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Progressive Contact Metamorphism of the
Biwabik Iron-formation, Mesabi
Range, Minnesota

BY
BEVAN M. FRENCH



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FOREWORD

The recent, spectacular growth of the taconite industry, and the expansion of taconite operations from the eastern to the central and western parts of the Mesabi range, emphasizes the importance of knowledge of the geology of the range. The earliest taconite plants were established in the Eastern Mesabi district, in areas in which the Biwabik Iron-formation was metamorphosed by the Duluth Gabbro Complex; most of the recent plants are in the Main and Western Mesabi districts, in areas of "unaltered" iron-formation.

This report describes the changes in mineralogy and texture from "unaltered" taconite in the Main Mesabi district to highly metamorphosed taconite in the Eastern Mesabi district. It describes not only the silicate minerals, but also the opaque iron oxides, carbonate minerals, and carbonaceous material. Knowledge of the mineralogic changes is extremely important to the practical problems related to beneficiating characteristics of the magnetic taconites.

The report is modified from a Ph.D. thesis submitted to the Graduate School at Johns Hopkins University by Bevan M. French.

P. K. SIMS

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H. L. James originally suggested the suitability of the Mesabi range for a detailed study of progressively metamorphosed iron-formation. The actual study would have been impossible without the generous and whole-hearted cooperation given to the writer by the many companies mining the Mesabi range, especially the Oliver Iron Mining Division of the United States Steel Corporation, Pickands Mather & Company, the Reserve Mining Company, the Hanna Mining Company, and the Meriden Iron Company. The assistance given by individuals cannot be acknowledged in full, but particular thanks are due to H. V. Wuerch and Henry Bakkila of the Oliver Iron Mining Division, to D. R. Croswell of the Erie Mining Company, to James Emanuelson of the Reserve Mining Company, and to C. A. Beckman of the Hanna Mining Company. In addition, the writer has benefited greatly from discussions with J. N. Gundersen, P. K. Sims, S. S. Goldich, J. W. Gruner, and R. L. Blake.

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ABSTRACT

The Biwabik Iron-formation, on the Mesabi range in northern Minnesota, extends for about 120 miles in a generally east-northeast direction, from west of Grand Rapids on the Mississippi River to Birch Lake, east of Babbitt. The formation is the middle unit of the Animikie Group of Middle Precambrian age. On the eastern end of the Mesabi range, the Animikie Group has been metamorphosed by the intrusive Duluth Gabbro Complex; mineralogical changes in the sediments, particularly in the iron-formation, appear to have been caused by the gabbro.

From the data of the present study, four metamorphic zones may be distinguished within the Biwabik Iron-formation by changes in mineralogy along the strike of the formation toward the gabbro contact:

1. *Unaltered taconite* extends from the western limit of the Mesabi range approximately to the town of Aurora. It is composed of quartz, magnetite, hematite, siderite, ankerite, talc, and the iron silicates chamosite, greenalite, minnesotaite, and stilpnomelane. Of these, only quartz, hematite, chamosite, greenalite, siderite, and some magnetite are considered primary. The textures of the other minerals indicate a secondary origin, possibly resulting from diagenesis or from an earlier period of low-grade metamorphism unrelated to the intrusion of the Duluth Gabbro Complex.

2. *Transitional taconite* contains the same mineralogy but exhibits extensive replacement by quartz and ankerite. Incipient metamorphic changes in this zone are the partial reduction of hematite to magnetite and the appearance of clinozoisite in the Pokegama Formation, the basal unit of the Animikie Group.

3. *Moderately metamorphosed taconite* is characterized by the development of the iron-rich amphibole grunerite and by the disappearance of original iron carbonates and silicates. Calcite appears in this zone as a product of the reaction of ankerite and quartz to form grunerite.

4. *Highly metamorphosed taconite*, within two miles of the contact of the Duluth Gabbro Complex, is completely recrystallized to a metamorphic fabric and is composed chiefly of quartz, iron amphiboles, iron pyroxenes, magnetite, and rare fayalite and calcite. Small veins and pegmatites reported from this zone may represent minor introduction of material from the gabbro.

The following mineralogical changes occur along the strike of the Biwabik Iron-formation toward the gabbro contact: partial reduction of hematite to magnetite; development of clinozoisite (in the Pokegama Formation); formation of grunerite; appearance of iron-rich clinopyroxene (hedenbergite); disappearance of hematite; appearance of iron-rich ortho-

pyroxene (ferrohypersthene); and development of graphite (from organic matter).

The mineralogical changes, which correspond to the complete transition from unmetamorphosed to highly metamorphosed taconite, occur within a horizontal distance of about 2 miles in the area of taconite workings of the Erie Mining Company near the old town of Mesaba.

Compositions of the carbonate minerals in the iron-formation were determined by combining refractive index measurements with X-ray powder diffraction data to obtain values for the Ca, Fe, and Mg components. In unaltered taconite, siderite compositions approximate $\text{Ca}_{45}\text{Fe}_{75}\text{Mg}_{20}$; ankerite compositions from the same material are quite uniform at approximately $\text{Ca}_{53}\text{Fe}_{24}\text{Mg}_{23}$. The calcites which appear in the metamorphosed taconite are Fe-rich and Mg-poor, approximating $\text{Ca}_{89}\text{Fe}_{10}\text{Mg}_1$.

No definite change in siderite or ankerite compositions is noted along the strike of the Biwabik Iron-formation; there is no indication of progressive removal of iron from the carbonate with increasing metamorphism. By contrast, calcites from the metamorphosed taconite increase in Ca, becoming virtually pure CaCO_3 near the gabbro.

Compositions of the cummingtonite-grunerite amphiboles, determined by refractive index measurements, indicate a progressive enrichment in Mg toward the gabbro contact.

Original hematite in units such as "Red basal taconite" is progressively reduced to magnetite toward the gabbro. Incipient reduction is observed at 3.5 miles from the gabbro contact, and reduction is virtually complete within 1.5 miles of the gabbro.

Acid-insoluble residues from the organic-rich "Intermediate Slate" and related units show a progressive increase in crystallinity with metamorphic level. Such material is amorphous in unaltered taconite, but is completely crystallized to graphite close to the gabbro.

The present study indicates that metamorphism of the Biwabik Iron-formation by the Duluth Gabbro Complex was largely isochemical and was characterized chiefly by progressive loss of H_2O and CO_2 . There is no indication that the original mineralogy consisted only of quartz and magnetite, or that large quantities of other components were introduced into the sediments from the gabbro.

The conditions of metamorphism cannot be definitely determined. A load pressure of between 2,000 and 4,000 atmospheres is considered reasonable on the basis of the estimated thickness of overlying rocks. Values of P_{O_2} within the stability field of magnetite + quartz prevailed over most of the iron-formation; the restricted formation of fayalite was apparently dependent on lower P_{O_2} values maintained locally by original organic matter (now graphite) in certain layers. The presence of wollastonite in a marble unit near the gabbro suggests a probable minimum temperature of 600°C at this location; temperatures of 300° to 400°C are indicated for moderately metamorphosed taconite 2-3 miles from the gabbro contact.

**PROGRESSIVE CONTACT METAMORPHISM OF THE
BIWABIK IRON-FORMATION, MESABI
RANGE, MINNESOTA**

INTRODUCTION

Iron-bearing minerals are of particular interest in petrogenetic studies because they may participate in reactions involving oxidation and reduction. The occurrence and composition of iron-bearing minerals thus reflect, in part, the value of P_{O_2} in the environment during their formation. Experimental studies of the stability of iron-bearing minerals as a function of temperature and P_{O_2} are important for estimating the conditions of temperature and pressure under which the corresponding natural assemblages have developed and may also provide data on the composition of coexisting volatile phases that are no longer available for direct study.

The work described here is intended to complement an experimental determination of the stability of siderite ($FeCO_3$) (French, 1964a; French and Rosenberg, 1965) by mineralogical study of the behavior of natural siderite-bearing assemblages in an area of progressive metamorphism. Detailed sampling of the Biwabik Iron-formation on the Mesabi range was carried out during a period of about eight weeks in the summer of 1962, covering the region between Mountain Iron and Babbitt and concentrating on the Eastern Mesabi district, where the iron-formation has been metamorphosed by the intrusive Duluth Gabbro Complex. In progressing from unaltered iron-formation into the contact aureole, marked changes occur in the iron carbonates and associated iron silicates, iron oxides, and organic matter. The present study constitutes a detailed mineralogical study of these changes and an attempt to deduce from them the conditions of metamorphism.

Approximately 160 samples of the Biwabik Iron-formation and associated rocks were collected; the gross mineralogy was determined for most of these by X-ray powder diffraction studies of the total rock samples, combined with petrographic study of about 70 thin sections. Approximately 75 of these specimens were selected for further mineralogical study; compositions of the carbonate minerals were determined by combining refractive index and X-ray powder diffraction measurements. Approximate compositions of metamorphic amphiboles were determined by refractive index measurements. Particular emphasis was given to changes in carbonate composition and mineralogy along the metamorphic gradient and to the reactions by which the iron carbonates decompose to form metamorphic minerals.

NATURE AND ORIGIN OF SEDIMENTARY IRON-FORMATION

GENERAL DISCUSSION

The term iron-formation is applied to rocks that are variable in mineralogy and texture, but that contain an abnormally high percentage of primary iron and are composed chiefly of iron-rich carbonates, iron silicates, iron oxides, and quartz or chert. James (1954, pp. 239-240) has used the term "iron-formation" to designate "a chemical sediment, typically thin-bedded or laminated, containing 15 percent or more iron of sedimentary origin, commonly but not necessarily containing layers of chert." This definition is applicable to most of the Biwabik Iron-formation, although it excludes beds that are mineralogically and texturally related to the iron-formation but that contain large amounts of chert or clastic material.

The problem of sedimentation and diagenesis of iron-formation has been studied by many authors (Gruner, 1922b; James, 1954; Pettijohn, 1957; Hunter, 1960). The deposits are generally regarded as chemical sediments whose composition, textures, and mineralogy reflect conditions in the depositional environment. Iron is derived during normal weathering and erosion of terrestrial rocks and is transported to the basin in streams, probably as a hydrosol stabilized by organic material. Volcanism and hydrothermal activity may introduce additional iron, but are not necessary; many iron-formations are not closely related to volcanic activity (James, 1954; Hunter, 1960).

James (1954) has distinguished four sedimentary facies of iron-formation on the basis of the dominant iron minerals: the sulfide, oxide, carbonate, and silicate facies. Pyrite and carbonaceous matter are characteristic of the sulfide facies. Hematite and magnetite, both of which may be primary, occur with chert or quartz in rocks of the oxide facies. The carbonate facies ideally consists of iron-rich carbonate (siderite and ankerite) and chert or quartz. The silicate facies is characterized by iron-rich phyllosilicates such as greenalite, chamosite, chlorite, minnesotaite, and stilpnomelane (Gruner, 1946; James, 1954; White, 1954). Commonly, sedimentary iron-formation consists of a complicated assemblage of quartz or chert, carbonates, silicates, and magnetite which is apparently gradational between the carbonate and silicate facies (see James, 1954, p. 252).

Each of the mineralogical facies is thought to represent a different environment of chemical deposition (James, 1954). Experimental and theoretical studies (Huber and Garrels, 1953; Huber, 1958) indicate that deposition of rocks of the oxide, carbonate, and sulfide facies is strongly affected by the value of the redox potential (Eh) of the environment; this

interpretation agrees with geological observations (James, 1954). The chemical conditions favoring deposition of the silicate facies are not so well understood; silicate-facies rocks seem to form in a fairly wide range of Eh values (James, 1954, pp. 263, 273).

EARLIER STUDIES OF METAMORPHOSED IRON-FORMATION

Minerals of sedimentary iron-formation which are generally regarded as primary are quartz and chert, pyrite, hematite, magnetite, siderite, ankerite, and the silicates greenalite, chamosite, and chlorite (Gruner, 1946; White, 1954; James, 1954, 1955). There is considerable disagreement about whether the silicates minnesotaite and stilpnomelane are primary or whether they have developed from earlier silicate material during low-grade metamorphism (Gruner, 1946; Tyler, 1949; James, 1954, pp. 266–267; 1955, pp. 1473–1474).

During progressive regional metamorphism of iron-formation, the first definite metamorphic change is the appearance of the amphibole grunerite at intermediate metamorphic levels (approximately the garnet zone) (Miles, 1943, 1946; James, 1955). The mineral is the most commonly observed iron silicate in metamorphosed iron-formation (Miles, 1943, 1946; Gundersen and Schwartz, 1962). In the carbonate and silicate facies of iron-formation, grunerite develops at the expense of iron carbonates and earlier iron silicates; grunerite in the oxide-facies rocks probably represents direct reaction between magnetite, quartz, and water (Miles, 1943, 1946).

High-grade regional metamorphism of iron-formation (sillimanite zone) is characterized by the development of iron pyroxenes. Clinopyroxenes near hedenbergite in composition appear more commonly than do orthopyroxenes, but both varieties may be present (Mueller, 1960; Kranck, 1961). Original silicates and carbonates are absent in such rocks, which consist chiefly of iron amphiboles, iron pyroxenes, magnetite, quartz, and minor calcite and garnet.

Quartz, hematite, magnetite, and pyrite are apparently the only original minerals of sedimentary iron-formation that remain stable at the highest grade of regional metamorphism (James, 1955; Mueller, 1960). In rocks of the oxide facies, both hematite and magnetite occur, with no indication of reduction during metamorphism. James (1955, p. 1473) has observed a regular increase in the grain size of quartz with metamorphic grade in rocks of the oxide facies, from less than 0.05 mm. in the chlorite zone to more than 0.2 mm. in the sillimanite zone.

Contact metamorphism of iron-formation by intrusive igneous rocks produces mineral assemblages strongly resembling those developed under high-grade regional metamorphism; iron pyroxenes and iron amphiboles are the dominant silicates.

Hematite is commonly altered to magnetite near igneous intrusives

(Zappfe, 1912; Grout and Broderick, 1919b; Ramdohr, 1927; Gundersen and Schwartz, 1962). The iron olivine fayalite (Fe_2SiO_4) is apparently restricted to contact-metamorphosed iron-formation. These two mineralogical characteristics have been interpreted as suggesting that conditions in contact aureoles are more reducing than those developed during regional metamorphism.

GEOLOGY AND METAMORPHISM OF BIWABIK IRON-FORMATION

GENERAL GEOLOGY OF THE MESABI RANGE

The Mesabi range is in northern Minnesota, 80 to 100 miles north of the city of Duluth, Minnesota (Fig. 1). The term Mesabi range refers to the preglacial outcrop of the Biwabik Iron-formation, most of which is now buried beneath glacial deposits. This outcrop belt, $\frac{1}{4}$ to 3 miles in width, extends for about 120 miles in an east-northeast direction, from west of Grand Rapids on the Mississippi River to Birch Lake, near Babbitt.

The iron-formation occupies the southern slope of the Giants range, a low group of hills whose summits reach 1,900 feet above sea level at the eastern end of the range. The eastern end of the Biwabik Iron-formation is truncated by the intrusive Duluth Gabbro Complex; the western end is covered by thick glacial deposits, and the extent and trend of the formation west of Grand Rapids are not definitely known (White, 1954).*

The Mesabi range and the Biwabik Iron-formation have been studied intensively for more than sixty years (H. V. Winchell, 1893; N. H. Winchell, 1893; Spurr, 1894; Van Hise and Leith, 1901, 1911; Leith, 1903; Wolff, 1917; Broderick, 1919; Grout, 1919; Gruner, 1922a, 1922b, 1924, 1946; White, 1954; Schwartz, 1956, p. 182). Detailed studies of the mineralogy of the highly metamorphosed iron-formation on the East Mesabi (Grout and Broderick, 1919b; Gundersen and Schwartz, 1962) were of considerable assistance in the present study. The guidebook of the Geological Society of America, *The Precambrian of Northeastern Minnesota*, edited by Schwartz (1956), contains a 1:62,500 scale map of the Mesabi range which served as a base map (Fig. 1).

The Biwabik Iron-formation is the middle unit of the threefold Animikie Group of Middle Precambrian age (Table 1). It is underlain by the quartzites and impure sandstones of the Pokegama Formation and overlain by the Virginia Formation, a thick succession of dark gray argillite and rare graywacke. On the Mesabi range, the Animikie Group rests with profound unconformity on metamorphosed slates and graywacke, which are correlated with the Knife Lake Group and on granitic rocks of the Giants range batholith, which intrude rocks of the Knife Lake Group.

The structure of the Animikie rocks on the Mesabi range is simple (White, 1954). Except at the extreme eastern end, the beds strike approximately N.75°E. and dip gently south-southeast. The major structure is the

* White (1954) has divided the Mesabi range into four subdivisions; the present study is concerned almost entirely with the Main Mesabi district (from Nashauk to Mesaba) and the Eastern Mesabi district (from Mesaba to Birch Lake).

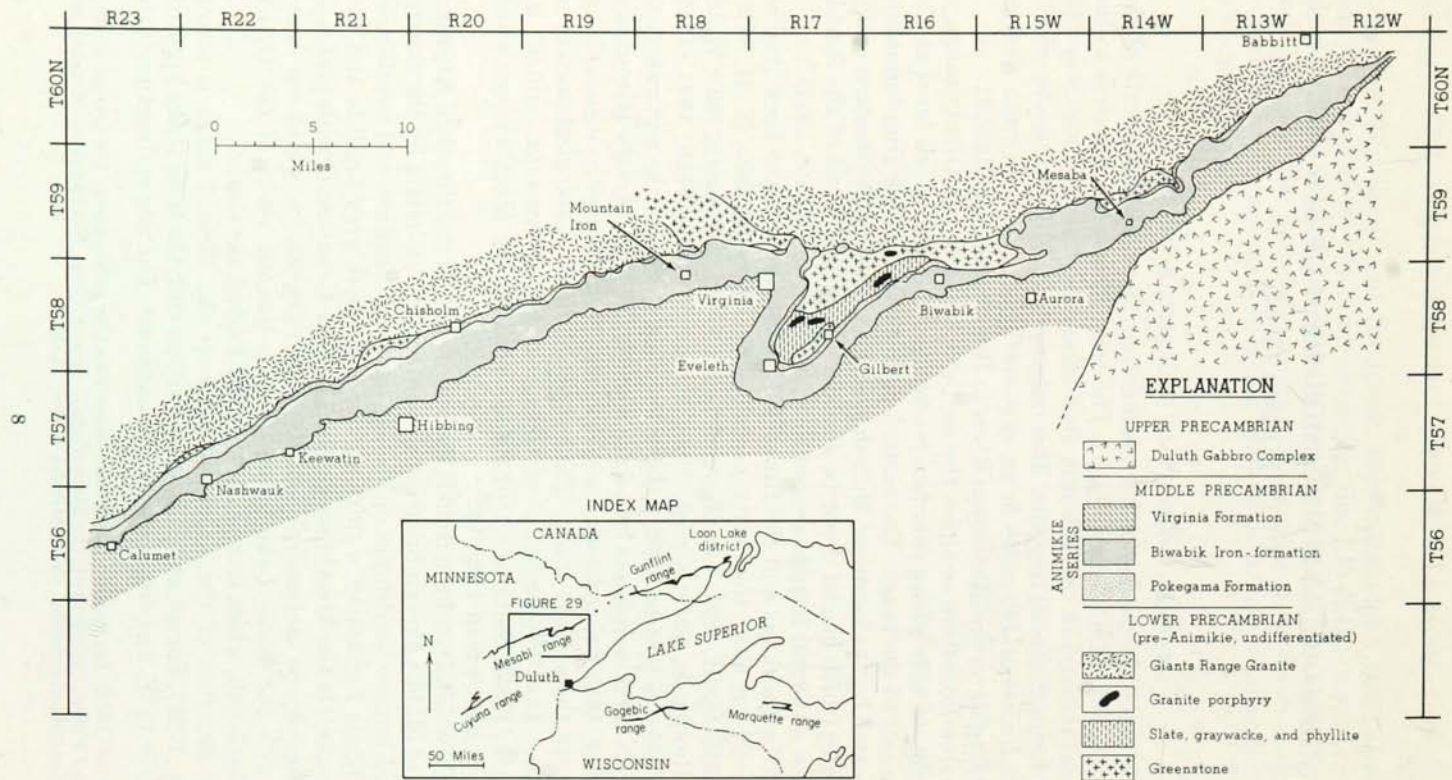


FIGURE 1.—Geologic map of part of the Mesabi range, Minnesota. Inset shows the location of the Mesabi range and other Lake Superior iron ranges.

TABLE 1. STRATIGRAPHIC SUCCESSION OF THE PRECAMBRIAN ROCKS OF NORTHERN MINNESOTA
(modified from Goldich and others, 1961)

Era	System	Major Sequence	Formation	Intrusive Rocks (age in billions of years)
Upper Precambrian	Keweenawan	North Shore Volcanic Group	<u>Hinckley Sandstone</u>	Duluth Gabbro Complex (1.1)
			<u>Fond du Lac Sandstone</u>	
		 unconformity	
			undivided	
Middle Precambrian	Animikie Group	Knife Lake Group	<u>Puckwunge Sandstone</u>	Vermilion and Giants Range batholiths (2.6)
		 unconformity	
			<u>Virginia = Rove = Thomson</u>	
			<u>Biwabik Iron-formation = Gunflint</u>	
			<u>Pokegama Quartzite</u>	
		 unconformity	
Lower Precambrian	Keewatin Group	Gneisses and other crystalline rocks (?)	<u>Soudan Iron-formation</u>	Saganaga Granite (2.7)
			<u>Ely Greenstone</u>	
		 unconformity (?)	

Virginia Horn, a Z-shaped bend in the outcrop belt in R.17W. produced by two broad folds whose axes plunge southwestward. Smaller gentle folds, a few feet to a few hundred feet in width, are common. Faults with large displacements have not been observed; the largest displacement detected does not exceed 200 feet (White, 1954).

MINERALOGY AND TEXTURES OF THE BIWABIK IRON-FORMATION

The Biwabik Iron-formation is generally a ferruginous chert which contains from 25 to 30 per cent iron. The thickness of the formation varies from less than 300 feet near Birch Lake to a maximum of about 800 feet near Eveleth.

Where the Biwabik Iron-formation is unaffected by the Duluth Gabbro Complex, it is typically a mineralogically complex rock that appears intermediate between the carbonate and silicate facies of iron-formation (James, 1954, p. 252). The chief minerals are quartz, magnetite, hematite, iron carbonates, and iron silicates (Gruner, 1946; White, 1954). Hematite-bearing units suggestive of the oxide facies are rare, and the sulfide facies apparently is absent.

The iron phyllosilicates greenalite, minnesotaite, and stilpnomelane are characteristically found in most units of the unmetamorphosed Biwabik Iron-formation; each mineral may occur singly or with any of the others (Gruner, 1946). Greenalite, originally described from the Mesabi range (Leith, 1903), is considered to be an iron serpentine containing little or no aluminum (Jolliffe, 1935; Gruner, 1936, 1946; Blake, 1958, 1965; Steadman and Youell, 1958). Minnesotaite, described as a new mineral from the Biwabik formation (Gruner, 1944b), is an iron-rich talc which may contain considerable magnesium (Gruner, 1946; Blake, 1958, 1965). Stilpnomelane is a complicated layer silicate with variable composition, which was identified on the Mesabi range first in veins in the Biwabik Iron-formation (Grout and Thiel, 1924) and subsequently as a component of the iron-formation itself (Gruner, 1937, 1944a; Blake, 1958, 1965).

Two fundamentally different kinds of iron-formation are distinguished on the Mesabi range (Wolff, 1917; Gruner, 1946; White, 1954). Cherty taconite is massive and quartz-rich, and characteristically has a granular texture produced by the occurrence of iron silicates in rounded, ovoid, or irregular granules commonly 0.5 to 2.0 mm. in diameter. Slaty taconite is generally dark, fine grained, and finely laminated; it is composed mainly of iron silicates and carbonates and contains much carbonaceous matter.*

*The term taconite was originally applied to unaltered iron-formation on the Mesabi range (H. V. Winchell, 1893). The term currently designates unoxidized iron-formation, without regard to whether or not it has been metamorphosed (Gruner, 1946; White, 1954; Gundersen and Schwartz, 1962).

The term slaty is actually a misnomer, for the beds so designated show only bedding fissility and have no true slaty cleavage. However, the term is in current and uniform use to designate the dark, nongranular, laminated iron-formation on the Mesabi range and is retained in the present study.

The two groups correspond approximately to James's "granular" and "nongranular" silicate facies of iron-formation (James, 1954, pp. 249, 267-270).

There is general agreement that the Animikie Group is sedimentary and that the Biwabik Iron-formation is a chemical sediment containing minor quantities of clastic material (Gruner, 1946; White, 1954; Schwartz, 1956, p. 182). There is less agreement about the actual chemical processes of sedimentation. Quartz, greenalite, carbonates, magnetite, and hematite are generally regarded as primary (Gruner, 1946; James, 1954; White, 1954); minnesotaite and stilpnomelane may be primary (Gruner, 1946; Schwartz, 1956) or may have developed during low-grade metamorphism (Tyler, 1949; James, 1954, pp. 266-267).

The Biwabik Iron-formation has been subdivided into four units (Wolff, 1917) on the basis of the dominant kind of taconite present: from the base of the formation upward, Lower Cherty, Lower Slaty, Upper Cherty, and Upper Slaty (Fig. 2). These units, which have been retained as members by later workers (Gruner, 1946; White, 1954; Schwartz, 1956), can be traced along most of the Main range and are recognizable even in the highly metamorphosed rocks near the Duluth Gabbro Complex (Grout and Broderick, 1919b; Gundersen and Schwartz, 1962). Most of the writer's samples are taken from the lower two members, which have been the most extensively mined; apparently there is no recognizable difference in mineralogy between corresponding lithologies in different parts of the formation (Gruner, 1946, p. 27).

Two zones are significant as marker beds and were sampled in detail. The Red Basal taconite, which occurs at the base of the Lower Cherty, is a hematite-bearing, partly clastic unit which is easily recognized along the greater part of the Mesabi range. The so-called Intermediate slate occurs in the lowest part of the Lower Slaty; it is a dark gray to black unit composed of slaty taconite which contains a larger amount of carbonaceous material than the overlying Lower Slaty.

