).

GLAUCONITIC ROCKS

Glauconite, (see table 15) though of widespread occurrence as a minor constituent of ironstones, rarely forms discrete deposits with ironstone associations. An exception is the Seend ironstone of England, represented by analysis I. Most of the larger glauconite deposits (greensands), such as those of New Jersey, have been studied as sources of potash rather than iron. Nevertheless, in the ironstone districts, glauconite as a disseminated mineral bears definite facies relation to other iron minerals. The oolitic hematite-chamosite ironstones of the Clinton Group, for example, are shown by Hunter (See footnote p. W7) to grade to the east into semicontinental hematitic sandstone and to the west into glauconite-bearing marine strata.

The compositions of the glauconitic rocks (table 15) have a wide range, in considerable part due to the variable proportions of clastic material, interstitial calcite, and secondary siderite. Though glauconite, like chamosite, probably in large part originates by reactions between solids and sea water, the actual accumulation into deposits is accomplished by transport and deposition of granules and pellets, along with more usual clastic components. The typical glauconite is dominantly ferric and—depending upon its "maturity"—with a substantial content of K_2O (see table 5). The compositions of the Gulf Coast greensands (analyses E-H, table 15) are therefore unusual, in that the rocks are more ferrous than normal glauconitic rocks and have a very low content of K_2O. In part the ferrous aspect is due to secondary siderite, but this can account only partially for the relatively low ferric-ferrous ratio. The rocks are also high in Al_2O_3. Evidently the pelletal material making up these greensands is far removed from the ordered mica structure of ideal glauconite; quite possibly it includes some chamosite. The association glauconite-chamosite is not particularly common, but it has been described. Chillingar (1956) reviews several occurrences of glauconite and chamosite in the U.S.S.R. Of interest is the extremely low content of K_2O (0.14 percent) of a chamosite-bearing glauconite of Mesozoic age (Chillingar, 1956, p. 495).

CARBONATE FACIES

Aside from the "blackband" and "clayband" siderites, which are discussed later, the rocks included in the carbonate facies are divided into those of Precambrian and post-Precambrian age. These groups are strikingly different in chemical composition and physical character, but they bear entirely comparable facies

TABLE 14.—*Analyses of silicate iron-formation, mostly Precambrian*

	A	B	C	D	E	F	G	H	I	J	K	L
SiO_2	50.96	42.48	65.42	51.18	48.11	29.35	38.51	30.26	52.18	38.85	45.10	71.08
Al_2O_3	1.09	.53	.08	11.95	3.27	.70	2.70	2.26	3.08	2.23	2.16	.55
Fe_2O_3	5.01	5.63	4.19	8.09	13.62	4.41	13.57	16.47	18.30	13.20	17.41	.78
FeO	30.37	33.76	23.63	12.15	16.69	39.51	21.47	37.00	16.68	26.58	20.83	18.53
MnO	.00	----	----	2.71	3.27	1.02	1.81	.78	----	.57	.47	.00
MgO	5.26	4.29	2.45	2.42	2.91	3.81	3.53	2.09	4.36	2.02	1.81	.18
CaO	.04	----	----	1.12	.80	2.10	3.55	Tr	2.90	2.09	2.66	Tr
Na_2O	.00	----	----	2.12	.24	.00	.01	.16	.58	.11	.12	----
K_2O	.00	----	----	1.86	2.32	.00	.09	.14		.11		----
H_2O+	6.41	4.80	4.16	1.19	1.74	2.79	----	8.73	[1].94	.59	.67	6.40
H_2O-	.75	(2)	(2)	.07	.44	.06	----	2.15		----	----	
TiO_2	----	----	----	.51	.52	.01	.144	.03	----	.15	.10	.13
P_2O_5	.00	----	----	.54	.44	.14	----	.01	.28	.23	.18	----
CO_2	.00	7.44	Tr	3.70	5.62	16.37	12.70	Tr	(1)	13.52	8.52	.44
S	Tr	----	----	----	----	.06	.005	----	[3].32	.37	.59	----
C	.21	----	----	----	----	.08	.027	----	----	----	----	----
Subtotal	100.10	98.93	99.93	99.61	99.99	100.41	98.12	100.08	99.62	[4]100.87	[5]100.85	98.09
Less O	----	----	----	----	----	.03	----	----	----	.19	.28	----
Total	100.10	98.93	99.93	99.61	99.99	100.38	98.12	100.08	99.62	100.68	100.57	98.09

[1] Loss on ignition, presumably includes CO_2.

[2] Samples dried at 100° C. before analysis.

[3] SO_3.

[4] Includes 0.25 percent SO_3. Total given as 100.69 in origina reference—apparently corrected O for S.

[5] Includes 0.23 percent SO_3. Total given as 100.56 in original reference—apparently corrected O for S.

A. Greenalite rock, Biwabik Iron-Formation, Mesabi district, Minnesota (Leith, 1903, p. 108). Analysis by George Steiger, U.S. Geological Survey.

B. "Taconite consisting of about 8.5 percent quartz, 19 percent carbonate, and 71 percent minnesotaite and greenalite" (Gruner, 1946, pp. 56-57). From "Lower Slaty division," Biwabik Iron-Formation, Mesabi district, Minnesota. Analysis by Mines Experiment Station, University of Minnesota; W. E. Apuli, chief chemist.

C. "Taconite consisting of about 28 percent quartz and 72 percent minnesotaite" (Gruner, 1956, pp. 56-57). From "Lower Cherty division," Biwabik Iron-Formation, Mesabi district, Minnesota. Analysis by Mines Experiment Station, University of Minnesota, W. E. Apuli, chief chemist.

D-E. Laminated chlorite-siderite-magnetite-quartz rock, Stambaugh Formation, Iron River district, Michigan (James, 1954, p. 271). Analyses by Leonard Shapiro and W. W. Brannock, U.S. Geological Survey.

F. Sideritic silicate iron-formation, Gogebic district, Michigan (Huber, 1959,.p 91). Calculated mode: minnesotaite 46.3 percent sideritic carbonate 40.8 percent, magnetite 6.4 percent, quartz 5.8 percent, excess constituents 1.0 percent. Represents 14 feet of drill core. Lucile N. Tarrant, analyst, U.S. Geological Survey.

G. "Upper argillite" member, Temiscamie Iron-Formation, Lake Albanel range, Quebec (Quirke, 1961, p. 306; also Quirke, Goldich, and Krueger, 1960). Main elements determined in laboratories of Cleveland-Cliffs Iron Co., Owen Hassett, chief chemist; C and CO_2 by Mines Experiment Station, University of Minnesota.

H. Magnetite-bearing oolitic greenalite rock, Roper River, Northern Territory, Australia (Cochrane and Edwards, 1960, p. 17; also Edwards, 1958). F. J. J. Sinnott, analyst.

I. Stilpnomelane-actinolite-magnetite-quartz rock, Krivoi Rog Series (Semenenko and others, 1956, p. 374). Verkhtsevskovo region, U.S.S.R. Analyzed in laboratories of Ukrainian Geologic Administration.

J-K. Thuringite-magnetite-siderite-quartz rocks, Krivoi Rog Series (Semenenko and others, 1956, p. 387). Verkhtsevskovo region, U.S.S.R. Analyzed in laboratories of Ukrainian Geologic Administration.

L. Black cherty rock with granules of greenalite, Ordovician in age (Kennedy, 1936, p. 435). From near Glenluce, Wigtownshire, Scotland. W. J. Skilling, analyst.

TABLE 15.—*Analyses of glauconitic rocks (greensand)*

[Values in parentheses reported separately; not included in total]

	A	B	C	D	E	F	G	H	I
SiO_2	68.90	50.74	51.83	50.32	29.40	32.10	28.67	27.21	21.61
Al_2O_3	3.52	1.93	6.23	7.53	7.46	15.54	16.80	18.87	5.82
Fe_2O_3	8.91	17.36	17.15	18.38	5.60	12.71	8.41	9.32	17.48
FeO	1.52	3.34	2.93	3.02	14.54	20.39	20.74	18.55	25.69
MnO	----	----	----	----	----	----	.11	.12	.52
MgO	1.90	3.76	3.66	3.82	2.88	5.20	1.55	1.49	.59
CaO	2.10	2.86	.52	.65	20.00	1.98	.45	.38	2.88
Na_2O	.82	1.53	.76	.22	Tr	2.37	.03	.11	.14
K_2O	3.56	6.68	6.60	7.88	3.41	3.62	.70	.43	.83
H_2O+	7.68	9.08	9.98	8.58	[1]2.20	[1]5.20	11.76	13.12	3.05
H_2O-									2.59
TiO_2							.30	.42	.25
P_2O_5	1.05	1.79	.31	.34	Tr	Tr	.25	.31	.96
CO_2	1.00	.88	.36	.15	14.80	----	10.03	9.85	16.68
FeS_2	----	----	----	----	----	----	----	----	.50
Organic C	(.21)	(.10)	(.24)	(.07)	----	----	([2])	([2])	.79
Total	100.96	99.95	[3]100.33	100.89	100.29	[4]100.09	99.80	100.18	100.38

[1] Includes organic matter.
[2] Reported as "present."
[3] Given as 100.42 in original reference.
[4] Total included 0.98 percent SO_3.

A–D. Greensand from Eocene Manasquan Formation (A) and Paleocene Hornerstown Sand, New Jersey (Mansfield, 1922, p. 124). R. K. Bailey, analyst; organic matter by E. T. Erickson (reported separately on p. 130).
E. Greensand, Texas (Schock, 1918, p. 170). Eocene. Analyst's name not given.
F. Greensand marl of Eocene age, Texas (Schock, 1918, p. 170; see also Baker, 1935) L. E. Magnenat, analyst.
G–H. Greensand, Weches Greensand Member of Mount Selman Formation, Texas; of Eocene age (Eckel, E. B., 1938, p. 25). J. J. Fahey, analyst.
I. Glauconite-limonite oolite from Seend ironstone, Wiltshire, England (Hallimond, 1925, p. 89). Lower Cretaceous. Analyzed in laboratories of Geological Survey of Great Britain.

relations to silicate and oxide rocks in their respective associations.

SIDERITIC ROCKS OF POST-PRECAMBRIAN AGE

The range of physical and chemical characters of sideritic ironstone is exceptionally well displayed in the Northampton Sand ironstone, as described by Taylor (1949, especially pp. 23–29, 33–35) and represented in part by analyses B–G, table 16. In the more common varieties of the Northampton Sand, the siderite may form a groundmass for chamosite or limonite oolite, typically with considerable diagenetic replacement of the ooliths; it may occur in fine-grained sideritic mudstone with sandy and argillaceous material; it may occur in limestone as matrix and partial replacements of shell fragments and calcite ooliths, or replacements of matrix calcite; or it may occur as "sphaerosiderite"—rounded masses and nodules in chamositic or kaolinitic ironstone. Of these several varieties, probably only sideritic mudstone represents a primary sediment. This rock generally is fine grained and massive. In the other varieties the bulk of the siderite is diagenetic, as shown by textural relations to other rock components; it is commonly more coarsely grained; and it has greater range in relative molecular proportions of FeO, MgO, and CaO.

As with other ironstone types, the sideritic rocks have a considerable spread in chemical composition—only in part reflected by the selected analyses in table 16—as a result of gradations into chamositic and limonitic facies and into normal mudstone, sandstone, limestone, and dolomite. Granules of collophane and phosphatized organic debris occur in the varieties containing ooliths of chamosite or limonite; the content of P_2O_5 ranges from low (< 0.2 percent) to high (> 2 percent), approximately in direct relation to the oolitic component.

SIDERITIC IRON-FORMATION OF PRECAMBRIAN AGE

The typical sideritic iron-formation (see table 17) is a thinly bedded or laminated rock made up almost wholly of alternating layers of dominantly chert and dominantly iron-rich carbonate, in roughly equal proportions by volume. It may grade into or be interbedded with pyritic facies, on the one hand, as in the Iron River district of Michigan (James, 1951) and the Michipicoten area of Ontario (Goodwin, 1962), and into silicate or silicate-magnetite facies, on the other, as in the Mesabi district (Gruner, 1946; White, 1954), the Gogebic district of Wisconsin and Michigan (Huber, 1959), the Gunflint district of Ontario (Goodwin, 1956), and the Labrador trough (Harrison, 1953; Gastil and Knowles, 1960). The transitions into silicate or silicate-magnetite are well illustrated by analyses D to G in table 17 and analysis F in table 14, and accompanying modes of rock from the Gogebic district, in which the silicate is minnesotaite.

Chemically, the greatest range is in the $SiO_2:(FeO+CO_2)$ relation, reflecting the variable proportions of chert and siderite. As in most Precambrian iron-formation, the alkali content is very low or actually zero. In rocks containing carbonaceous material or associated with pyritic facies the carbonate is notably higher in Mn content (analyses A–C, M–N) and the P_2O_5 content is distinctly higher than in rocks with silicate association. Sideritic iron-formation from the Cuyuna district, Minnesota, contains as much as 12.9 percent MnO (Schmidt, 1963, p. 21).

TABLE 16.—*Analyses of siderite rocks of post-Precambrian age*

	A	B	C	D	E	F	G	H	I	J	K	L[1]	M[1]	N	O	P	Q	R
SiO_2	7.56	9.20	8.03	4.42	4.88	12.73	2.3	8.51	13.5	32.71	7.75	12.70	18.60	9.09	8.20	7.36	13.5	18.63
Al_2O_3	4.10	8.95	8.86	5.40	3.38	9.10	1.3	6.12	10.2	5.54	8.35	4.65	5.31	7.11	5.84	3.77	.7	5.90
Fe_2O_3	1.83	2.64	23.76	1.20	1.20	7.12	1.4	1.77	3.0	2.58	1.71	16.83	21.47	7.34	3.25	4.57	1.8	1.22
FeO	43.86	39.53	27.58	45.14	49.32	32.62	23.4	36.91	32.5	25.17	35.61	27.93	23.06	44.90	42.72	43.23	43.8	42.10
MnO	.13	.05	.17	.18	.37	.16	----	.42	.7	.46	.37	.76	.76	.20	.36	.84	1.5	.61
MgO	3.92	2.06	3.13	3.69	1.51	4.37	2.4	3.75	3.5	2.30	4.03	4.34	3.26	.53	.84	.33	1.7	1.58
CaO	2.90	6.73	4.65	6.03	3.46	8.70	28.7	5.54	5.0	3.27	10.53	5.98	4.47	2.37	3.94	4.97	3.1	.99
Na_2O	.11	----	----	----	----	----	----	.05	----	----	.18	----	----	.01	.05	.12	----	----
K_2O	1.13	----	----	----	----	----	----	.03	----	----		----	----	.34	.51	.70	----	----
H_2O+	.81	4.32	3.95	.14	2.33	.44	.9	4.05	2.90	.72	4.15	4.73	5.77	3.73	1.78	2.11	.9	.58
H_2O-	.28	----	----	----	----	----	.2	10.00	8.00	1.27	(2)	(1)	(1)	.80	1.43	.77		
TiO_2	.18	----	----	----	----	----	----	.36	.3	----	.18	----	----	2.44	.39	.24	.03	.28
P_2O_5	.11	2.70	1.84	.108	.618	2.18	.3	1.30	1.0	1.80	1.28	1.53	.60	.81	.21	.39	2.45	.33
CO_2	32.84	23.01	17.35	33.06	32.70	21.78	38.8	20.70	19.0	20.80	25.25	20.80	16.30	19.78	29.41	29.91	29.6	[3] 24.31
S	----	.036	.014	.111	.119	.216	.4	.05	.2	----	.102	.11	.21	[4] .013	[4] .19	[4] .16	----	.44
FeS_2	----	----	----	----	----	----	----	----	----	1.62	----	----	----	----	----	----	----	----
C	----	----	----	----	----	----	----	.27	.2	[5] 1.33	[6] .36	----	----	.28	.62	.61	----	----
Subtotal	[7] 99.82	99.23	99.33	99.48	99.89	99.42	100.1	[8] 99.96	100.0	99.57	99.85	[9] 100.36	[10] 99.81	99.74	99.74	100.08	[11] 99.08	96.97
Less O	.03	.02	.01	.06	.06	.11	.2	.03	.1	----	.05	.06	.11	----	.10	.08	----	.22
Total	[7] 99.79	99.21	99.32	99.42	99.83	99.31	99.9	[8] 99.93	99.9	99.57	99.80	[9] 100.30	[10] 99.70	99.74	99.64	100.00	[11] 99.1	96.75

[1] Sample dried before analysis. Moisture content ("hydratationgrad") of L reported as 2.49 percent; that of M as 2.38 percent.

[2] Sample dried at 212°F before analysis. Moisture loss reported as 6.48 percent.

[3] Reported as loss on ignition in analysis of acid-soluble fraction.

[4] Reported as S_2.

[5] "Coaly matter."

[6] "Carbonaceous matter."

[7] Contains 0.06 percent F.

[8] Total includes 0.03 percent Cr_2O_3, 0.08 "V. oxide," 0.02 As.

[9] Total does not include 0.60 reported as insoluble.

[10] Total does not include 0.80 reported as insoluble.

[11] Contains 0.0005 percent V_2O_5.

A. Siderite bed in upper 6 feet of Brassfield Dolomite of Silurian age. Rose Run pits, Owingsville, Bath County, Ky. Analysis F2641 by Paula M. Buschman, U.S. Geol. Survey, of sample collected by R. P. Sheldon. Subtotal contains 0.06 percent F. Analysis also shows zero SO_3.

B–G. Sideritic rocks from the Northampton Sand ironstone, Middle Jurassic age (Taylor, 1949, pp. 60–61). B, described as "ooliths of chamosite in siderite matrix"; C, "Ooliths of limonite and subordinate chamosite in siderite matrix"; D, "fine-grained siderite mudstone"; E, "fine-grained siderite mudstone [with] scattered chamosite ooliths"; F, "siderite mudstone with chamositic cement and local calcareous debris;" G, "siderite granules scattered through calcite groundmass" (Taylor, 1949, p. 58). Calculated mineral compositions given in original reference. Analyses B–F by Stewarts and Lloyds, Ltd.; Analysis G by G. A. Sergeant, Geological Survey of Great Britain.