METAMORPHISM OF THE BIWABIK IRON-FORMATION

The Duluth Gabbro Complex, an intrusive mass of gabbro and related igneous rocks (Taylor, 1964), underlies a considerable area of northeastern Minnesota and separates the originally continuous Mesabi and Gunflint ranges. At the east end of the Mesabi range, the gabbro truncates the outcrop belt of the Biwabik Iron-formation at a slight angle (Fig. 1). The gabbro overlies the iron-formation almost concordantly and the base dips a maximum of about 30°SSE.

The development of iron-rich pyroxenes, amphiboles, and olivine in the Biwabik Iron-formation near the contact of the Duluth Gabbro Complex was recognized in early studies of the Mesabi range (N. H. Winchell and H. V. Winchell, 1891; Bayley, 1893; H. V. Winchell, 1893; Elftmann, 1894; Grant, 1900; Leith, 1903; Grout and Broderick, 1919b; Richarz, 1927a,

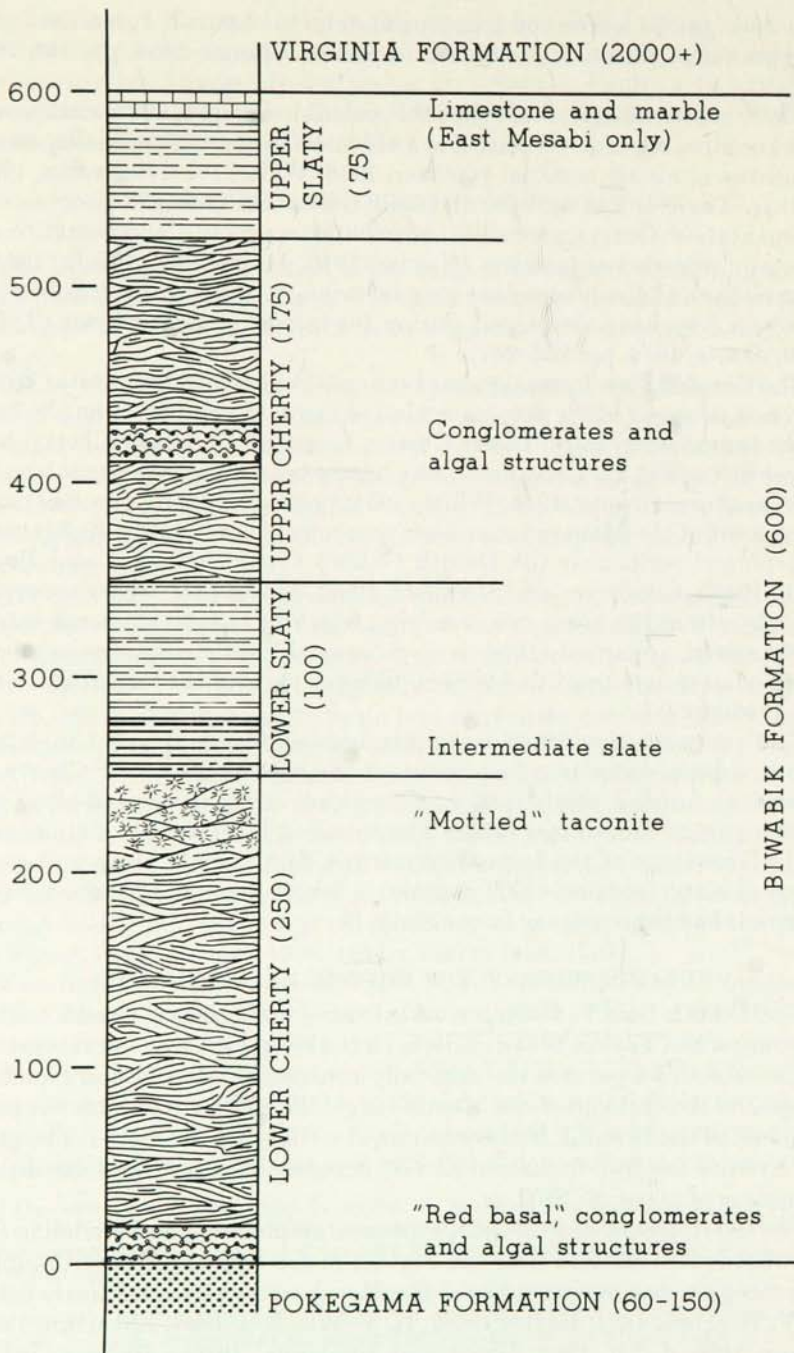


FIGURE 2.—Generalized stratigraphic section of the Biwabik Iron-formation.

1927b). The mineralogy of the highly metamorphosed taconite has been studied in detail (Gundersen and Schwartz, 1962).

Minor intrusive bodies, apparently associated with the intrusion of the Duluth Gabbro Complex, also occur in the Eastern Mesabi district; contact effects adjacent to these minor intrusions are insignificant or absent (White, 1954; Gundersen and Schwartz, 1962).

Mineralogical changes in the Biwabik Iron-formation in the Eastern Mesabi district appear related only to the contact of the Duluth Gabbro Complex, as described by White (1954, p. 36): "The taconites of the East Mesabi range, which were metamorphosed by the Duluth gabbro, contain a rather high-grade metamorphic mineral assemblage consisting of relatively coarse quartz, grunerite, carbonate, garnet, fayalite, magnetite, and minor pyroxene. Near Mesaba, these rocks grade rather abruptly into taconites composed dominantly of fine quartz, greenalite, minnesotaite, stilpnomelane, magnetite, and siderite. Such taconites are characteristic of the entire Main and West parts of the range, and no further lateral metamorphic gradient is evident."

The gabbro was not studied by the writer, but has been described briefly in earlier studies (Gundersen and Schwartz, 1962, p. 71).

METHODS OF STUDY

SUBDIVISION OF THE MESABI RANGE

Several factors make the Mesabi range eminently suitable for detailed study of progressive metamorphism of iron-formation. The geology is simple and has been studied in detail. The stratigraphy of the Biwabik Iron-formation is well defined, and can be distinguished even in the metamorphosed rocks. Structural deformation of the rocks is slight, even near the contact of the Duluth Gabbro Complex (White, 1954), and relations between different units of the Biwabik Iron-formation or between the iron-formation and the gabbro have not been obscured. In addition, adequate samples can be obtained from the numerous artificial exposures of the Aunimikie rocks, particularly in the open-pit taconite operations.

Detailed studies of the mineralogy of both the unaltered and highly metamorphosed iron-formation have been made (Gruner, 1946; White, 1954; Gundersen and Schwartz, 1962), but no detailed work has been done on the nature of the transition between the two.

It is convenient to divide the outcrop belt of the Biwabik Iron-formation into four zones that have characteristic textural and mineralogical features observable in the field (Fig. 3). These zones reflect mineralogical changes produced by the gabbro.

Zone 1, unaltered taconite, extends from the western limit of sampled area (Nashwauk) east beyond Biwabik. The eastern limit is the boundary between R.15W. and R.16W. In this zone the taconite is fine grained and consists of quartz, iron oxides, iron carbonates, and the iron silicates chamossite, greenalite, minnesotaite, and stilpnomelane.

Zone 2, transitional taconite, extends from the R.15W.-R.16W. boundary to the town of Mesaba (21:59-14).^{*} No mineralogical differences are observed, but there is considerable secondary replacement of the taconite by quartz and ankerite.

Zone 3, moderately metamorphosed taconite, extends from Mesaba (21:59-14) approximately to the boundary between R.13W. and R.14W. Taconite in this zone is characterized by the development of grunerite and by the disappearance of layered silicates and carbonates.

Zone 4, highly metamorphosed taconite. This zone extends from about 14:59-14 east to Argo Lake (16:60-12). Taconite in this zone is highly recrystallized and is characterized by increased hardness and grain size and by the formation of iron-bearing pyroxenes. Coarse-grained pods and lenses of iron-rich minerals are found in this zone. Except for calcite, carbon-

^{*} Sections are designated here by the abbreviated notation used by White (1954). Thus, SESE 21:59-14 indicates the SE $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 21, T.59N., R.14W.

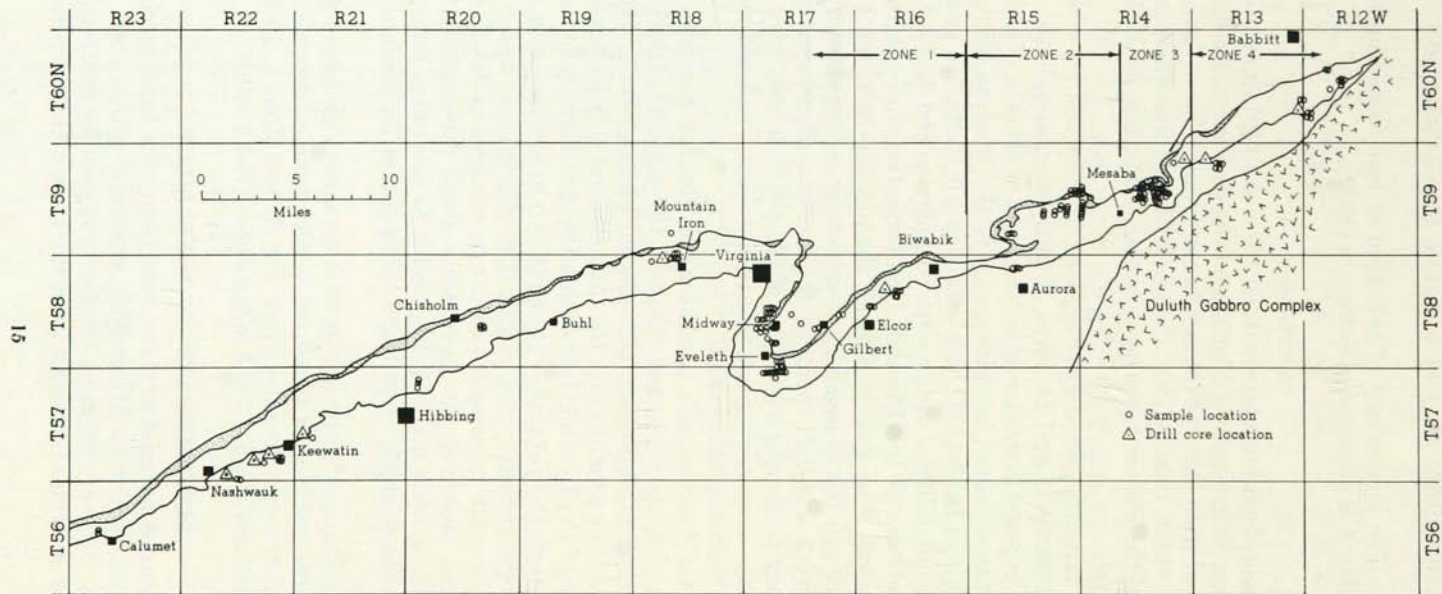


FIGURE 3.—Generalized geologic map of part of the Mesabi range, showing location of samples and boundaries of the four metamorphic zones distinguished in this study.

ates are absent. The mineralogy of this kind of iron-formation has been studied in detail by Gundersen and Schwartz (1962).

SAMPLING

The unmetamorphosed taconite in Zone 1 was sampled from a few natural exposures near Virginia and Gilbert and from drill cores. Fresh taconite also was obtained from some of the soft ore open-pit mines — the Auburn (Midway) (Schwartz, 1956, p. 160), Pierce (Hibbing), and Sherman (Chisholm), and from the Pilotac taconite operation of the U.S. Steel Company at Mountain Iron.

Transitional taconite (Zone 2) is exposed in Erie Mining Company's taconite pits in 28:59-15 and 24:59-15. Slightly metamorphosed taconite (Zone 3) is well exposed in similar operations east of Mesaba (14,15:59-14). The highly metamorphosed taconite occurs in the Reserve Mining Company's operations in R.13-14W.; this area was not studied in great detail because of the availability of earlier work (Gundersen and Schwartz, 1962).

About 160 samples of the Biwabik Iron-formation and the associated Animikie sediments were collected along the outcrop belt (see Fig. 3 for sample distribution). Where possible, samples were collected from definitely located outcrops and drill cores. In the taconite pits, however, it was usually necessary to sample loose piles of blasted material; such samples were typical of the surrounding taconite and probably were not more than 100 yards from their original position.

The Duluth Gabbro Complex truncates the Biwabik Iron-formation at a slight angle, and, in the region near Babbitt, the contact is locally parallel to bedding in the iron-formation (Gundersen and Schwartz, 1962). The metamorphic aureole produced by the intrusion extends for several miles along the strike of the Biwabik Iron-formation, but because of the nearly concordant contact, the distance is probably two to five times the straight-line distance to the gabbro contact at the time of intrusion. As a result, the metamorphic zones are spread out and can be sampled in detail over relatively large areas. However, the uncertainty about pre-erosional attitude and extent of the gabbro makes it impossible to determine the exact distance between the original contact and any point in the metamorphosed iron-formation.

Metamorphic changes in the iron-formation show a uniform relation to distance from the gabbro, as measured in the manner described above. Limits on the four zones described (see Fig. 3) are: Zone 1, 10-60 miles; Zone 2, 2.6-10 miles; Zone 3, 1.7-2.6 miles; Zone 4, 0-1.7 miles.

DETERMINATION OF MINERALOGY

About 20 grams of material were removed from each hand specimen and ground in a Spex Industries Mixer/Mill, equipped with a steel vial and steel balls. The -120 or -230 mesh fraction was used for analysis.

Separation of individual minerals from the taconite is hampered by the

TABLE 2. STRONG X-RAY REFLECTIONS OF MINERALS IN THE TACONITE
OF THE BIWABIK IRON-FORMATION, $\text{CuK}\alpha$ RADIATION

Mineral	hkl	d (Å)	2θ (degree)	Mineral	hkl	d (Å)	2θ (degree)
Quartz	100	4.255	20.9	Chlorite (14A)	001	14.20	6.2
	101	3.343	26.7		002	7.10	12.5
Magnetite	220	2.97	30.1	Minnesotaite	002	9.53	9.3
	311	2.53	35.5		004	4.77	18.6
Hematite	104	2.69	33.3		006	3.18	28.1
	110	2.51	35.8	Talc	002	9.30	9.5
Goethite	100	4.18	21.3		004	4.57	19.4
	110	2.51	35.8		006	3.10	28.8
Siderite	110	3.59	24.8	Stilpnomelane	001	11.9	7.5
	211	2.79	32.1		003	4.04	22.1
Ankerite	211	2.90	30.8	Grunerite	110	8.38	10.6
Calcite	211	3.04	29.4		310	3.08	29.0
	Greenalite	001	7.21	12.3	Fe-hornblende	110	8.38
002		3.60	24.7	310		3.03	29.5
201		2.59	34.6	Fayalite	130	2.83	31.6
Chamosite (7A)	001	7.12	12.4		Fe-hypersthene		3.21
	002	3.55	25.1	Hedenbergite	310, 211	3.00	29.8
	201	2.53	35.5		Graphite	002	3.35

fine grain size, by the fibrous and commonly intergrown character of the silicates, and, in particular, by fine disseminated magnetite. Separation procedures are complicated and often unrewarding (Blake, 1958). Magnetite separations were carried out on only a few suitable specimens.

The mineralogy of the taconite makes it suitable for identification and study by X-ray powder diffraction, using total rock samples. The powder sample was mounted on a glass slide in an acetone-Duco cement mixture. Diffraction patterns from 5° to $40^{\circ} 2\theta$ were obtained on a Norelco instrument, using $\text{CuK}\alpha$ radiation, a scanning speed of 1° per minute, and a chart speed of $\frac{1}{2}$ inch per minute. Divergent, scatter, and receiving slits were 1° , 1° , and 0.006 inch, respectively. Scale factor, time constant, and multiplier factor were generally 4, 1, and 8, respectively.

The minerals of unaltered taconite — quartz, hematite, magnetite, siderite, ankerite, chamosite, chlorite, greenalite, stilpnomelane, minnesotaite, and talc — can be identified by their characteristic reflections (Table 2). X-ray diffraction is particularly useful for distinguishing between the iron-rich layered silicates, using the basal reflections in the range 9° – $13^{\circ} 2\theta$. Except for the closeness of the hematite (110) and magnetite (311) peaks, there is no significant interference between major peaks. Secondary peaks, however, are needed to distinguish between chamosite and greenalite and between minnesotaite and talc.

In metamorphosed taconite, which contains grunerite, hornblende, hedenbergite, ferrohypersthene, and calcite (Gundersen and Schwartz, 1962), grunerite and hornblende can be distinguished by the position of the (310) peak.

Probably this method of identification is suitable to detect quantities of less than 10 per cent present of any given mineral. The quartz which is almost always present serves as a useful internal standard for exact measurement of peak locations.

The identification of minerals by X-ray powder diffraction was supplemented by petrographic examination of about 70 thin sections. Comparison between the thin sections and the X-ray patterns of the same samples made mineral identifications more exact and provided textural data for recognition of the replacement or reaction relations between minerals. These data allowed more reliable interpretations of the mineralogy of the additional specimens for which only X-ray powder patterns were obtained.

PROGRESSIVE METAMORPHISM OF THE BIWABIK IRON-FORMATION AND RELATED ROCKS

UNALTERED TACONITE (ZONE 1)

INTRODUCTION

The mineralogy of the taconite in Zone 1 is quite uniform (Gruner, 1946; White, 1954). There is considerable uncertainty about whether the present mineralogy is primary or partly metamorphic; the writer favors the view that the mineralogy reflects an episode of low-grade metamorphism unrelated to the intrusion of the Duluth Gabbro Complex (see p. 11). To avoid confusion, the term unaltered is applied to the taconite in Zone 1, to indicate that it shows no features related to the intrusion of the Duluth gabbro.

CHERTY TACONITE

Introduction. Cherty taconite is the dominant lithology in the Lower Cherty and Upper Cherty Members of the Biwabik Iron-formation (Wolff, 1917; Gruner, 1946; White, 1954); these members underlie all natural outcrops of the formation. In outcrop, cherty taconite is massive and medium- to thin-bedded and consists of individual layers commonly two inches to two feet thick. Specimens are characterized by a high percentage of quartz and by a granular texture which is often visible in hand specimen. In the Lower and Upper Cherty, cherty taconite beds are interbedded with thin dark layers of slaty taconite, which may constitute 10 to 30 per cent of a given section. These slaty layers, rich in carbonate and magnetite, are generally irregular in shape, as in the so-called wavy-bedded taconite (Gruner, 1946, Pl. 14A).

Primary Mineralogy and Textures. Well-developed granule texture is characteristic of specimens of cherty taconite examined by the writer (Figs. 4 and 5). The granules, which form a framework within a matrix of crystalline quartz, are generally 0.2 to 2 mm. in long dimension, rounded, and ovoid to elliptical in shape. Commonly, they are irregular in shape and may be stretched to sharp points suggestive of rupture when soft. Granules with concave surfaces are not uncommon, and dumbbell-shaped granules are occasionally observed. Where closely packed, the granules are often deformed against each other, indicating compaction when soft.

Most granules are composed of featureless, isotropic, dark-green to brownish green greenalite; they show no concentric or radial structures and contain no recognizable central nucleus. Small circular bodies of uncertain origin rarely occur within the granules (see Gruner, 1946, Pl. 4; James, 1954, Figs. 26 and 27). Finely divided opaque material commonly is scattered through the greenalite; it may be either magnetite or organic matter.

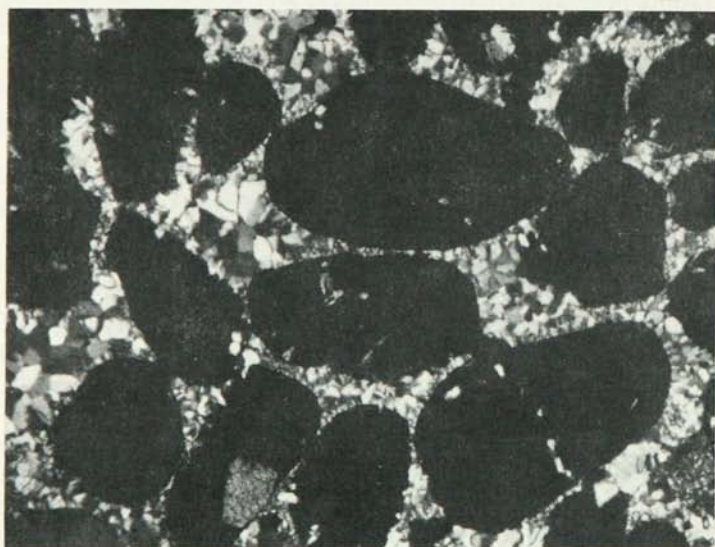
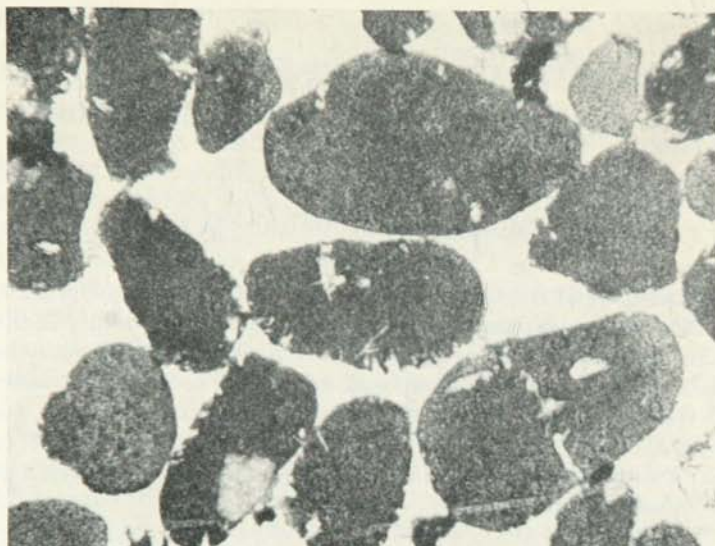


FIGURE 4.—Greenalite granule taconite from unaltered Biwabik Iron-formation (Zone 1). Plane polarized light, 61x. Featureless greenalite in the granules (dark gray) is slightly replaced by the quartz matrix (white) near the margins of the granules. FIGURE 5.—Greenalite granule taconite from unaltered Biwabik Iron-formation (Zone 1); same view as Figure 4; crossed nicols. Fine-grained quartz occurs around the rims of the granules; coarser quartz occupies the centers of voids between granules. The texture of the cement suggests a later introduction of quartz into spaces between a framework of greenalite granules.

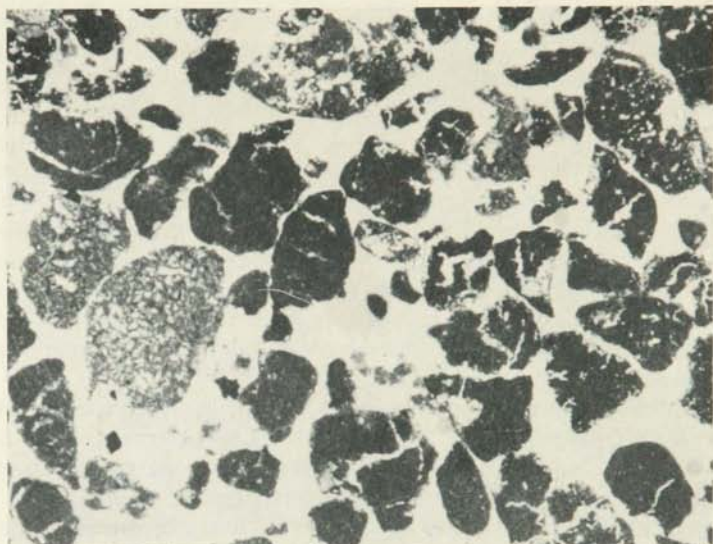


FIGURE 6.—Stilpnomelane granule taconite from unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 19x. Featureless stilpnomelane (dark gray) forms irregular granules in a quartz matrix (white). It is partly replaced by fibrous talc (light gray) and siderite (gray rhombs). The stilpnomelane in this specimen may be primary.

Irregular granules composed of featureless brown stilpnomelane were observed in one specimen of cherty taconite (Fig. 6); the granules are surrounded by rims of pleochroic fibrous stilpnomelane. No other silicate material is observed within the granules; this occurrence of stilpnomelane may be primary.

The matrix of the granules is crystalline quartz. Two kinds of quartz can generally be distinguished in specimens of cherty taconite: (1) very fine quartz, 0.005–0.01 mm., which forms a rim a few grains thick around the granules and is generally absent where the granules are in contact with one another; (2) coarser quartz, 0.05–0.5 mm., which fills interstices between granules. There is a definite increase in grain size of the quartz from the margin of the granule toward the center of the pore space, which suggests that the quartz is a pore filling (Fig. 5). Similar textures in a Paleozoic siliceous oolite (Choquette, 1955) have been interpreted as evidence for postdepositional introduction of quartz into a framework of ooliths.

Secondary Minerals and Textures. Partial to complete replacement of the original greenalite granules by minnesotaite, stilpnomelane, siderite, and magnetite is characteristic of the cherty taconite in Zone 1; the quartz matrix may also be partly replaced. Such replacement is characterized by development of coarser-grained crystals and aggregates of the secondary minerals within the original greenalite and quartz. No specimens containing completely unaltered greenalite were observed by the writer.

Silicates. Minnesotaitite commonly occurs in cherty taconite as small fibrous sheaves about 0.05 mm. long, in which the individual fibers may be parallel or radiating, or as individual fibers and patches of very fine shreds. The mineral is colorless to pale green and highly birefringent; the fibers show parallel extinction.

Minnesotaitite is the most common mineral observed to replace greenalite in the granules; sparse minnesotaitite occurs in the quartz matrix as well (Fig. 7, this report; also see Gruner, 1946, Pls. 2 and 3; LaBerge, 1964). Replacement by minnesotaitite commonly produces granules in which small irregular remnants of dark greenalite occur within a minnesotaitite matrix. Rarely, the entire granule is completely altered to an aggregate of fine quartz and minnesotaitite fibers; in such rocks, minnesotaitite may constitute as much as 40 per cent of the taconite.

Stilpnomelane is uncommon in cherty taconite and only rarely exceeds 5 per cent. It forms rosettes of fibers 0.05 to 0.1 mm. long. Most of the stilpnomelane observed by the writer is brown and strongly pleochroic, suggesting a ferric variety (Hutton, 1938; Gruner, 1946).

Talc was identified in several specimens of cherty taconite, where it replaces granules and occurs in some specimens of slaty taconite. Where such replacement has been intense, it constitutes as much as 40 per cent of the rock, and the original granule texture is reduced to blotchy ovoid aggregates of fine quartz and irregular shreds of talc.

The value of $d(006)$ for talc was determined for one specimen which consisted almost entirely of talc and quartz. Six oscillations between 25° and $30^\circ 2\theta$ were averaged, using the quartz as an internal standard. The value of $d(006)$ obtained (3.124 Å) is close to that of natural talc (3.10 Å; Brown, 1961), and it is quite distinct from that of minnesotaitite (3.18 Å; Blake, 1958).

Talc was previously reported (Blake, 1958, p. 83) associated with stilpnomelane in a cavity in altered iron ore a few miles from where the present specimen was collected, suggesting that talc might have formed in the taconite during a later event connected with formation of the soft ores. The occurrence of talc in several specimens of otherwise unaltered taconite, however, indicates to the writer that such occurrences probably are not related to the alteration that produced the soft ores.

Carbonates. Both siderite and ankerite have been observed by the writer in cherty taconite; both minerals are apparently secondary. Siderite is more common; it occurs as individual rhombohedra and anhedral grains that replace both greenalite granules and the adjacent quartz matrix (Fig. 4); the mineral constitutes from 5 to 10 per cent of the taconite. Such replacement is particularly intense for a few millimeters adjacent to thin slaty bands which are rich in fine-grained, apparently primary siderite (Fig. 8). Strong replacement may produce a granule composed of a single crystal of carbonate that pseudomorphs the granule shape. Replacement of the quartz matrix is less marked.

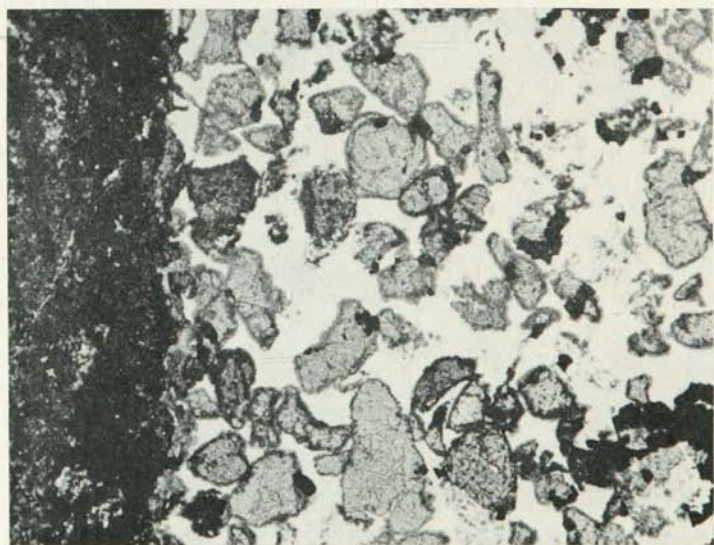
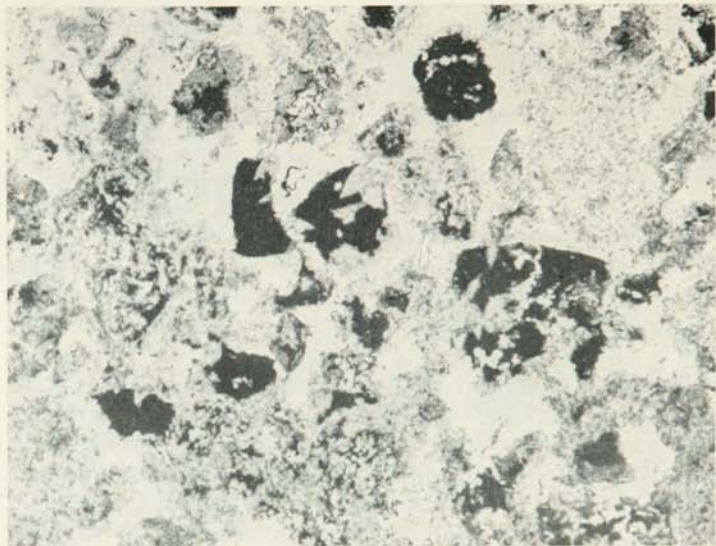


FIGURE 7.—Intense replacement of greenalite granule taconite by minnesotaite in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 22x. A few remnants of greenalite (dark gray) remain in quartz matrix (white). Most of the granules have been converted to aggregates of fine-grained minnesotaite (light gray) and quartz. FIGURE 8.—Strong replacement of granule taconite by carbonate in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 19x. The dark band at left is a mixture of fine-grained siderite and magnetite. Adjacent to this band, original silicate granules have been replaced by single crystals of siderite (light gray), which preserve the original granule shape.

The term ankerite is applied to a dolomite-like carbonate that contains a significant amount of iron; ankerite from the unmetamorphosed taconite generally contains 50–55 mole per cent more $\text{CaFe}(\text{CO}_3)_2$ (Table 4), and can be distinguished from siderite by X-ray diffraction and by the closeness of the n_c index to that of quartz.

Ankerite occurs in taconite that is richer in quartz and contains less silicate material; such beds may resemble the banded carbonate-quartz rocks characteristic of the carbonate facies (James, 1954). Commonly, ankerite is present as isolated rhombohedra 0.01 to 0.1 mm. in size that replace the quartz; rarely, fine-grained quartz is included within the crystals. The ankerite rhombohedra are often zoned, with a darker outer rim and a clear interior (Fig. 9).

Replacement by ankerite commonly develops patches of ankerite crystals several millimeters across, which give the taconite a mottled appearance (Figs. 9 and 10). In such specimens, the mottles contain remnants of earlier granules, which are outlined by fine opaque matter. Ankerite constitutes 10–30 per cent of individual specimens of taconite; the higher percentages correspond to the more intensely replaced mottled taconite.

Ankerite occurs less frequently in the carbonate-rich slaty layers associated with cherty taconite, forming irregular bands and patches of anhedral about 0.05 mm. in diameter that surround and apparently replace earlier siderite grains 0.01 mm. or less in size.

Other Minerals. Magnetite is a minor constituent of cherty taconite, and generally makes up 5 to 15 per cent of the rock. The mineral has been considered to be primary or diagenetic by other investigators (Gruner, 1946; White, 1954). However, LaBerge (1964) has concluded that petrographic relations indicate a secondary origin for most, if not all, of the magnetite in the Biwabik Iron-formation; he has suggested that the magnetite was formed during a period of low-grade regional metamorphism.

Very fine-grained magnetite, which occurs in both granules and matrix as disseminated crystals 5 microns or less in size, is probably primary in origin. The finer opaque dust within the granules may also be primary.

Definite secondary magnetite occurs as coarser euhedra 0.05 to 0.1 mm. in size, which are grouped in bunches and lenses as much as 1 mm. across. Such magnetite commonly replaces earlier iron silicates in granules and also occurs with fine-grained siderite in the thin slaty bands associated with cherty taconite (Fig. 8). These textures and relations are identical to those described independently by LaBerge (1964, figs. 7–9, 13–14) in a detailed petrographic study of unaltered Mesabi range taconite. The writer's observations support LaBerge's conclusions that the magnetite and minnesotaite in such occurrences are clearly secondary.

Replacement of the granules by magnetite is most common at the margins and may yield an inner core of greenalite or minnesotaite surrounded by a rim of coarser magnetite crystals that preserves the outline of the granule; the crystals commonly show octahedral cross-sections. More rare-

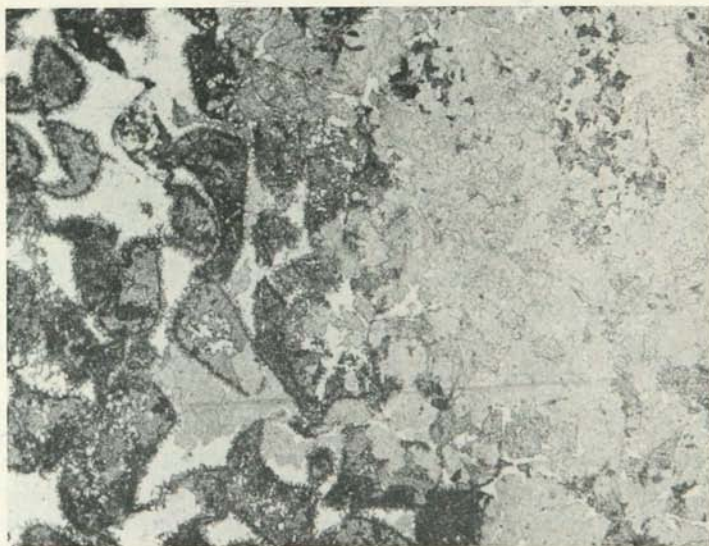
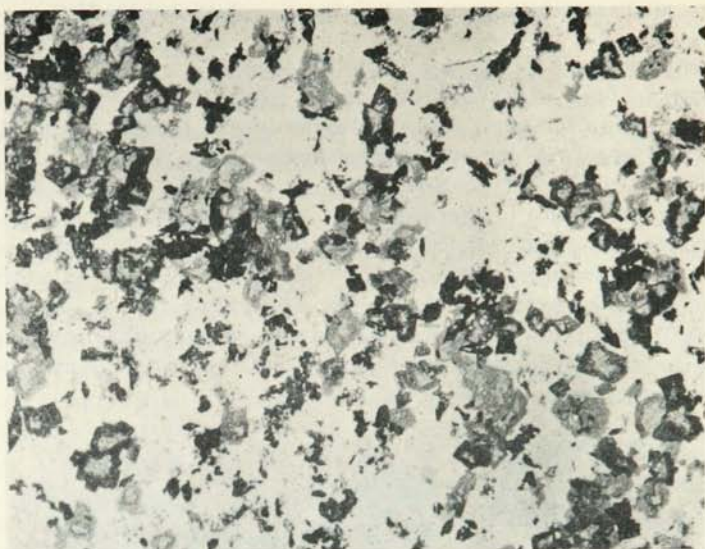


FIGURE 9.—Ankerite-rich cherty taconite from unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 20x. Ankerite (gray) occurs as small rhombs replacing fine-grained quartz (white) and is associated with fine-grained magnetite (black). The rhombs are commonly zoned, with a dark outer zone and a light interior. FIGURE 10.—Strong replacement of silicate granule taconite by coarse-grained ankerite in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 20x. The original granules, shown at left, consist of greenalite (dark gray) and occur in a matrix of crystalline quartz (white). Medium- to coarse-grained ankerite (light gray) at right forms a patch several millimeters in diameter, and replaces both the granules and the quartz matrix. A small amount of magnetite (black) occurs in the ankerite.

In this specimen, such replacement largely destroys the granule texture; however, ghosts of granules commonly can be seen in such ankerite.

ly, the entire granule may be pseudomorphed by magnetite (Fig. 11). Identical structures are commonly present in highly metamorphosed taconite; the preservation of original granule texture despite thorough recrystallization of the taconite allows the original character of the rock to be recognized (Grout and Broderick, 1919b; Gundersen and Schwartz, 1962).

Quartz in the matrix of cherty taconite constitutes 20–30 per cent of the rock. Quartz also apparently develops within the granules simultaneously with the formation of minnesotaite at the expense of the original greenalite, and constitutes as much as 60 per cent of highly replaced taconite. Replacement of granules by quartz alone is uncommon and generally is confined to the granule margins; rarely, small euhedra of quartz are observed within the greenalite.

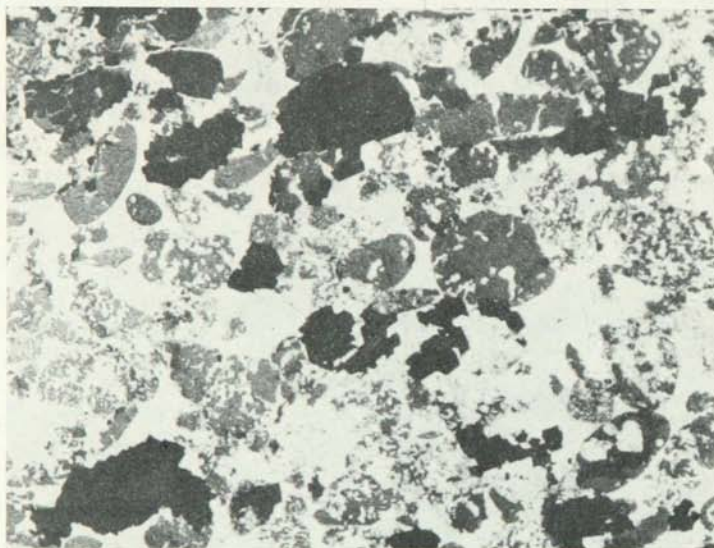


FIGURE 11.—Strong replacement of silicate granule taconite by magnetite in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 20x. Original granules of greenalite or chlorite (light gray) in a matrix of crystalline quartz (white) are partly to completely replaced by groups of magnetite euhedra (black), which preserve the general shape of the granule. Partial replacement by magnetite is illustrated by the granules at upper left and lower right; the large granules in the upper center and lower left have been completely replaced.

Summary. The granule cherty taconite of the Biwabik Iron-formation strongly resembles in texture the oolitic silicate units of younger iron-formations, which are believed to have originated by the sedimentary accumulation of chemically precipitated ooliths (Pettijohn, 1957; Hunter, 1960). It is generally believed that the cherty units of the Biwabik Formation originated through the same mechanism (Gruner, 1946; James, 1954; White, 1954).

Certain features of cherty taconite had been thought to be unique to the

Precambrian: the strong mineralogical banding, the presence of featureless granules instead of ooliths, and the occurrence of greenalite instead of chamosite or chlorite. These distinctions no longer appear rigorous; banded iron-formations do occur in Paleozoic rocks (O'Rourke, 1961), and a greenalite-bearing iron-formation resembling cherty taconite has been described from the Ordovician (Kennedy, 1936).

Estimated percentages of minerals in typical specimens of unaltered cherty taconite examined by the writer are: quartz 30–60 per cent, minnesotaite 10–40 per cent, greenalite 0–20 per cent, stilpnomelane 0–5 per cent, siderite 0–20 per cent, ankerite 0–30 per cent, magnetite 5–15 per cent. Hematite is generally absent; its occurrence is apparently restricted to distinct layers such as the Red Basal taconite at the base of the Lower Cherty member. Talc constitutes as much as 40 per cent of some specimens, but is rare.

The most common mineral assemblages are: minnesotaite-greenalite, minnesotaite-greenalite-siderite, minnesotaite-siderite, siderite-ankerite, and ankerite. Magnetite and quartz are ubiquitous in all assemblages.

It was not determined in the present study whether the mineralogical changes observed in unaltered cherty taconite have been produced by diagenesis or by low-grade metamorphism. Similar replacements are observed in unmetamorphosed sedimentary iron-formations of both Precambrian and post-Precambrian age (James, 1954; Hunter, 1960).

SLATY TACONITE AND THE INTERMEDIATE SLATE (ZONES 1 AND 2)

Introduction. Slaty taconite was collected chiefly from the Lower Slaty member of the Biwabik Formation (Wolff, 1917; Gruner, 1946; White, 1954). Small slaty bands rich in carbonate and magnetite that occur with cherty taconite in the Lower Cherty member also were studied. No differences were observed between specimens collected from Zones 1 and 2; accordingly, the two zones are discussed together in this section. Detailed study of slaty taconite was hampered because the Lower Slaty member forms no natural outcrops and is readily altered near ore bodies and because the fine grain size and the included dark organic matter make recognition of textural relations between minerals extremely difficult.

Mineralogy of Slaty Taconite. Slaty taconite is characterized by fine laminations that reflect differences in mineral composition, by very fine-grained minerals, and by a general absence of granules. The most common minerals are stilpnomelane, minnesotaite, siderite, and quartz; any of these may form essentially monomineralic layers (Gruner, 1946).

Silicate-carbonate slaty taconite is a finely laminated rock composed of alternating buff and dark-green laminae 0.2 to 4 mm. thick. In a typical specimen (Fig. 12), the buff bands consist dominantly of fine grains of siderite about 2 microns in size and lesser amounts of green stilpnomelane. Commonly, very small dark nuclei occur in the centers of the siderite grains. The dark-green layers contain no siderite and are almost entirely

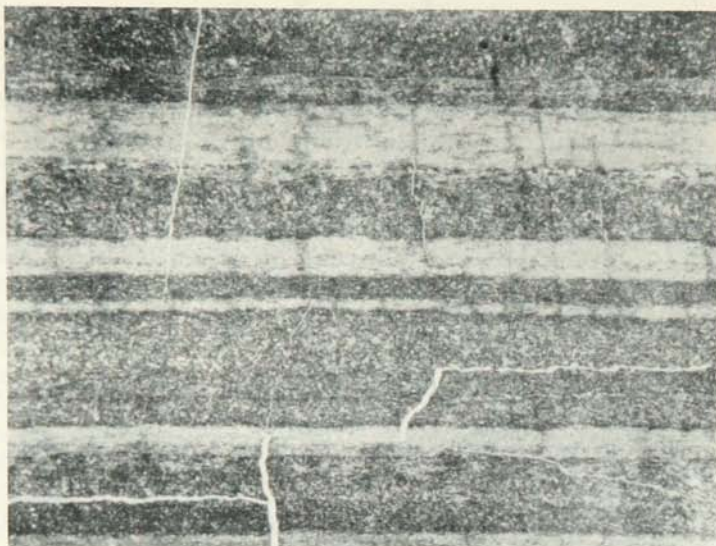


FIGURE 12.—Finely laminated slaty taconite composed of alternating carbonate- and silicate-rich bands, in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 8x. Silicate-rich laminae (light gray) consist of a fine-grained aggregate of stilpnomelane flakes oriented parallel to the banding, together with minor quartz and magnetite. Carbonate-rich bands (dark gray) are composed chiefly of fine-grained siderite and minor stilpnomelane, quartz, and organic matter.

composed of pleochroic green stilpnomelane, which occurs as platy grains smaller than 10 microns. The stilpnomelane crystals are parallel to banding in the taconite and show aggregate polarization in thin section. Contacts between the laminae are sharp. The material closely resembles iron-formation from Crystal Falls, Michigan (James, 1954, Fig. 32; Pettijohn, 1957, p. 447). In other specimens, minnesotaite may be the dominant silicate.

Silicate slaty taconite corresponds essentially to the nongranular silicate facies iron-formation of James (1954, pp. 268-270). Carbonate generally accounts for less than 30 per cent; the dominant minerals are stilpnomelane and minnesotaite. Small amounts of chlorite* are rarely observed as irregular green pleochoric flakes as much as 50 microns long; this material commonly is altered to stilpnomelane.

*Both true chlorite (14 A) and chamosite (7 A) were identified by the writer in the Pokegama and Biwabik formations. Where possible, the two are distinguished on the basis of the presence or absence of the 14 A peak in the X-ray pattern. The following terms are applied: (1) *chlorite* designates light-green, pleochoric, low-birefringent silicate minerals that occur in amounts too small for exact identification; (2) *chlorite* (14 A) designates true chlorite identified by X-ray diffraction; (3) *chamosite* designates material for which only a 7 A peak is observed. Exact identification is possible only for specimens containing considerable chlorite, and it is possible that both polymorphs may exist in the same specimen (Hunter, 1960). A more detailed classification is not required for the present study (see, e.g., Hunter, 1960; Brown, 1961).

In silicate-rich slaty taconite, quartz and magnetite are present in minor quantities, rarely in excess of 10 per cent. Commonly, quartz occurs in small irregular lenses, less than 1 mm. long, elongated parallel to the laminations; such quartz is very fine grained and some is possibly amorphous chert. Magnetite occurs as euhedra 1 to 50 microns in size and rarely constitutes as much as 60 per cent of a layer; much magnetite is secondary, forming from siderite in carbonate-rich bands (Fig. 8).

Some specimens of slaty taconite studied consist only of alternating bands of fine-grained carbonate and quartz a few millimeters thick (Gruner, 1946, Pl. 19); these rocks correspond to ideal representatives of the carbonate facies (James, 1954, pp. 249, 251).

The carbonate bands are light brown in hand specimen and contain as much as 80 per cent of siderite anhedral 1 to 10 microns in size. A small amount of ankerite, in crystals 0.1 to 0.2 mm. in diameter, apparently replaces the siderite. Very fine quartz less than 5 microns in size constitutes 20 to 30 per cent of the band; a small amount of coarser quartz (10 microns) occurs as irregular patches.

The quartz-rich bands appear black in hand specimen and resemble chert; they consist commonly of more than 95 per cent microcrystalline quartz less than 10 microns in size, together with a small amount of coarser quartz. The remainder is euhedral ankerite and fibrous silicates.

Some layers of slaty taconite contain small granules of iron silicate 0.05 to 0.2 mm. in diameter, much smaller than granules found in cherty taconite; the granules do not form a framework and generally appear to float in a fine matrix. Chamosite was identified by the writer in one specimen of otherwise nongranular slaty taconite. In this specimen, thin layers of chamosite-bearing granules in a matrix of hematite alternate with nongranular layers containing either hematite or a mixture of siderite and chamosite (Fig. 13). The granules are irregular, elongate, and commonly compressed against one another. The chamosite occurs in the granules as small pleochroic green flakes that are slightly birefringent, associated with finely crystalline quartz. These granules resemble strongly the quartz-chlorite clasts observed in the Pokegama Formation.

Slaty taconite contains small amounts of dark-brown to black carbonaceous material designated as graphite by Gruner (1946, p. 21). This material occurs as thin partings parallel to the layering which have a wavy jagged appearance suggestive of stylolites.

Mineralogy of the Intermediate Slate. The lowermost 30 to 60 feet of the Lower Slaty member of the Biwabik Iron-formation is a dark-gray to black slaty taconite with a high content of organic matter* (3 to 4 per cent carbon by weight) (Gruner, 1946). This unit is strikingly different from the overlying Lower Slaty and rests on the Lower Cherty member with a sharp contact that can be recognized throughout the Main Mesabi

*The term organic is used here to describe the carbonaceous material that contains a considerable amount of hydrocarbons. It does not necessarily imply a biogenic origin.

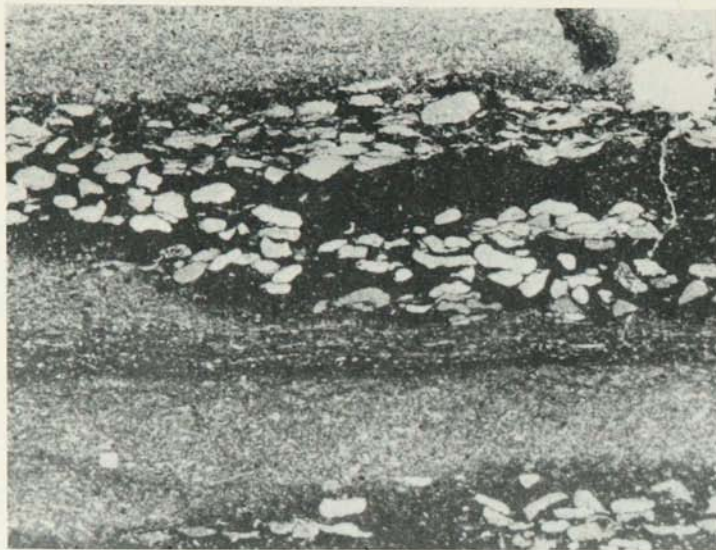


FIGURE 13.—Finely laminated granule-bearing slaty taconite in unaltered Biwabik Iron-formation (Zone 1). Ordinary light, 9x. The specimen consists of alternating granule-bearing and granule-free laminae. The small, elongate, and commonly distorted granules, composed of fine-grained chlorite and quartz (light gray), are surrounded by a fine-grained matrix of apparently primary hematite and quartz (dark gray to black). The granules appear to float in the matrix and do not form a framework. The granule-bearing layers alternate with granule-free laminae composed of fine-grained siderite or of siderite and chlorite.
(The mark at upper right is caused by a hole in the section.)

and Eastern Mesabi districts (Gruner, 1946; White, 1954; Gundersen and Schwartz, 1962).

The Intermediate slate is fine grained and nearly opaque in thin section; mineral identifications are based on X-ray diffraction alone. Specimens of unaltered Intermediate slate are composed dominantly of siderite and chamosite; either mineral may constitute as much as 80 per cent of the rock. Minor components, which rarely exceed 10 per cent, are quartz, magnetite, and stilpnomelane. Amorphous organic matter was not determined, but may constitute 5 to 10 per cent. Small amounts of pyrite occur in the acid-insoluble residues of some specimens.

Summary. The finely laminated character of the slaty taconite and the occurrence of rare isolated small granules are consistent with an origin through chemical deposition in quiet water. White (1954) has concluded that the slaty units of the Biwabik Iron-formation were deposited farther from shore than the granule-bearing cherty taconite.

The chief components of slaty taconite are siderite, stilpnomelane, minnesotaite, and quartz, each of which may constitute more than 90 per cent of a given lamina. An estimated composition for the majority of specimens examined is: siderite 30–60 per cent, silicate 30–60 per cent, quartz 5–10 per cent, magnetite 5–15 per cent. No greenalite was detected.

Typical mineral assemblages are: stilpnomelane-siderite-quartz-magnetite, stilpnomelane-quartz-magnetite, minnesotaite-stilpnomelane-quartz-magnetite, stilpnomelane-chamosite-magnetite-quartz, and siderite-ankerite-quartz.

Hematite is an uncommon component of slaty taconite; the rare hematite-siderite and hematite-chamosite-quartz layers are believed to be primary (Gruner, 1946, p. 31; C. A. Beckman, oral communication, 1962), but they constitute a negligible amount of the total thickness of slaty taconite.

Chlorite has been observed in small amounts in slaty taconite and in the partly clastic units at the base of the Biwabik Formation (Gruner, 1946, pp. 22, 25); chlorite minerals also occur in other Precambrian iron-formations (James, 1951, 1954; Moorhouse, 1960).