H. Cleveland ironstone (Middle Jurassic), Eston, England (Hallimond, 1925, p. 51). Main seam. Rock contains about equal amounts of siderite and chamosite (34 percent each). J. E. Stead, analyst.

I. Cleveland ironstone (Middle Jurassic), Cleveland, England (Hallimond, 1925, p. 51). Main seam. Rock contains approximately equal amounts of siderite and chamosite (about 30 percent each). J. E. Stead, analyst.

J. Cleveland ironstone, "Pecten Seam" (Whitehead and others, 1952, p. 61; analysis quoted from older report). From Glaisdale Mine, Yorkshire, England.

K. Cleveland ironstone, "Two-foot Seam" (Whitehead and others, 1952, pp. 59–60). Analysis by J. and H. S. Pattison, Newcastle upon Tyne.

L. Minette ore from Luxemburg, Jurassic (Aalenian) in age. From upper part of "Grunes" horizon, Lager IV (Lucius, table B). Quartz content reported separately as 1.14 percent, included in total SiO_2. Analysis by laboratory of Konzern, A.R.B.E.D.

M. Minette ore from Luxemburg, Jurassic (Aalenian) in age. From near base of "Schwarzes" horizon, Lager III (Lucius, table B). Quartz content reported separately as 9.48 percent, included in total SiO_2. Analysis by laboratory of Konzern, A.R.B.E.D.

N. Ilmenite-bearing gray oolite, chamositic, from Kurremolla, southern Sweden (Palmqvist, 1935, p. 53). Jurassic (Lias) age. Analysis by Sven Palmqvist. SiO_2 is total of values for "sand" 3.10 percent, "SiO_2 (sol.)" 5.70 percent, "SiO_2" 0.29 percent. Al_2O_3 is total of values for "Al_2O_3" 6.86 percent, and "Al_2O_3 (clay)" 0.25 percent.

O. Greenish-gray, dense siderite rock, locality as for N (Palmqvist, 1935, p. 58). Analysis by Sven Palmqvist. SiO_2 is total of values for "sand" 1.41 percent, SiO_2 (sol.) 1.71 percent, and SiO_2 5.08 percent. Al_2O_3 is total of values of "Al_2O_3" 1.49 percent, and "Al_2O_3 (clay)" 4.35 percent.

P. Light-gray, dense siderite rock, locality as for N (Palmqvist, 1935, p. 89.) Analysis by Sven Palmqvist. SiO_2 is total of values for "sand" 0.15 percent, "SiO_2 (sol.)" 3.03 percent, and "SiO_2" 4.18 percent. Al_2O_3 is total of values for "Al_2O_3" 0.25 percent, and "Al_2O_3 (clay)" 3.52 percent.

Q. Siderite rock ("Weisseisenerzen"), Auerback, Germany (Harder, 1955, p. 516); Analysis by H. Harder. Cretaceous. Contains 0.0005 percent V_2O_5.

R. Siderite rock from western Bashkiria, U.S.S.R., of Devonian age (Florensky, V. P., and Balshina, B. V., 1948, p. 690; sample 702/4). Analyst, B. V. Balshina. Associated with chamositic ironstone. Analysis is total of two parts, acid-soluble, and acid-insoluble (26.36 percent), given in original reference. All TiO_2, Al_2O_3, and Fe_2O_3 is in "acid-insoluble" fraction, as is all but 0.39 percent of the SiO_2. Calculated mode as follows (ibid., p. 691): detrital material 26.36 percent, siderite 67.27 percent, calcite 0.43 percent, magnesite 2.19 percent, pyrite 0.82 percent, apatite 0.78 percent, other 2.58 percent.

SULFIDE FACIES

Although sulfide, principally pyrite, is a constituent of many or most iron-rich sedimentary rocks, rarely does it assume major proportions. As a facies, the sulfide rocks (see table 16) are distinctly subordinate to those of the oxide, carbonate, and silicate, and the defining mineral is almost wholly of diagenetic origin. With a few exceptions, such as the previously noted thin pyritic beds of the Cleveland district of England and at Wabana, Newfoundland, the heavily pyritic rocks are black shales or their equivalents, with a large content of organic matter or carbon. The absence of direct precipitates, the scarcity of rocks of this facies, and the typical association with organic shales are all to some degree reflections of the extraordinarily slow rate at which sulfate in natural solutions is reduced, even in the thermodynamically stable realms of sulfide, except when catalyzed by biochemical agents. Viewed differently, it may also be said that the presence of organic matter, which permits the development of anaerobic sulfate-reducing bacteria, commonly is necessary to create the requisite low Eh for sulfide formation in sedimentary environments.

In table 18 are tabulated chemical analyses of a variety of sulfide-rich sedimentary rocks. The only complete analysis available (analysis A) is of a 50-foot bed of graphitic pyritic slate, the Wauseca Pyritic Member of the Dunn Creek Slate, which underlies the sideritic Riverton Iron-Formation in the Iron River district of Michigan (James; 1951, 1958). The pyrite occurs mostly in separated grains of about 3 microns diameter, and most show crystal outlines. The content of pyrite is nearly constant over a known strike length of about 20 miles. The fine-grained matrix is black with scattered fine flakes of mica and particles of quartz. Similar concentrations of pyrite in slate are known elsewhere, most notably at Mount Isa, Australia (Love and Zimmerman, 1961), and other localities in Australia (Skinner, 1958; Baker, 1960); lesser but still significant concentrations occur in units such as the

TABLE 17.—*Analyses of sideritic iron-formation, Precambrian*

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
SiO_2	24.25	18.11	22.97	39.26	40.09	32.87	30.62	26.97	46.46	45.4	48.10	27.43	30.15	13.91	38.58	58.22
Al_2O_3	1.71	.18	1.08	2.88	2.23	2.46	.41	1.30	.24	1.8	.47	.23	.40	3.63	3.27	.48
Fe_2O_3	.71	.34	3.59	.63	9.96	4.78	.46	2.31	.64	8.4	6.79	1.64	5.27	3.28	4.90	2.40
FeO	35.22	40.68	33.17	24.94	25.84	30.84	34.50	39.77	26.28	21.1	22.36	30.28	31.34	28.62	28.07	20.90
MnO	2.11	2.56	6.77	1.23	1.25	1.33	.93	.29	.21	1.7	--------	.77	[1] 2.53	1.73	.04	.01
MgO	3.16	3.59	2.02	4.62	2.79	3.58	4.41	1.99	3.10	1.9	2.91	5.04	4.77	5.73	.47	.44
CaO	1.78	1.31	1.48	4.62	.50	.62	1.45	.66	1.87	1.1	.74	6.64	1.25	4.34	1.79	1.33
Na_2O	.04	.06	.06	.00	.03	.00	.00	.09	--------	.05	--------	--------	--------	.94	.39	.27
K_2O	.20	.04	.10	.00	.40	.00	.00		--------	.07	--------	--------	--------	.45	.12	.04
H_2O+	.00	.05	.00	1.23	1.80	1.69	.02	.51	1.15	.50	1.80	--------	.36	1.30	.81	.50
H_2O-	.21	.09	.17	.11	.56	.28	.03	.10	.07		(2)	--------	(2)	.10	1.76	2.26
TiO_2	.00	Tr	.10	.07	.23	.27	.02	--------	Tr	.03	--------	--------	.02	.09	.03	.02
P_2O_5	.91	.47	.62	.11	.13	.09	.10	.03	.13	.41	.087	--------	.665	.23	--------	--------
CO_2	27.60	30.52	26.50	20.46	14.38	20.94	27.03	26.20	19.96	16.7	15.32	28.03	24.65	27.06	19.02	13.00
S	--------	.06	--------	.04	.01	.09	.07	--------	[3] .11	--------	--------	--------	--------	--------	--------	--------
FeS	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	[4] 8.43	--------	--------
C	1.96	1.41	2.02	.07	.05	.45	.06	--------	--------	--------	.40	.016	--------	--------	--------	--------
Subtotal	99.86	99.47	100.65	100.27	[5] 100.26	100.29	100.11	100.22	100.22	99.16	98.98	100.08	101.40	99.84	99.25	99.87
Less O	--------	.03	--------	.02	.01	.05	.04	--------	--------	--------	--------	--------	--------	--------	--------	--------
Total	99.86	99.44	100.65	100.25	[5] 100.25	100.24	100.07	100.22	100.22	99.2	98.98	100.08	101.40	99.84	99.25	99.87

[1] Reported as Mn_2O_3.

[2] Sample dried at 100° C. before analysis.

[3] Given as FeS_2.

[4] Reported as 5.08 percent Fe, 3.35 percent S, with text notation that sulfide is mainly pyrrhotite (8.31 percent) with minor pyrite (0.12 percent).

[5] Total contains 0.01 percent V_2O_3.

A. Banded chert-carbonate rock, Riverton Iron-Formation, Iron River district, Michigan (James, 1951, p. 257); analyst, Leonard Shapiro, U.S. Geol. Survey. Sample represents 3 feet of drill core.

B–C. Carbonate-rich layers in Riverton Iron-Formation, Iron River district, Michigan, (James, 1951, p. 257). Analysis B by Leonard Shapiro; analysis C by Charlotte Warshaw, U.S. Geol. Survey.

D–G. Banded chert-carbonate from the Ironwood Iron-Formation, Gogebic district, Wisconsin-Michigan (Huber, 1959, p. 91). Analyses D and G, by Lucile N. Tarrant, analyses E and F by Lucille M. Kehl, U.S. Geol. Survey. Analyses D, E, F, and G represent, respectively, 17, 12, 14, and 12 feet of drill core. Calculated modes in percent, as follows:

	D	E	F	G
Sideritic carbonate	49.6	35.9	52.4	67.2
Quartz	31.8	34.7	29.5	29.7
Minnesotaite	14.5	10.2	6.5	1.7
Magnetite	.9	14.4	6.9	.7
Excess constituents	3.4	5.0	5.0	.7

H. Carbonate iron-formation, Negaunee Iron-Formation, Marquette district, Michigan (Van Hise and Bayley, 1897, p. 337). Analyses given separately for acid-soluble and acid-insoluble fractions. George Steiger, analyst.

I. Carbonate iron-formation, Gunflint Iron-Formation. From north side Gunflint Lake, Gunflint district, Ontario (Irving and Van Hise, 1892, p. 192; see also Goodwin, 1956). T. M. Chatard, analyst.

J. Chert-siderite rock, Welch mine, Florence County, Wis. Sample 150004, collected by C. E. Dutton; analysis by P. L. D. Elmore, S. D. Botts, M. D. Mack, U.S. Geol. Survey, using "rapid analysis" methods described in U.S. Geol. Survey Bull. 1036–C.

K. Siderite-rich bed in "Lower Slaty division", Biwabik Iron-Formation, Mesabi district near Hibbing, Minn. (Gruner, 1946, p. 59). Sample represents 15 feet of drill core. Analysis by Mines Experiment Station, University of Minnesota; W. E. Apuli, Chief Chemist.

L. Upper sideritic chert member, Temiscamie Iron-Formation, Lake Albanel range, Quebec (Quirke, 1961, p. 308). Sample represents 10 feet of drill core. Major elements determined in laboratory of Cleveland-Cliffs Iron Co.; organic C and CO_2 by Mines Experiment Station, Univ. of Minnesota.

M. Siliceous iron carbonate rock from the Kennedy mine, Cuyuna district, Minnesota (Harder and Johnston, 1918, p. 120–121). Analyst: J. H. McCarthy, Mines Experiment Station, University of Minnesota.

N. Lowermost member of iron-formation at Helen mine, Michipicoten district, Ontario (Collins, Quirke, and Thomson, 1926, p. 69; see also Goodwin, 1962).

O. Quartz-siderite rock, Krivoi Rog Series, Ukraine, U.S.S.R. (Semenenko and others, 1956, p. 147); S. A. Panchenko, analyst.

P. Quartz-rich siderite iron-formation, Krivoi Rog Series, Ukraine, U.S.S.R. (Semenenko and others, 1956, p. 149); analyses by laboratories of Ukraine Geologic Administration.

Chattanooga Shale of the United States (about 11 percent, according to Bates and Strahl, 1957), the Upper Cambrian "alum shale" of Sweden (about 12 percent in the *Peltura* zone, written communication from V. E. McKelvey), and the Kupferschiefer of Germany and its equivalent, the Marl Slate of England. The pyritic deposit of Meggen, Germany, is thought by some to be of sedimentary origin (Lindgren, 1933, p. 269), and by others to be epigenetic; Ehrenberg, Pilger, and Schroder (1954) conclude that it formed as a result of submarine exudation of magmatically derived fluids—that is, it is of "exhalative-sedimentary" origin. In several of these units—notably the Mount Isa rock and the Kupferschiefer—the pyrite is accompanied by a variety of other sulfides.

Analyses G to H, table 18 are of a Precambrian pyritic slate in Minnesota that has been metamorphosed to yield some pyrrhotite—a hydrothermal origin for the sulfides, as proposed by Thiel (1924), seems very unlikely. Analysis F represents a thick unit of pyritic rock—as much as 120 feet thick, with associated pyrrhotite, siderite, magnetite, and quartz—of the Michipicoten district of Ontario; according to Goodwin (1962) the rock is the product of sedimentation of materials derived from submarine hot spring and fumarolic activity—that is, it is of the "exhalative-sedimentary" type. A similar origin is suggested for pyrrhotite-pyrite bodies at Samreid Lake, Ontario (Friedman, 1959).

The occurrence of sulfide as diagenetic replacements in limestone is well known, particularly because of the spectacular preservation of fossils converted entirely to pyrite. In a few places the pyritic replacements assume major proportions as rock constituents; analyzed samples of a 4-foot bed in the Greenhorn Limestone of the Black Hills, for example, contain as much as 25.2 percent pyrite (Rubey, 1930, p. 8).

BLACKBAND AND CLAYBAND SIDERITE

The so-called blackband and clayband (or clay-ironstone) siderites (table 19) occur in clays and shales as thin layers rarely more than a foot or so thick, or as disconnected lenses and nodules. They consist of fine-grained siderite for the most part, with variable amounts of clastic material—sand and clay—and organic matter. Spherulitic structure is common.

TABLE 18.—*Analyses of sulfide-rich rocks*

[Values given in percent]

Sample A. Complete analysis

SiO_2	36.67	Na_2O	0.26	FeS_2	38.70
Al_2O_3	6.90	K_2O	1.81	SO_3	2.60
Fe_2O_3	-----	H_2O+	1.25	C	[1] 7.60
FeO	2.35	H_2O-	.55	Total	100.21
MnO	.002	TiO_2	.39		
MgO	.65	P_2O_5	.20		
CaO	.13	V_2O_5	.15		

Samples B–H. Partial analyses

	B	C	D	E	F	G	H
SiO_2	9.91	-----	13.20	-----	4.69	42.11	36.57
Al_2O_3	-----	-----	-----	-----	.56	8.72	5.28
Fe	35.18	29.00	28.60	31.10	42.1	18.88	27.84
Mn	-----	-----	-----	-----	1.0	.75	.16
MgO	-----	-----	-----	-----	1.90	.20	1.69
CaO	.54	-----	2.80	-----	3.87	.19	1.70
P_2O_5	.35	-----	.52	-----	-----	-----	-----
P	-----	-----	-----	-----	-----	.063	.119
S	34.46	25.00	24.58	25.70	32.6	14.8	15.6
SO_3	-----	-----	-----	-----	-----	-----	-----
CuO	-----	.015	-----	-----	-----	-----	-----
PbO	-----	.140	-----	-----	-----	-----	-----
Ni, Co	-----	.11	-----	-----	-----	-----	-----
H_2O	-----	-----	-----	-----	-----	-----	-----
Loss on ignition	-----	-----	-----	-----	-----	16.24	10.96

[1] Includes organic matter.

A. Pyritic graphitic slate, Iron River district, Michigan. Precambrian (James, 1951). Charlotte M. Warshaw, analyst.

B. Oolitic pyrite, Wabana, Newfoundland (Hayes, 1915, p. 49). Ordovician. A. V. Seaborn, analyst.

C. "Sulphur band" of Cleveland ironstone, Cleveland district, England (Hallimond, 1925, p. 54). Middle Jurassic. J. E. Stead, analyst.

D–E. "Sulphur band" of Cleveland ironstone (Lamplugh, Wedd, and Pringle, 1920, p. 53). Analysis D by A. A. Street, analysis E by Ridsdale and Co., Middlesbrough.

F. Pyritic member of Precambrian iron-formation of Michipicoten district, Goodreau A deposit, Ontario (Goodwin, 1962, p. 577). J. H. Dann, analyst.

G–H. Sulfide-bearing graphitic slate (Precambrian), Aitkin County, Minn. (Pennington and Davis, 1953, p. 9, 14). Sulfides are pyrite, pryrrhotite, and marcasite. Sample G represents 66 feet of drill core; sample H represents 70 feet. Analyses by Lerch Bros., Crosby, Minn.

The typical occurrence is in rocks associated with coal beds, notably those of Carboniferous or Permian age. They are abundant in the Appalachian coal field (see, for example, Stout, 1944; Singewald, 1911), and they are reported to occur at 75 horizons in the lower coal measures of Wales (Tyler, 1950, p. 518). In the U.S.S.R., in the foreland of the Urals in the general vicinity of Perm, siderite forms irregular and lenticular beds as much as several meters thick over a region of thousands of square miles (Belousov, 1933; Miropolskaya, 1949).

The rocks tend to be higher in FeO relative to MnO, CaO, and MgO than the marine siderite facies. The $FeCO_3$ content of the carbonate commonly is 90 percent or more. The calculated molecular composition of siderite from the coal measures of the Lvov basin of the U.S.S.R., for example, in molecular percent is 95.07 percent $FeCO_3$, 2.15 percent $MnCO_3$, and 2.77 percent $CaCO_3$ (Vartanova, Artemenko, and Galkina, 1950, p. 302). The blackband ores are significantly higher in C or organic content than those of the clayband variety and commonly contain several percent marcasite.

Much of the blackband and clayband siderite is of diagenetic origin, but some of the more continuous layers may represent primary sediments, deposited in brackish waters or marine swamps in the presence of abundant vegetal matter.