Chamosite has been identified by the writer in small granules in slaty taconite and as a major constituent of the Intermediate slate. This material may represent the "greenalite" identified by X-ray diffraction from slaty taconite (Gruner, 1946, p. 31). No chlorite or chamosite was observed in cherty taconite.

Mineral assemblages determined by X-ray diffraction for unaltered Intermediate slate are: siderite-chamosite-stilpnomelane-quartz-magnetite, siderite-chamosite-quartz (\pm magnetite), and chamosite-quartz-magnetite.

Slaty taconite contains a higher percentage of Al_2O_3 (as much as 7 per cent) than cherty taconite (about 1 per cent) (Gruner, 1946). This difference probably reflects the higher percentages of aluminum-bearing stilpnomelane and chamosite in slaty taconite.

TRANSITIONAL TACONITE (ZONE 2)

CHERTY TACONITE

Cherty taconite in Zone 2 is mineralogically identical to that in Zone 1, and there is no detectable increase in grain size. However, where the Lower Cherty member was sampled in the Erie Mining Company taconite operations in 23, 24, and 28:59-15, considerable, widespread replacement of the iron silicates by quartz and ankerite was observed. It is not certain whether this replacement is related to the Duluth Gabbro Complex or whether it is characteristic of the rather narrow stratigraphic interval studied.

Replacement by quartz appears more common than in the cherty taconite in Zone 1. Quartz commonly replaces the iron silicate in the granules (Figs. 14 and 15), forming aggregates of quartz grains 0.05 to 0.1 mm. in size. In such silicified rocks, the granule texture is preserved by the arrangement of fine dust originally present in the granules and by the preservation of finer quartz (0.005 to 0.02 mm. size), which originally constituted the matrix.

As in Zone 1, replacement of cherty taconite by secondary siderite is common, particularly when it lies adjacent to thin slaty layers. In one specimen, fine-grained siderite has replaced the cement, whereas the granules

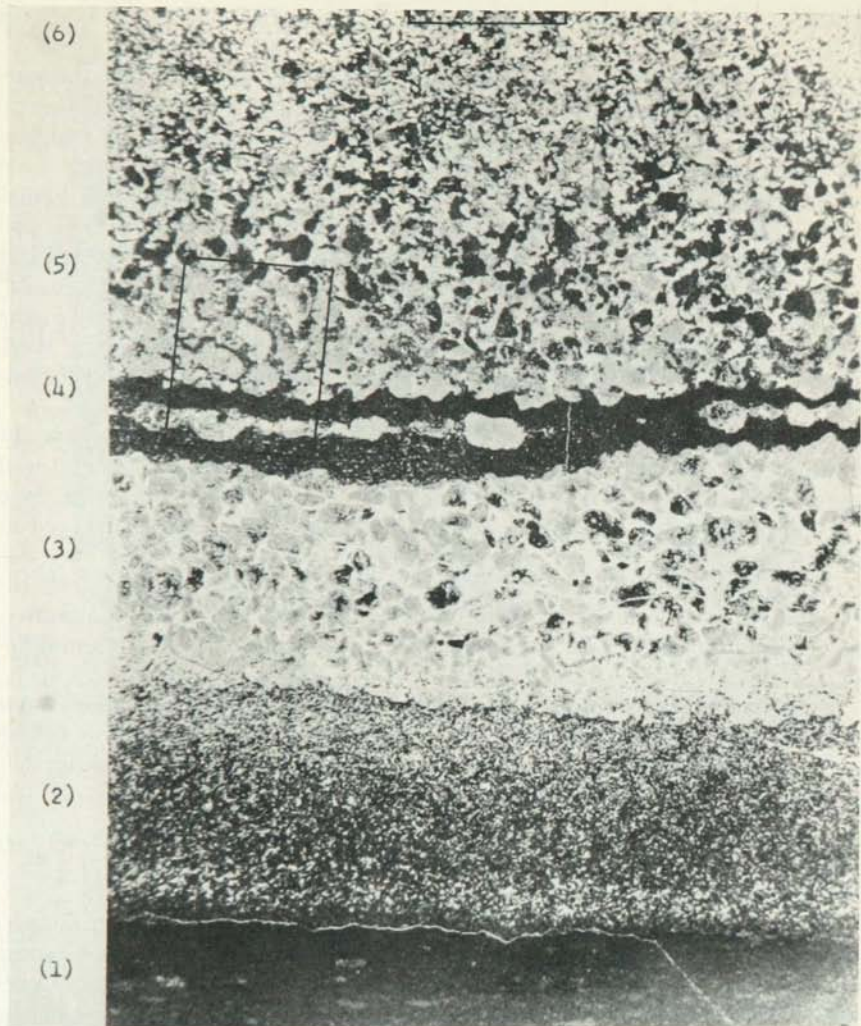


FIGURE 14.—Banded granule-bearing cherty taconite, showing intense secondary replacement by silica and carbonate, from transitional Biwabik Iron-formation (Zone 2). 5.6x. From bottom up, the following layers are distinguished: (1) Dark gray slaty band, consisting of fine-grained siderite and organic matter. (2) Coarser-grained, light-gray, apparently secondary siderite, which partially replaces the overlying granule taconite. (3) Original granule taconite, almost completely replaced by crystalline quartz (white), in which the shape of the original granules (light gray) is preserved by fine-grained dust; remnants of original silicate (dark gray), either greenalite or chlorite, remain in some granules. (4) Thin layer of fine-grained siderite, probably a second slaty band. Fine-grained siderite has replaced the matrix of the overlying granule taconite. (5) Granule-bearing layer, similar to (2). The granules are replaced by crystalline quartz, and much of the intergranular matrix is now fine-grained siderite. Original silicate material (dark gray) remains. This layer apparently grades upward into (6). (6) Clastic lamina, consisting of fine-grained, apparently detrital quartz, cemented by interstitial silicate (dark gray), possibly chlorite.

Outlines indicate the location of Figure 15.

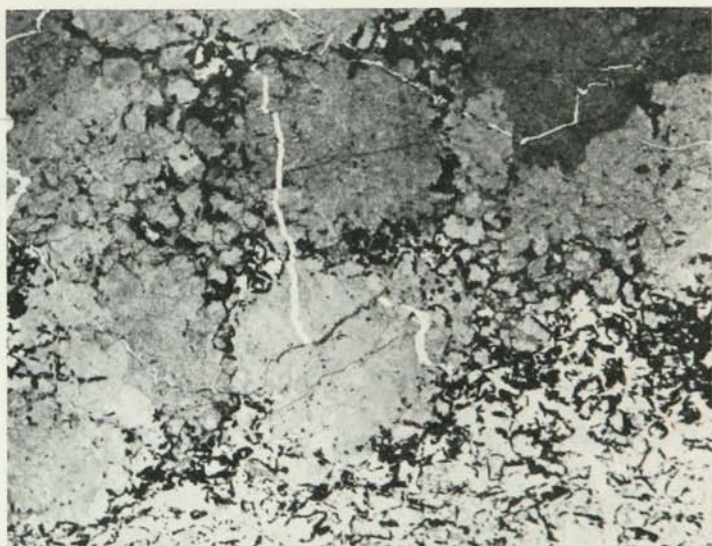
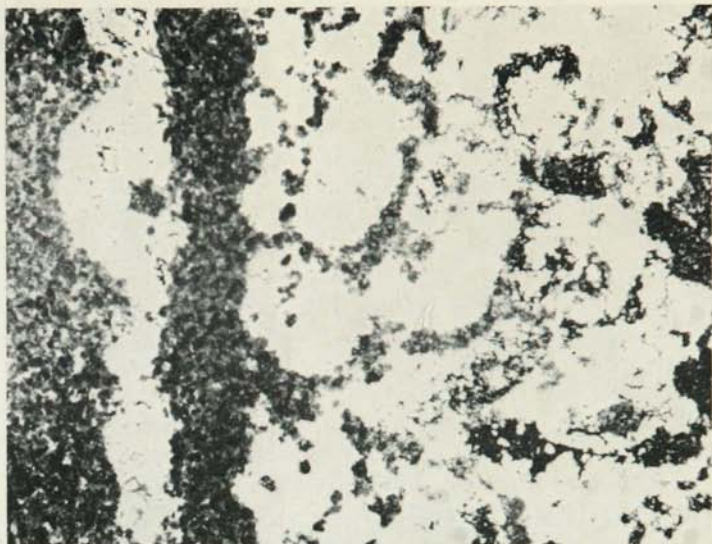


FIGURE 15.—Enlarged view of Figure 14, showing intense replacement of original granule-bearing taconite by quartz and siderite. Ordinary light, 20x. Siderite-rich layer (4) is shown at left; immediately adjacent to it, granules in the overlying layer (5) have been replaced by crystalline quartz (white), whereas intergranular spaces have been replaced by siderite (light gray). Unreplaced original silicate material (dark gray) is shown at right. FIGURE 16.—Intense replacement of granule-bearing cherty taconite by very coarse-grained ankerite "mottles" in transitional Biwabik Iron-formation (Zone 2). Ordinary light, 7x. Original granule-bearing taconite has been replaced by a "mottle" composed of coarse ankerite crystals (light gray); the remainder of the taconite consists of magnetite (black), which replaces original granules and quartz (white) (lower part of figure). Original granule texture may be seen in the ankerite crystals, preserved by magnetite or by fine dust within the original granule (particularly, at upper left and center right).

themselves are replaced by quartz (Figs. 14 and 15). The specimen shown in Figure 14 contains one of the few partly clastic layers observed in the Lower Cherty member; it consists of a quartz-bearing siltstone, cemented by chlorite, into which the underlying cherty taconite grades.

A characteristic feature of the Lower Cherty in Zone 2 is replacement of the taconite by coarse ankerite. The ankerite forms closely spaced patches as much as 10 mm. in diameter, which give the taconite a mottled appearance. The patches are pink or cream-colored when fresh, and gradually darken after being exposed to air. Such texture is particularly characteristic of the part of the Lower Cherty immediately beneath the Lower Slaty contact; the term mottled cherty taconite is applied to this rock. The patches consist of ankerite anhedral generally 0.5 to 1 mm. in size. The crystals are irregular, have undulose to slightly sutured boundaries, and commonly show strained extinction. Within the ankerite patches, original granule texture can be distinguished at times by the circular arrangement of original dust in the granule (Fig. 16).

The ankerite-bearing mottled cherty taconite found in the uppermost part of the Lower Cherty member near Mesaba apparently occurs along the entire length of the Main Mesabi district. Similar material is found at the same stratigraphic position at the towns of Midway and Keewatin; in this taconite, an identical relation can be observed between secondary ankerite patches and original granule texture (Fig. 10).

The uniformity in mineralogy of specimens from Zone 1 and Zone 2 lends support to the interpretation that replacement by ankerite is characteristic of these particular units of the Lower Cherty member and is not related to the intrusion of the Duluth Gabbro Complex.

MODERATELY METAMORPHOSED TACONITE (ZONE 3)

CHERTY TACONITE

Introduction. As the Duluth Gabbro Complex is approached, the first detectable change in mineralogy of the cherty taconite is the development of the amphibole grunerite. Grunerite, which contains 75 to 85 mole per cent $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, apparently develops simultaneously in all lithologies from both earlier iron silicates and iron carbonates.

In silicate-bearing cherty taconite, grunerite forms from the silicates; the following assemblages are commonly observed: grunerite-minnesotaite-quartz, grunerite-stilpnomelane-quartz, and grunerite-quartz.

In carbonate-rich cherty taconite, grunerite forms by reaction between carbonate and quartz to produce the following assemblages: grunerite-ankerite-quartz, grunerite-ankerite-calcite-quartz, grunerite-calcite-quartz, grunerite-ankerite-calcite, grunerite-calcite. Magnetite is a minor component in all assemblages.

The relative amounts of minerals in grunerite-bearing cherty taconite vary widely; the following percentages are typical of the majority of specimens studied by the writer: grunerite 20–50 per cent, rarely higher; anker-



FIGURE 17.—Development of grunerite in stilpnomelane granule taconite in moderately metamorphosed Biwabik Iron-formation (Zone 3). Ordinary light, 21x. The original granules are largely replaced and somewhat obscured by grunerite (light gray), which occurs as small fibrous sheaves and as lath-shaped crystals that cut through the granules. A small amount of pleochroic brown stilpnomelane (dark gray) remains between the crystals. Magnetite (black) replaces the rims of the two granules at upper left, and apparently coexists with the quartz matrix (white) without reaction. FIGURE 18.—Destruction of granule texture of cherty taconite through replacement by metamorphic grunerite in moderately metamorphosed Biwabik Iron-formation (Zone 3). Plane-polarized light, 21x. Original silicate-bearing granules in a quartz matrix (white) are replaced by fibrous grunerite (light gray), which truncates the original granules. A minor amount of magnetite (black) is present.

No earlier silicate minerals were detected by X-ray diffraction studies.

ite 10–40 per cent; earlier silicates 10–20 per cent; quartz 30–50 per cent, rarely absent; and magnetite 10–20 per cent.

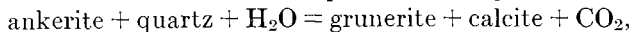
Formation of Grunerite. In cherty taconite, grunerite develops as tabular crystals and fibrous radiating sheaves composed of fine needles, which cut and surround the original granules. These sheaves resemble minnesotaite, and X-ray diffraction may be required to distinguish between the two minerals. The grunerite rosettes and sheaves are commonly 0.1 to 0.3 mm. long and locally consist of a central crystal about 0.1 mm. long, surrounded by smaller radiating fibers. The larger crystals have sharp contacts against the original silicate minerals in the granule. The ends of the crystals are commonly frayed; some of the larger crystals show typical grunerite polysynthetic twinning.

In some specimens of grunerite-bearing granular cherty taconite, recrystallization is not complete, and patches of earlier minnesotaite or stilpnomelane remain in the granules between the larger elongate grunerite crystals (Fig. 17). Granules that have been partly or completely replaced by magnetite apparently are unaffected by the formation of grunerite.

The quantity of earlier silicates decreases as grunerite increases in abundance; eventually, fibrous grunerite may completely pseudomorph the granule texture (Fig. 18). In the more intensely recrystallized rocks, grunerite crystals are invariably decussate and randomly oriented. No preferred orientation was observed.

In carbonate-rich cherty taconite, grunerite develops by reaction between ankerite and quartz. Such reaction is well-demonstrated in the mottled cherty taconite exposed in the open-pit workings of Erie Mining Company. As one passes from unmetamorphosed taconite in 24:59-15 to grunerite-bearing taconite in 15:59-14, the original mottled appearance is preserved, but the ankerite patches are converted to an aggregate of ankerite, fibrous greenish-yellow grunerite, and coarsely crystalline white calcite. The amount of grunerite formed in these rocks varies. The mineral may develop only at the edge of the patch where ankerite and quartz are in contact (Fig. 19). Elsewhere, both ankerite and quartz are penetrated and replaced by fibrous grunerite (Fig. 20).

The reaction between ankerite and quartz to form grunerite,



is also indicated by the depletion of quartz in some specimens of grunerite-carbonate taconite. No siderite-grunerite assemblages were observed, but an analogous reaction between siderite and quartz is probable.

Other Minerals. Small amounts of pleochroic blue-green amphibole are present locally as irregular patches within felted masses of grunerite. This mineral generally constitutes less than 5 per cent of cherty taconite in Zone 3, although it appears more commonly in slaty taconite from Zone 3 and in specimens of both kinds of taconite from Zone 4.

Similar amphiboles from metamorphosed iron-formation have been called blue-green hornblende; they are strongly pleochroic in olive green

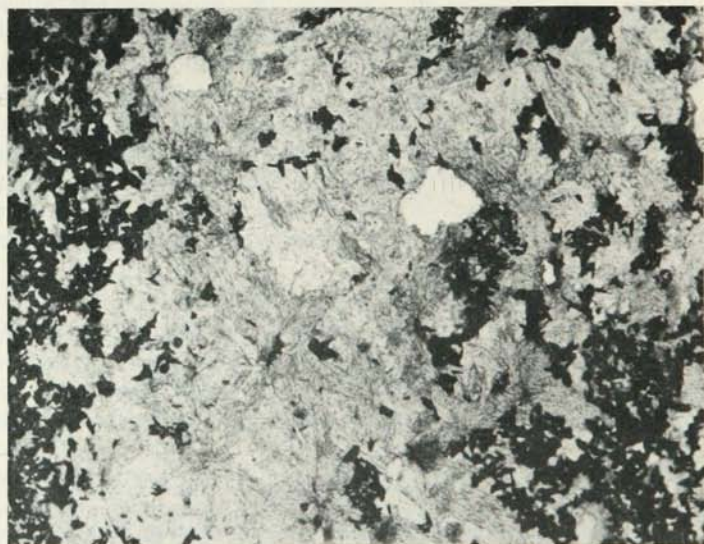
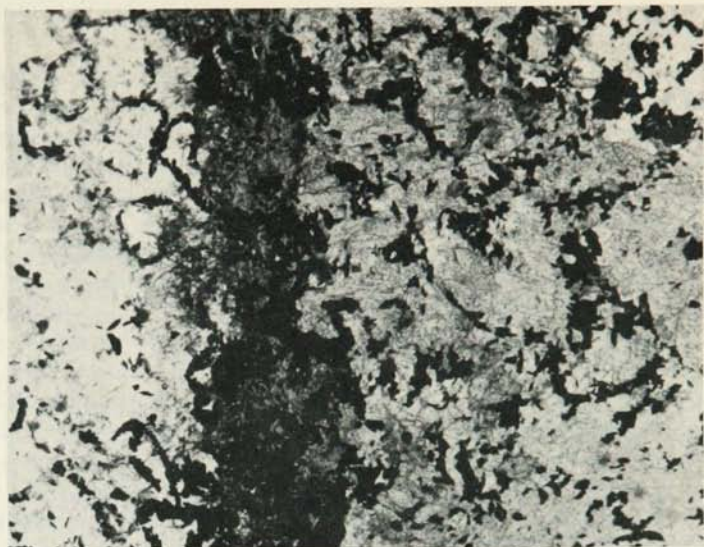


FIGURE 19.—Development of grunerite by reaction between carbonate and quartz in moderately metamorphosed Bwababik Iron-formation (Zone 3). Plane-polarized light, 19x. Fibrous grunerite (dark gray) has developed at the contact between coarsely crystalline ankerite (gray, right) and quartz (white). The quartz-rich matrix, on left, contains original granules outlined by magnetite. Fibrous grunerite also occurs in the carbonate adjacent to the contact. Considerable euhedral magnetite (black) occurs in the ankerite and appears concentrated with grunerite at the contact. FIGURE 20.—Nearly complete alteration of ankerite to metamorphic grunerite in moderately metamorphosed Bwababik Formation (Zone 3). Ordinary light, 20x. Fibrous radiating grunerite (light gray, high relief) has almost completely penetrated and replaced an original "mottle" of coarsely crystalline ankerite (light gray, low relief). Euhedral magnetite (black) and small unreplaced areas of quartz (white) also are present.

and bluish green shades and are associated with cummingtonite-grunerite and pyroxenes. Analyses of this material from other areas show 6–10 per cent CaO, 10–15 per cent Al_2O_3 , and as much as 9 per cent Fe_2O_3 ; total alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) is less than 5 per cent (Richarz, 1930; Miles, 1943; James, 1955; Kranck, 1961; Gundersen and Schwartz, 1962). In the highly metamorphosed iron-formation on the Mesabi range (Zone 4), some single amphibole grains consist of intergrown hornblende and cummingtonite (Gundersen and Schwartz, 1962, p. 87).

Quartz commonly constitutes 30 to 50 per cent of metamorphosed cherty taconite; it occurs as the matrix of original granules and surrounds ankerite patches in the mottled cherty taconite. There has been no detectable increase in grain size of the quartz with development of grunerite. The distinction between fine quartz in the granules (0.005 to 0.03 mm.) and coarser quartz in the matrix (0.05 to 0.1 mm.) can still be observed even in grunerite-rich specimens.

Magnetite generally constitutes 10 to 20 per cent of metamorphosed cherty taconite, as aggregates of euhedra 0.05 to 0.1 mm. in size. Some magnetite partly or completely pseudomorphs the original granules. Such textures, which are believed to represent replacement in unaltered taconite, preserve the original granule texture despite widespread development of grunerite.

Both magnetite and quartz in grunerite-bearing taconite are believed to be original (premetamorphic) components. Although some magnetite possibly developed from other minerals (particularly siderite) during metamorphism, no great increase in magnetite, as compared with unaltered taconite, has been observed either in the present study or in earlier work (Gruner, 1946; James, 1955).

Grunerite has been reported to form during metamorphism of banded magnetite-quartz iron-formation, by reaction between magnetite and quartz (Miles, 1943, 1946; James, 1955). In the complex cherty taconite examined by the writer, definite evidence for or against such a reaction is absent; there are virtually no banded magnetite-quartz rocks on the Mesabi range.

SLATY TACONITE

Only a few specimens of slaty taconite were studied in Zone 3; these were chiefly slaty bands associated with grunerite-bearing cherty taconite in the Lower Cherty member. In slaty taconite, grunerite apparently develops simultaneously with its appearance in the associated cherty taconite.

Metamorphism of slaty taconite produces a distinctively banded rock, in which the individual layers, 5 to 20 mm. thick, contain widely varying amounts of grunerite, quartz, magnetite, and blue-green hornblende. No carbonates were detected.

Grunerite is the dominant mineral in metamorphosed slaty taconite. It occurs as interlocking fibrous masses composed of elongate crystals 0.1 to

0.3 mm. long. Grunerite may constitute as much as 80 per cent of individual layers, occurring with quartz, magnetite, and blue-green hornblende. Other layers consist chiefly of magnetite or quartz with subordinate grunerite.

Blue-green hornblende possibly constitutes 5 to 10 per cent of the grunerite-rich layers; it occurs both as irregular pleochroic patches within felted masses of grunerite and as individual sheaves of needles 0.2 to 0.3 mm. long. The mineral also occurs with grunerite in small cross-fiber veins, a few tenths of a millimeter to a few millimeters wide, which cut through the individual layers.

THE INTERMEDIATE SLATE

Development of grunerite in place of premetamorphic silicates and carbonates is also characteristic of the metamorphosed Intermediate slate sampled in Zone 3. Some specimens examined by the writer are almost completely composed of felted masses of fibrous grunerite, with minor magnetite and graphite; such rocks are almost completely opaque in thin section.

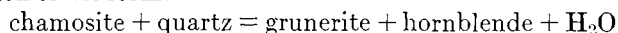
The change in the Intermediate slate during metamorphism is well illustrated in the workings of Erie Mining Company in 14 and 15:59-14, about one half mile east of the boundary between Zone 2 and Zone 3 (see Fig. 3). Unmetamorphosed Intermediate slate here is a massive, dark gray to black, moderately fissile rock resembling argillite. Toward the east, the development of grunerite converts the rock into a hard, massive, dark gray hornfels that is cut by numerous small veinlets of fibrous amphibole a few millimeters wide. Much of the amphibole in these veinlets is blue-green hornblende.

Since identifications of the minerals within the Intermediate slate were made only by X-ray diffraction, there are no textural data, and a detailed comparison of the metamorphosed unit with its equivalents in Zones 1 and 2 is impossible. The following assemblages were observed in the Intermediate slate in Zone 3: hornblende-grunerite-quartz, grunerite, chamosite-grunerite-quartz, and chamosite-quartz. No carbonates were observed. Magnetite and carbonaceous material (generally graphite) are additional phases in all assemblages.

Comparison of the assemblages with those determined for unmetamorphosed Intermediate slate (see above, p. 31) suggests that grunerite forms from reaction between the pairs siderite-quartz and chamosite-quartz. The absence of siderite and the persistence of chamosite in Zone 3 suggest that the siderite-quartz pair becomes unstable first during metamorphism, forming grunerite by the reaction:



Since chamosite contains considerable aluminum, it probably decomposes by a reaction of the form:



Variations in composition of chamosite and amphiboles (particularly in Al content) may allow the assemblage chamosite + quartz to persist over

a considerable range of physical conditions. In slaty taconite, quartz is probably exhausted first, and chamosite in quartz-free rocks probably persists to even higher temperatures before decomposing to such possible products as grunerite + garnet or cordierite + magnetite.

HIGHLY METAMORPHOSED TACONITE (ZONE 4)

INTRODUCTION

The boundary between Zones 3 and 4 at 1.7 miles from the gabbro contact corresponds with the appearance of iron pyroxenes, generally hedenbergite, in the taconite. Since a detailed mineralogical and petrographic study was made by Gundersen and Schwartz (1962), and since no iron carbonates are in this zone, detailed examinations of the taconite in Zone 4 were not undertaken; the writer's studies were confined to the eastern part of 14:59-14 and to a few specimens collected from the area examined by Gundersen and Schwartz (1962).

MINERALOGY

Gundersen and Schwartz (1962) have studied the highly metamorphosed Biwabik Formation in detail where it is exposed in the Reserve Mining Company's taconite operations, which extend from 16:60-12 to 24:60-13. The taconite in this area is completely recrystallized and contains cummingtonite, hedenbergite, ferrohypersthene, blue-green hornblende, quartz, magnetite, minor fayalite, and other accessory minerals. Despite intense metamorphism and recrystallization of the taconite, the original banded and laminated texture is preserved and emphasized by differences in mineralogy. Granule texture commonly is preserved by fine magnetite or graphite dust which outlines the shape of the granule (Gundersen and Schwartz, 1962, pp. 79, 121); granules completely replaced by magnetite are also preserved. Cummingtonite is the dominant iron silicate in this zone; it is commonly associated with blue-green hornblende. Much of the cummingtonite and hornblende occurs as fibrous masses that surround and replace coarser crystals of fayalite and pyroxene (Gundersen and Schwartz, 1962, pp. 41, 84, and 107). Calcite is the only carbonate present.

A typical specimen of highly metamorphosed taconite collected by the writer (Fig. 21) contains coarse quartz grains 0.1 to 1 mm. in size, intergrown with very irregular crystals of iron silicates that locally exceed 1 mm. in size. The iron silicate crystals are generally poikilitic and include numerous small grains of quartz and magnetite.