TABLE 19.—*Analyses of blackband and clay-ironstone siderite*

	A	B	C	D	E	F	G	H	I	J
SiO_2	5.10	6.46	13.50	10.04	12.86	6.83	13.35	0.48	8.67	10.72
Al_2O_3	2.35	2.64	6.13	5.57	6.16	2.85	5.79	.37	4.47	4.45
Fe_2O_3	.00	6.85	1.30	1.49	.39	.43	.41	1.18	.42	1.11
FeO	50.92	42.08	39.87	37.99	43.81	51.45	41.03	41.37	43.11	38.08
MnO	.58	2.32	1.38	1.51	.98	.54	.55	.89	2.07	1.06
MgO	.30	1.76	2.77	3.37	1.15	.42	3.36	4.00	2.09	3.75
CaO	.70	3.87	2.12	4.59	1.67	2.13	3.00	4.53	5.15	5.19
Na_2O	-----	-----	-----	-----	-----	-----	-----	-----	-----	.12
K_2O	-----	-----	.18	.55	.42	.16	.86	-----	-----	.19
H_2O+	2.70	Tr	1.21	1.47	1.32	.54	1.36	4.10	[1] .25	1.10
H_2O-		.15	.59	.74	.54	.19	.57		[2] .12	.77
TiO_2	-----	.21	-----	-----	-----	-----	-----	.02	-----	.22
P_2O_5	.33	.65	.69	.80	.83	.23	.70	1.87	1.176	1.83
CO_2	31.80	32.70	28.47	29.92	28.22	33.31	28.49	31.34	32.74	30.20
S	.18	-----	-----	-----	-----	-----	-----	-----	.178	-----
SO_3	-----	.20	Tr	Tr	Tr	-----	-----	.30	-----	.02
FeS_2	-----	.11	.05	.06	.30	.02	-----	1.28	-----	.42
C	5.00	-----	[3] .83	[3] 1.42	[3] .88	[3] .67	[3] .07	[3] 8.25	-----	[4] 1.04
Subtotal	99.96	100.00	99.09	99.52	99.53	99.77	99.54	[5] 100.00	100.44	100.27
Less O	.09	-----	-----	-----	-----	-----	-----	-----	.09	-----
Total	99.87	100.00	99.09	99.52	99.53	99.77	99.54	100.00	100.35	100.27

[1] "Water and organic matter."

[2] "Moisture."

[3] "Organic matter."

[4] Total of carbon, organic 0.92 percent, and hydrogen, organic 0.12 percent.

[5] Total includes 0.02 "arsenic acid."

A. Siderite ironstone ("blackband"), Prestwick Mine, Natal, South Africa (Wagner, 1928, p. 127–128). R. R. Walton, analyst. Associated with coal beds of Karoo System (Carboniferous to Triassic). Calculated mode: quartz 2.33 percent, "clay substance" 7.82 percent, siderite 83.24 percent, calcite 0.48 percent, apatite 0.76 percent, pyrite 0.34 percent, carbon 5.00 percent. Some of "clay substance" is chamosite.

B. "Clay ironstone," Ashburnham, Sussex, England (Lamplugh, *in* Lamplugh, Wedd, and Pringle, 1920, p. 227). Bed in Wadhurst Clay (Cretaceous). Analysis by R.R. Tatlock and Thomson, Glasgow.

C. "Clayband ironstone," Pargate. Yorkshire (Gibson, *in* Strahan and others (1920). Bed of siderite nodules in Coal Measures (Carboniferous). Analysis reported here is total of acid-soluble and ignited acid-insoluble residue. All SiO_2 is in insoluble portion. Analyst not known.

D. Siderite ironstone, Brown Rake, Butterley, Derbyshire, England (Gibson, *in* Strahan and others, 1920, p. 52). Bed in Coal Measures (Carboniferous). Analysis reported here is total of acid-soluble and ignited acid-insoluble residue. Analyst not known.

E. Brooch ironstone, Corngreaves, Staffordshire, England (Gibson, *in* Strahan and others, 1920, p. 62). Thin layer in Coal Measures (Carboniferous). Analysis reported here is total of acid-soluble and ignited acid-insoluble residue. Analyst not known.

F. Sideritic ironstone ("Crawstone"), Madeley Wood, Shropshire, England (Dewey, *in* Strahan and others, 1920, p. 93). Irregular masses in fine-grained sandstone of Coal Measures (Carboniferous). Specific gravity 3.68. Analysis reported here is total of acid-soluble and acid-insoluble residue. Analyst not known.

G. Clay ironstone, Rosser Vein Mine, Dowlais, South Wales (Strahan, *in* Strahan and others, 1920, p. 114). Bed in Coal Measures (Carboniferous). Analyst not known.

H. Blackband ironstone, Dundonald Colliery, Fifeshire, Scotland (MacGregor, Lee, and Wison, 1920, p. 142). Analysis by Lochgelly Iron and Coal Co. Layer 4–6 inches thick above coal bed of early Carboniferous age.

I. Blackband ore, Holmes County, Ohio (Stout,1944. pp. 168–169). Nodular siderite in Pennsylvanian strata. Analysis by Ohio Geological Survey.

J. Blackband ore, Tuscarawas County, Ohio (Stout, 1944, p. 172). Nodular siderite above Lower Kittanning coal (Pennsylvanian). D. Schaaf, analyst.

DISTRIBUTION OF DEPOSITS IN SPACE AND TIME

The size, position, and duration of basins of deposition, the dimensions of the deposits, and the facies relations both within the iron-rich sedimentary rocks and other rocks formed contemporaneously—all these are of importance to the geochemistry of iron sedimentation, particularly with respect to problems of genesis. Though volumetrically of minor proportions, the iron-rich rocks throughout the world have been studied extensively, both because of intrinsic interest and economic value. The literature on the subject is immense (see Luttrell, 1955, for a partial bibliography). Fortunately, three compendia of relatively recent vintage are available: "Die Eisenerzvorräte der Welt" (Einecke, 1950); "Symposium sur les gisements de fer du monde" (edited by Blondel and Marvier, 1952); and "Survey of World iron resources" (United Nations, 1955). These are excellent source books.

In the succeeding paragraphs and accompanying tables, the occurrence and character of iron-rich sedimentary rocks are summarized briefly. The time aspect can be delineated accurately only for deposits of post-Precambrian age; for the Precambrian, assignments of age can be made in a relative sense within some individual regions but absolute age is not readily established.

DEPOSITS OF TERTIARY AGE

Deposits of Tertiary age (see table 20) are widespread in northern Europe, northern Africa, and southern United States, but most are of minor dimensions. The only unit of significant size is that of the Kerch district of the Crimea. The rock—mostly limonite-chamosite oolite—was deposited in a Pliocene embayment of the Black Sea, in an area of about 150 by 50 km. The iron deposits were formed in/the central part of the embayment and grade laterally into sands and clays (see facies map in Markevich, 1960, p. 370).

DEPOSITS OF MESOZOIC AGE

The principal Mesozoic deposits (see table 21) are those of Jurassic age in northern Europe. These include the famous minette beds of eastern France, Luxembourg, Belgium, and western Germany, the major

TABLE 20.—*Occurrences of iron-rich sedimentary rocks of Tertiary age*

	Locality	Character	Thickness	Remarks	Key References
Pliocene	Kerch Basin, U.S.S.R.	Oolitic limonite and chamosite.	$\leqq$ 22m	Youngest major ironstone. Deposited in embayment of Black Sea. Lateral gradation into ferruginous sands and clays.	Konstantov and others, 1933; Putzer, 1943; Malakhovsky, 1956 and 1959; Markevich, 1957.
	Gelrode, Belgium	Sandy glauconite	Few meters		Ancion, 1952.
Miocene	Vogelsberg, Germany.	Siliceous limonite			Blondel and others, 1955.
Oligocene	Semnan area, Iran	Oolitic limonite, hematite.			Mahmoudi, 1952.
	Caucasus, U.S.S.R.	Siderite			Arkhangelskii and Kopchenova, 1934.
	East side of Urals, U.S.S.R.	Oolitic limonite and chamosite(?).	$\leqq$ 15 m	Nonmarine	Davidson, 1961.
Eocene	Tunisia	Oolitic limonite	3.5 m		Gottis, 1952.
	Algeria	do	8–15 m		Betier, 1952.
	Kandi region, French W. Africa.	do			Blondel, 1952.
	Kressenberg, Germany.	do	Few meters		Gudden and others, 1952.
	Weald, England	Siderite beds and nodules (clay ironstone).			Sweeting, 1944.
	India	Siderite (clay ironstone).			Krishnan, 1952.
	Colombia	Oolitic hematite	2–6 m	May be Oligocene in age.	Colombia, 1952, Hubach, 1953.
	Texas, U.S.A	Glauconitic sands and clays.	$\leqq$ 100 ft	Weches Greensand Member of Mount Selman Formation.	Eckel, 1938.
	Mississippi, U.S.A	Siderite		Wilcox Formation and Ackerman Formation (Wilcox age).of former usage.	Vestal, 1954; Lowe, 1914.

ironstones of England (Northampton, Cleveland), and others of lesser importance. At first glance, the picture would appear to be one of simultaneous deposition of iron over broad areas, in a transgressive epicontinental sea bordering the deep Tethys seaway to the south. In detail, however, this breaks down, and it becomes apparent that the present deposits reflect dozens of separated basins, few of which exceeded 50 miles in maximum dimension. Furthermore, even for those formed within the same stage—the Aalenian, for example, which is the age of the major deposits—the iron-rich beds in adjoining basins may not be stratigraphically equivalent (see fig. 9 in Lucius, 1945, for the relations between the Esch and Differengen basins). At any one time, therefore, there existed at most perhaps one or two basins of modest size within which iron-rich rocks were being laid down—surely less than 1 percent of the total area of the epicontinental sea. This fact, not readily apparent because of the relatively coarse units of time normally dealt with, emerges as a result of the extraordinarily detailed stratigraphic analysis made possible by the rich fossil record; it is a fact of major importance to bear in mind in appraising the geochemical processes involved in the deposition of these and other much less accurately dated ironstones.

TABLE 21.—*Occurrences of iron-rich sedimentary rocks of Mesozoic age*

	Locality	Character	Thickness	Remarks [1]	Key references
Cretaceous:					
Upper	Salzgitter, Germany	Oolitic and pisolitic limonite.	≦100 m	Much rock is clastic, derived from erosion of older ironstones on diapiric uplifts. In part of pre-Cretaceous age.	Kolbe, 1952; Blondel and others, 1955; Seitz and others, 1952.
	Gross Iselde, Peine, Damme, West Hannover, Germany.	Siliceous limonite	≦30 m		Seitz and others, 1952.
	Scania, Sweden	Glauconitic sandstones.		Thick	Hadding, 1932.
	Mugai, Khoper districts, Russia.	Limonite oolite			Arkhangelskii and Kopchenova, 1934.
	Aswan, Egypt	Oolitic hematite	1–2 m	Area 50 by 20 km	Little and Attia, 1943; Nassim, 1950; Attia, 1954.
	New Jersey, U.S.A.	Glauconite	≦40 ft	In several formations; area 160 by 16 km.	Mansfield, 1922.
	New Jersey	Clay ironstone		Hornerstown sand (now considered to be Paleocene).	Mansfield, 1922.
	Alberta, Canada	Oolitic limonite-chamosite.	≦30 ft	Areal extent not yet defined.	Mellon, 1962.
Lower	Claxby, England	Oolitic limonite, glauconite.	6 m aggregate		Hallimond, 1925.
	Wassy, Point Varin, Metabief, Sommevoire, France.	Oolitic limonite			Blondel and others, 1955.
	Maryland, U.S.A.	Clay ironstone		Arundel Formation (now considered to be Upper Cretaceous).	Singewald, 1909.
Cretaceous undivided.	Moravia, Czechoslovakia.	Arenaceous siderite			Roth and Matejka, 1953.
	Carpathia, Poland	Clay ironstone			Einecke, 1950.
	Agbaja plateau, Nigeria.	Oolitic limonite	>40 ft	Chamosite and siderite, minor magnetite found in deeper drill holes.	Jones, 1958.
	Udi plateau, Nigeria.	"Rubbly" ironstone.	2–28 ft	Probably clastic deposit.	Hazell, 1958.
Jurassic:					
Upper (Malm)	Yugoslavia	Interbedded limonite and limestone.	≦4 m		Nöth, 1952.
	Giphorn, Wessergebiet, Germany.	Limonite oolite, in part.	≦9 m	Oxfordian age	Seitz, Hoffman, and Preul, 1952.

See footnote at end of table.

TABLE 21.—*Occurrences of iron-rich sedimentary rocks of Mesozoic age*—Continued

	Locality	Character	Thickness	Remarks [1]	Key references
Middle (Dogger)	Chamoson,, Erzegg, Fricktal, Switzerland.	Limonite, chamosite oolite.	1–2 m	Separate beds of Callovian and Bathonian age.	Déverin, 1945.
	Hungary	Limonite	—	—	Panto, 1952.
	"Minette" beds of eastern France, Belgium, Luxemburg, Western Germany.	Oolitic limonite and chamosite, mainly.	To 9 m	Aalenian in age. As many as 12 beds in several basins within region 120 by 40 km.	Cayeux, 1909; Coche, Dastillon and others, 1954, 1955; Bichelonne and Angot, 1939; Lucius, 1945; and many others.
	Northampton, England.	Chamosite and limonite oolite; siderite.	To 25 feet	Aalenian (lower Dogger) age. Original basin 100 by 20 miles.	Taylor, 1949.
Lower (Lias)	Cleveland, England	Sideritic chamosite oolite.	Main seam 2½–5 feet.	Uppermost middle Lias in age. Four separate beds.	Whitehead and others, 1952; Rastall and Hemingway, 1949.
	East Midland, Banbury, England.	Sideritic chamosite oolite (Marlstone ironstone).	To 25 feet	Same age as Cleveland ironstone. With Cleveland, deposited in individual basins about 30 by 15 miles in region 250 by 30 miles.	Whitehead and others, 1952.
	Northern Göttingen	Hematite oolite and hematite-chamosite oolite.	4–5 m	Lias-γ age, equivalent to Pliensbachian.	Harder, 1951.
	Fredericke Basin, Germany.	Oolitic limonite and chamosite, mainly.	Beds few meters thick.	Lias-α–3 age, equivalent to lower Sinemurian. Four beds.	Kolbe, 1952.
	Vares, Yugoslavia	Siderite and hematite, locally oolitic.	To 60 m	Considered to be of "exhalative-sedimentary" type.	Latal, 1952.
	Frodingham, England.	Mainly limonite oolite.	To 32 feet	Lower Lias age (approximately Sinemurian).	Whitehead and others, 1952.
	Austria	Clay ironstone	—	—	Kern, 1952.
	Scania, Sweden	Sandy siderite, some chamosite and limonite oolite.	Many meters.	Oldest Jurassic ironstone in Europe.	Palmqvist, 1935; Hadding, 1929, Hadding, 1933.
Triassic	No deposits of significance known.				

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[1] Nomenclature of Jurassic stages follows Kolbe (1953). It differs from French usage (Cusset, de Torcy, and Maubeuge, 1952, p. 147), which places the Malm-Dogger boundary above the Oxfordian and places the Aalenian in the Lias. It also differs from British usage (Arkell, 1956, p. 10-11) which includes the Aalenian with the Bajocian, the Domerian with the Pliensbachian, and the Lotharingian with the Sinemurian.

The Triassic Period, one of widespread aridity during which continental areas stood high and the oceans were confined largely to the major basins, is the most barren interval of post-Precambrian time insofar as iron sediments are concerned. Clearly such conditions are not favorable for sedimentary concentration of iron, as the known deposits are of trivial size.

DEPOSITS OF PALEOZOIC AGE

The Carboniferous and the Permian, marked by major coal beds in many parts of the world, are also marked by extensive development of the blackband siderite, but ironstones of normal character are relatively scarce. The strata of middle and lower Paleozoic age (see table 22), in contrast, contain many iron-rich units. Two types are of particular interest: the Lahn-Dill type of Devonian age, associated with volcanic rocks and believed to represent sedimentary deposition of the products of submarine volcanic and fumarolic activity (the "exhalative-sedimentary" ores); and the somewhat comparable deposits formed in eugeosynclinal (orthogeosynclinal) tracts, as typified by the Ordovician ironstones of northwest France, Wales, Portugal, and Spain. The latter deposits generally are characterized by the presence of abundant thuringite and magnetite.

The youngest rocks of "iron-formation" aspect—that is, with interbedded chert—are of Paleozoic age. The outstanding example is that of the Lesser Khingan range of Manchuria, the age of which is established by the presence of an Early Cambrian brachiopod (*Modioloides priscus* Walcott). The iron-formation, 65 to 80 feet thick, consists of banded hematite-chert and magnetite-chert (Chebotarev, 1958); it is underlain by a 25-foot bed of manganese carbonate which grades into the overlying iron-formation through a transitional zone of braunite-hematite. The unit is traced for a strike length of 60 km and, according to Chebotarev, there is no evidence of igneous activity during the period of deposition. A second major example, as yet incompletely described in available literature, is in the Snake River region between the Yukon and Northwest Territories, Canada. According to C. D. A. Dahlstrom (oral communication to the Annual Convention of the Canadian Institute of Mining and Metallurgy, Montreal, Canada, April 1964), a jasper-hematite iron-formation several hundred feet thick is overlain by fossiliferous rocks of Middle Cambrian age and underlain by an evaporite-bearing sequence that is correlated with nearby strata of Early Cambrian age. Other iron-formation units of possible or probable Paleozoic age are those of Morro do Urucum, Brazil; Relun, Chile; and the Mandi district of northern Pakistan and the Chisapani Garhi area of south-central Nepal (O'Rourke, 1962).

TABLE 22.—*Occurrences of iron-rich sedimentary rocks of Paleozoic age*

[Locality names given in brackets are according to the Columbia Lippincott Gazetteer of the World (1961)]

	Locality	Character	Thickness	Remarks	Key references
Permian	Desert Basin, Australia.	Limonite oolite, possibly chamositic.	≦30 ft	Lenses in marine sandstone and shale.	Edwards, 1958.
	Szechwan, China	Pisolitic hematite shale.	2–4 m		Krishnan, 1955.
	Kiangai, China	Oolitic hematite	1–5 m	In quartzite	Do.
	Opaczna and Ostrawice, Poland.	Chamositic ironstone.		Locally manganiferous	Einecke, 1950.
	Perm, Russia	Siderite (clay ironstone).		Lenses	Miropolskaya, 1949; Belousov, 1933.
	Karroo beds, South Africa and Southern Rhodesia.	Blackband siderite. Chamosite reported locally.	Lenticular	Associated with coal beds. Some layers many square miles in area.	Wagner, 1928; Tyndale-Biscoe, 1952.
Carboniferous	Wyoming, U.S.A	Oolitic limonite and glauconite, also shale with "buckshot ore".		Three thin beds in Amsden Formation.	Wanless, Belknap, and Foster, 1955; Branson, 1939.
	do.	Limonitic and hematitic shale.		In Sacajawea Formation of C. C. Branson, Wind River Mts.	Branson and Branson, 1941.
	England, Wales, Scotland.	Blackband and clayband siderite.		Thin layers and lenses occur at many horizons in Coal Measures.	Strahan and others, 1920; MacGregor and others, 1920.
	Lvov Basin, U.S.S.R.	do.		Thin layers and lenses associated with coal beds.	Bartonova and others, 1950.
	Shansi and Hunan provinces, China.	do.		Thin layers and lenses associated with coal beds.	Juan, 1946.
	Appalachian region U.S.A.	do.		Thin layers and lenses associated with coal beds.	Stout, 1944; Singewald, 1911.
Devonian	Lahn-Dill district Germany.	Bedded hematite, chamosite, siderite, magnetite.	Beds≦ 16 m thick.	Type area of the "exhalative-sedimentary" class of ores, believed related to volcanism.	Kolbe, 1953; Borchert, 1960b; Harder, 1954.
	Thuringia, Harz, and Westfalen, Germany.	Oolitic hematite and chamosite (or orthochlorite), siderite.	2 m	Lahn-Dill type	Von Gaertner, 1952; Beyschlag, Krusch, and Vogt, 1915; Hesemann, 1952.
	Ribera area, Spain	Bedded hematite		Lahn-Dill type	Quiring, 1955.
	Belgium	Oolitic hematite	≦4 m	Separate beds of Late, Middle and Early Devonian age.	Ancion, 1952.
	Lanschakogel, Austria.	Bedded limonite		Thin beds	Kern, 1952.
	Macedonia, Yugoslavia.	Oolitic chamosite, siderite, minor magnetite.	Beds 1–20 m	Three or more beds in phyllite in area of 60 by 30 km.	Page, 1958.
	Dielette, l'Hermitage-Lorge, and Trelon, France.	Bedded specularite, magnetite, quartz.		Thin beds	Caillère and Kraut, 1957; Blondel, 1955.
	Camdag-Ferizla area, Turkey.	Oolitic oxides, siderite, chlorite.	Lenses ≦25 m thick.	Fossiliferous	Krishnan, 1955.

TABLE 22.—*Occurrences of iron-rich sedimentary rocks of Paleozoic age*—Continued

	Locality	Character	Thickness	Remarks	Key references
Devonian—Con.	Rates, Portugal	Bedded ironstone		Thin beds	De Jesus and Cotelo Neiva, 1952.
	Volga-Ural region, U.S.S.R.	Oolitic chamosite; bedded siderite and limonite.		Lower Frasnian in age. Many beds.	Strakhov and others, 1959.
	Bashkira and Tatar republics, U.S.S.R.	Oolitic ironstone			Miropolsky, 1949.
	Tindouf region, Algeria.	do		Three lenticular beds known.	Matheron, 1955.
	Arizona, U.S.A	Oolitic hematite	5–7 ft	Upper part of Martin Formation.	Willden, 1960, 1961.
	Nova Scotia, Canada.	Oolitic magnetite, hematite, "green silicate", quartz.			Hayes, 1919.
	Hunan, Kiangsi, Hupeh provinces, China.	Oolitic hematite	<2 m	Several beds	Juan, 1946; Krishnan, 1955.
	Meggen, Germany	Pyrite	4 m	Grades into baritic rock, also into limestone; may not be sedimentary.	Lindgren, 1933; Bergeat, 1914; Ehrenberg, H. and others, 1954.
	Sierra Grande, Argentina.	Oolitic hematite		In sequence of "Devonian to Carboniferous" age.	Argentina, 1952.
Silurian [1]	Eastern U.S.A	Oolitic hematite (Clinton iron ores).	30 ft max. in Ala.	Sporadic occurrence from New York to Ala. generally four beds.	Burchard, Butts, and Eckel, 1910; Burchard, 1913; Newland and Hartnagel, 1908; Alling, 1947; Lesure, 1957; Hunter, 1960 (see footnote p. W7).
	Aroostook County, Maine, U.S.A.	Hematitic shale, siliceous carbonate.	Aggregate 150 ft.	Manganiferous	Pavlides, 1960, 1962.
	Sardinia, Italy	Oolitic thuringite-chamosite with siderite and magnetite.	15 m		Penta, 1952.
	Hupeh province, China.	Oolitic hematite			Krishnan, 1955.
Ordovician [1]	Thuringia, Germany	Oolitic chamosite-thuringite, magnetite.	Aggregate ≦25 m.	Three beds. Arenig age.	Von Gaertner, 1952; Engelhardt, 1942.
	Holoubkha [Holoubkov], Czechoslovakia.	Oolitic chamosite and hematite.		Tremadoc age	Blondel, 1955.
	Zdice and Krusna Hora [Krusne Hory], Czechoslovakia.	do		Arenig age	Do.
	Nucitz [Nutschitz], Czecholsovakia.	do	≦22 m	Caradoc age. Can be traced for 40 km.	Beyschlag, Krusch, and Vogt, 1915.
	Dimmersdorf and Einodtal, Austria.	Ironstone		Tremadoc age	Einecke, 1950.
	Anjou, France	Magnetite and bavalite; oolitic.	≦ 6 m	Arenig age, metamorphosed.	Tröger, 1950; Hoenes and Tröger, 1945.
	Normandy, France	Siderite, hematite, Fe-chlorite; oolitic.	≦6 m	Arenig-Llandeilian age.	Do.
	North Wales	Oolitic chlorite		Several beds of Arenig and younger age.	Strahan and others, 1920; Pulfrey, 1933.
	Southern Highlands, Scotland.	Greenalite chert			Kennedy, 1936.

See footnote at end of table.

TABLE 22.—*Occurrences of iron-rich sedimentary rocks of Paleozoic age*—Continued

	Locality	Character	Thickness	Remarks	Key references
Ordovician[1]—Con.	Quadramil, Portugal.	Oolitic chamosite, siderite.	≦ 9 m	Approx. Arenig age	Cotelo Neiva, 1953.
	Moncoro and Vila Cova, Portugal.	Hematite (Moncorvo); magnetite-quartz.	Several meters.	do	Do.
	Vivaldi, Spain	Magnetite, thuringite, siderite; oolitic.	2 m–8 m	Two beds in schist	Rechenberg, 1956.
	Siljan district, Sweden.	Oolitic limonite, chamosite, minor glauconite.	------	Similar beds found in Estonia, Latvia, and Gotland.	Hessland, 1949.
	Oland, Sweden	Glauconite	------	Ordovician and Cambrian age.	Hadding, 1932.
	French West Africa	Hematite and red jasper.	------	In schist	Blondel, 1952.
	French Morocco	Magnetite, chlorite; oolitic.	≦ 25 m	Llandeilian age; 41 localities known.	Agard, Destombes, Naudet, and van Leckwijck, 1952; Percival, 1955.
	Wabana, Newfoundland.	Oolitic chamosite and hematite.	Beds 5–30 ft	12 or more beds in 5 zones in sandstone and shale of Arenig age.	Hayes; 1919, 1929.
	Nova Scotia, Canada.	do	≦ 8 ft	------	Hayes, 1919.
	Mayville, Wis. U.S.A.	Oolitic limonite	≦ 55 ft	In Neda Formation; also noted in Illinois (Workman, 1950).	Hawley and Beavan, 1934.
	Zapla, Argentina	Hematite, thuringite	Few meters	Widespread unit	Argentina, 1952.
Cambrian	Dunderland, Norway.	Banded quartz-magnetite, quartz-hematite.	≦ 50 ft	Several beds at two horizons 3,000 ft apart in marble-schist-quartzite sequence. Some manganiferous beds.	Bugge, 1948; Foslie, 1949; Carstens, 1955.
	Georgia, U.S.A	Oolitic hematite	1–3 ft	In Shady Formation	Kesler, 1950.
	Virginia, U.S.A	Siliceous specular hematite.	≦ 6 ft	In shale and quartzite	Harder, 1908.
	Talladega, Ala. U.S.A.	Magnetite, hematite, quartz.	Lenses ≦ 50 ft.	------	Reed, 1949; Pallister, 1953.
	New Mexico, U.S.A.	Arenaceous oolitic hematite, minor glauconite.	≦ 15 ft	Found over lateral distance of 100 miles; occur in Bliss Sandstone.	Kelly, 1951.
	Lesser Khingan Range, eastern U.S.S.R.	Banded cherty iron-formation.	20–25 m	Underlain by manganiferous bed. Contains Lower Cambrian brachiopod.	Nalivkin, 1960; Chebotarev, 1958; O'Rourke, 1961.
Paleozoic (?)	Relun, Chile	Siliceous hematite	20 m	Area 8 by 15 km	Nef, 1952, Valdes, 1955.
	Morro do Urucum Brazil.	Banded hematite-jasper with manganese beds.	300 m	------	Dorr, 1945; Dorr, Guild, and Barbosa, 1952.

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[1] In much of French and German literature, the Silurian comprised both Ordovician and Silurian of British and American usage; by some, it included the Cambrian as well. Where stage names are given, these have been converted into standard American usage; where they are not, the original terminology is retained.

DEPOSITS OF PRECAMBRIAN AGE

Every shield area of the world has been found to contain beds of iron-formation, much of it only weakly metamorphosed. The principal occurrences are summarized in tables 23, 24, and 25, according to area and—for those of the Canadian Shield and South Africa—to some degree according to relative stratigraphic position. The only region not included in the tables is that of central Africa, where iron-formation is known to be present in thick beds at many places (see for example, Woodtli, 1961) but for which published data are as yet too fragmentary to present a coherent picture.

The iron-formations of South Africa, Brazil, India, and the Krivoi Rog-Kursk areas of the U.S.S.R. all are of imposing thickness and extent, but probably the most impressive assemblage is to be found in the Canadian Shield. Here, in a discontinuous chain surrounding a northeastward-trending core area of older and more highly metamorphosed rocks, is a remarkable series of "ranges" of rudely equivalent age. The Belcher Island-Nastapoka Island area is on the northwest flank of this block, the Labrador-Quebec "trough" is on the northeast end, the Lake Albanel range is on the southeast flank, and the Marquette, Menominee, Gogebic, Gunflint, Mesabi, and Cuyuna districts are on the south margin. The principal iron-formation units are bracketed in age between about 1,800 million years and 2,500 million years (Lowdon and others, 1963; Goldich and others, 1961).

TABLE 23.—*Occurrences of iron-rich beds of Precambrian age in North America and South America*[1]

Region	Locality	Character	Thickness	Remarks	Key references
Canadian shield: Approximately Animikie (or Huronian) age.	Iron-River-Crystal Falls district, Mich.	Cherty iron-formation, mostly siderite facies.	≦600 ft	Riverton Iron-Formation; youngest iron-formation of Animikie Series.	James, 1951, 1954, 1958; James and others, 1959.
	Amasa Oval and West Marquette, Michigan.	Chert-magnetite, chert-hematite, chert-siderite.	≦800 ft	In Animikie Series, but younger than major iron-formation units. Four separate units (Mansfield, Bird, Fence River and Amasa of Amasa Oval: Bijiki of West Marquette).	Leith, Lund, and Leith, 1935; Gair and Wier, 1956; Bayley, 1959; James, 1958.
	Belcher-Nastapoka Islands, Canada.	Cherty iron-formation; oxide, silicate (greenalite), siderite facies.	270 ft	Overlain by basalt	Moore, 1919.
	Labrador trough, Labrador-Quebec.	Cherty iron-formation; oxide, silicate-siderite facies.	≦600 ft	Sokoman Formation; Wabash Lake Iron-Formation. Belt 600 miles long, 60 miles wide.	Harrison, 1952; Westervelt, 1957; Auger, 1954; Gastil and Knowles, 1960.
	Lake Albanel range, Mistassini district, Quebec.	Cherty iron-formation; oxide, silicate, siderite facies.	≦700 ft		Quirke, Goldich, and Krueger, 1960; Quirke, 1961.
	Mesabi-Gunflint range, Minnesota-Ontario.	Cherty iron-formation; oxide, silicate, siderite facies.	≦800 ft	Biwabik Iron-Formation; Gunflint Iron-Formation. Total length 200 miles, interrupted by Duluth Gabbro Complex.	Gruner, 1946; White, 1954; Goodwin, 1956.
	Cuyuna district, Minnesota.	Mostly silicate-siderite iron-formation.	Several hundred feet.	Manganiferous. Possibly correlative with Biwabik Iron-Formation.	Grout and Wolff, 1955; Schmidt, 1963.
	Gogebic, Marquette, and Menominee districts, Wisc.-Mich.	Cherty iron-formation; oxide, silicate siderite facies.	≦ 2,000 ft, Marquette district.	Ironwood Iron-formation (Gogebic); Negaunee Iron-Formation (Marquette); Vulcan Iron-Formation (Menominee). Probably correlative but deposited in separate basins.	Leith, Lund, and Leith, 1935; Huber, 1959; James, 1958.

See footnote at end of table.

TABLE 23.—*Occurrences of iron-rich beds of Precambrian age in North America and South America*[1]—Continued

Region	Locality	Character	Thickness	Remarks	Key references
Canadian shield—Continued Pre-Animikie age.	Michipicoten district, Ontario.	Helen Iron-Formation: chert, siderite, pyrite.	Siderite beds to 350 ft; pyrite beds to 120 ft.	Helen Iron-formation considered to be of exhalative-sedimentary type.	Goodwin, 1962.
		Lower iron-formation: chert-magnetite, chert-hematite.	Lenticular, typically to 300 ft thick, 3,000 ft long.		
	Vermilion district, Minnesota.	Mostly chert-hematite, chert-magnetite.	Few hundred feet or less.	Soudan Iron-Formation, underlain by Ely Greenstone (lower Precambrian).	Grout and others, 1951; Goldich and others, 1961.
	Skunk Creek belt, Mich.	Banded magnetite-quartz-silicate.	100 ft	In Dickinson Group	James and others, 1961.
Rocky Mountain	Southwest Montana	Banded quartz-magnetite, mostly.	Beds ≦50 ft	Many occurrences, probably not correlative.	DeMunck, 1956; James and Wier, 1961, 1962.
	Atlantic City, Wyo	Banded quartz-magnetite.	150 ft		Bayley, 1963.
	Seminoe Mountains, Wyo.	do	≦300 ft		Lovering, 1929.
	Arizona-New Mexico	Banded jasper-magnetite.	≦30 ft, lenticular.	In Jerome area, Arizona, interbedded with dacite flows.	Burchard, 1931; Anderson and Creasey, 1958; Bertholf, 1960.
South America	Guiana Shield, Venezuela.	Banded magnetite-quartz, hematite-quartz.	≦700 ft (Cerro Bolivar).	Includes El Pao, Cerro Bolivar, Santa Barbara areas.	Stam, 1963, Ruckmick, 1963.
	Amapa, Brazil	Banded quartz-hematite.	75m		Dorr, Guild, and Barbosa, 1952.
	Mato Grosso, Brazil, and Santa Cruz, Bolivia.	do	≦300 m (Morro do Urucum).	Manganiferous; possibly Paleozoic in age.	Dorr, 1945; Dorr, Guild, and Barbosa, 1952.
	Minas Gerais, Brazil (Quadrilatero Ferrifero).	Banded quartz-hematite (itabirite).	To 1000 m; average about 250 m.	Cauê Itabirite, of Minas Series; original extent probably more than 10,000 square miles.	Dorr, Guild, and Barbosa, 1952; Johnson, 1962; Guild, 1957; Dorr and Barbosa, 1963.
	Minas Gerais, Brazil	Siderite iron-formation.	Lenses to 50 ft.	In pre-Minas Rio das Velhas Series.	Gair, 1962.

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[1] Not a complete list. Does not include some highly metamorphosed rocks in Canada, nor some recent discoveries for which information is scant.