In the taconite studied by the writer in 14:59-14, the dominant pyroxene is an iron-rich clinopyroxene; following the convention of Gundersen and Schwartz (1962), this mineral is referred to as hedenbergite. It occurs as irregular anhedra about 0.5 mm. in size, and was not observed to constitute more than 10 per cent of the taconite. The hedenbergite is commonly surrounded by and penetrated by fibrous cummingtonite that clearly replaces it; in some specimens, hedenbergite is represented only by a few isolated ir-

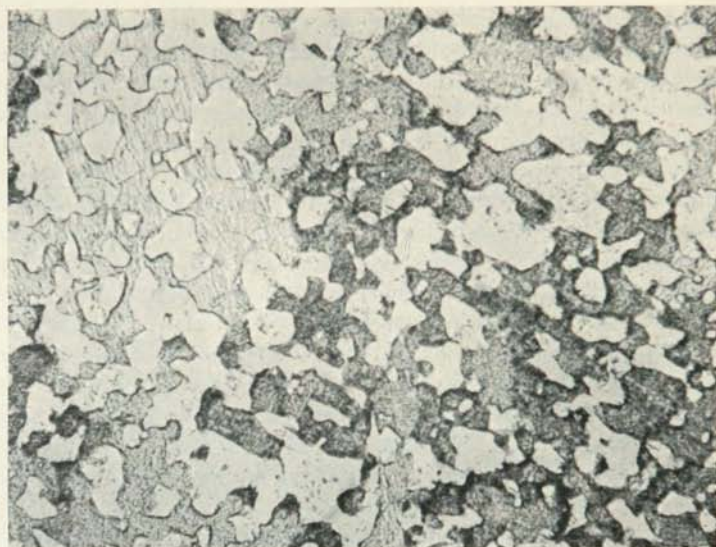


FIGURE 21.—Completely recrystallized cherty taconite from highly metamorphosed Biwabik Iron-formation (Zone 4). Ordinary light, 56x. Specimen is a granoblastic aggregate of large, irregular, and extremely poikilitic anhedral ferrohypersthene (dark gray), cummingtonite (light gray) and quartz (white). In this specimen, cummingtonite and ferrohypersthene appear to coexist stably. A small fringe of fibrous material, possibly amphibole, occurs at the margins of some of the ferrohypersthene grains (center and lower left).

regular masses in optical continuity, within a matrix of fine fibrous amphibole.

Near the Duluth Gabbro Complex, the Intermediate slate contains fayalite (about Fa_{90}) in association with ferrohypersthene, quartz, magnetite, and pyrrhotite (Gundersen and Schwartz, 1962, pp. 31–34). Some layers contain the assemblage quartz-fayalite-magnetite, with minor amphibole. The carbonaceous material in this zone is graphite (see below, p. 72).

VEINS AND SMALL PEGMATITE BODIES

Small crosscutting veins and pegmatite bodies are characteristic of the highly metamorphosed taconite in the Peter Mitchell Mine of the Reserve Mining Company. In their study, Gundersen and Schwartz (1962) distinguished two distinct types: pegmatites, which consist chiefly of quartz and alkali feldspars, and lamprophyres, which are composed mainly of hornblende. The most common minerals in these bodies are quartz, albite, oligoclase, hornblende, and biotite (Gundersen and Schwartz, 1962, pp. 72–74). The borosilicate axinite was identified by the writer in a sample of pegmatite from the same location; the mineral occurs as bunches of clove-brown crystals associated with coarse pink feldspar and quartz. Epidote and garnet were also observed in other specimens of similar pegmatitic material.

Gundersen and Schwartz (1962, pp. 73, 116) have argued that the occurrence of most of the metamorphic iron silicates in the taconite is controlled by these crosscutting veins and pegmatites, which acted as channels for the metasomatic introduction of necessary materials into an essentially anhydrous iron-formation. According to their interpretation, thermal metamorphism of an iron-formation consisting originally of only quartz and magnetite developed fayalite- and ferrohypersthene-bearing rocks. Subsequent metasomatic introduction of H_2O , CO_2 , Ca, Mg, and other elements, accompanying the emplacement of the crosscutting bodies, converted these rocks into the assemblages of cummingtonite, hornblende, and hedenbergite which now are observed.

Because of the implications of this theory for considerations of the nature of the metamorphism and the original character of the iron-formation, the writer searched for similar bodies in the highly metamorphosed, hedenbergite-bearing taconite in 14:59-14, at the eastern end of the Erie Mining Company operations. No large crosscutting bodies of the type described by Gundersen and Schwartz were observed, although the taconite contains the same metamorphic minerals as at the Peter Mitchell Mine to the east.



FIGURE 22.—Coarse-grained hedenbergite-calcite veinlet in cherty taconite in highly metamorphosed Biwabik Iron-formation (Zone 4). Plane-polarized light, 4.5x. The veinlet consists of large, partly replaced anhedral hedenbergite (gray), together with coarse calcite (light gray, upper left), quartz (white), and pyrrhotite (black). Minor amounts of magnetite and fibrous green amphibole are present. The diagonal black band at the right consists of fine-grained magnetite and is continuous with similar layers in the enclosing cherty taconite, indicating that the coarse-grained veinlet has developed by replacement of the taconite.

In the highly metamorphosed taconite studied by the writer, the only coarse-grained bodies observed were small lenses and veinlets composed of iron silicates and other minerals. The taconite enclosing these bodies contains hedenbergite, cummingtonite, blue-green hornblende, quartz, and magnetite.

The coarse-grained lenses and veinlets are discontinuous, elongate, somewhat irregular in size, and generally concordant to layering in the enclosing taconite; they are 6 inches to 2 feet long. The lenses are generally subparallel lengthwise to the taconite layers; rarely, bodies having a variable orientation cut across individual layers for short distances. Fairly sharp contacts between the lenses and the taconite can be distinguished on the basis of the large difference in grain size.

The veinlets and lenses contain coarse-grained hedenbergite, calcite, quartz, and pyrrhotite; the anhedral crystals, generally several mm. long, are commonly intergrown (Fig. 22). A small amount of pleochroic green amphibole (actinolite?) occurs as smaller crystals about 1 mm. long. Both fibrous green amphibole and calcite occur in patches and fractures within hedenbergite crystals, indicating slight retrograde alteration of the hedenbergite.

Petrographic evidence suggests that the bodies were developed by replacement of the enclosing taconite. Small patches of fine-grained quartz occur locally within hedenbergite crystals, and, in one specimen, a magnetite-rich band with a vague granule texture persists across a veinlet despite the development of coarse hedenbergite around it (Fig. 22).

The general concordance of these bodies to the layering and their mineralogical similarity to the enclosing taconite distinguish them from the larger crosscutting bodies that occur in the iron-formation nearer the gabbro (Gundersen and Schwartz, 1962). These features, combined with textural evidence for a replacement origin, indicate to the writer that these veinlets and lenses were derived from the taconite itself during metamorphism and do not represent material introduced from external sources.

METAMORPHISM OF HEMATITE-BEARING UNITS OF THE BIWABIK IRON-FORMATION

INTRODUCTION

Layers containing primary hematite are present in the unmetamorphosed Biwabik Formation; the best known is the so-called Red Basal taconite, which occurs at the base of the Biwabik and apparently is transitional with the underlying clastic Pokegama Formation (Gruner, 1946; White, 1954). This unit contains hematite oolite beds (Gruner, 1946, Pl. 4A) and intraformational conglomerates that contain elongate chips composed of fine-grained hematite and quartz. Minor quantities of carbonate and iron silicates, chiefly stilpnomelane, occur in this unit.

The most striking feature in the Red Basal taconite is finely banded al-

gal structures; a layer of similar material occurs in the Upper Cherty member (Gruner, 1946; Gundersen and Schwartz, 1962). The structures resemble the stromatolites found in younger calcareous rocks (see Gruner, 1946, Pls. 9 and 12), and are composed of thin bands of alternating hematite-rich and hematite-free chert which produce a distinctive red and white appearance.

The biological origin of these structures is generally accepted (Grout, 1919; Grout and Broderick, 1919a; Gruner, 1946; White, 1954). The mineralogy is considered primary likewise, and no remnants of carbonate have been observed within the structures; possibly, the algal material acted as a mat to entrap chemically precipitated silica (Pettijohn, 1957, p. 221).

Hematite, as noted earlier (see above, p. 30) also occurs as the matrix of chlorite-bearing granules in thin slaty layers in the Upper Cherty member (Fig. 13).

Where hematite-bearing beds are traced into the contact aureole of the Duluth Gabbro complex, magnetite occurs in the place of hematite. There is general agreement that original hematite has been reduced to magnetite by the effects of gabbro intrusion (Grout and Broderick, 1919b; White, 1954; Gundersen and Schwartz, 1962).

METAMORPHISM

Specimens of the hematite-bearing units, chiefly the algal zones of the Red Basal taconite and the Upper Cherty member, were examined by X-ray diffraction to determine the relative amounts of hematite and magnetite. Because of interference between the strong hematite (110) and magnetite (311) peaks, an approximate estimation of relative amounts of hematite and magnetite was made by comparing visually the hematite (104) and magnetite (220) peaks and assuming that $I(104) = 3 \times I(220)$. If more specimens had been available for study, a more rigorous calibration using known hematite-magnetite mixtures would have been carried out.

The Red Basal taconite in Zone 1 contains a small amount of magnetite associated with hematite; the magnetite generally occurs in the centers of oolites and as chips in the conglomeratic units. Magnetite in these rocks does not appear in the X-ray pattern and does not exceed 5 per cent; it is believed to result from postdepositional reduction (White, 1954).

In Zone 2 near Aurora (59:14), the Red Basal taconite contains considerable magnetite. Both hematite and magnetite peaks can be observed in the X-ray patterns, and locally magnetite is dominant. At the Erie taconite pits about 3.5 miles from the present gabbro contact (SESE 18:59-14), the Red Basal taconite contains considerable algal material, which is more coarsely banded than usual and contains algal columns 1 to 2 inches across. These beds are associated with conglomerates composed of hematite-bearing chips, and contain minor amounts of chlorite, stilpnomelane, and calcite. The Red Basal taconite is associated with clastic units of the Pokey-

ama Formation; one bed of coarse quartz-pebble conglomerate contains isolated pieces of algal material several centimeters across.

In the rocks at the Erie pit, replacement of the Red Basal taconite by magnetite is common and widespread in both the algal beds and the flat-pebble intraformational conglomerates. The matrix and the smaller pebbles are more strongly altered to magnetite; the larger chips and the algal structures themselves show less replacement. Rarely, conversion to magnetite is nearly complete; such rocks are gray and contrast sharply with the normal red color of less altered specimens. Two kinds of magnetite replacement are observed: rarely, the original fine hematite in the chips and algal bands is replaced by gray magnetite of the same grain size; more commonly, irregular patches and lenses of coarser magnetite replace both hematite and quartz. In a polished section of this material, hematite is observed with chert in the chips and granules, occurring as small distinct crystals generally 5 to 15 microns across; such material may be recrystallized from original finely disseminated hematite. Magnetite occurs as aggregates of sharply defined euhedra commonly 30 to 100 microns in size. The magnetite crystals have sharp boundaries against both hematite and quartz and appear to replace both minerals.

No hematite was detected in X-ray patterns of taconite sampled by the writer within 1.5 miles of the gabbro contact. Within one mile of the gabbro contact, the Red Basal taconite and other originally hematite-bearing units contain only magnetite.

METAMORPHISM OF THE POKEGAMA FORMATION

INTRODUCTION

The contact between the clastic beds of the Pokegama Formation and the overlying Biwabik Iron-formation apparently is somewhat gradational; near the contact, hematite-bearing cherts and clastic sandstones may be interlayered (White, 1954; Gundersen and Schwartz, 1962). The strata that generally are immediately below the Biwabik Formation are pure white, massive orthoquartzites. Other units of the formation are conglomerates, micaceous and feldspathic quartzites, and argillites (White, 1954; Dolence, 1961).

The Pokegama Formation forms few natural exposures on the Mesabi range and is rarely encountered in mines and drill cores; accordingly, only a few specimens were available for study, and a detailed description of the metamorphism of the formation was not possible.

UNALTERED POKEGAMA FORMATION (ZONE 1)

The contact between the Pokegama and Biwabik formations is well exposed in the Auburn Mine near Eveleth (Schwartz, 1956, p. 160). The white, massive orthoquartzite beneath the Biwabik Formation is composed of rounded, well-sorted detrital quartz grains 0.2 to 0.8 mm. in di-

ameter and is cemented by quartz and a small amount of fibrous green chlorite. A few detrital grains are aggregates of fine quartz and chlorite that resemble the granules observed in specimens of laminated iron-formation (Fig. 13). Some chlorite in the matrix is partly altered to pleochroic brown flakes that may be stilpnomelane.

Below the orthoquartzite at this locality is a greenish sandstone composed of poorly rounded, well-sorted clastic grains 0.02 to 0.1 mm. in size. Quartz is the dominant detrital material; lesser amounts of K-feldspar and mica flakes are present. The matrix constitutes 10 to 25 per cent of the rock and consists of fine green chlorite that is dominantly chamosite; no 14 A peak is observed in the X-ray pattern. The matrix partly or completely replaces some clastic quartz grains.

A similar bed occurs within the Biwabik Formation at this locality, a few feet above the contact (Schwartz, 1956, p. 160). Clastic quartz, fairly well-sorted with variable rounding, constitutes about 75 per cent of the rock. The chlorite matrix has partly replaced the quartz grains. The X-ray pattern shows a definite 14 A peak, but both chlorite (14 A) and chamosite may be present. The refractive index of the matrix material is $n_w = 1.640 \pm 0.005$; for a true chlorite, this corresponds to an iron-rich variety such as brunsvigite or daphnite (Deer, Howie, and Zussman, 1962, v. 3, pp. 138-152).

METAMORPHOSED POKEGAMA FORMATION

Near Mesaba, the Pokegama Formation associated with the Red Basal taconite consists of massive conglomeratic quartzite. This unit is coarser grained than specimens from Zone 1, and contains a higher percentage of fine-grained quartz-chlorite granules. The latter may constitute as much as 5 per cent of the detrital fraction; the remainder is rounded quartz grains 0.3 to 2.0 mm. in size. The matrix is a clear quartz cement.

Chlorite in the granules shows definite alteration to fibrous sheaves of brown pleochroic stilpnomelane. In another specimen from the same area, the matrix is composed of green chlorite and a few colorless euhedra of clinozoisite about 0.05 mm. in size. The chlorite mineral in both specimens may be a mixture of 7 A and 14 A polymorphs; a strong 14 A peak is observed in one. The refractive index of chlorite in both specimens, $n_w = 1.65 \pm 0.01$, suggests iron-rich varieties.

The Pokegama Formation from the highly metamorphosed area near the Duluth Gabbro Complex was not studied by the writer. Metamorphic minerals reported from the formation in this area include cordierite (Dolence, 1961), amphiboles, and biotite (Gundersen and Schwartz, 1962).

Quartz is the dominant detrital component of the Pokegama Formation; minor feldspar and mica occur locally. Iron-rich chlorite (14 A) and chamosite constitute a significant portion of the matrix of the impure varieties. In Zone 2, stilpnomelane definitely has developed from chlorite. Since stilpnomelane occurs in both the Pokegama and Biwabik formations in Zone

1, it is uncertain whether this change is related to the gabbro. The occurrence of small amounts of clinozoisite in the matrix in Zone 2 probably has resulted from metamorphism by the gabbro.

METAMORPHISM OF THE VIRGINIA FORMATION

The Virginia Formation consists of at least 2,000 feet of dark gray massive argillite and local siltstone and graywacke, and apparently overlies the Biwabik Iron-formation conformably (White, 1954). The formation forms no natural outcrops and is rarely penetrated in drilling; accordingly, little can be said about its metamorphism at present.

Specimens of unmetamorphosed Virginia Formation were obtained from artificial exposures in the St. James Mine near Aurora (3:58-15). In a siltstone bed, quartz is the dominant clastic component and occurs as poorly rounded, well-sorted grains 0.02 to 0.05 mm. in size. A small amount of detrital albite is present; mica occurs both as scattered detrital flakes and as fine-grained material in the matrix. Chlorite of undetermined composition also occurs in the matrix. The same mineralogy is observed in the dark-gray argillite associated with the siltstone, which constitutes more than 90 per cent of the observed stratigraphic section.

At a distance of 1.1 miles from the gabbro, the Virginia Formation is recrystallized to a massive, fine-grained, quartz-albite-biotite hornfels that contains small amounts of opaque minerals (see also Gundersen and Schwartz, 1962, pp. 68-69). Cordierite has been reported to occur in the Virginia Formation in the same area (Leith, 1903).

MINERALOGICAL CHANGES DURING PROGRESSIVE METAMORPHISM OF THE BIWABIK IRON-FORMATION

GENERAL DISCUSSION

The first mineralogical changes attributed to contact metamorphism by the Duluth Gabbro Complex are observed in Zone 2, about 3.5 miles from the gabbro contact. They are: the large-scale replacement of hematite by magnetite in the Red Basal taconite; and, the minor development of clinozoisite in the chloritic matrix of the Pokegama Formation.

The mineralogy of slaty and cherty taconite of the Biwabik Formation remains unchanged in Zone 2, although replacement by ankerite and quartz may be more prevalent than in Zone 1.

The first widespread contact-metamorphic effect observed in the cherty and slaty taconite units of the Biwabik Iron-formation is the development of grunerite from original silicates and carbonates in Zone 3, within 3 miles of the gabbro contact. The grunerite-bearing assemblages that develop in Zone 3 are characterized by: gradual disappearance of the original silicates minnesotaite and stilpnomelane concomitantly with development of grunerite (no greenalite was observed); disappearance of ankerite from cherty taconite and absence of siderite from slaty taconite as grunerite appears; appearance of calcite with grunerite in originally ankerite-bearing cherty taconite; and gradual disappearance of chamosite in the Intermediate slate as grunerite appears — some chamosite in quartz-free slaty taconite persists through Zone 3 to about 1.5 miles from the gabbro.

Contact metamorphism in Zone 4 is well expressed by complete recrystallization of the taconite and by the appearance of iron pyroxenes. Characteristic mineralogical features of this zone are: development of iron pyroxenes (hedenbergite apparently occurs in the outer part of the zone; it is joined by ferrohypersthene near the gabbro contact); general absence of original silicates and iron carbonates (calcite is the only carbonate present); occurrence of magnetite alone in units that originally contained hematite; development of fayalite in slaty taconite (Gundersen and Schwartz, 1962, pp. 95–96, 115); and occurrence of pyrrhotite and absence of pyrite in slaty taconite (Gundersen and Schwartz, 1962, p. 78).

These mineralogical changes are summarized graphically in Figure 23. Except for the absence of hematite and the occurrence of fayalite in the highly metamorphosed taconite, the changes are virtually identical to those observed during progressive regional metamorphism of iron-formation by James (1955) (Fig. 24, this report).

A progressive increase in the grain size of quartz with increasing metamorphism has been observed in iron-formation composed only of quartz

Distance from Contact (D) (miles)

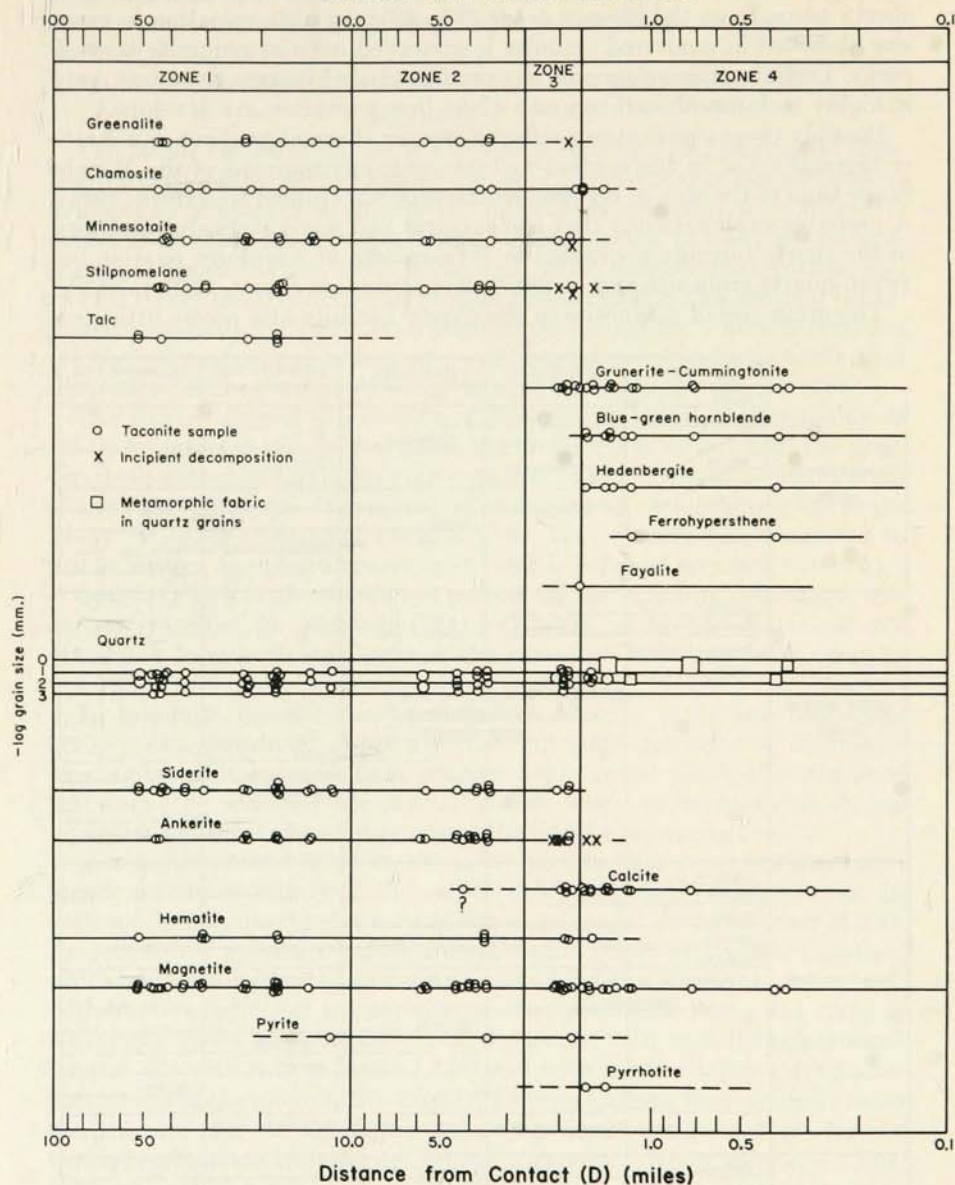


FIGURE 23.—Diagram showing the mineralogy of the Biwabik Iron-formation in different metamorphic zones as a function of distance from the Duluth Gabbro contact. Small circles indicate location of specimens; dashed lines indicate uncertainty in occurrence.

and iron oxides (James, 1955). No such progressive relation is detected in cherty taconite on the Mesabi range (Fig. 23); the wide variation in grain size observed in unaltered taconite is preserved even in grunerite-bearing rocks. Definite coarsening and recrystallization of quartz is evident only in highly metamorphosed taconite where iron pyroxenes are developed.

Possibly these observations reflect a steeper thermal gradient or a shorter thermal event in the contact-metamorphic environment of the Mesabi range than in the area of regional metamorphism studied by James (1955). A probable explanation is that the textural and mineralogical complexity of the cherty taconite prevents the development of a uniform relation between quartz grain size and metamorphic grade (see James, 1955, p. 1473).

The grain size of magnetite in the cherty taconite also shows little uni-

	CHLORITE ZONE	BIOTITE ZONE	GARNET ZONE	STAUROLITE ZONE	SILLIMANITE ZONE
ARGILLACEOUS ROCKS	Quartz				
	Feldspar (clastic)	-----			
	Chlorite	-----	Oligoclase		
	Muscovite	-----			
		Biotite	Garnet	Staurolite	Sillimanite
BASIC IGNEOUS ROCKS	Chlorite	-----			
	Epidote	-----			
	Actinolitic hornblende	-----			
	Albite	-----			
		Green-brown biotite			
		Blue-green hornblende			
		Albite-oligoclase		Brown biotite	
				Green hornblende	Andesine
IRON-FORMATION	Greenalite	-----			
	Chlorite	-----			
	Siderite	-----			
	Hematite	-----			
	Magnetite	-----			
	Minnesotite	-----			
	Stilpnomelane	-----			
			Grunerite		
			Blue-green hornblende		
			Garnet		Pyroxene
	0.05	0.10	0.15	0.20	
	Approximate diameter of typical quartz grains, in purer layers of "chart." Values in mm.				
DOLOMITE	Carbonate				
			Tremolite	Diopside	

FIGURE 24.—Mineral assemblages of some common rocks in the metamorphic zones of northern Michigan (adapted from James, 1955). Dashed lines indicate uncertainty about classification. Some minor minerals are not shown.

form variation with metamorphism (Gundersen and Schwartz, 1962, pp. 80-81); however, coarse magnetite occurs at the gabbro contact.

MINERALOGY AND COMPOSITION OF THE CARBONATES

METHODS OF STUDY

The major emphasis in the study was placed on the behavior of iron-bearing carbonates during metamorphism. Compositions of the carbonates in about 55 samples of taconite were determined indirectly from measurements of 2θ (211) and n_o (Rosenberg, 1960). Studies of natural and synthetic carbonates (Ford, 1917; Rosenberg, 1960) indicate that both n_o and 2θ (211) vary linearly between the pure end-members. This method is particularly suitable for unmetamorphosed iron-formation, whose carbonates are fine grained and so intergrown with iron silicates and magnetite that separation for chemical analysis is difficult and unreliable (Blake, 1958).

The writer followed the method of Rosenberg (1960) in determining 2θ (211). An internal standard of cadmium fluoride was mixed with the powdered taconite. For CdF_2 , 2θ (111) = 28.701° (French, 1964a, p. 62). Values of $\Delta 2\theta$ (211-111) were determined by averaging six oscillations in the range $27-33^\circ 2\theta$, using a setting of 1 inch = $1^\circ 2\theta$. Peak centers were measured to $\pm 0.01^\circ$ with a Vernier rule; averaged value is believed accurate to $\pm 0.01^\circ$.

Quartz, which is almost always present in the taconite, provides a secondary standard, for which 2θ (101) was taken as 26.664° . Values of $\Delta 2\theta$ calculated from both standards in the same specimen generally agree to $\pm 0.01^\circ$.