TABLE 24.—*Occurrences of iron-rich beds of Precambrian age in Europe and Asia*[1]

Area	Locality	Character	Thickness	Remarks	Key references
Scandinavia	Sydvaranger and others, Norway; Stripa and others, central Sweden; Porkonen and Jussaari, Finland.	Banded quartz-hematite, quartz-magnetite.	Generally few tens of meters or less.	Strongly metamorphosed in most places.	Norway: Bugge, 1953; Poulsen, 1952. Sweden: Geijer, 1938; Geijer and Magnussen, 1948, 1952. Finland: Marmo, 1952.
U.S.S.R.	Krivoi Rog, Ukraine.	Cherty iron-formation; oxide, silicate, carbonate facies.	≦200 m	Tightly folded belt 250 km long.	Svitalsky, 1937; Semenenko and others, 1956; Belevtsen, 1957.
	Kursk (Kursk magnetic anomaly).	Banded quartz-hematite, quartz-magnetite.	≦500 m	Covered in places with several hundred meters of Paleozoic and younger strata.	Plaksenko, 1959.
	Belozerkoye area, Zaporozh'ye region.	Banded quartz-hematite.	≦500 m	Stratigraphy similar to both Krivoi Rog and Kursk.	Alexandrov, 1962.
	Central Kazakhstan	Banded iron-formation.	Believed to be thick.	---	Polovinkina and Rozina, 1956 (as reported in published annotated bibliographies).
	Southern Urals	Siderite layers in shale and limestone.	Lenses ≦60 m.	Part of Burzyansk Series (Riphean).	Starostina, 1959.
	Eastern Siberia (Bakal upland).	Hematite-jasper	Lenses in zone 200 m thick.	Classed as exhalative-sedimentary.	Pavlosky and Belichenko, 1958.
China	Chahar province, northern China.	Oolitic hematite (minette type).	4 m or less	In Sinian System, with sandstone and shale. Shows stromatolitic structures.	Tegregen, 1921; Krishnan, 1955; Matsuzawa, 1953.
	Southern Manchuria and adjacent areas of Korea.	Banded hematite-quartz, magnetite-quartz.	≦400 m (at Miao Erh Kou).	In middle Precambrian Wu-t'ai-shan System.	Tegregen, 1921; Tsuro, 1931; Murakami, 1922; Asano, 1953; Krishnan, 1955.
India	Singhbhum and adjoining areas of Bonai and Keonjar.	Banded hematite-jasper.	≦3,000 ft (possible fold repetition).	Area of 40 by 25 miles.	Krishnan, 1955 Spencer and Percival, 1952.
	Bailadila, Rowgat, and adjacent deposits of Madhya Pradesh.	Banded quartz-magnetite, quartz-hematite.	≦1,500 ft	---	Krishnan, 1955.
	Hyderabad	Quartz-magnetite, quartz-hematite schist.	≦150 ft	In Dharwar System ("Archean").	Krishnan, 1952.
	Mysore State	Banded hematite-quartz.	≦200 ft	In Dharwar System	Krishnan, 1952 Radhakrishna, 1951.
	Salem-Trichinopoly district, southern India.	Banded magnetite-quartz.	Beds to 100 ft.	At least 3 beds known	Krishnan, 1952.

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[1] Not a complete list. Includes iron-rich beds of major thickness and (or) significance. Grouped deposits, as in India, may include formations not stratigraphically equivalent.

TABLE 25.—*Occurrences of iron-rich beds of Precambrian age in Australia and South Africa*

Australia

Locality	Character	Thickness	Remarks	Key references
Roper Bar, northern Australia	Oolitic hematite and greenalite; magnetite, siderite.	Beds ≦40 ft	Three beds separated by sandstone and shale. "Upper Proterozoic."	Edwards, 1958; Cochrane and Edwards, 1960.
Constance Range, northern Australia	Oolitic hematite and greenalite (?); siderite.	≦30 ft	Two beds separated by sandstone. "Upper Proterozoic."	Edwards, 1958.
Yampi Sound, northwestern Australia	Banded hematite-quartz, magnetite-quartz.	≦130 ft	"Middle Precambrian."	Canavan, 1953.
Western Australia	do	Many thin beds.	Widespread in occurrence ("jasper bars"). "Archean."	Miles, 1953.
Middleback Ranges, South Australia	do	≦200 ft	Possibly two separate formations.	Rudd and Miles, 1953; Percival, 1955b; Edwards, 1953; Miles, 1954.

South Africa

Locality	Stratigraphic position	Character	Thickness	Remarks	Key references
Transvaal System of Transvaal.	Pretoria Series, 5 horizons:				
	1. Waaikraal	Magnetite and silicates.	≦12 ft	Crop out in belts partly encircling Bushveld Complex. Magnetic quartzite (Timeball Hill horizon) can be traced for 300 miles.	Wagner, 1928.
	2. Daspoort	Oolitic hematite and chamosite.	Av. 3 ft		
	3. Clayband	Magnetite-chamosite-siderite oolite.	≦4 ft		
	4. Pisolitic ironstone.	Arenaceous hematite chamosite.	≦6 ft		
	5. Magnetic quartzite (lowest unit).	Magnetite-hematite-chamosite oolite.	≦27 ft		
	Dolomite Series, Thabazimbi.	Banded quartz-hematite.	200–260 m	Stratigraphically below Pretoria Series.	Du Preez, 1945.
Transvaal System of Cape Province.	Pretoria Series, Griquatown Stage: Postmasburg belt (Gamagara Rand).	Banded chert, magnetite, silicates, siderite.	2,500 ft in south, 1,000 ft in north.	Belt 320 miles long	Wagner, 1928; Cilliers and others, 1961; Cullen, 1963.
Witswatersrand System of Transvaal and adjacent areas.	Three horizons, main one in Hospital Hill Slate Zone.	Banded quartz-hematite, quartz-magnetite.	As much as several hundred ft.		Wagner, 1928.
Swaziland System of Transvaal, Natal, Zululand, Northern Cape Province; also Southern Rhodesia.	Beds at different horizons.	Banded quartz-magnetite, quartz-hematite; magnetite-chamosite-siderite in places.	Generally 20–100 ft.		Do.

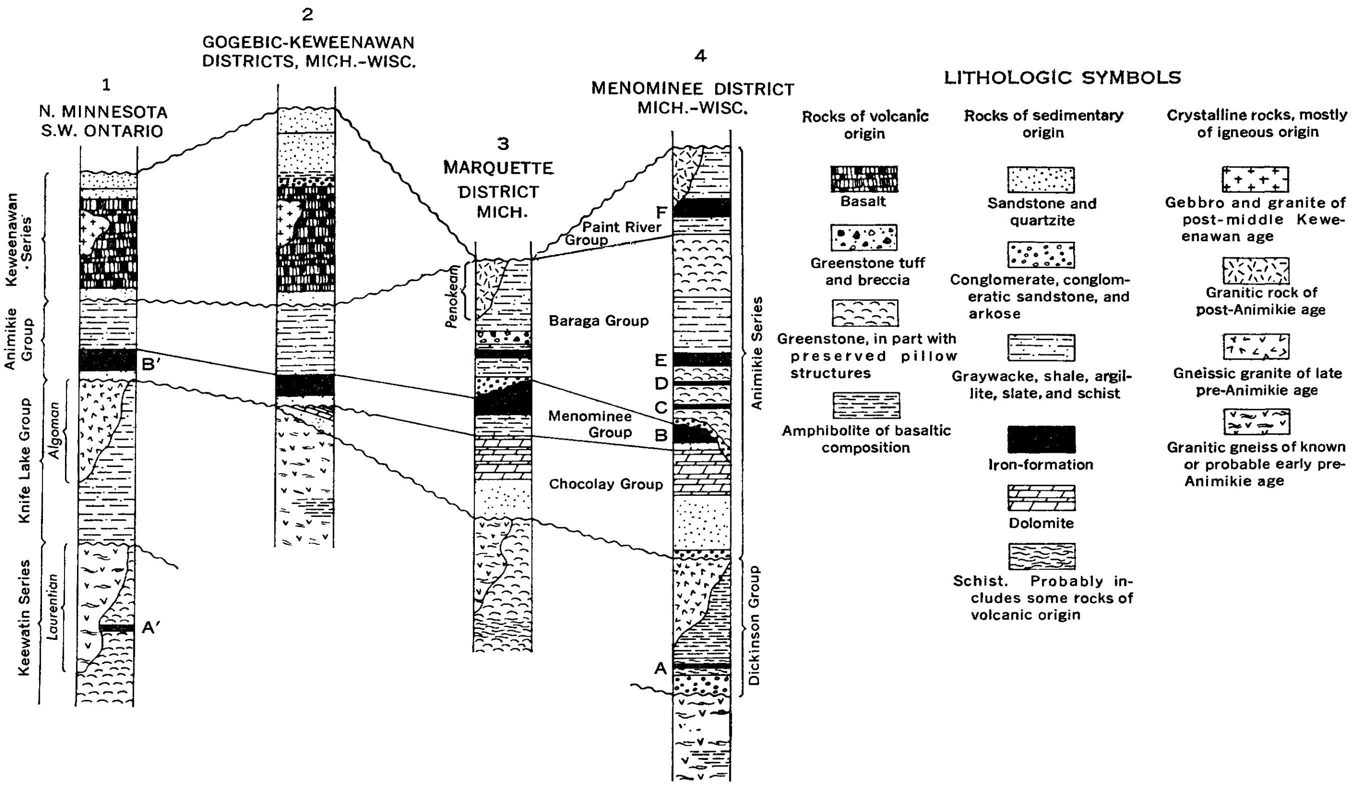

FIGURE 6.—Generalized stratigraphic successions of Precambrian rocks of the Lake Superior region, showing occurrence of iron-formation units (modified from James, 1960).

The iron-rich rocks of the Canadian shield attain maximum thickness and complexity on the south side of Lake Superior (fig. 6). The main iron-formation unit of the Animikie Series (unit B of fig. 6, which represents the Vulcan, Negaunee, Ironwood, Biwabik, and Gunflint Iron-Formations of the various districts) attains a thickness of 2,000 feet in the Marquette district. In the Menominee and Iron River-Crystal Falls districts and adjoining areas, the main iron-formation is succeeded by at least four other units having thicknesses of 100 to 800 feet; in column 4, in ascending order, these are the Mansfield and Bird Iron-bearing Members of the Hemlock Formation (C,D), the Amasa Formation (E), and the Riverton Iron-Formation (F). The aggregate thickness of the Animikie Series in the area illustrated by column 4 (fig. 6) is about 50,000 feet, of which iron-formations in maximum thickness comprise about 4,000 feet. All the facies of iron-formation are represented—sulfide, carbonate, silicate, and oxide (both hematite and magnetite varieties). Of particular interest are the local development of algal structures in the Biwabik Iron-Formation (unit B′), as described by Grout and Broderick (1919) and by Gruner (1946), and the magnificent preservation of algal forms in basal chert of the Gunflint Iron-Formation of Ontario (Barghoorn, 1957).

Also shown in figure 6 are the pre-Animikie iron-formation units of Minnesota and Michigan (units A and A′). Unit A′, in particular—the Soudan Iron-Formation of the Vermilion district—is representative of "Keewatin-type" iron-formation, of common occurrence in the pre-Animikie mafic volcanic rocks elsewhere in the Shield. The Soudan is more than 2,500 million years old (Goldich and others, 1961), and is separated from the Animikie Group by two profound unconformities.

The main iron-formations of the Lake Superior region appear to be approximately equivalent in age to those of Krivoi Rog and Kursk in Russia, which have been assigned an age of 1,800–2,000 million years (Semenenko, 1959), and to the Transvaal System of South Africa, which contains the major iron-formations of that region and which is estimated to be about 2,000 million years in age (Nicolaysen, 1962). The Cauê Itabirite of Brazil, which was thought to be bracketed between 500 and 1,350 million years (Herz and others, 1961), is now believed to have an age between 2,600 and 1,300 million years (P. W. Guild, written communication, March 19, 1964). In India the rocks associated with iron-formation of the Singhbhum district yield apparent ages of about 1,500 million years (Pichamuthu, 1962). The oldest iron-formation units known are those of "Keewatin-type" in the Swaziland System of South Africa, the age of which is believed to be in excess of 3,100 million years (Nicolaysen, 1962).

IRON IN NATURAL WATERS

Iron is held and transported in natural waters in three forms: (1) as dissolved iron, mainly ferrous; (2) in suspension as a colloid or particulate form; and (3) as a constituent of clastic particles.

IRON IN SOLUTION

The solubility product of $Fe(OH)_3$, which is the stable (or metastable) species of iron in the Eh-pH range of most natural surface waters, is extremely low. Published values range from 10^{-36} to 10^{-40} (Hem, 1960a, p. 53). Consequently the amount of iron that theoretically can be held in true solution is vanishingly small except at abnormally low values of pH (5 or below), or in equilibrium with abnormally high concentrations of SO_4^{-2} or Cl^{-1}—certain oilfield brines and volcanic waters (see White, Hem, and Waring, 1963, p. 32, 44). The low theoretical solubility of iron in the normal environmental range is indicated by figure 7, which is one of a family of Eh-pH diagrams that can be drawn for specified anionic concentrations (Hem, 1960b, p. 69). As Hem states, the usefulness of such diagrams is restricted by the arbitrary selection of anionic values and by the implicit assumptions of equilibrium and absence of unspecified complex ions.

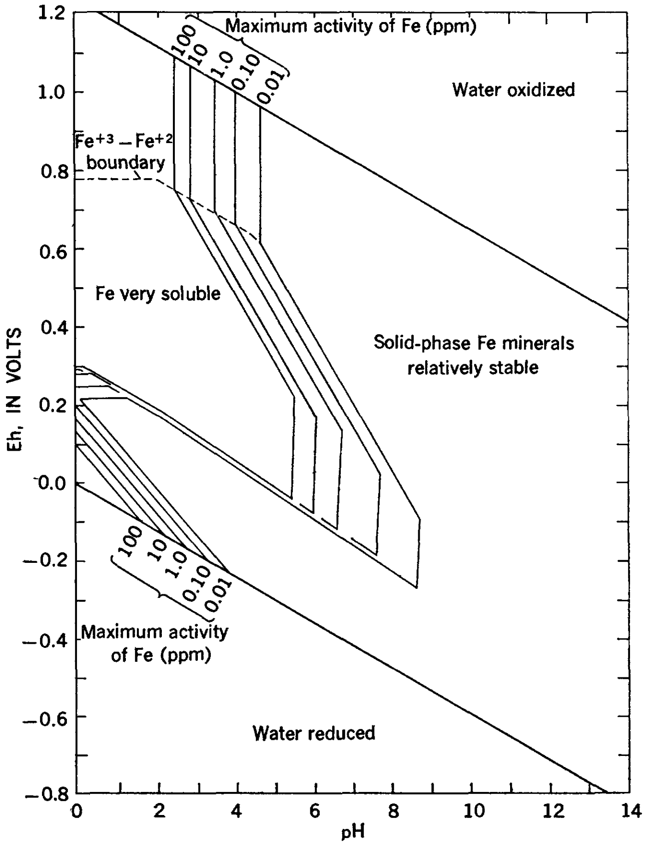

Figure 7.—Activity of dissolved iron in equilibrium with total sulfur at activity 10^{-3} (equivalent to 96 ppm SO_4^{-2} and total carbonate at activity 5×10^{-3} (equivalent to 305 ppm HCO_3^{-1}). (From Hem, 1960b).

According to Lewis and Goldberg (1954), the average content of soluble iron in the ocean is 0.0034 mg/l both at surface and at depth (mg/l=ppm, in water of unit density). Dobrzhanskaia and Pshenina (1958) record the soluble iron content of the Black Sea as zero at the surface and at depth in most places, but locally in the "deep layer", at 1,000–2,000 m in depth, the concentration is as high as 0.020 mg/l. The content of soluble iron of ground waters in common rocks generally is less than 1 ppm, but values of as much as 5 ppm are not rare (White, Hem, and Waring, 1963). The higher values doubtless reflect the presence of ferrous iron in water of either low pH or low Eh, or both. According to Hem and Cropper (1959, p. 16) iron concentrations of as much as 50 ppm are stable in natural ground waters. The redox potentials of such waters will be raised in near-surface environments by contact with oxygen, with consequent precipitation of ferric iron. Hem notes, however, that ferrous iron commonly is present in emerging natural waters and attributes its preservation to lack of equilibrium. The dissolved-iron content of stream waters generally is low; the average for streams of the world has been computed to be 0.73 ppm (Strakhov, 1948).[4]

Iron may also be in solution as organic complexes, including chelates, many of which are well known in laboratory procedures (Bjerrum, Schwarzenbach, and Sillen, 1957). Information on such possible complexes in natural environments is scant, but the complexes of tannic acid have been investigated experimentally by Hem (1960c). The complexing of ferrous iron was noted to be particularly strong in fairly concentrated solutions of tannic acid (500 ppm, or about 1.5×10^{-3} molarity); colored complexes were formed over a pH range of 2 to 9, with Fe concentrations after a month's time of 10 to 2 ppm. Hem (1960c, p. 94) concludes that the mechanism may be effective in solution and tansport of iron in forested regions. Hutchinson (1957) discusses at some length the relation between iron content and organic matter in lake waters, noting that some lakes in northern Sweden contain as much as 2,500 mg Fe m^{-3} (p. 711). He concludes (p. 714) that

> * * * apart from particulate iron compounds in organisms and perhaps in suspended silt, the main forms of iron in lake water are ferric hydroxide in particulate form or adsorbed to particles of microscopic dimensions, and an organic iron complex or series of complexes.

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[4] Some uncertainty exists as to the validity of Strakhov's values. In the published discussion accompanying the paper, A. P. Vinogradov expresses the view that the division made between soluble and suspended iron seemed arbitrary and that in fact the amount of iron in true solution is much lower.

Shapiro (1964) also notes that iron is present in many natural waters in vastly greater quantity than that predicted by physicochemical argument, and he shows experimentally that much of this excess iron must be in the form of ferric colloid peptized by organic acids.

As previously mentioned, certain waters of volcanic association may contain large amounts of iron in equilibrium with SO_4^{-2} or Cl^{-1}. White, Hem, and Waring (1963, p. 44) record values of as high as 5,100 ppm. A particularly interesting example is the iron-rich water of hot springs related to Ebeko volcano, Paramushir Island, and its transport to the Okhotsk Sea (Zelenov, 1958). For the main stream carrying iron-rich waters to the sea, the data are as follows:

Distance below confluence of hot-spring waters	pH	Iron content (mg/l)	
		Fe^{+2}	Fe^{+3}
0	1.3	150	120
700–800 m	1.4	20	200
1700–1800 m	1.6	10	320
Mouth of stream (≈ 3 km)			
Sample 1	1.4	5	320
Sample 2	1.5	---------	220

The discharge is 1.8/m^3/sec, and the total iron delivered to the sea is 400–500 gms/sec or 35–50 tons per day. The iron-rich waters extend into the sea as a colored band a few hundred meters wide and several kilometers long. The band is divided into three zones: (1) a near-shore zone of poisonously green water out to 50–80 m from the river mouth; (2) a zone about 1.5 km long colored yellow by precipitation of yellow iron oxides, and (3) a zone out to the open sea of bluish-yellow water without precipitated iron oxides. The pH increases steadily from 1.7 in the surf zone to 7.6 in the normal sea water. The content of iron decreases steadily to 1 mg/l.

IRON IN SUSPENSION

Ferric hydroxide readily forms colloidal suspensions, which are fairly stable and have a positive charge. Iron sols are reportedly stabilized by organic colloids; Moore and Maynard (1929, p. 375) state, "Natural streams, therefore, in which the content of organic matter is at least 4.5 ppm, will have no difficulty in transporting 30 ppm colloidal silica and 10 ppm colloidal ferric oxide.* * *" Iron in particulate form, which is defined by Lewis and Goldberg (1954) to be that of plus 5-micron dimensions, is present in considerably greater amounts than dissolved iron in sea water and displays much greater range—0.0045 mg/l in deep waters (more than 500 m) and as high as 3.25 mg/l in shoal water. The maximum amount of particulate iron in the Gulf of Panama is 0.863 mg/l. in near-shore positions (Schaefer and Bishop, 1958). Plankton such as diatoms absorb particulate ferric hydroxide, and Harvey (1932–33) comments that there is "* * * little more ionic iron in a cubic metre of water than found in a diatom of moderate size."

Strakhov (1948 table 7), in his extensive study of suspended iron in natural waters, shows that for streams in the U.S.S.R. the ratio of suspended iron to dissolved iron—which here appears to include particles of true colloidal dimension—ranges from about 1:1 to 100:1. It must be noted, however, that for some streams the amount of suspended iron was computed from the turbidity of the water and the Fe content of the total load; this would include iron carried on or chemically as part of clay minerals.

IRON AS A CONSTITUENT OF TRANSPORTED OR SUSPENDED CLAYS

Iron is associated with clays as an essential ion in the clay structure, as in nontronite, or as surface films of oxides on the clay micelles (Carroll, 1958). Of these two principal modes, the surface films on oxides appear to be quantitatively the more important; the iron-bearing clays are relatively scarce in occurrence. As quoted by Carroll (p. 4), the average ferric oxide content of the colloid fraction of 162 soils in the United States is 10.3 percent. Presumably, an appreciable fraction of this is as separated particles, rather than clay-bound, which would separate from the clay host during erosion and transportation; nevertheless, although quantitative data are few, there seems little doubt but that much iron is transported as oxide films on clays. If the clay fraction is accumulated in an environment of low Eh, the oxide iron may return to solution and redeposit as glauconite, chamosite, siderite, or sulfide (Carroll, 1958, p. 24; Strakhov, 1948).

Iron also of course may be transported in coarser clastic fractions as an essential constituent of such minerals as pyroxene or hornblende or of volcanic materials, and similarly can be recycled through sea-bottom reactions—a process labelled "halmyrolse" by Hummel (1922). This mobilization of iron from clays and other clastic materials may take place both on sea-bottom or below the depositional interface. Bruevich (1938b) describes such mobilization and reconcentration of iron (and manganese) in bottom deposits of the Barents Sea.

CONCLUSIONS

The amount of iron in true solution in the oceans and most natural bodies of water is extremely small, and is controlled by the very low ($\approx 10^{-38}$) solubility-product of $Fe(OH)_3$. Concentrations typically are about 0.003 mg/l in ocean water and considerably less than 1 mg/l in most streams and ground waters. The only natural waters carrying significantly large quantities of iron (to 10 mg/l) in solution are certain bicarbonate or bicarbonate-sulfate ground waters and rare hot spring waters in some volcanic areas (to 5,000 mg/l). Some natural fresh waters may also contain relatively large concentrations of iron as an organically peptized ferric colloid, or, to a lesser degree, as organic complexes.

The bulk of the iron produced by present-day erosion is transported to the ocean as colloidal ferric hydroxide, as adhering oxide on clay, or as chemically bound ions in clastic mineral particles. This iron may be remobilized by sea-bottom reactions to form local concentrations, such as concretions, fossil replacements, and perhaps glauconite pellets, but in general it must remain associated with, and be much subordinate to, the dominantly clastic deposits; it is not a likely source of iron for the main deposits of ironstone and iron formation.

IRON IN PRESENT-DAY SEDIMENTS

With the exception of "bog ores" in lakes of higher latitudes (see next page), there is no example in present-day environments of deposition of material approaching in composition the iron-rich units of past eras. Hematite-coated quartz grains and hematite oolite dredged from the North Sea have been regarded as contemporary formation of iron oolite (Pratje, 1930), but there is considerable doubt as to the interpretation; the material may be reworked from older beds, and certainly the North Sea is not the site of modern-day ironstone deposition.

The general sedimentation pattern of present-day marine regions is that of relatively iron-poor sediments near the coasts and progressive increase in iron content toward the deeps, the highest iron content being found in the red clays far from shore. In a chemical and mineralogical study of deep-sea sediments, Wakeel and Riley (1961, p. 125) write:

> With the exception of the highly calcareous sediments, the iron content of the deep-sea sediments, calculated as Fe_2O_3, on a carbonate and water-free basis, is surprisingly uniform. This is particularly true of the argillaceous samples, which contain average concentrations of 8.23 percent total Fe_2O_3 (7.04 percent Fe_2O_3 and 1.13 percent FeO on original clay). [In table 3 in Wakeel and Riley, the average Fe_2O_3 content of argillaceous sediments, on a carbonate and water-free basis, is given as 8.93 percent rather than 8.23 percent. H.L.J.] The mean iron contents of the sediments of the three oceans are similar, but those from the Pacific are slightly higher * * *.
>
> Certain of the highly calcareous samples from the Atlantic (Nos. 2, 6, and 11) and their acid-insoluble residues have Fe_2O_3 contents (on a water- and carbonate-free basis) considerably higher than the argillaceous sediments. This effect has been observed previously by Revelle (1944) who found that sediments containing less than 30 percent of carbonates contained on the average about 7.0 percent of Fe_2O_3 (on a water- and carbonate-free basis), whereas those containing over 80 percent of carbonates had much greater concentrations of Fe_2O_3 amounting to as much as 16 percent in some cases. This excess iron over that contained in the argillaceous sediments is probably derived from globigerina or other organisms, the highly insoluble iron oxide or hydoxide content of which remains after their calcareous parts have dissolved away during sedimentation.

The relating of iron content to organisms had been proposed by Correns (1937, 1952b), who noted that foraminiferal tests contain 0.16 to 0.65 percent Fe_2O_3. Correns also noted that the far-reaching deltaic deposits of the Amazon River, which is higher in Fe content than most major streams, are not enriched in iron, doubtless because of dilution by a heavy clastic load.

The pattern of iron distribution in bottom deposits of lakes and seas has been studied by many. In general, however, the total amount of iron is relatively moderate—less than that of the deep-sea deposits and much less than that of the sedimentary ironstones. Tabulations by Strakhov (1959, table 4) for bottom deposits of the Black Sea, for example, show total iron to range from 3.07 percent to 4.94 percent of which a quarter to a half is in detrital material. The exceptionally high iron content (to 11.11 percent) found locally in the bottom sediments of the Okhotsk Sea, particularly near the Kurile Islands, doubtless is related to incorporation and dissolution of volcanic materials (Ostroumov, 1955).

A submarine iron-rich deposit similar to that being deposited off Paramushir Island (see p. W40) is reported to be present near Santorin, Greece. According to Harder (1960), the deposit, the extent of which is not specified, consists mainly of ferrous and ferric hydroxides and is related to recent volcanic or fumarolic activity. The chemical composition of the deposit is as follows, in weight percent:

SiO_2	18	TiO_2	0.01
Fe_2O_3 [1]	58	MnO_2	.1
Al_2O_3	.05	CaO	.15
P_2O_5	.3	MgO	.2
V_2O_5	.0	H_2O	21
MnO [2]	.15		

[1] Presumably total iron given as Fe_2O_3.

[2] As given.

BOG IRON DEPOSITS

The so-called bog iron ores—including "lake ore", "meadow ore"; "raseneisenstein"—are found in many swamps and lakes in recently glaciated regions, notably in North America, northern Europe, and northern Asia. Prior to about 1900 these deposits were significant sources of iron ore and were studied by many investigators, particularly in Europe, but modern literature on the subject is scarce. Nevertheless, as Lindgren (1933, p. 263) says, "* * * the easily traceable processes of their formation gives us a most welcome key to the origin of other and more obscure deposits." The most significant work of relatively recent years is that of

Ljunggren (1953, 1955a, 1955b), on the bog ores of Sweden; and that of Strakhov (1948) and Krotov (1950) on the bog ores of the U.S.S.R.

The ores exhibit a wide range of characters—in composition (manganiferous to nonmanganiferous), in occurrence, and in physical properties. Harder (1919, p. 53) divides them into two general groups on the basis of occurrence: (1) those formed in agitated or flowing water at lake margins, and (2) those formed in marshes, bogs, or other shallow depressions.

Type 1, lake ore, is found most abundantly between depths of 1 to 5 m and rarely at depths of as much as 10 m. The ores consist of oolitic or pisolitic grains, 2 to 7 mm in diameter, commonly cemented into discs ranging in diameter from an inch or so—the "penny-ore" of Sweden—to a foot or more. These grains and discs, together with fragments of similar material and clastic detritus, coalesce to form more or less continuous masses generally less than 1 m thick. Krotov (1950) reports the alternation of iron and manganese oxides, locally with chamositic chlorite, in some of the concretionary forms in Russian lakes.

The bog ores of type 2 occur as thin layers of earthy to pisolitic yellow to black oxides, both at the surface and below as much as several feet of porous soil or peat. Much of the material is cemented sand and encrusted plant remains. These ores commonly contain nests of white fine-grained siderite, and in places the siderite is the major iron mineral; the analyses given by Clarke (1924, p. 538) of "raseneisenstein" from the Netherlands show as much as 37.70 percent $FeCO_3$. Vivianite also is a common mineral, in amounts to several percent or more.

The chemical compositions of "lake ores" have considerably greater range in manganese and lesser range in phosphate (and carbonate) than the bog ores of type 2. Many analyses are quoted by Beyschlag, Krusch, and Vogt (1909); those of Finnish lake ores show the following range:

	Percent
Fe_2O_3	20. 5–69. 5
MnO_2	3. 3–40. 3
SiO_2	7. 1–19. 3
Al_2O_3	. 9– 3. 2
CaO	0. 4– 0. 8
MgO	Tr.– . 3
P_2O_5	0. 45–1. 25
Loss on ignition	12. 9–21. 9

Further analyses of Finnish ores, giving Fe and Mn contents together with minor elements, are presented in table 26. In many of the deposits, layers of iron-rich material alternate with, are encrusted by, or grade into manganese-rich ore.

Goethite is the only identifiable iron oxide of the bog ores. In a differential thermal and X-ray study of the Swedish ores, Ljunggren (1955b) finds that the soft earthy ores yield diffuse patterns in X-ray powder photographs, only the major reflections of goethite being identifiable, whereas the hard varieties of lake ore are much better crystallized. The DTA curves are significantly different from standards of any of the crystalline iron oxides, probably owing to the presence of oxide and oxide hydrate gels. The manganese mineral associated with the Swedish ores probably is mainly delta-MnO_2, but the identification is not certain (Ljunggren, 1955b, p. 145–146). The manganiferous ores are enriched in minor elements and have higher radioactivity than the predominantly iron ores (Ljunggren, 1955a).

The distribution of the deposits appears to have little relation to the nature of bedrock, nor do the deposits in bogs and lakes have any necessary relation to tributary streams. On the basis of a study of bog iron deposits in Finland, Aarnio (1920) concluded that the deposits were found only in or adjacent to water-permeable ground, usually sand, in areas of humous podzolic soil. These soils are strongly acid; iron (and manganese) are leached in the A-horizon and are removed, probably as soluble humates or bicarbonate. Formation of bog ores occurs when the subsoil water enters water courses, lake shallows, or more aerated ground (Ljunggren, 1955a; Aarnio, 1920; Strakhov, 1948; Borchert, 1960a). In general, the precipitation is in response to the predictable rise in Eh when the waters become aerated, and the increase in pH with loss of CO_2.

Bog ores of quite different origin are present in areas of recent or present-day volcanic activity in Japan. According to Zelenov (1960, p. 50), one deposit is 2,000 m long, 30–200 m wide, and as much as 20 m thick. The iron in these deposits apparently has been precipitated from emerging thermal waters.

MINOR ELEMENTS

The systematics of minor-element distribution in the iron-rich sedimentary rocks are poorly known, for three principal reasons: (1) relatively few rocks have been analyzed; (2) most investigations have covered only a few of the minor elements and these are different from one study to another; and (3) the values obtained by different methods, or by different laboratories, are not necessarily comparable. Reason 3 may be illustrated by reference to the published values for boron content of Finnish lake ores, as determined by highly reputable analysts: Goldschmidt (1954, p. 286–87) reports that of 12 samples analyzed, 9 had no boron, 2 contained 5 ppm, and only one contained as much as 10 ppm, whereas Landergren (1948; see table 26 in this report) finds boron to be present in all analyzed samples of entirely similar ore, with amounts in the range of 20 to 40 ppm.

For reasons 2 and 3 above, it is not feasible to present a single tabulation of available analyses, nor is it feasible

TABLE 26.—*Iron, manganese, and minor-element contents of bog iron ores from deposits in Finland*[1]

[Adapted from Landergren, 1948. Values are given in weight percent]

Element[2]		1	2	3	4	5	6	7	8	9	10	11	12	13	14	Average[3]
Name	Estimated error (percent)															
Fe	--------	18.8	34.8	12.0	31.0	49.9	26.1	44.22	33.43	44.22	26.35	42.44	25.4	28.27	40.4	32.7
Mn	--------	14.1	5.9	8.9	12.0	.6	16.7	1.65	1.10	.89	2.92	.83	23.3	15.35	.20	7.45
B	--------	0.003	0.003	0.003	0.003	0.003	0.002	0.003	0.002	0.003	0.003	0.003	0.004	0.003	0.002	0.0029
Be	±25	<.001	<.001	<.001	.001	<.001	.001	<.001	<.001	.001	<.001	<.001	.001	.0008	<.001	.0007
Co	±25	.01	.02	.008	.01	.03	.008	.01	.006	.008	.008	.02	.007	.02	.01	.013
Cr	±30	<.001	<.001	<.001	<.001	≦.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
K	±20	--------	--------	.06	.04	≦.04	.05	--------	.07	--------	--------	--------	.05	.004	--------	--------
Li	±15-20	.004	.0005	.001	.0006	≦.0005	<.0005	.004	.0005	≦.005	≦.0005	≦.0005	.0005	.0007	≦.0005	.001
Mg	±10-15	.1	.1	.5	.1	≦.1	.1	.3	.2	≦.1	≦.1	≦.1	.09	.66	≦.1	--------
Mo	±20	<.005	<.005	.006	.005	≦.005	<.005	<.005	<.005	≦.005	≦.005	≦.005	<.005	<.005	≦.005	--------
Ni	±10	.003	.006	.002	.01	.001	.004	.001	.001	.004	<.001	<.001	.008	.01	.003	.004
Rb	±15	≦.001	<.001	.001	<.001	≦.001	.001	--------	.001	<.001	--------	--------	.001	.001	--------	.008
Ti	±40	≦.001	.01	1.0	.03	≦.01	.03	.15	.08	.10	<.01	.03	.20	.20	.02	.15
V	±25	≦.01	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	≦.001	<.001
W	±20	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	--------

[1] Samples numbered as in Landergren (1948). From collection by E. H. Kranck.

[2] Fe and Mn determined "in Helsingfors;" uame of analyst not given. Ti determined chemically and other elements spectrographically by S. Landergren in laboratories of Geological Survey of Sweden; estimated errors as given by Landergren.

[3] As given by Landergren, 1948, p. 108, 110.

TABLE 27.—*Iron, manganese, and minor-element contents of some iron-rich rocks.*

[Adapted from Landergren, 1948. Values in weight percent]

Element[1]		Sideritic ironstone		Chamositic ironstone				Limonitic ironstone	Hematitic iron-formation		Magnetite iron-formation		Averages[3]		
													Oolitic ironstone[2]	Sideritic ironstone	Quartz-banded ore, Sweden
Element	Estimated error (percent)	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Fe	--------	38.9	53.4	35.3	(4)	35.7	nd	nd	52.0	52.2	46.6	nd	31	38	52
Mn	--------	.2	.1	.05	0.1	.2	1.2	0.5	.09	.3	.08	0.25	.16	.26	.12
B	--------	0.01	0.001	0.01	0.002	0.005	0.001	0.01	<0.001	0.001	<0.001	<0.001	0.0073	0.0028	0.0006
Be	±25	<.001	.002	<.001	.001	.001	<.001	.001	.007	<.001	<.001	<.001	.001	.001	.0029
Co	±25	.04	.008	.02	.01	.03	.03	.005	.005	<.003	<.003	<.003	.02	.03	.0027
Cr	±30	.001	.01	.01	.003	.03	.02	.03	.008	.001	.005	.001	.024	.002	.005
K	±20	.4	nd	.06	.2	.11	nd	.07	.2	nd	.32	nd	--------	--------	--------
Li	±15-20	.01	.004	.003	.004	.02	.003	.01	.001	<.0005	.002	<.0005	.012	.01	.0006
Mg	±10-15	.04	.7	1.2	.9	.4	1.0	2.1	4.8	.8	1.48	1.0	--------	--------	--------
Mo	±20	<.001	<.003	<.001	<.001	<.001	<.001	<.001	<.003	<.001	<.003	<.001	--------	--------	--------
Ni	±10	.01	.01	.01	.01	.03	.04	.02	.001	.003	.001	.01	.02	.005	.002
Rb	±15	.001	<.001	<.001	.002	<.001	<.001	.001	.001	<.001	.01	<.001	.0007	.0005	.0006
Ti	±40	.2	.09	.3	.2	.3	.05	.10	.02	.02	.08	.02	.39	.20	.01
V	±25	.01	.05	.05	.05	.06	.05	.03	.02	.003	.002	.004	.05	.007	.0085
W	±20	<.03	.03	<.03	<.03	<.03	.1	<.03	<.03	<.03	<.03	<.03	--------	--------	--------

[1] Fe and Mn determined in laboratories of Geological Survey of Sweden. Ti determined chemically and other elements spectrographically by S. Landergren in laboratories of Geological Survey of Sweden; estimated errors as given by Landergren.

[2] Dominantly chamositic ironstone.

[3] As given by Landergren, 1948, p. 108, 110.

[4] Given as 5.4 percent by Landergren; probably a typographical error.