To minimize interference between the ankerite (211) and magnetite (220) peaks, powdered samples containing large amounts of magnetite were agitated in water. A hand magnet held against the beaker removed the magnetite, allowing the carbonate-rich slurry to be decanted. A few repetitions of this treatment removed the interfering magnetite.

In metamorphosed taconite, the (301) peak of both grunerite and hornblende interferes with both the calcite (211) and CdF_2 (111) peaks. In such specimens, quartz was used as the standard for determination of $\Delta 2\theta$. In quartz-free specimens, quartz from Lake Toxaway, North Carolina, which had been calibrated with CdF_2 , was added as a standard.

Refractive indices of the carbonates were determined on a flat stage in NaD light. Index oils were calibrated before use with an Abbe refractometer (for oils with indices below 1.720) and with a Leitz Jelyey refractometer (for oils in the range 1.720-1.880). * Determinations were made at room temperature ($24^\circ-26^\circ\text{C}$). Estimated accuracies of determinations for the various carbonates are: siderite, ± 0.005 ; ankerite, ± 0.003 ; calcite, ± 0.002 .

The determined values of n_o and $\Delta 2\theta$ for the carbonates, plotted on a triangular graph (Rosenberg, 1960) (Fig. 25), give the composition of the carbonate in terms of the end-members CaCO_3 , MgCO_3 , and FeCO_3 .

*The writer acknowledges the kind assistance of Alice Weeks and Ed Williams of the United States Geological Survey in calibrating the high-index oils.

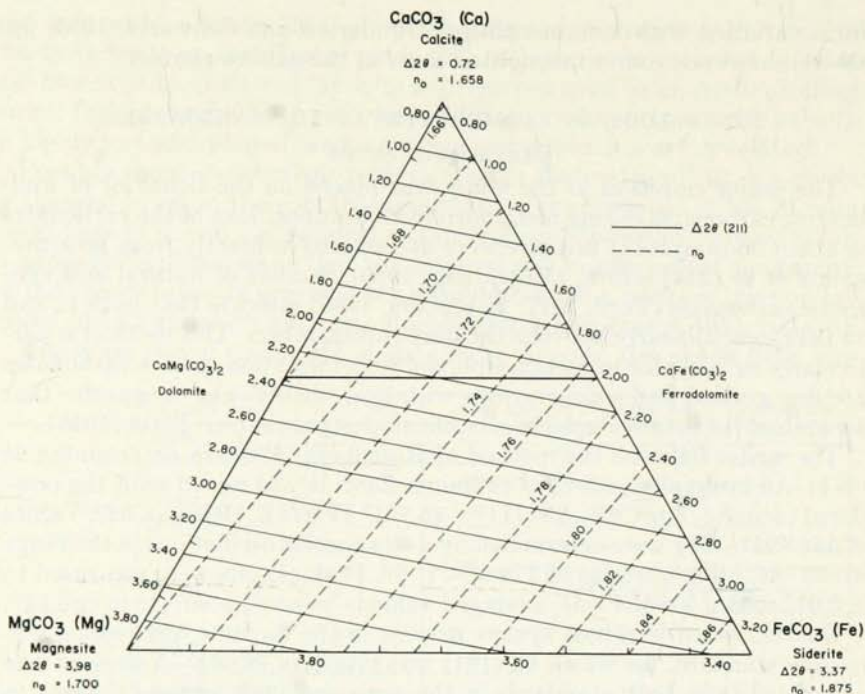


FIGURE 25.—Triangular diagram for determination of carbonate compositions from measured values of n_0 and $\Delta 2\theta$ (211) (after Rosenberg, 1960). MnCO_3 is neglected as a component, and the data are not applicable to carbonates which contain large amounts of MnCO_3 . Data indicated by $\Delta 2\theta$ (211) actually designate the value of $\Delta 2\theta$ (211) for the carbonate, measured against the (111) reflection of CdF_2 , $28.701^\circ 2\theta$ for CuK_α radiation.

Two sources of error occur in this method (Rosenberg, 1960, pp. 76–78). First, dolomites have parameters that are not exact linear functions of the end-members (Graf, 1961); however, the uncertainties caused by the deviations are slight. More seriously, the method neglects manganese as a component in the carbonate. The presence of MnCO_3 in the carbonate will produce lower values of n_0 and $\Delta 2\theta$; the resulting compositions will be too low in FeCO_3 and too high in CaCO_3 . However, the parameters of MnCO_3 and FeCO_3 are similar, and a large amount of MnCO_3 must occur to produce serious errors in the estimated composition. Rosenberg (1960, pp. 75–80) reports good agreement between calculated and analyzed compositions of synthetic and natural carbonates. In most natural carbonates, the Fe/Mn ratio exceeds 5:1; analytical data (see below, p. 53) indicate that the carbonates of the Mesabi range satisfy this criterion.

EXPERIMENTAL RESULTS

Values of $\Delta 2\theta$ and n_0 were determined for the carbonates in 55 taconite samples collected along the strike of the Biwabik Formation from Nash-

wauk to Birch Lake. From these two quantities, the composition of the carbonate may be determined on a triangular diagram (Rosenberg, 1960) in terms of the end-members Ca (CaCO_3), Mg (MgCO_3), and Fe (FeCO_3) (Fig. 25).

The values of Fe and Mg determined for the carbonates will be strongly affected by uncertainties in n_0 ; these determinations are probably accurate to ± 3 mole per cent. The value of Ca, which is dependent chiefly on the more exact value of $\Delta 2\theta$, is probably accurate to ± 1 mole per cent. As indicated below, Mn is probably a minor component in the Mesabi carbonates. Considering both experimental uncertainties and the possible effect of Mn, it is believed that the determined values for Ca are accurate to ± 2 mole per cent, and that the values of Fe and Mg are accurate to ± 5 per cent.

To estimate the probable effect of MnCO_3 on the determinations (Rosenberg, 1960, p. 76), a partial analysis of a siderite-rich slaty layer in the Lower Cherty was obtained through the kindness of Miss S. Rettig and Blair Jones of the United States Geological Survey. The sample contained over 90 per cent siderite as determined by X-ray diffraction, and minor amounts of quartz, stilpnomelane, and organic matter. The analysis gave: Fe 38.1, Mn 2.3, Na 0.1, K 0.8, and Ca + Mg 4.9 — total 46.1. These data correspond to an Fe/Mn ratio of 16:1,* well above the value of 5:1 considered desirable for use of the method (Rosenberg, 1960, p. 79).

Low amounts of manganese are also reported in analyses of the taconite itself; MnO is less than 2 weight per cent (Gruner, 1946, p. 57), even in taconite containing large quantities of carbonate. Further evidence of low manganese content is the compositions of iron silicates from the highly metamorphosed taconite (Gundersen and Schwartz, 1962, p. 76). The highest amount occurs in hedenbergite and corresponds to only 7 mole per cent of the johanssenite ($\text{CaMnSi}_2\text{O}_6$) end-member; cummingtonite and fayalite contain under 3 mole per cent of the respective Mn end-members.

To determine possible variations in carbonate within the same hand specimen, compositions of duplicate samples, including different layers from the same specimen, were determined (Table 3).† In most specimens, the variation between samples is within the experimental error. In others, the slight differences possibly represent actual variations between different

* Potassium in the analysis probably is produced by solution of the small amount of contained stilpnomelane. Additional iron could also have been introduced from this mineral, but it is doubtful whether such solution would change the value of Fe/Mn greatly.

† Complete compositional data for samples of taconite that contained two carbonates could not always be obtained if only a small amount (under 5 per cent) of the second carbonate was present. Measurement of $\Delta 2\theta$ and n_0 for the dominant carbonate were routine. For the second carbonate, a fairly accurate value of $\Delta 2\theta$ could be obtained, but, in most cases, it proved impossible to isolate grains of the second carbonate from the fine-grained, carbonate-rich aggregate in order to measure n_0 . Accordingly, only $\Delta 2\theta$ values are given for a second carbonate which occurs in minor amounts. Approximate compositions (indicated in the tables by parentheses) were obtained by assuming the following contents, which are typical of Mesabi carbonates: siderite, Ca₃; ankerite, Ca₃₃; calcite, Mg₁.

TABLE 3. DUPLICATE DETERMINATIONS OF CARBONATE COMPOSITIONS FROM SAMPLES OF TACONITE FROM THE BIWABIK IRON-FORMATION *

No.†	D‡	Zone	Carbon-ate	$\Delta 2\theta$	n_o	Ca	Fe	Mg
26A	17.4	1	S	3.35	1.804	7.6	61.3	31.1
26B	17.4		S	3.35	1.809	4.3	63.4	32.3
30A	17.4	1	S	3.43	1.814	4.2	66.2	29.6
30B	17.4		S	3.43	1.823	3.3	71.5	25.2
31 sid	17.4	1	S	3.41	1.828	4.6	68.8	26.6
31 mt			S	3.37	1.833	4.3	77.3	18.4
51A-1	22.1	1	S	3.43	1.830	2.8	75.0	22.2
			A	2.10		(53.0)	24.2	22.8
51A-2	22.1		S	3.43	1.828	3.0	74.0	23.0
			A	2.12		(53.0)	20.9	26.1
51A-3	22.1		S	3.43	1.833	2.0	76.9	21.1
			A	2.12		(53.0)	20.7	26.3
51B-1	22.1		S	3.44	1.833	2.0	76.7	21.3
51B-2	22.1		S	3.42	1.833	2.7	77.0	20.3
51B-3	22.1		S	3.44	1.828	2.3	74.0	23.7
54A	22.4	1	A	2.07	1.720	53.8	24.5	21.7
54B	22.4		A	2.06	1.725	53.9	27.7	18.4
			S	3.36		(5.0)	75.0	20.0
61 sil	3.49	2	S	3.37	1.833	4.6	77.5	17.9
			A	2.08	1.725	53.2	27.4	19.4
61 sil			S	3.38	1.838	3.4	79.8	16.8
			A	2.08	1.725	52.9	27.4	19.6
61 dk			S	3.27	1.828	7.8	75.3	16.9
61 lt			S	3.32	1.833	5.8	77.3	16.9
95A	1.90	3	A	2.08	1.715	54.0	21.7	24.3
			C	1.00	1.682	89.0	11.0	0.0
95B	1.90		A	2.00	1.715	56.5	22.3	21.3
			C	1.00	1.683	88.9	11.1	0.0
96A	1.90	3	A	2.07	1.712	54.7	19.9	25.4
			C	1.00	1.682	89.2	10.8	0.0
96B			A	2.08	1.712	54.3	20.0	25.7
			C	1.02	1.680	88.9	10.1	1.0
128A	1.86	3	S	3.32	1.830	6.0	76.1	17.9
			A	2.02	1.735	53.8	33.2	13.0
128B			S	3.30	1.828	6.9	75.3	17.8
			A	2.01	1.725	55.2	27.9	16.9

* Abbreviations for minerals in the Biwabik Iron-formation used in this and subsequent tables follow. Parentheses on the tables indicate that only trace amounts are present.

Unmetamorphosed

A: ankerite	Gth: goethite	Q: quartz
C: calcite	H: hematite	S: siderite
Chl: chlorite (14A)	M: magnetite	St: stilpnomelane
Chm: chamosite	Mi: minnesotaite	Tc: talc
Gr: greenalite		

Metamorphosed

Andr: andradite	Fe-Hyp: ferrohyperssthene	Gt: grunerite
Ax: axinite	Gar: garnet	Hd: hedenbergite
Bio: biotite	Gr: crystalline	Kfs: K-feldspar
Cu: cummingtonite	graphite (3.36 A)	Pyr: pyrite
Fay: fayalite	d-Gr: disordered graphite	Pyrrh: pyrrhotite
Fe-Hbd: blue-green hornblende	(3.43 A, diffuse)	Tour: tourmaline

† Abbreviations after the number refer to different layers in the same specimen or to multiple determinations on the same layer. Abbreviations: sil, silicate-rich; dk, dark (organic-rich); lt, light (no organics); sid, siderite-rich; mt, magnetite-rich.

‡ Distance in miles from the Duluth Gabbro contact.

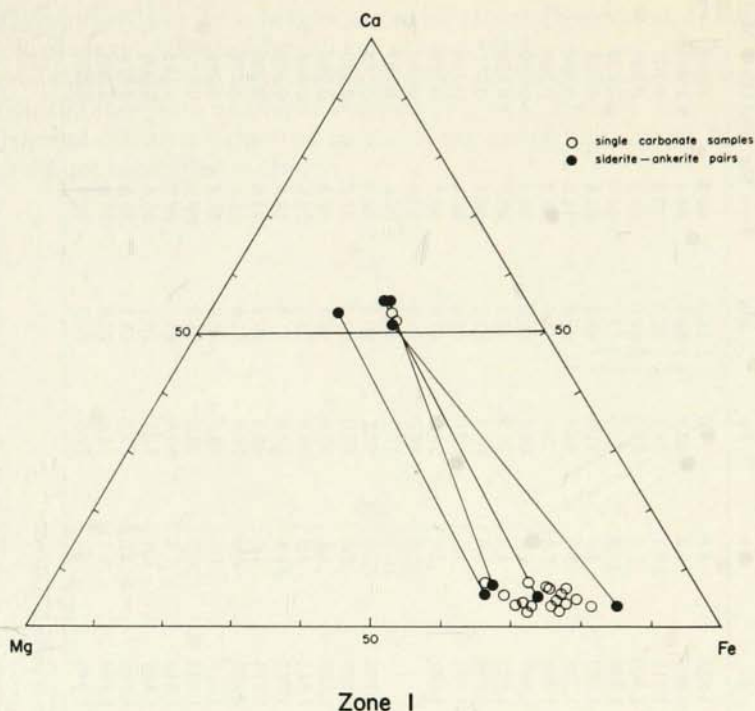


FIGURE 26.—Compositions of siderite and ankerite from unaltered Biwabik Iron-formation (Zone 1).

laminae of layered taconite. The average of these multiple determinations is plotted in the subsequent figures.

The unmetamorphosed taconite (Zone 1) contains both siderite and ankerite; rarely, coexisting siderite-ankerite pairs are present (Table 4; Fig. 26).^{*} Siderite compositions are fairly uniform; FeCO_3 contents range from 63 to 83 mole per cent, and the average composition is $\text{Ca}_5\text{Fe}_{72}\text{Mg}_{23}$. The ankerite compositions are quite consistent around an average value of $\text{Ca}_{53}\text{Fe}_{25}\text{Mg}_{22}$, corresponding to 53 mole per cent $\text{CaFe}(\text{CO}_3)_2$; ankerites are invariably more magnesian than the coexisting siderite.

The tie lines between coexisting siderites and ankerites are approximately parallel to the Ca-Fe edge of the triangle, suggesting that equilibrium between the two phases is approached if not attained (Rosenberg, 1960, pp. 75-86).

The Mesabi ankerites contain several mole per cent CaCO_3 in excess of the 50 per cent required for the ideal dolomite composition; such excess

^{*} The word *coexistence* does not imply that chemical equilibrium necessarily existed between the phases. In some specimens, where ankerite replaces siderite, or where ankerite reacts to form grunerite and calcite, equilibrium may be maintained between the phases despite textural evidence suggesting disequilibrium (see Zen, 1963).

TABLE 4. COMPOSITIONS OF CARBONATES FROM THE BIWABIK IRON-FORMATION, ZONE 1 (UNALTERED TACONITE) *

No.	D†	Carbonate	$\Delta 2\theta$	n_s	Ca	Fe	Mg	Fe + Mg	Fe/(Fe + Mg)
1	13.5	S	3.38	1.833	4.8	77.0	18.2	95.2	0.809
10	17.4	S	3.41	1.809	5.3	63.8	30.9	94.7	0.674
		A	2.12	1.710	53.4	18.7	27.9	46.6	0.401
12	17.6	S	3.36	1.809	7.0	64.0	29.0	93.0	0.688
		A	2.02	1.720	55.3	25.0	19.7	44.7	0.559
13	17.6	S	3.38	1.823	5.0	71.4	23.6	95.0	0.752
		A	2.02	1.718	55.5	24.2	20.3	44.5	0.456
19	17.3	S	3.37	1.838	3.8	79.7	16.5	96.2	0.828
26	17.4	S (2)‡	3.35	1.807	7.6	62.8	29.6	92.4	0.680
27	17.4	S	3.42	1.823	3.7	71.2	25.1	96.3	0.739
30	17.4	S (2)‡	3.43	1.819	3.9	68.9	27.2	96.1	0.717
31	17.4	S (2)‡	3.39	1.831	4.0	76.0	20.0	96.0	0.792
51	22.1	S (6)‡	3.43	1.831	2.8	75.6	21.6	97.2	0.778
		A (3)‡	2.11		(53.0)	23.0	24.0	47.0	0.489
54	22.4	S (1)‡	3.36		(5.0)	75.7	19.3	95.0	0.797
		A (2)‡	2.07	1.723	53.6	26.1	20.3	46.4	0.563
56	45.8	S	3.45	1.823	2.8	71.0	26.2	97.2	0.730
57	45.8	S	3.41	1.820	4.1	69.6	26.3	95.9	0.726
58	44.1	S	3.36	1.844	3.6	83.3	13.1	96.4	0.864
		A	2.13	1.725	51.4	27.3	21.3	48.6	0.562
102	43.3	S	3.40	1.814	5.2	66.4	28.4	94.8	0.700
103	43.3	S	3.31	1.823	6.9	71.9	21.2	93.1	0.772
104	43.3	A	2.12	1.715	51.8	27.3	20.9	48.2	0.566
119	35.8	S	3.32	1.823	6.7	72.0	21.3	93.3	0.772
120	35.8	S (b)‡	3.32	1.818	7.3	69.0	23.7	92.7	0.744
121	35.8	S	3.31	1.828	6.6	74.7	18.7	93.4	0.800
122	41.4	S	3.36	1.828	4.7	74.2	21.1	95.3	0.779
123	41.4	S	3.40	1.828	3.7	74.0	22.3	96.3	0.768
152	11.3	S	3.40	1.828	3.7	74.0	22.3	96.3	0.768

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

‡ Compositions shown are averaged values from duplicate determinations (see Table 3). Number of determinations is shown in parentheses. (b) indicates a broad (211) peak.

CaCO_3 in ankerite has also been reported by others (Smythe and Dunham, 1947; Rosenberg, 1960; Goldsmith and others, 1962).

Carbonates from the transitional taconite (Zone 2) are similar in composition to those from unaltered taconite (Table 5; Fig. 27). The presence of a trace of calcite is suggested by the X-ray pattern of sample MF-161, but could not be verified optically.

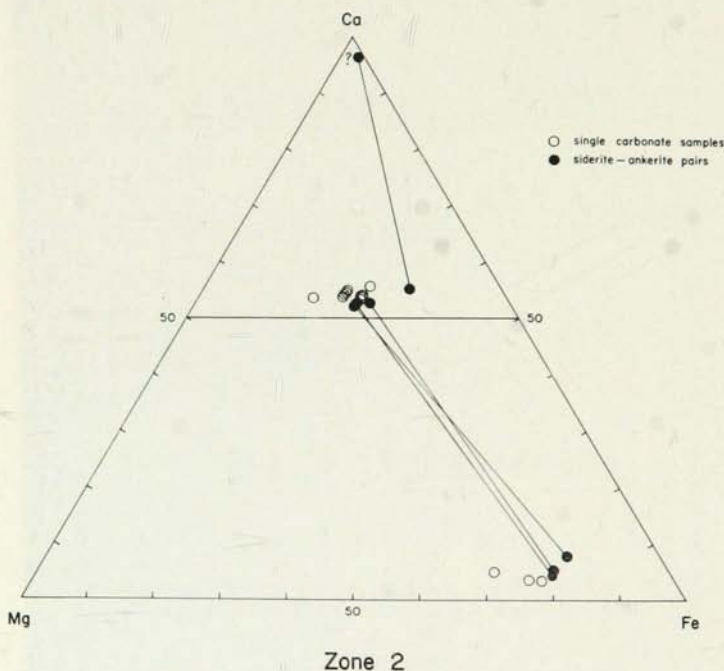


FIGURE 27.—Compositions of carbonate minerals from transitional Biwabik Iron-formation (Zone 2). The occurrence of calcite shown is doubtful.

Compositions of siderite and ankerite show little variation; the close parallelism of tie lines between coexisting siderite-ankerite pairs suggests that equilibrium was attained in these specimens (see Rosenberg, 1960, pp. 79–82). The average composition of the ankerites from Zone 2 is $\text{Ca}_{5.4}\text{Mg}_{2.4}\text{Fe}_{2.2}$, essentially that of Zone 1. However, the specimens studied represent a restricted sample of iron-formation and this interpretation is uncertain.

Carbonate assemblages in grunerite-bearing taconite (Zone 3) are characterized by the appearance of calcite (Table 6; Fig. 28). No three-carbonate assemblages were observed; ankerite coexists with either calcite or siderite but not with both. The calcite contains negligible MgCO_3 and may contain 9–11 mole per cent FeCO_3 . The siderite-ankerite pairs have inter-

TABLE 5. COMPOSITIONS OF CARBONATES FROM THE BIWABIK IRON-FORMATION, ZONE 2 (TRANSITIONAL TACONITE) *

No.	D†	Carbonate	$\Delta 2\theta$	n_o	Ca	Fe	Mg	Fe + Mg	Fe/(Fe + Mg)
60	3.49	S	3.36	1.833	4.6	77.6	17.8	95.4	0.813
		A	2.11	1.720	52.7	24.2	23.1	47.3	0.512
61	3.49	S (4) ‡	3.34	1.833	5.2	77.4	17.4	94.8	0.816
		A (2) ‡	2.08	1.725	53.0	27.3	19.7	46.9	0.580
62	3.49	A	2.11	1.720	52.7	24.2	23.1	47.3	0.512
63	3.49	S	3.39	1.833	3.4	76.6	20.0	96.6	0.793
64	3.49	S	3.25	1.833	7.8	78.2	14.0	92.2	0.848
		A	2.13	1.720	52.2	24.1	23.7	47.8	0.504
66	3.76	A	2.09	1.720	53.4	24.4	22.2	46.6	0.524
67	3.76	A	2.09	1.715	53.8	21.8	24.4	46.2	0.472
68	3.76	A	2.09	1.720	53.4	24.5	22.1	46.6	0.526
69	3.76	S	3.40	1.818	5.0	68.7	26.3	95.0	0.723
		A	2.08		(53.0)	27.6	19.4	47.0	0.587
92	4.39	A	2.01	1.720	55.7	25.0	19.3	44.3	0.564
158	5.70	A	2.08	1.715	54.1	21.9	24.0	25.9	0.477
159	5.54	S	3.40	1.828	3.8	74.5	21.7	96.2	0.774
160	5.54	A	2.07	1.720	53.8	24.5	21.7	46.2	0.530
161	4.14	A	1.99	1.720	55.2	31.0	13.8	44.8	0.692
		C	0.82		96.3	2.7	(1.0)	3.7	(0.730)
162	4.14	S	3.36		(5.0)	75.0	20.0	95.0	0.789
		A	2.06	1.715	54.7	21.9	23.3	45.3	0.483
163	3.93	A	2.07	1.715	54.2	21.9	23.9	45.8	0.478
164	3.93	A	2.12	1.707	53.7	17.2	29.1	46.3	0.371

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

‡ Compositions shown are averaged values of duplicate determinations (see Table 3). Number of determinations is given in parentheses.

TABLE 6. COMPOSITIONS OF CARBONATES FROM THE BIWABIK IRON-FORMATION, ZONE 3 (MODERATELY METAMORPHOSED TACONITE) *

No.	D†	Carbonate	$\Delta 2\theta$	n_s	Ca	Fe	Mg	Fe + Mg	Fe/(Fe + Mg)
70	1.94	A	2.08	1.715	54.0	21.9	24.1	46.0	0.476
		C	0.98	1.677	90.2	9.1	0.7	9.8	0.929
72	1.92	A	2.11	1.710	54.1	18.7	27.2	45.9	0.407
		C	0.98	1.678	90.0	9.2	0.8	10.0	0.920
73	1.91	A	1.96	1.713	57.8	21.5	20.7	42.2	0.509
		C	1.02	1.675	89.4	7.4	3.2	10.6	0.698
74	1.78	C	1.01	1.681	89.1	10.6	0.3	10.9	0.972
94	2.03	S	3.06	1.828	13.7	77.0	9.3	86.3	0.892
		A	1.92	1.710	59.4	20.0	20.6	40.6	0.493
95	1.90	A (2) ‡	2.04	1.715	55.1	22.1	22.8	44.9	0.492
		C (2) ‡	1.00	1.683	88.9	11.1	0.0	11.1	1.000
96	1.90	A (2) ‡	2.08	1.712	54.3	20.0	25.7	45.7	0.438
		C (2) ‡	1.01	1.681	89.1	10.7	0.2	10.9	0.982
127	1.86	S	3.44		(5.0)	60.0	35.0	95.0	0.632
		A	2.08	1.720	53.5	24.4	22.1	46.5	0.525
128	1.86	S (2) ‡	3.31	1.829	6.4	75.6	18.0	93.6	0.808
		A (2) ‡	2.02	1.730	54.2	30.7	15.1	45.8	0.670

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

‡ Compositions shown are averaged values from duplicate determinations (see Table 3). Number of determinations is shown in parentheses.