EXPLANATION OF SAMPLES

A. Unweathered sideritic mudstone, Northampton, England—Northampton Sand ironstone. No. 3 in tables 44, 45, 46 in Landergren, 1948.
B. Minette ore, gray bed, Luxembourg. No. 5 in tables 53, 54, 55 in Landergren, 1948
C. Unweathered chamosite oolite—oolites of chamosite and subordinate limonite in sideritic groundmass—Northampton, England. No. 1 in tables 44, 45, 46 in Landergren, 1948.
D. Gray green chamosite ore, Frodingham ironstone, Lincolnshire, England. No. 6 in tables 44, 45, 46 in Landergren, 1948.
E. Marlstone ironstone, Oxfordshire, England. Average of 7 analyses 8a to 8g, in tables 44, 45, 46 in Landergren, 1948.
F. Minette ore, green bed, Luxembourg. No. 8 in tables 53, 54, 55 in Landergren, 1948.
G. Minette ore, brown bed, Luxembourg. No. 6 in tables 53, 54, 55 in Landergren, 1948. Rock is assumed to be a limonite oolite.
H. Quartz-hematite ore, banded; from the Stripa mine, Sweden. No. 24 in tables 15, 23, 27 in Landergren 1948.
I. Jaspilite, Marquette, Michigan. No. 32 in tables 53, 54, 55 in Landergren, 1948.
J. Quartz-magnetite ore, from the Strassa mine, Sweden. No. 27 in tables 15, 23, 27 in Landergren, 1948.
K. Quartz-banded magnetite ore, South Varanger, Norway. No. 1 in tables 53, 54, 55 in Landergren, 1948.

to separate them according to the schemes of classification used for the bulk analyses given in previous tables. Instead, on the assumption that most results will have a fair degree of internal consistency, some of the available data on minor elements are presented in separate tables, each of which represents the results from a single investigator or a single laboratory. Table 27 is a selection of analyses from the tremendous work of Landergren, which is unparalleled both in volume and in the clarity with which the methods, estimated errors, and results are presented. Table 26, previously referred to, also is drawn from this work. Table 28 contains analyses from a tabulation of average values for some Russian deposits, as given by Arkhangelskii and Kopchenova (1934). The results were based on an extensive analytical project carried out at the Institute of Geology and Mineralogy (Moscow); the methods of analysis (colorimetric) and individual values are reported in a separate publication (Arkhangelskii and Kopchenova, 1935).

TABLE 28.—*Average contents of iron, manganese, and minor elements*[1] *of some iron-rich rocks from U.S.S.R.*

[Adapted from Arkhangelskii and Kopchenova, 1934.[2]; nd., not determined; Tr., trace. Values in weight percent]

	Bog ore; Karelia and Moscow districts	Chamosite-limonite oolite, Kerch, Pliocene	Limonite oolite, Cretaceous		Clay ironstone, Caucasus		Iron-formation, Kursk, Precambrian
			Mugai	Khoper	Oligocene	Jurassic	
	A	B	C	D	E	F	G
Fe	37.66	39.83	28.80	42.21	33.94	42.17	47.46
Mn	.84	1.88	.37	1.21	4.17	.79	.13
As	.01	.08	.01	0	Tr.	Tr.	Tr.
Co	0	.019	nd	Tr.	0	0	0
Cr	.01	.17	Tr.	Tr.	0	0	Tr.
Cu	.004	.002	.011	Tr.	.003	.003	.01
Ni	0	.008	Tr.	.007	0	Tr.	0
P	1.57	1.12	.45	1.21	.51	.11	.12
Ti	.22	.16	nd	.11	.13	.07	.08
V	.03	.06	.08	.03	0	0	0

[1] Qualitative analyses for Pb, W, Zn, Mo, and Sn contents also reported for individual samples. Results generally negative, but W present in trace amounts in samples from Kerch and Kursk, and Pb present "in appreciable amounts" in one Kursk sample.

[2] The seven average compositions selected are from a table containing 14, including some for deposits of questionable origin. The 14 averages are reported to be based on analyses of about 200 samples.

Table 29 gives the contents of six metals from the eight separated minette ironstone beds of Luxemburg, assembled by Lucius (1945) from the work of R. Stumper; it is one of the few compilations available for stratigraphic units within a single basin. Table 30 presents a few analyses from the Liassic beds of southern Sweden, arranged according to lithologic character of the ironstone by Palmqvist (1935); the work was done in V. M. Goldschmidt's laboratory at the University of Göttingen. Table 31 contains semiquantitative data by the U.S. Geological Survey on 11 samples from the ironstones of the Clinton Group of New York and Pennsylvania and the Martin Formation of Arizona. These data, though suitable for statistical analysis, must be used with caution; individual values may or may not be significant. Finally, in table 32, the maximum and minimum values of the assembled data are compared with crustal abundance.

An extensive study by Hegemann and Albrecht (1954) of the oxide ores of iron provides a valuable comparison of minor-element contents of the sedimentary ores as compared with those of magmatic or hydrothermal origin. Individual analyses are not given—the results are grouped and assembled in graphic form—but it is evident that in general the minor element content of the sedimentary types is low. The ores of the Lahn-Dill type ("exhalative-sedimentary") are considered to be distinctly higher in Zn and Cu, and possibly Ag, Pb, and Mo, than the normal ironstones. The results also show a several-fold enrichment over crustal abundance of Ni, Co, and V in the minette ores of Lorraine, which confirms the results reported by Lucius (1945) presented in table 29.

TABLE 29.—*Contents of* Cu, As, V, Ni, Ti, *and* Zn *in minette ironstone of Luxembourg*

[As quoted in Lucius (1945, p. 159, adapted from work of R. Stumper). Values in weight percent]

	Stratum[1] and location	Cu	As	V	Ni	Ti	Zn
A	Layer 3b, St. Michel (Upper red)	0.0068	0.019	0.060	0.0060	0.116	0.0147
B	Layer 3a, St. Michel (Middle red)	.0061	.019	.062	.0069	.118	.0145
C	Layer 3, Landergrund (Main red)	.0040	.020	.056	.0061	.111	.0100
D	Layer 2, Mont-Rouge, Enclave (Gold)	.0048	.020	.059	.0059	.093	.0157
E	Layer 1, Mont-Rouge (Gray)	.0051	.019	.060	.0078	.099	.0182
F	Layer I, Mont-Rouge West (Brown)	.0051	.026	.070	.0095	.111	.0212
G	Layer II, Mont-Rouge West (Black)	.0057	.023	.059	.0102	.126	.0239
H	Layer III, Mont-Rouge, Enclave (Green)	.0051	.023	.070	.0110	.113	.0230

[1] Units arranged in relative stratigraphic position (A is youngest, H is oldest).

TABLE 30.—*Minor element contents of glauconitic, chamositic, and sideritic ironstone of Lias (Jurassic) age of southern Sweden*

[Adapted from Palmqvist, 1935. Analyst: Cl. Peters, Mineralog. Inst., Göttingen, using spectrographic methods. Results (expressed as oxides) given in tables 5-11 in Palmqvist, 1935. Values in weight percent]

	A	B	C	D	E
	Glauconite, Baldringe Road	Brown cement, Baldringe Road	Oolite (chamosite?), Baldringe Road	Siderite, Kurremola, locality 2	Oolite with siderite and iron silicate, Kurremola, locality 5
As	nd	nd	nd	nd	0.013
B	0.03	0.016	0.016	0.016-0.003	0.016-0.003
Co	0	.0008	.0008	nd	nd
Cr	.07	.0007	.0035	nd	nd
Ge	.0004	.0004	.0004	.0004	nd
Ni	.0008	.04	.04	nd	nd
V	.007	.03	.7	nd	nd
Zn	nd	.008	.008	0	.004

A commonly held view is that the iron-oxide sediments are enriched in minor elements because of assumed origin as a positively charged colloid, able to adsorb other elements (Goldschmidt, 1954), or because ferric iron can form insoluble vanadate, arsenate, chromate, or selenate (Goldschmidt, 1954; Krauskopf, 1955). The concept of sedimentary iron oxides as scavengers for minor elements in natural environments does not seem to be borne out by the available data on the oxide ironstones, though it certainly appears true for the manganese-iron oxide concretions of present sea bottoms.

Except for phosphorus, the distribution and occurrence of which has been discussed in relation to major rock components, the minor-element content of ironstones is surprisingly low, with maximum concentrations no greater than or considerably below those of shale.

TABLE 31.—*Spectrographic analyses of ironstone of the Clinton Formation and Group (Silurian) and Martin Formation (Devonian), U.S.A.*

Analysts; Nancy M. Conklin (analyses A-E, I-K) and Paul R. Barnett (analyses F-H) ,U.S. Geol. Survey. Laboratory numbers are given at heads of columns. Values in weight percent]

	CLINTON [1]					MARTIN [2] [Oolitic hematite with glauconite]					
	A	B	C	D	E	F	G	H [3]	I	J [3]	K [3]
	(oolitic chamosite)	(oolitic hematite)	(siderite)	(oolitic chamosite)	(hematite)						
	F2639	F2640	F2641	F2642	F2635	F2726	F2727	F2728	G2892	G2893	G2894
Ba	0.0007	0.007	0.0015	0.003	0.0015	0.007	0.007	0.003	0.03	0.015	0.007
Be	.0003	0	0	.00015	0	0	0	0	.0003	.0003	.00015
Ce	0	0	0	0	0	0.03	0.03	.03	.03	.03	.03
Co	.0015	0	<.0015	.003	0	.0015	.0015	.0015	.003	.003	.003
Cr	.007	.007	.0007	.015	.007	.007	.007	.007	.007	.007	.007
Cu	.015	.0003	.0003	.015	.0003	.0007	.0003	.0003	.0015	.0007	.0015
Ga	.0003	.0003	.00015	.0015	.0007	.0007	.0007	.0007	.0007	.0003	.0007
La	0	.007	0	.007	0	.015	.015	.007	.015	.015	.015
Mo	<.002	<.002	0	<.002	<.002	0	0	0	<.005	<.005	<.005
Nb	nd	nd	nd	.0015	0	.0015	.0015	.0015	.0015	.0015	.0015
Nd	0	0	0	.015	0	.015	.015	.015	.015	.015	.015
Ni	.003	.003	.0007	.007	.0015	.0015	.0015	.0015	.003	.003	.003
Pb	0	0	0	0	0	.0015	.0015	.0015	.003	.003	.003
Sc	.0015	0	0	.003	.0007	.0007	.0007	.0007	.0015	.0015	.0015
Sr	.007	.007	.0007	.015	.03	.03	.03	.03	.03	.03	.03
V	.03	.03	.0015	.07	.015	.015	.015	.007	.03	.03	.03
Y	.007	.007	0	.007	.007	.003	.003	.003	.007	.007	.007
Yb	.0007	.0007	nd	.0015	.0007	.0007	.0007	.0007	.0007	.0007	.0007
Zr	.003	.007	0	.07	.007	.003	.007	.007	.015	.007	.007

[1] For chemical analyses, description, and location for A, see table 13, No. L; B, table 9, No. C; C, table 16, No. A, D, table 13, No. M, E, table 9, No. D.

[2] For chemical analysis, description, and location fr F, G, I, see table 9, Nos. N, P, O, respectively.

[3] Specific locations given in Willden, 1960, 1961.

NOTE.—Values, in percent, are reported to nearest number in the series 3, 1.5, 0.7, 0.3, 0.15, 0.07, ... These numbers represent midpoints of group data on a geometric scale. Comparisons of this type of semiquantitative results with data obtained by quantitative methods, either chemical or spectrographic, show that the assigned group includes the quantitative value about 60 percent of the time. Also looked for but not found: Ag, As, Au, Bi, Cd, Dy, Er, Eu, Gd, Ge, Hf, Hg, Ho. In, Ir, Li, Lu, Os, Pd, Pr, Pt, Re, Rh, Ru, Sb, Sn, Sm, Ta, Tb,Te, Th, Tl, Tm, U, W. and Zn. B reported in barely detectable amounts in several samples (limit of detection 0.002 percent).

TABLE 32.—*Minimum and maximum concentrations of minor elements given in tables 8–19, 27–31 as compared with crustal abundance*

[Values in weight percent]

Element	Crustal abundance (from Mason, 1958, p. 44)	Concentration from tables in this report		Reference for maximum	
		Minimum	Maximum	Table	Analysis
As	0.0002	0	0.026	29	F
B	.0003	0	.03	30	A
Ba	.0400	.0007	.03	31	I
Be	.0002	0	.007	27	H
Ce	.0046	0	.03	31	F–K
Co	.0023	0	.04	27	A
Cr	.0200	.0007	.17	28	B
Cu	.0045	.0003	.015	31	A, D
Ga	.0015	.00015	.0007	31	E–K
Ge	.0002	0	.0004	30	A–C
La	.0018	0	.015	31	G–K
Li	.0030	0	.02	27	E
Mo	.0001	0	<.003	27	B, H, J
Nb	.0024	0	.0015	31	D, F–K
Ni	.0080	.0007	.04	27 30	F B, C
P	.1180	0	2.62	11	F
Pb	.0015	0	.003	31	I, J, K
Rb	.012	0	.01	27	J
Sc	.0005	0	.003	31	D
Ti	.4400	.02	[1] .91	11	F
V	.0110	.0015	.7	30	C
W	.0001	0	.1	27	F
Y	.0040	0	.007	31	A, B, D, E, I, J, K
Yb	.0003	.0007	.0015	31	D
Zn	.0065	0	.0239	29	G
Zr	.0160	0	.07	31	D

[1] Excluding Ti-rich siderites of Sweden, which contain abundant clastic ilmenite.

With respect to copper, Goldschmidt (1954, p. 185) states:

> A concentration of copper in marine oxidate sediments, such as in ferric hydroxides and the higher oxides of iron and manganese, is well established even if adequate average data cannot be given.

The analyses now available, however, indicate the copper content commonly is less than crustal abundance. Again, Goldschmidt (p. 286–287) reports boron in the marine ferric ores, in amounts "* * * usually ranging from 50 to 500 ppm B_2O_3, sometimes reaching 1,000 ppm, and rarely as low as 30 ppm," and the Scania (Sweden) ironstone was found to contain 100 to 1,000 ppm B_2O_3 by Palmqvist (1935), who, like Goldschmidt, attributed the high content to a marine environment of origin. In striking contrast, however, is the absence of boron in the ironstones of the Clinton (see table 31). Quite evidently the boron content in itself is not a reliable criterion of marine versus nonmarine origin, particularly in view of the previously noted content of 20 to 40 ppm in the definitely nonmarine bog ores (table 26); the "very marked" difference noted by Goldschmidt does not appear to exist.

Goldschmidt (1954, p. 473) reports "conspicuous concentration" of arsenic, to 700 ppm, in marine ores of Mesozoic age, and the oolitic ores of the Kerch basin of Russia are very much enriched in this element. In a detailed discussion, accompanied by many analyses, Vasyutinsky and Nevoysa (1961) show the mean content of As of the Kerch ores to be 0.10–0.12 percent, the greatest concentration (to 0.29 percent) being in the iron oxide ooliths; the amount in siderite and chlorite (chamosite) is much less. The arsenic content of the mineralogically similar minette of Luxembourg (table 29) is about an order of magnitude lower than that of Kerch, and the ironstones of the Clinton Formation and Group and the Martin Formation (table 31) have a zero content.

On an deductive basis, a definite relation is to be expected between the pattern of minor-element distribution and the facies of ironstone. Analysis of these probable relations is difficult, however, because of scarcity of suitable data and because of the influence of local factors. The lack of data is particularly acute with respect to the Precambrian iron-formations, except for those of Sweden. The effect of local differences in the environment of deposition—specifically the geochemical aspect of the surrounding terrain—may be large and may in fact submerge differences due to the chemistry of precipitation. For example, in table 29 data for several metals are given for the several horizons of minette ironstone in Luxemburg. The 8 beds represented vary widely in mineralogic character; they include oxide, silicate, and siderite facies. The contents of Cu, As, V, Ni, Ti, and Zn all are relatively high and astonishingly similar from one horizon to another; the total range of each is scarcely greater than what might be expected in a single bed. Another example is that of the high lanthanide content (particularly La, Ce, and Nd) in the ironstone of the Martin Formation of Arizona (see table 31), which probably reflects a distinctive aspect of the region at the time of deposition; mineralogically similar facies of the Clinton have virtually no lanthanide content.

Arkhangelskii and Kopchenova (1934) conclude that significant differences in minor-element content exist between bog ores, limonite oolite, and clay ironstone, although the differences, as indicated by the average values listed in table 28, are not impressive. Landergren (1948, p. 91) notes the greater enrichment of Cr and V in chamositic ores of Great Britain as compared with sideritic rocks. This trend also is evident in the Russian ores (table 28) and to some degree in the Clinton ironstone (table 31). The chamositic rocks are generally higher in Al-content than other ironstones, and the increased amounts of Cr and V probably stem from an initial clay constituent.

Though data are still scarce except for Sweden, the Precambrian iron-formations doubtless are very much lower in minor-element content than the younger ironstones. Landergren (1948, p. 163) notes the remarkable deficiency of the ferrides—titanium, vanadium, chromium, manganese, cobalt, and nickel—in the banded ores of Sweden.

DIFFERENCES BETWEEN IRONSTONE AND IRON-FORMATION

Both ironstone and iron-formation have a wide range in characteristics and associations, but it seems worth while to summarize the differences that exist between the more abundant deposits that may be classed as typical of the two groups, namely ironstone of the minette type, and iron-formation of the Lake Superior type.

1. Age. *Ironstone:* Pliocene to middle Precambrian. Principal beds are of lower Paleozoic and of Jurassic age. Oldest known occurrence is in strata with approximate age of 2,000 million years (Transvaal Series, South Africa); youngest unit of significant size is of Pliocene age (Kerch basin, U.S.S.R.). *Iron-formation:* Cambrian to early Precambrian. Principal formations in the U.S.S.R., South Africa, and North America have an age of about 2,000 million years. "Keewatin-type" iron-formation, generally associated with volcanic rocks, occurs in the oldest known Precambrian strata of several shield areas of the world. Youngest proved age for iron-formation is Cambrian.
2. Thickness. *Ironstone:* major units a few meters to a few tens of meters. *Iron-formation:* major units 50 meters to 600 meters.
3. Original areal extent. *Ironstone:* individual basins of deposition probably rarely more than 100 miles in maximum dimension. *Iron-formation:* difficult to determine, but at least some units had continuity over linear distances of many hundred miles.
4. Physical character. *Ironstone:* massive to poorly banded; silicate and oxide facies oolitic. *Iron-formation:* thinly bedded; has layers of dominantly hematite, magnetite, siderite, or silicate alternating with chert that makes up about half the rock by volume; oolitic structure relatively rare except in hematitic and silicate facies of some areas.
5. Mineralogy. *Ironstone:* dominant oxide is goethite; hematite is fairly common, magnetite relatively rare; chamosite is primary silicate, glauconite (chlorite and stilpnomelane in metamorphosed ironstone) is minor; calcite and dolomite common constituents; pelletal collophane relatively abundant in some rocks. *Iron-formation:* no goethite; magnetite and hematite about equally abundant; primary silicate is greenalite, with minnesotaite, stilpnomelane, and chlorite in rocks of slightly higher metamorphic grade. Quartz (chert) a major constituent; dolomite present in some units

but calcite rare or absent. Pelletal phosphate, chamosite, glauconite absent.

6. Chemistry. *Ironstone:* except for high content of iron, no distinctive aspects. *Iron-formation:* remarkably low content of Na, K, Al, and minor elements; phosphorus content generally much lower than in ironstone (Geijer, 1962); Mn/Fe ratio believed by some to be higher (Lepp, 1963).
7. Associated rocks. No distinctive differences. Both ironstone and iron-formation typically are interbedded with shale, sandstone, or graywacke, or their metamorphosed equivalents. Carbonate rocks—limestone and (or) dolomite in the ironstone sequences and dolomite in iron-formation sequences—not rare but subordinate to clastic rocks in immediately associated strata.
8. Relative abundance of facies. No gross differences apparent. Probable order of abundance for ironstone: oxide, silicate (chamosite), siderite, sulfide; for iron-formation, order is similar but siderite facies may be more abundant than silicate facies. Within oxide facies, however, magnetite is far more abundant in iron-formation than in ironstone.

Some of the differences in the above summary can be ascribed to greater degree of metamorphism or simple "aging" of the (generally) older rocks, which result in change of goethite to hematite, chamosite to chlorite, and possibly glauconite to stilpnomelane, but many features remain as distinctive to iron-formation. Chief among them are the notably greater abundance in the Precambrian, the greater dimensions, the interlayered chert, and the extremely low content of the alkalis, alumina, phosphorus, and minor elements.

ORIGIN

The lack of modern-day examples of ironstone and iron-formation deposition makes the subject of origin a fertile one for speculation. Furthermore, the question is not a simple one: it has many facets, some interrelated and some for the most part independent. Fairly definite conclusions can be drawn as to the distribution patterns and basic chemistry of iron deposition: both ironstone and iron-formation were formed as chemical sediments in marine or brackish-water basins of restricted circulation, or in marginal seas of modest extent, the mineralogy of the iron precipitates being governed principally by relative availability of oxygen, carbon dioxide, and sulfur. Beyond this, many major and minor problems remain unsettled. Chief among them are the source and mode of transport of iron (and, for the iron-formation, also silica) and the relation between ironstone and iron-formation.

The various mechanisms that have been proposed for derivation of the iron are as follows:

1. Iron is derived from weathering of land masses under humid tropical or subtropical conditions (Gruner, 1922; Gill, 1927; Moore and Maynard, 1929; Taylor, 1949; Sakamoto, 1950; Alexandrov, 1955; Hough, 1958); under arid conditions (Woolnough, 1941); or by weathering under an atmosphere of lower oxygen and higher CO_2 content than at present (MacGregor, 1927; Tyler and Twenhofel, 1952).
2. The iron is derived from sea-bottom reactions on chiefly clastic materials (Strakhov, 1959; Borchert, 1960a; Braun, 1964), and concentrated by solution and selective sea-bottom precipitation (Borchert), or mainly by diagenetic reactions (Strakhov).
3. The iron (and also silica in the iron-formations) is derived from processes related to contemporaneous volcanic and igneous activity (Van Hise and Leith, 1911; Moore, *in* Moore and Maynard, 1929; Goodwin, 1956; Oftedahl, 1958; Gruner, 1959, written communication, a reversal of views published in 1922; Harder, 1963).

Each of these mechanisms—other than that calling for atmospheric modification—can be either observed or reasonably inferred on a small-scale basis at the present. For example, the bog iron deposits represent leaching of iron from surface and subsurface materials and lateral movement to sites of deposition—essentially a weathering process; sideritic concretions and some glauconite concentrations surely represent mobilization of iron from surrounding sediments by sea-bottom or diagenetic reaction; present-day deposition of iron related to volcanism is known from at least a few localities. None of the processes are mutually exclusive; the question is one of scale and of which process is dominant. Of the three possibilities, it would seem to the present writer that the second—sea-bottom or diagnetic reactions—is quantitatively inadequate, particularly with respect to the iron-formations, unless the chemistry of seawater differed profoundly from that of today. If this judgment is accepted, then only two major possibilities need to be considered: derivation of iron by weathering processes, and derivation of iron by processes related to volcanism and igneous activity.

Assessment of the role of volcanism and related processes to iron deposition is not easily made, as it depends largely upon inferences drawn from associated rocks. Nevertheless, a close and probable genetic relation seems reasonably proved for a few ironstones and iron-formations—for example, the Devonian ironstone of the Lahn-Dill district of Germany, and the "Keewatin-type" Precambrian iron-formations, exemplified in the Michipicoten district of Canada. Another well-documented example is that of Meggen, Germany (Ehrenberg, Pilger, and Schroder, 1954), where pyritic beds of Devonian age grade laterally into barite. In others, such as the deposits of Kazah, U.S.S.R. (Maksimov, 1958), the iron-rich strata interfinger with and grade into manganese-rich beds. These various deposits, which have been classed as exhalative-sedimentary, typically exhibit rapid changes in thickness and lithic facies, and all have close spatial relations to volcanic rocks or other evidence of volcanic and igneous activity.

For most of the major ironstone units of younger age, however, for which time-equivalent relations can be established with other rocks—so that contemporaneous volcanic or igneous activity in surrounding regions can be excluded—derivation of iron by weathering processes, or at least nonvolcanic processes, seems certain. Typical of the deposits of nonvolcanic association are the many ironstone beds of Jurassic age of northern Europe, which were deposited in isolated or semi-isolated marine basins on the order of several tens of miles in maximum dimension, marginal to or within an epicontinental sea. The iron seemingly can only have been derived from weathering of adjoining land areas, as concluded by Taylor (1949) for the Northampton Sand ironstone of England.

Most of the major iron-formations of the world similarly are devoid of apparent volcanic associations, although the possibility of a relationship cannot be as readily dismissed, at least for units of Precambrian age, in view of the great difficulty or perhaps (at present) impossibility of establishing true time-equivalence between dissimilar rocks of separated areas. Nevertheless, sufficient information on the enclosing geology of these areas is at hand to show that the relationship, if it existed, was not an immediate one; the iron and silica were not derived from thermal waters of volcanic or igneous source within the basins of deposition.

Deposition of both ironstone and iron-formation of nonvolcanic affiliation requires a more efficient means of transporting iron to the site of deposition and of separation from other materials than that now evident in dominant surface processes, in which the bulk of the iron is transported in the form of colloidal iron oxide and is inextricably tied up with the clastic fraction.

For the ironstones of nonvolcanic origin, with ages as young as Pliocene, significant atmospheric or biospheric modification seems an unlikely possibility: the range of environmental conditions in the Pliocene could not have differed greatly from those of the present except in relative importance. The only process now yielding iron concentrations, other than by volcanic contributions, is that of bog-ore formation, which involves shallow subsurface leaching of iron from permeable sands, and transportation in bicarbonate ground waters of low Eh and pH. It does not seem unreasonable to invoke this process on a much larger scale. The process and general setting may be visualized as follows: during a period of widespread and dominantly clastic sedimentation in a shallow epicontinental sea, local warping resulted in emergence of low broad island areas separated by shallow and generally interconnected basins. Climatic conditions—probably warm and humid—permitted development of a thick cover of deeply rooted vegetation on the emergent blocks of permeable and weakly lithified sediments. Deep penetration of ground waters rich in CO_2 and organic acids—the CO_2 content augmented by subsurface production from root processes—resulted in leaching of fine-grained iron oxides and iron sulfides in near-surface zones, with the products of leaching being transported by acid ground waters to bordering seas via subsurface routes. If the sites of debouchement of the ground waters were fully open to oceanic circulation, then most of the dissolved material was dispersed, but if the site was a relatively small basin with restricted circulation, then the iron could be trapped and ultimately precipitated according to the Eh–pH conditions prevailing. Clastic components—sand and clay—and associated clastic rocks would represent contribution and periodic influx of surface-transported materials, which would be interlayered and in part intermixed with the products of chemical precipitation.

For several reasons the process suggested for deposition of ironstone appears inadequate to explain deposition of iron-formation. Chief among these are the far greater dimensions of the depositional units, the more complete separation of iron from constituents other than silica, and the presence of interbedded chert. Most layers within iron-formation are finely laminated, with thicknesses of laminae being on the order of 0.1 mm. If these represent yearly precipitations, an iron-formation 200 m thick would take about a million years to accumulate, even assuming no breaks in sedimentation. It is more likely that the laminae represent longer time intervals, and that sedimentation was not continuous, so that a thick iron-formation may well have taken some tens of millions of years to accumulate. Maintenance for such a long period of time of topographic conditions appropriate for continued groundwater flow of the type outlined seems improbable. Furthermore, in pre-Devonian time the landscape would not be covered with deeply rooted vegetation, if indeed it was covered at all.

Finally, the ground water hypothesis would offer no obvious explanation for the interbedded chert.

Neither the dual occurrence of ironstone and iron-formation in strata at least as young as Cambrian, nor the fact that ironstone could be deposited both in Pliocene time and in a period far back in the Precambrian, eliminates the possibility of a significant relation between evolution of the earth's atmosphere and origin of iron-formation. An atmosphere appreciably different from that of the present could have persisted at least into early Paleozoic time. Strong limits on this speculation are imposed, however, by evidence from within the iron-formation units and their associated rocks. Any proposed system must permit or account for the following facts:

1. Depositional environments for iron had comparable ranges in Eh to those inferred for younger ironstone. This fact is derived from the observed range in facies (oxide to sulfide), from the relative abundance of facies types, and from the relation of the facies to physical features of the rocks that give independent evidence on environment of origin. Oolitic structure, for example, which surely in part reflects deposition in shallow and turbulent—and therefore well-aerated—water, is confined to oxide and silicate facies, as it is in younger ironstone; never is it present in sideritic facies.
2. The precipitation of calcium, magnesium, and minor elements was strongly repressed during the iron-formation cycles.
3. Chert rarely occurs as separate units in strata associated with iron-formation. Furthermore, within iron-formation the amount of chert varies systematically with the facies defined by iron minerals. The implication, therefore, is that precipitation of silica was not independent of that of iron.
4. Thick units of dolomite are present in strata associated with some units of iron-formation. The dolomite actually interbedded with or adjacent to iron-formation commonly contains magnetite, but the principal units—as much as 2,000 feet thick—contain no more iron than dolomites of younger age.
5. Associated clastic rocks, such as quartzite, graywacke, and argillite, are quite similar in mineralogy and chemistry to equivalent rocks of younger age. Clastic feldspar is common in the quartzites and graywackes, which indicates that chemical breakdown of rocks during erosion was not entirely dominant over physical processes.

A number of workers have suggested that the earth's atmosphere during the time of iron-formation deposition was higher in CO_2 than during later eras. The existence of thick and widespread oxidic facies seemingly eliminates the possibility that an actual reducing atmosphere prevailed, but it does not eliminate the possibility that the partial pressure of CO_2 was significantly greater. If, for example, in a dominantly oxidizing atmosphere, though perhaps much lower in oxygen than today, the partial pressure of CO_2 were 0.03 atmosphere, instead of the present 0.0003 atmosphere, the equilibrium pH of surface waters would be reduced from 8.17 to about 6.1 (Rubey, 1951, p. 1129). If the total volume of surface waters were less than at present, the pH would be still lower. Surface waters would then to some degree have similar chemical attributes, particularly the capacity to leach and transport iron, that is now characteristic of acid ground waters. Furthermore, if the pH of marine water in fact was much lower than at present, either because of the direct equilibration with CO_2 of the atmosphere or because of higher concentration of some other constituent—chlorine, for example—then an additional important factor is introduced: namely, that the sea itself could have been a major reservoir for iron in solution.

The validity of this model is open to some question. Revelle and Fairbridge (1957, p. 246) conclude that the present CO_2 content of the atmosphere is an approximate equilibrium value, controlled in large part by carbonate precipitation and silicate weathering. The specific situation analyzed, however, is that of a sudden increase in partial pressure of CO_2 and its effects on seawater equilibrium, with the implicit assumption of element concentrations similar to those of present oceans. This assumption is not necessarily an acceptable one; conceivably, for example, seawater at the time of iron-formation deposition might have been much undersaturated with respect to elements such as calcium. Cloud (1965) questions the existence of an oxygen-bearing atmosphere in early and middle Precambrian time, as do Lepp and Goldich (1964). Cloud develops the concept of photosynthetically generated oxygen to provide local oxidizing environments. The concept is a valuable one, but whether local generation of oxygen is quantitatively adequate for precipitation of thick oxidic sediments remains to be demonstrated.

It is clear, however, that an increase in the partial pressure of CO_2 to relatively modest levels would have profound effect on the cycle of iron, and vastly increase the efficiency of iron extraction and transport. Accepting this as a probable condition, and considering the limiting factors previously outlined, the proposition is here presented that—

1. The earth's atmosphere has been dominantly oxidizing since at least mid-Precambrian time—that is, for the past 2 billion years—and that oxygen,

perhaps locally generated by photosynthesis, was available even at the time of formation of the oldest known stratified rocks (3 billion years or more in age).

2. During mid-Precambrian time, the atmosphere contained a considerably greater amount of CO_2 than at present, and that this relatively high CO_2 content persisted but in diminishing amounts until at least early Cambrian time.
3. The iron-formations typically were deposited adjacent to long-exposed low-lying land masses during intervals in which clastic contributions to the sea were almost nil. Reduction of the land surface during the iron-formation cycle was almost entirely by deep chemical weathering, with complete chemical breakdown of silicates so as to yield abundant iron and silica in solution.
4. An important event leading to the deposition of major iron-formations was the formation of shallow restricted troughs or basins, marginal to the old landmass, in which the products of chemical weathering could be accumulated, and in which abnormal bottom conditions, particularly of Eh, could exist. Some units of iron-formation consisting only of oxide facies, however, could have been deposited in the relatively unrestricted shallows of low-sloping continental shelves.
5. The precipitation of such elements as Ca, Mg, K, and Na was inhibited by the low pH of the sea water, possibly also by low concentrations; whereas iron, transported as bicarbonate, and silica, derived from breakdown of silicates and transported as monomeric H_2SiO_4 (Siever, 1962), reached saturation levels. The intimate association of iron minerals and chert, therefore, is due to the manner in which the elements were extracted from the landmass and trapped: the breakdown of silicates to yield the necessary amounts of iron in solution would at the same time place large amounts of silica in solution. The fractionation of iron and silica from other elements was not accomplished at the source, but rather during the precipitation process.
6. The rhythmic layering so characteristic of iron-formation is due to some periodic, perhaps seasonal change in environment. Sakamoto (1950) suggests that this change is one of alternating wet and dry seasons, with consequent effect on the pH of waters tributary to the basin of deposition; Hough (1958), by analogy to present-day lakes, concludes that the layering is due to seasonal overturn. It is here proposed that the layering is due to explosive growth of silica-secreting organisms in response to periodic (seasonal?) increase in either the nutrient content or the temperature of surface waters in the basin of deposition. According to this concept, iron would be precipitated at a slow and nearly constant rate, whereas the silica-rich layers would represent relatively brief interludes during which organically precipitated silica was showered down from near-surface levels in the water.
7. Periodic influx of clastic material, now represented by rocks such as graywacke and quartzite, represent intervals of structural disturbance during which chemical weathering became subordinate to physical disintegration of the land surface. During these periods the supply of iron and silica in solution was greatly reduced, so that iron-formation and clastic sedimentary rocks, in general, now are mutually exclusive.
8. Thick units of iron-free dolomite, which, if present in the iron-formation sequences generally are separated by some distance stratigraphically from the main iron-formation units, were formed either before the restriction on open-sea circulation was established or during periods when it was destroyed. During these intervals the iron and silica being contributed were lost to the open sea, whereas the carbonate rock could have been precipitated from water not significantly different in composition from that of the oceanic reservoir, in response to some special conditions such as those now prevailing on the Bahama Banks.
9. The time of maximum development of iron-formation, about 2,000 million years ago, was near or at the close of a very long and perhaps world-wide period of stable structural conditions. In the Canadian Shield, at least, to judge from the geochronologic data now available, this structural stability had lasted for about 500 million years. In this, the region of greatest iron-formation occurrence, the formation of the necessary marginal basins was the earliest stage of what was to develop into a eugeosynclinal and orogenic cycle of major proportions.

Both ironstone and iron-formation, therefore, may have been formed by essentially similar processes—extraction of iron by weathering from adjacent land areas and precipitation in (generally) restricted basins. The great differences between the rocks could be ascribed to primarily two factors: (1) the greater efficiency of the weathering process in Precambrian time, which would permit the close association of abundant iron and abundant silica in solution; and (2) the far lengthier periods of structural stability, two of which had durations as long as from the Cambrian to the present—approximately from 2,500 to 2,000 million years and from 1,000 to 500 million years ago. The lesser, though by no means insignificant, amount of iron-formation of Cambrian age could be due to a diminished CO_2 content of the atmosphere.

These suggestions for origin of ironstone and iron-formation should be taken for what they are—that is, plausible speculations. They are offered to provide targets for further research, by means of which specific aspects can be either verified or rejected; most surely they are not final answers.

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