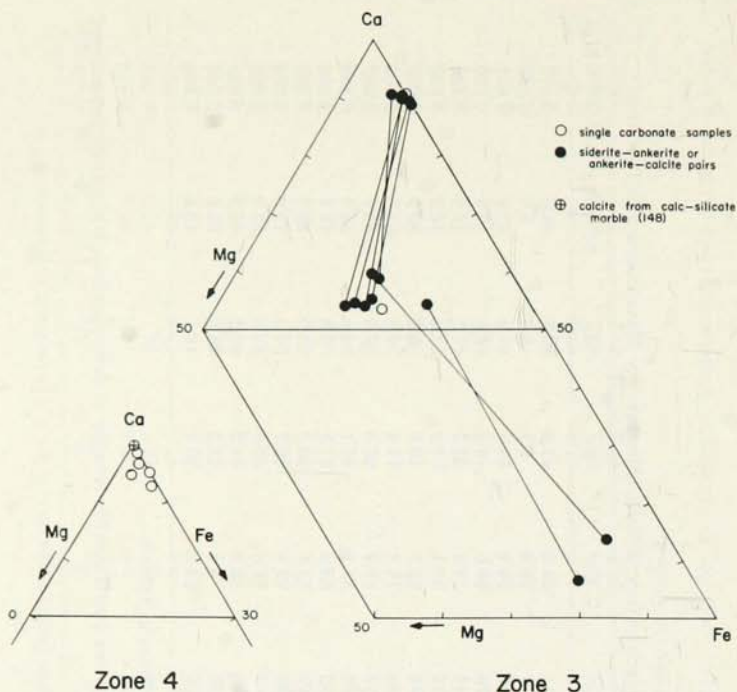


FIGURE 28.—Compositions of carbonate minerals from metamorphosed Biwabik Iron-formation (Zones 3 and 4). The calcite-ankerite assemblages of Zone 3 (large incomplete triangle) coexist with grunerite; grunerite is not observed with the siderite-ankerite assemblages. Only calcite is observed in Zone 4 (small triangle at lower left); calcite from a calc-silicate marble (crossed circle) is nearly pure CaCO_3 .

secting tie lines that suggest disequilibrium. It is possible that ankerites coexisting with calcite are more magnesian than those coexisting with siderite, but there are too few siderite-ankerite pairs in the taconite of Zone 3 to demonstrate such a relation.

Although the range of ankerite compositions in Zone 3 is greater than in the other two zones, the average composition, $\text{Ca}_{55}\text{Fe}_{23}\text{Mg}_{22}$, is similar. The highest percentages of CaCO_3 (59) and FeCO_3 (31) in ankerite are found in this zone; the latter value corresponds to 67 mole per cent $\text{CaFe}(\text{CO}_3)_2$.

Calcite is the only carbonate found in Zone 4 (Table 7; Fig. 28). Calcites from the iron-formation contain over 95 mole per cent CaCO_3 . Calcite from a wollastonite-bearing calc-silicate marble at the top of the Biwabik Formation (Gundersen and Schwartz, 1962) is essentially pure calcite, containing over 99 mole per cent CaCO_3 .

The behavior of the original carbonates of the Biwabik Iron-formation along the metamorphic gradient can be examined by plotting mole per cent CaCO_3 and the ratio $\text{Fe}/(\text{Fe} + \text{Mg})$ as a function of distance from the gab-

TABLE 7. COMPOSITIONS OF CARBONATES FROM THE BIWABIK IRON-FORMATION, ZONE 4 (HIGHLY METAMORPHOSED TACONITE) *

No.	D†	Carbonate	$\Delta\varrho\theta$	n_o	Ca	Fe	Mg	Fe + Mg	Fe/(Fe + Mg)
76	1.57	C	0.88	1.664	94.7	2.4	2.9	5.3	0.453
77	1.57	C	0.85	1.671	95.0	5.0	0.0	5.0	1.000
87	0.29	C	0.76	1.661	98.4	1.2	0.4	1.6	0.750
97	1.63	C	0.92	1.673	92.7	6.4	0.9	7.3	0.877
148‡	1.10	C	0.73	1.659	99.6	0.3	0.1	0.4	0.750
166	1.40	C	0.81	1.664	96.5	2.9	0.6	3.5	0.829

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

‡ From a calcite marble unit at the top of the Biwabik Iron-formation; Member A (Gundersen and Schwartz, 1962). Other samples from iron-silicate taconite.

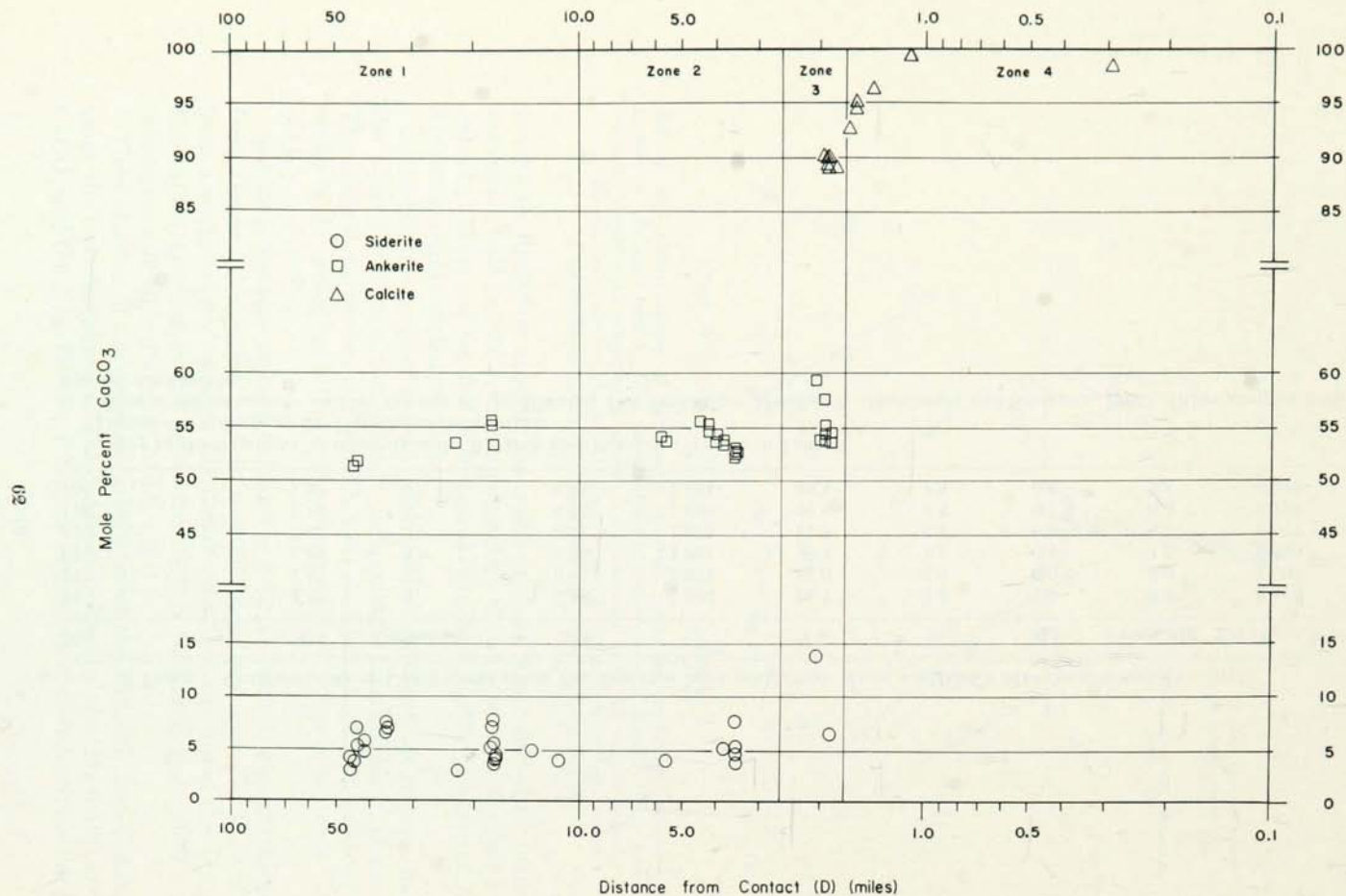


FIGURE 29.—Graph of mole per cent CaCO_3 in carbonates from Biwabik Iron-formation as a function of distance from the gabbro contact. Siderites and ankerites show no progressive change in composition with distance. However, calcite, which appears in metamorphosed taconite, becomes progressively richer in CaCO_3 toward the contact.

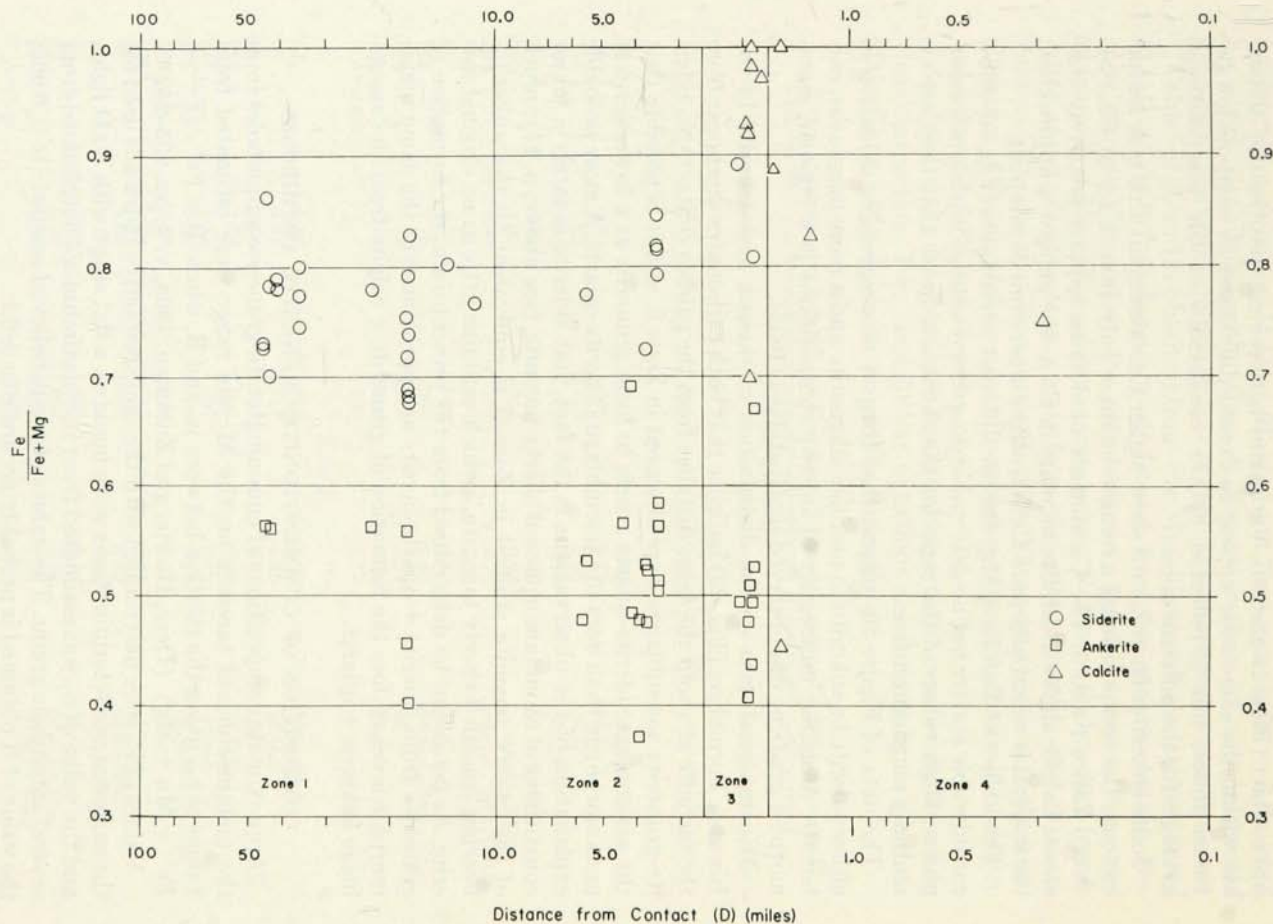


FIGURE 30.—Graph of the ratio $Fe/(Fe + Mg)$ in carbonates from the Biwabik Iron-formation as a function of distance from the gabbro contact. There is no observable change in composition with distance, indicating that siderite and ankerite do not progressively lose Fe with metamorphism.

bro contact (Figs. 29 and 30). Variations between compositions of carbonate within the same zone appear to exceed differences in composition between zones; this is reflected by the consistency of the compositional averages for the different zones.

Some ankerites from Zone 3 show higher Ca values, but this may be fortuitous; the compositional averages increase only from Ca_{54} to Ca_{55} between Zones 1 and 3. The Ca content of siderite appears relatively constant. Calcite shows a definite increase in Ca as the gabbro is approached; the mineral is essentially pure CaCO_3 at the inner limit of sampling.

The values of $\text{Fe}/(\text{Fe} + \text{Mg})$ for the different carbonates (Fig. 30) show considerable scatter but no detectable progressive change during metamorphism. High values of the ratio for the calcites indicate that they are essentially magnesium-free.

The data of Figure 30 suggest that there is no progressive oxidation of either siderite or ankerite to produce magnetite and a more magnesian carbonate. A similar uniformity of siderite compositions in a regional metamorphic gradient was observed by Gustafson (1933).

Mineralogical data on the distribution of siderite and ankerite in the Biwabik Formation (Fig. 23) indicate that both carbonates disappear from the taconite at about the same distance from the gabbro contact. No siderite-grunerite assemblages were observed in Zone 3, and it is possible that the assemblage siderite-quartz reacts to form grunerite at a lower level of metamorphism than does the assemblage ankerite-quartz. A more probable explanation of the observations is the fact that siderite is rarely a major constituent of unmetamorphosed cherty taconite (see above, p. 27); much of the cherty taconite studied in Zone 3 is equivalent to the ankerite-bearing "mottled cherty taconite," which contains little or no original siderite. As far as can be determined from the present data, the formation of grunerite from siderite + quartz occurs at approximately the same metamorphic level as does the formation of grunerite + calcite from the assemblage ankerite + quartz.

COMPOSITION OF CUMMINGTONITE-GRUNERITE AMPHIBOLES

Approximate compositions of cummingtonite-grunerite amphiboles from the metamorphosed taconite on the Mesabi range were estimated from values of n_γ , using the relation between n_γ and R , where $R = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn} + \text{Mg})$ (Deer, Howie, and Zussman, 1963, v. 2, pp. 235-242).

Values of n_γ were determined with the same refractive index oils used for the carbonates. Determinations were made on a flat stage with NaD light, and the value of n_γ was estimated from the maximum n'_γ determined from several amphibole grains. The values of n_γ are believed accurate to ± 0.003 ; the value of R obtained is probably accurate to ± 0.1 .

Several conflicting nomenclatures have been proposed for amphiboles of this series (Sundius, 1931; Jaffe and others, 1961). The present study

follows the convention of Deer, Howie, and Zussman (1963, v. 2, p. 235), by which amphiboles with values of R greater than 0.7 are designated grunerite. The term cummingtonite is applied to more magnesian varieties.

Values of n_γ and R obtained from the Mesabi amphiboles are presented (Table 8; Fig. 31) as functions of distance from the gabbro contact. Despite considerable scatter, the data indicate a general decrease in n_γ and an increase in Mg as the gabbro is approached. Values of R above 0.7 (grunerite) appear farther than 1 mile from the gabbro; within this distance values of R are below 0.7 (cummingtonite). These data agree with the identification of the amphibole near the gabbro as cummingtonite (Gundersen and Schwartz, 1962, pp. 83-84).

Analysis of the data by Least Squares supports the conclusions based on visual inspection. Two straight-line equations are derived from the data (D is distance in miles from the gabbro contact).

TABLE 8. REFRACTIVE INDICES AND ESTIMATED COMPOSITIONS OF CUMMINGTONITE-GRUNERITE AMPHIBOLES FROM THE METAMORPHOSED BIWABIK IRON-FORMATION (ZONES 3 AND 4) *

No.	D^\dagger	n_γ	Fe^{2+}		Associated Minerals
			$Fe^{2+} + Fe^{3+} + Mg + Mn$		
<i>Zone 3</i>					
125	2.01	1.707		0.79	M,Q,(St?)
70	1.94	1.701		0.73	M,Q,C,A
138	1.93	1.713		0.85	M,Q
72	1.92	1.702		0.74	M,Q,C,A
95A	1.90	1.704		0.76	M,C,A,(Q?)
95B	1.90	1.704		0.76	same as 95A
96A	1.90	1.704		0.76	M,C,A,(Q?), (Mi?)
96B	1.90	1.702		0.74	same as 96A
74	1.78	1.713		0.85	M,C,(Q)
124	1.75	1.690		0.63	M,Q,A,(Mi),(St)
140	1.71	1.712		0.84	M
141	1.71	1.702		0.74	Fay?
Average		1.705		0.77	
<i>Zone 4</i>					
75	1.57	1.718		0.89	M,Q,(St?)
76	1.57	1.717		0.89	M,Q,C
77	1.57	1.715		0.87	Q,C
131	1.53	1.696		0.69	M,Q,H,(A?)
136	1.47	1.707		0.79	none
133	1.38	1.700		0.73	M,Q,Hd,Fe-Hbd
150	1.36	1.679		0.53	M,Q
135A	1.28	1.712		0.84	none
80	1.24	1.696		0.69	Q,Fe-Hbd
99	1.15	1.712		0.84	M,Q,Fe-Hyp,(C?)
82	0.73	1.682		0.56	M,Q,(Bio?)
83	0.73	1.680		0.54	M,Q,Fe-Hbd
88	0.39	1.691		0.64	M,Q,Fe-Hyp
Average		1.700		0.73	

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

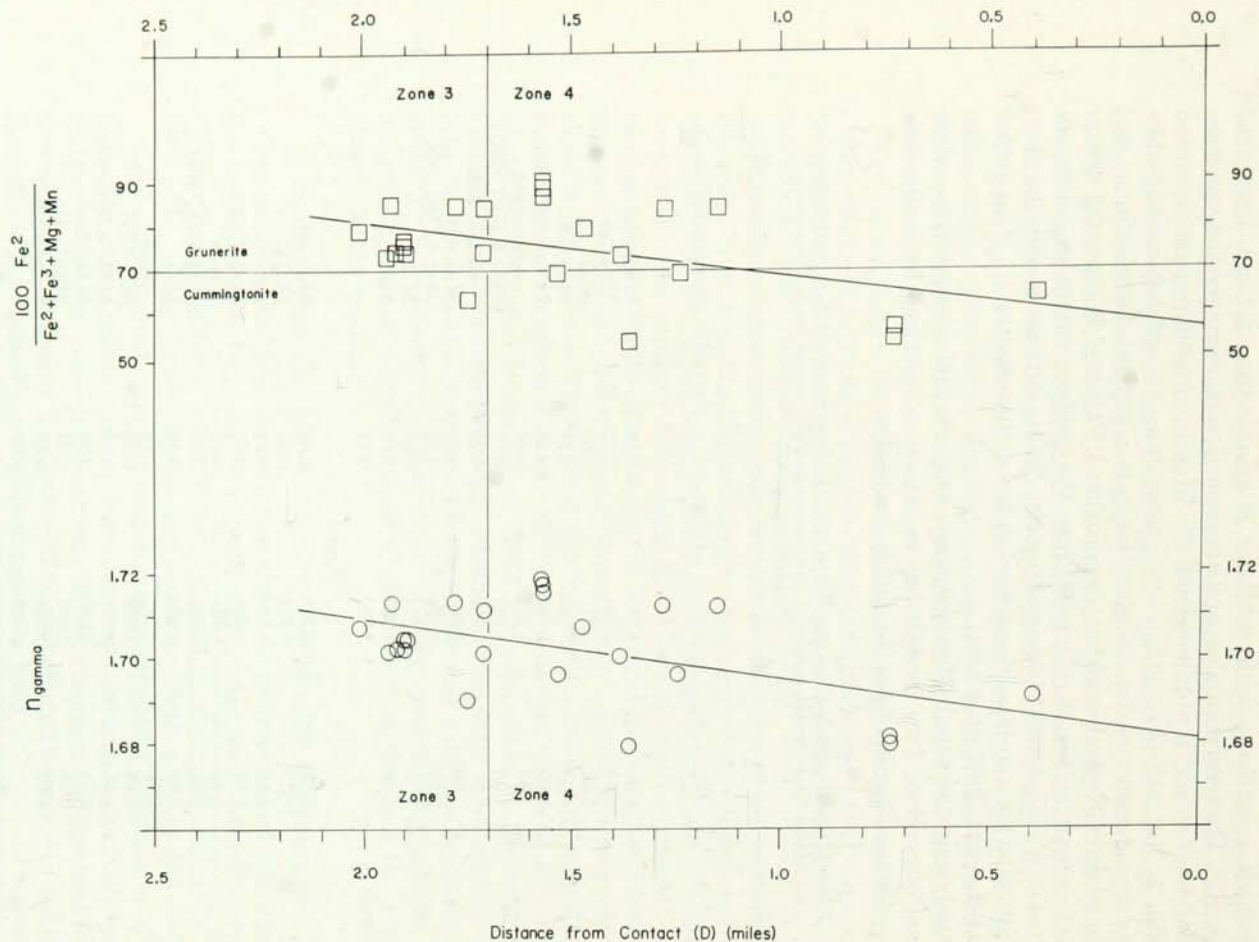


FIGURE 31.—Graph of compositions of cummingtonite-grunerite amphiboles in the metamorphosed Biwabik Iron-formation as a function of distance from the gabbro contact. Compositions are estimated from measured values of n_{γ} . The solid lines represent equations derived by Least Squares reduction of the data.

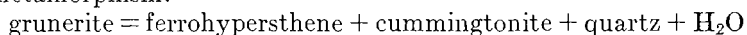
$$n_{\gamma} = 1.682 + 0.014 D$$

$$100 R = 55.4 + 12.4 D$$

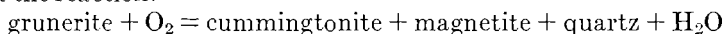
The data obtained indicate that amphiboles of the cummingtonite-grunerite series, coexisting with magnetite and quartz, become more magnesian at higher temperatures. This behavior is in agreement with results of natural and experimental studies on iron-magnesium silicates (Ramberg, 1952, pp. 30-34; Eugster and Wones, 1958).

The transition of grunerite to cummingtonite with increasing metamorphism may occur either during reaction to form iron pyroxene or by progressive oxidation of the grunerite.

Data on coexisting cummingtonite and iron pyroxenes (Mueller, 1960; Kranck, 1961) indicate that coexisting cummingtonite and hedenbergite have approximately the same Fe/(Fe + Mg) ratio, whereas ferrohypsthene is slightly richer in Fe than the coexisting cummingtonite. These data suggest that a reaction of the following type may occur with increasing metamorphism:



Alternatively, production of cummingtonite in pyroxene-free rocks could reflect the reaction:



COMPOSITIONS OF COEXISTING GRUNERITE AND CARBONATES

Recent studies have emphasized the dependence of mineral stabilities upon the composition of the vapor phase with which the minerals are in equilibrium (Thompson, 1955; Greenwood, 1961, 1962). Mineral assemblages in metamorphic rocks have recently been studied to determine the composition of the coexisting vapor and to decide whether chemical potentials of volatile components such as H₂O, CO₂, and O₂ are controlled by the mineral assemblage or are specified externally (Korzhinskii, 1959; Zen, 1963).

Iron-formations are of particular interest for such studies because of the response of the component minerals to variations in P_{O₂} (Eugster, 1959). In studies of the compositions of coexisting phases in highly metamorphosed iron-formation, Mueller (1960) developed theoretical relations between mineral compositions and the composition of the vapor phase. Kranck (1961), in a similar study, attempted to use data from mineral assemblages to reach conclusions about the mobility of volatile components during metamorphism.

The metamorphosed Biwabik Iron-formation in Zone 3 commonly contains the assemblages grunerite-ankerite-calcite and grunerite-calcite (quartz and magnetite are additional phases in both assemblages). This rock may be described approximately by the seven components CaO, MgO, FeO, SiO₂, H₂O, CO₂, and O₂. If equilibrium exists between the six phases grunerite, ankerite, calcite, quartz, magnetite, and vapor, the Gibbs Phase Rule ($F + P = C + 2$) indicates that the system will have three degrees of

freedom. It is reasonable to suppose that the samples studied formed at approximately the same specified temperature and total pressure; thus, if the chemical potential (or fugacity) of one volatile component is specified outside the system, the compositions of the coexisting phases are uniquely determined (more than one volatile component cannot be specified if the six phases are in equilibrium).

Compositions of coexisting carbonate and grunerite were determined for several samples (Table 9; Fig. 32). The compositions of all phases in the assemblage grunerite-ankerite-calcite are quite uniform and well within the experimental uncertainty; the value of R for grunerite is 0.75 ± 0.02 . Grunerites that coexist with calcite alone show R values from 0.85 to 0.89, which represent a significant increase in iron content; the compositions of the coexisting calcites are also significantly variable.

TABLE 9. COMPOSITIONS OF COEXISTING GRUNERITE AND CARBONATES IN THE METAMORPHOSED BIWABIK IRON-FORMATION*

No.	D†	Ankerite			Calcite			Grunerite	
		Ca	Fe	Mg	Ca	Mg	Fe	n_γ	R
<i>Zone 3</i>									
70	1.94	54.0	21.9	24.1	90.2	9.1	0.7	1.701	0.73
72	1.92	54.1	18.7	27.2	90.0	9.2	0.8	1.702	0.74
95‡	1.90	55.1	22.1	22.8	88.9	11.1	0.0	1.704	0.76
96‡	1.90	54.3	20.0	25.7	89.1	10.7	0.2	1.703	0.75
74	1.78		none		89.1	10.6	0.3	1.713	0.85
<i>Zone 4</i>									
76	1.57		none		94.7	2.4	2.9	1.717	0.89
77	1.57		none		95.0	5.0	0.0	1.715	0.87

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3.

† Distance in miles from the Duluth Gabbro contact.

‡ Average of data for A and B samples (see Tables 3 and 8).

The assemblage siderite-grunerite was not detected in the taconite specimens studied.

The observed relations are consistent with the assumption of equilibrium at a specified temperature, total pressure, and chemical potential of one volatile component. Under these conditions, the assemblage grunerite-ankerite-calcite is invariant; the grunerite-calcite assemblage is univariant, and variations in compositions of the coexisting grunerite and calcite are therefore permissible.

It should be noted that the three grunerite-calcite assemblages lie closer to the gabbro (1.57–1.78 mi.) than do the grunerite-ankerite-calcite assemblages (1.74–1.90 mi.) and possibly developed at higher temperatures.

Despite this uncertainty about temperature, the data in Figure 32 indicate that the composition of grunerite at approximately the same metamorphic grade can vary considerably, depending on whether the grunerite coexists with one or with two carbonates. Approaching about 0.3 mile

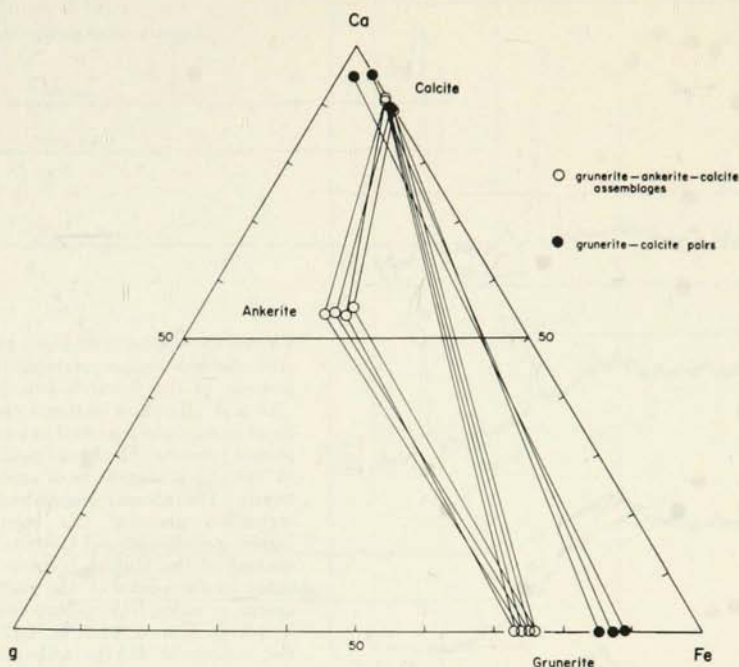


FIGURE 32.—Compositions of coexisting carbonates and grunerite in metamorphosed Biwabik Iron-formation.

closer to the gabbro contact apparently leads to the disappearance of ankerite from the assemblage and to the development of a less ferrous calcite and a more ferrous grunerite. The change in grunerite composition over this short interval is the reverse of the general trend observed in amphiboles from both carbonate-free and carbonate-bearing rocks, which tend to become more magnesian as the gabbro is approached.

Although the relations shown in Figure 32 are consistent with the assumption of equilibrium, they do not prove that equilibrium was actually established; compositional data from more grunerite-carbonate assemblages will be necessary to reach a definite conclusion.

CHANGES IN THE ORGANIC MATERIAL DURING METAMORPHISM

Recent examinations of the carbonaceous material from unmetamorphosed Precambrian sediments (Swain and others, 1958; Hoering, 1962a, 1962b) have shown that such material is not crystalline graphite, but is amorphous and consists of numerous complex hydrocarbon compounds. It is thus probable that much of the material from other Precambrian rocks is not crystalline graphite. A study of the organic material from the Intermediate slate was therefore undertaken to determine its nature and

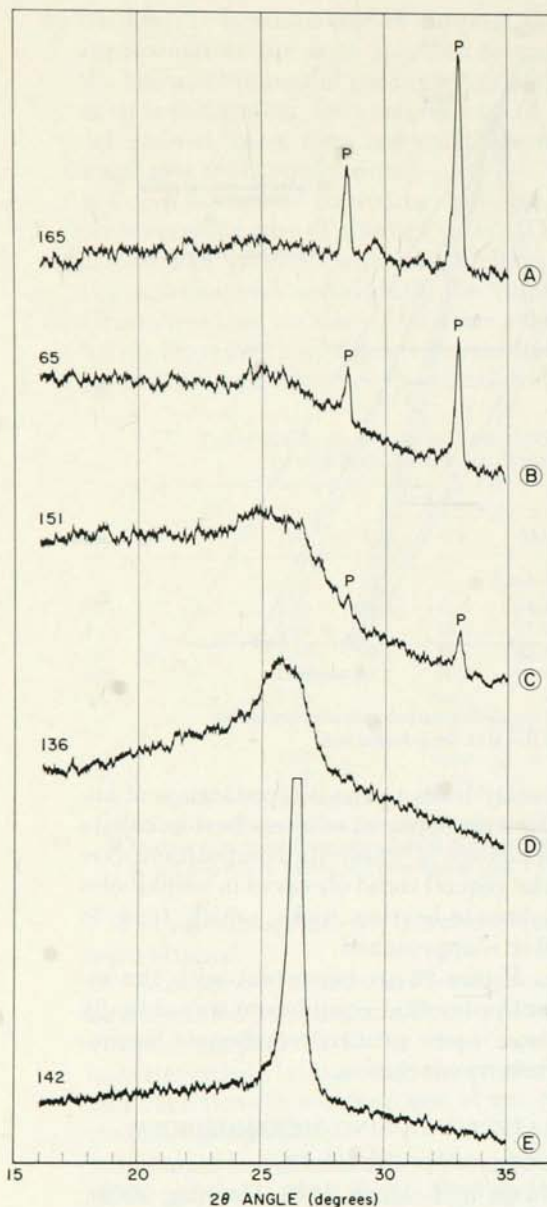


FIGURE 33.—X-ray diffraction patterns of acid-insoluble organic material from slaty taconite of the Biwabik Iron-formation. (A) and (B) show patterns characteristic of amorphous material in unmetamorphosed taconite. The broad peak at about $25^{\circ} 2\theta$ (C) is suggestive of asphaltic materials. Disordered graphite (D) and crystalline graphite (E) occur in the highly metamorphosed taconite near the contact of the Duluth Gabbro. *P* designates pyrite peaks in the residue. Distances, in miles, from gabbro contact are: A, 1.8; B, 3.49; C, 11.3; D, 1.47; E, 1.71. For samples A–D, the scale factor is 8, the multiplier is 1, and the time constant is 8; for sample E these factors are 16: 1: 4.

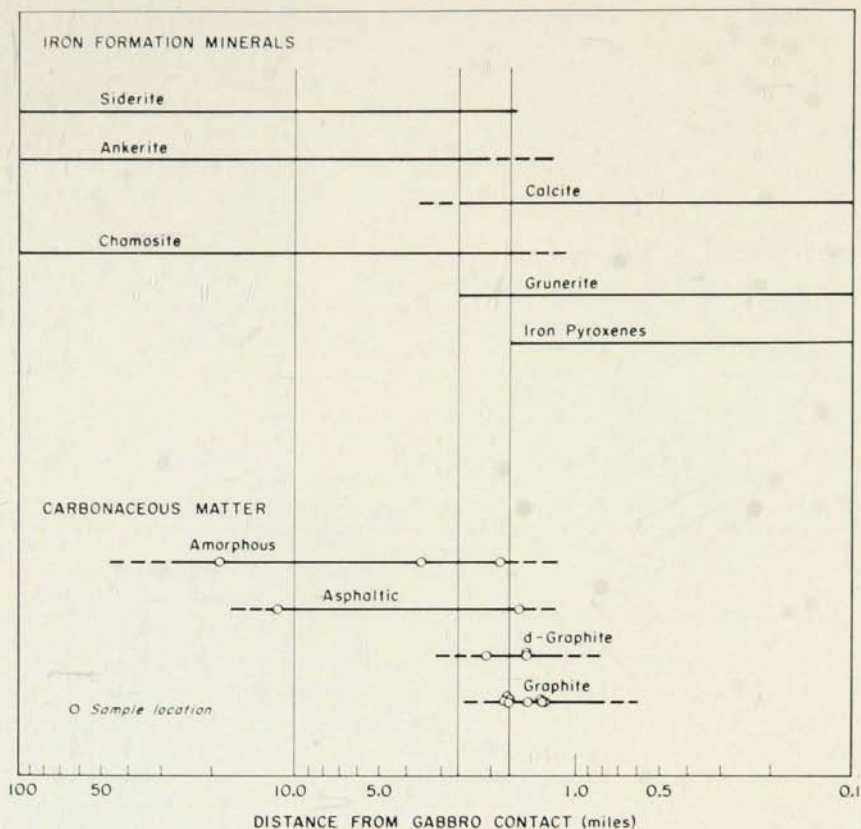


FIGURE 34.—Crystallinity of organic matter in the metamorphosed Biwabik Iron-formation as a function of distance from the Duluth Gabbro Complex.

to detect, if possible, the development of graphite from such material during metamorphism (French, 1964b).

Samples of about 100 grams from the Intermediate slate were ground to -230 mesh and dissolved in hydrofluoric acid to remove silicate and carbonate minerals.* The residue obtained was further treated with hot concentrated hydrochloric acid to remove fluorides and fluosilicates; residues were X-rayed after each step to check completion of the process.

After complete treatment, 1-2 grams of black or dark gray material remained; this residue was studied by X-ray diffraction to determine the degree of crystallinity of the carbonaceous material. Small amounts of pyrite and tourmaline contained in the specimens survived treatment and were detected in the X-ray pattern.

* Particularly quartz, whose (101) peak will completely mask the graphite (002) reflection if even a small amount is present.

TABLE 10. CRYSTALLOGRAPHIC CHARACTER OF CARBONACEOUS MATERIAL FROM SLATY TACONITE OF THE BIWABIK IRON-FORMATION IN DIFFERENT METAMORPHIC ZONES *

No.	Zone	D [†]	Peak (2θ) [‡]	Material	Acid-Soluble Minerals	Acid-Insoluble Minerals
18	1	17.4	none	Amor.	S,Mi,M	
151§	1	11.3	25.4 v.br.	Asph.	Chm,St,S,M	Pyr
65§	2	3.49	none	Amor.	Chm,S	Pyr
93	3	2.03	26.0 br.	d-Gr	S,M	Pyr
165§	3	1.80	none	Amor.	Chm	
140	3	1.71	26.4	Gr	Cu,M	
141	3	1.71	26.5	Gr	Cu,Chm,Fay?	Tour
142§	3	1.71	26.5	Gr	Chm,M	
143§	3	1.71	26.4	Gr	Cu,Chm,Bio	Tour
59	4	1.53	25.0 v.br.	Asph.	C,A	
136	4	1.47	26.0 br.	d-Gr	Cu	
137§	4	1.47	26.0 br. 23.3?	d-Gr (+Gr?)	Chm,Cu	
135§	4	1.28	26.4	Gr	Cu	
80§	4	1.24	26.4	Gr	Fe-Hbd, Cu	

* A key to abbreviations for minerals in the Biwabik Iron-formation is given in Table 3. Others used here are: v.br., very broad; br., broad; Amor., amorphous; Asph., asphaltic.

[†] Distance in miles from the the Duluth Gabbro contact.

[‡] When $2\theta = 25.0-25.4$, $d = 3.56-3.51$; when $2\theta = 26.0$, $d = 3.43$; when $2\theta = 26.4$, $d = 3.38$; and when $2\theta = 26.5$, $d = 3.36$.

§ Specimens collected from Intermediate slate.

The X-ray patterns obtained may be classified into four groups (Fig. 33): (1) No peaks, indicating completely amorphous material. Such patterns were obtained from material found only in unmetamorphosed taconite. Some patterns showed minor peaks owing to pyrite. (2) A very broad peak at about $25^\circ 2\theta$ (3.5 A.), resembling patterns of coals and asphalts. One specimen which produced such a pattern (MF-59) consisted of patches of black, brittle, resinous hydrocarbon in carbonate-bearing cherty taconite. Detailed analysis of this material (T. C. Hoering, oral communication, 1964) showed a richness in pyridine-extractible hydrocarbon material. (3) A slightly diffuse peak at 26.0° (3.43 A.), indicating poorly crystallized graphite. Such spacing may represent a graphite with considerable disorder in layer stacking (turbostratic) (Ubbelohde and Lewis, 1960, p. 79). The term d-graphite is used for this. (4) A sharp peak at about 26.5° (3.36 A.), corresponding to well-crystallized graphite. No data were obtained for percentages of organic material in taconite at different metamorphic levels.

There is a general correspondence between degree of crystallinity of the organic material and distance from the gabbro contact (Fig. 34; Table 10). The organic fraction is amorphous in unmetamorphosed taconite, whereas near the contact both d-graphite and crystalline graphite are developed. A similar increase in crystallinity and graphite development with increasing metamorphic grade has been observed in regionally metamorphosed coal beds (Quinn and Glass, 1958). The definite occurrence of crystalline graphite in the highly metamorphosed iron-formation has important implications for determining the conditions of metamorphism (see p. 88).

CHARACTER OF PROGRESSIVE METAMORPHISM OF THE BIWABIK IRON-FORMATION

NATURE OF THE BIWABIK IRON-FORMATION BEFORE INTRUSION OF THE DULUTH GABBRO COMPLEX

The present study of unaltered taconite reinforces the conclusion that the Biwabik Iron-formation originated as a chemical sediment containing iron silicates, iron carbonates, quartz, hematite, and magnetite (Gruner, 1946; White, 1954). Greenalite, quartz, hematite, and fine-grained magnetite are considered original components of cherty taconite. Relations in the unaltered cherty taconite of Zone 1 indicate that siderite, ankerite, minnesotaite, stilpnomelane, talc, and coarser magnetite have developed subsequently by replacement of the original minerals.

The distinction between primary and secondary minerals in slaty taconite is more difficult because of finer grain size and uncertain textural relations. Chamosite, siderite, and quartz are regarded by the writer as primary; all observation of ankerite indicate that it has developed by replacement of original siderite.

It was not possible in the present study to decide whether all stilpnomelane and minnesotaite are original or secondary. Some stilpnomelane has clearly developed from chamosite.

There is no evidence from the mineralogy of the unaltered taconite itself to indicate whether the observed replacements have occurred during diagenesis or whether they are the result of low-grade metamorphism (chlorite grade). The writer favors the interpretation that the mineralogy of the unaltered Biwabik Formation reflects a period of low-grade metamorphism preceding, and unrelated to, the intrusion of the Duluth Gabbro Complex. Mineralogical evidence for such a view is indirect and consists chiefly of the occurrences of minnesotaite and stilpnomelane in definitely metamorphosed rocks in other areas. Secondary minnesotaite has been observed on the Cuyuna range (Blake, 1958, 1965), developing parallel to rock cleavage oriented at a steep angle to original bedding. Stilpnomelane is commonly found in slightly metamorphosed pelitic rocks, associated with chlorite, muscovite, albite, epidote, and actinolite; in these rocks stilpnomelane is clearly metamorphic and may develop from chlorite (Hutton, 1938; Zen, 1960). The mineral has also been found in quartz-bearing veins that cut low-grade schists and Precambrian iron-formation (Grout and Thiel, 1924; Hallimond, 1924).

The Gunflint Iron-formation, which is correlative with the Biwabik Formation, has a mineralogy suggestive of a lower grade of metamorphism (James, 1954, p. 265). Siderite, ankerite, chamosite, and unrecrystallized

silica are the dominant components; stilpnomelane and minnesotaite are rarely observed (James, 1954; Moorhouse, 1960).

Indirect mineralogical and stratigraphic evidence are thus consistent with the conclusion that the unaltered taconite of the Biwabik Formation was subjected to a previous period of low-grade metamorphism unrelated to the intrusion of the Duluth Gabbro (James, 1954; James and Clayton, 1962). LaBerge (1964) has recently reached the same conclusion as a result of similar but independent petrographic studies on the Biwabik Iron-formation and other iron-formations from the Lake Superior region. The slight deformation of the Animikian rocks on the Mesabi range may have been produced at the same time. Such metamorphism may be related to an event at 1,600 to 1,700 m.y., which is recognized on the Cuyuna range and in east-central Minnesota (Goldich and others, 1961).

The exact metamorphic grade of the unaltered taconite is not, however, crucial to a study of the contact metamorphism. The present study and the results of earlier investigators (Gruner, 1946; White, 1954; LaBerge, 1964) indicate that, before the intrusion of the Duluth Gabbro, the Biwabik Formation was a mineralogically and texturally complex rock containing quartz, siderite, ankerite, greenalite, minnesotaite, stilpnomelane, and magnetite, together with minor hematite, chamosite, and talc. There is no evidence from the unaltered taconite for the presence of significant amounts of magnetite-quartz iron-formation, as suggested by Gundersen and Schwartz (1962).

NATURE OF METAMORPHISM OF THE BIWABIK IRON-FORMATION

Before metamorphism, the unaltered taconite apparently contained sufficient Ca, Fe, Mg, Si, H₂O, and CO₂ to yield the mineral assemblages observed in the metamorphosed taconites of Zones 3 and 4. The progressive mineralogical changes resulting from metamorphism indicate to the writer that contact metamorphism of the Biwabik Formation by the Duluth Gabbro Complex was largely isochemical, except for the loss of H₂O and CO₂ during metamorphism. This interpretation is favored by the close chemical similarity between unmetamorphosed and metamorphosed iron-formation from the Mesabi range and elsewhere (Gruner, 1946, pp. 63-64; James, 1955, p. 1476).

The Duluth Gabbro Complex acted only as a source of heat for metamorphic processes. Minor elements (e.g., sulfur and the boron in tourmaline and axinite) possibly were introduced from the gabbro, but large-scale introduction of major elements such as Ca and Mg was not necessary. These conclusions are in agreement with the results of earlier studies (e.g., Grant, 1900; Gruner, 1946; White, 1954). This interpretation was perceptively presented by Grant (1900, pp. 506-508) at a time when the exact mineralogy of the Biwabik Formation was still uncertain:

"The original rock is regarded as a glauconitic greensand, in which there is more or less iron carbonate. The rock has been altered to a quartz-

magnetite-amphibole slate, the amphibole being in the form of actinolite, grünerite, cummingtonite, and hornblende. This quartz-magnetite-amphibole slate, commonly known in the Lake Superior region as actinolite schist, has been profoundly changed by the gabbro, and the resulting rock is a coarse grained aggregate of quartz, magnetite, olivine (which is frequently fayalite), hypersthene, augite-hornblende, and occasionally grünerite and cummingtonite. These rocks, like the rocks from which they are derived, are beautifully banded, the separate bands being composed of quartz, or of magnetite, or of silicates, or of a mixture of any two or more of the minerals. . . . It is thus clear that the materials necessary for the formation of the minerals of the metamorphic rocks were all present in the original quartz-magnetite-amphibole slates."

The observations of the present study do not support the conclusions of Gundersen and Schwartz (1962), who suggest that complicated metasomatic effects accompanying intrusion of the Duluth Gabbro affected an iron-formation composed only of quartz and magnetite. Gundersen and Schwartz (1962, pp. xv-xvi) state:

"Considerable field and petrographic evidence exists to indicate that the constituents of quartz and magnetite are recombined to form most of the metamorphic and metasomatic mineral assemblages observed. There is, on the other hand, no evidence indicating the previous existence of the so-called primary silicates or carbonates of the iron formation nor any evidence supporting the concept of progressive metamorphism of these minerals into any of the mineral assemblages now found in the district. . . .

"The emplacement of the Duluth gabbro resulted in thermal metamorphism of the adjacent rocks, which was manifested largely by simple recrystallization and formation of fayalite-magnetite-quartz assemblages in the iron formation. Almost contemporaneously, the injection of numerous pegmatite-like veins was accompanied by the introduction of magnesium- and calcium-bearing aqueous solutions into the adjacent taconites, which resulted in the widespread formation of cummingtonite, hedenbergite, and some calcium-bearing ferrous amphiboles."

There are several theoretical difficulties in this interpretation. It should be emphasized that magnetite and quartz are the only original components of unaltered taconite which remain stable at the highest levels of metamorphism (Fig. 23), so that examination of highly metamorphosed taconite may give an incorrect estimate of the original mineralogy of the pre-metamorphic iron-formation. However, even in the metamorphosed taconite, quartz and magnetite commonly coexist intimately without formation of silicates (Grout and Broderick, 1919b, pp. 8-9; Gundersen and Schwartz, 1962, p. 117). Gundersen and Schwartz have suggested no source for the necessary solutions, and it may be questioned whether the Duluth Gabbro Complex could have been the source of sufficient water, for instance, to produce all of the amphibole in the metamorphosed taconite. It seems more reasonable to suggest that water was originally present in the iron-

formation or in the overlying Virginia Formation, in which case no mechanism is required for localized introduction of solutions into the metamorphosed taconite.

However, the most serious defects in their interpretation are: First, the metamorphosed Biwabik Iron-formation is stratigraphically continuous with unaltered taconite characterized by a diverse mineralogy. There is no evidence for any significant magnetite-quartz units existing in the Biwabik Formation before intrusion of the Duluth Gabbro. Second, in Zone 3, grunerite is clearly a prograde mineral which is observed in the process of formation from earlier iron silicates and carbonates (Figs. 17-20). Pegmatites of the type described by Gundersen and Schwartz (1962) were not observed in this zone. Retrograde formation of amphibole from hedenbergite occurs only in the eastern end of the area studied by the writer; possibly such retrograde formation of amphibole reflects falling temperature and does not require sudden introduction of water and other components.

MINERAL ASSEMBLAGES AND ISOGRADS IN THE METAMORPHOSED BIWABIK IRON-FORMATION

MINERAL ASSEMBLAGES IN CHERTY AND SLATY TACONITE

The mineralogical changes that are observed among the silicates in cherty taconite during progressive metamorphism correspond to those predicted on the basis of theoretical and experimental studies of the system $\text{FeO-SiO}_2\text{-H}_2\text{O}$ (Yoder, 1957; Flaschen and Osborn, 1957).

The unaltered cherty taconite of the Biwabik Formation contains considerable carbonate, and can be represented approximately by the system $\text{FeO-SiO}_2\text{-H}_2\text{O-CO}_2$. At a specified temperature and total pressure, a four-phase assemblage of three solids plus vapor is invariant and the composition of the vapor is fixed. Two solid phases form a univariant assemblage with a vapor of variable composition.

The mineral assemblages that develop during metamorphism of cherty taconite are shown in Figure 35; assemblages in the simplified system $\text{FeO-SiO}_2\text{-H}_2\text{O}$ (Yoder, 1957) are shown by dashed lines for comparison.

Assemblage 1 corresponds to ideal cherty taconite consisting of greenalite, magnetite, and quartz. Development of siderite and minnesotaite produces assemblage 2, which represents unaltered cherty taconite on the Mesabi range.

Assemblages 3-6 develop during progressive metamorphism and correspond, respectively, to reactions involving: 3, decomposition of greenalite; 4, formation of grunerite; 5, decomposition of minnesotaite and siderite; and 6, decomposition of grunerite. The latter reaction is not observed to occur on the Mesabi range.

At P_{O_2} values within the stability field of fayalite, assemblages 5a and 6a are produced, respectively, by formation of fayalite and by decomposition of grunerite.

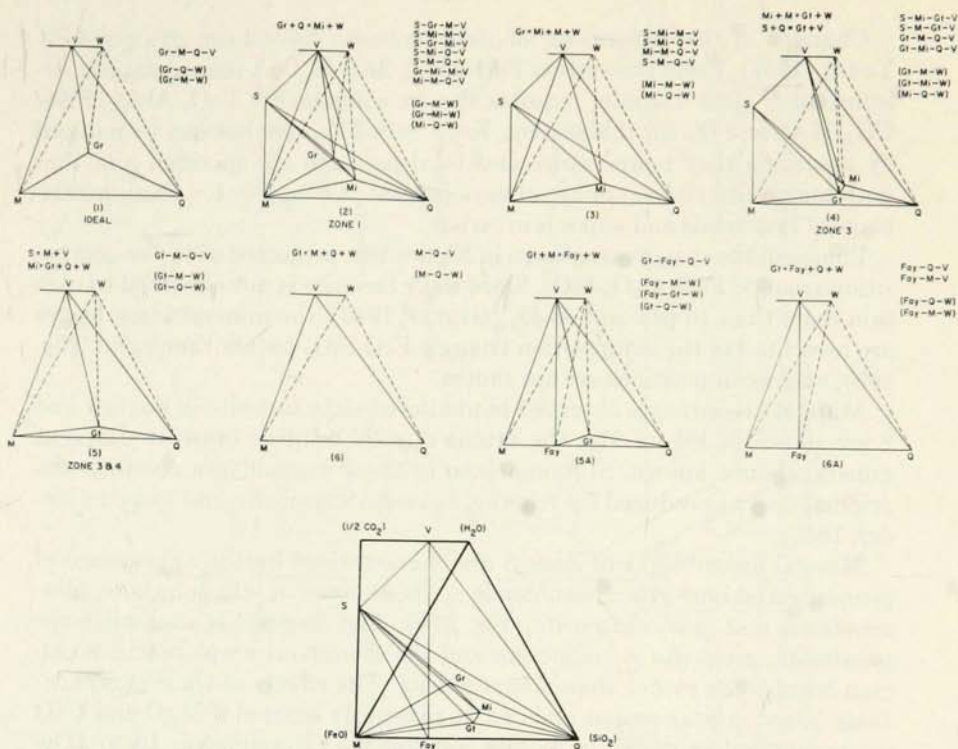


FIGURE 35.—Schematic diagrams of mineral assemblages produced in cherty taconite with progressive metamorphism. Assemblages produced in the system $\text{FeO-SiO}_2\text{-H}_2\text{O-CO}_2$ are shown in solid lines; assemblages in the simpler system $\text{FeO-SiO}_2\text{-H}_2\text{O}$ (Yoder, 1957) are indicated by dashed lines and are listed in parentheses.

Diagrams 1-6, from upper left to left center, show assemblages which develop by progressive metamorphism of ideal cherty taconite (1, upper left) composed of greenalite, magnetite, and quartz in equilibrium with a vapor composed of H_2O and CO_2 . Assemblage (2) (upper center) contains siderite and minnesotaite and corresponds to unaltered cherty taconite in the Biwabik Iron-formation (Zone 1). Assemblages (5a) and (6a) (right center), represent reactions occurring only at values of P_{O_2} within the stability field of fayalite.

The larger figure at bottom indicates the compositions of the mineral phases in the system $\text{FeO-SiO}_2\text{-H}_2\text{O-CO}_2$.

Changes in the mineralogy of slaty taconite have been discussed by Yoder (1957), using the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. A more complete description of slaty taconite requires the six components FeO , Al_2O_3 , SiO_2 , CO_2 , H_2O , and O_2 ; for this system, $F = 8 - P$. The variance can be reduced by assuming that temperature and total pressure are specified and that both magnetite and vapor are always present. Then, $F = 4 - P$; an assemblage of four solids and vapor is invariant.

Phases in the system are shown in Figure 36a, projected onto the composition triangle $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$. Since slaty taconite is not observed to contain more than 10 per cent Al_2O_3 (Gruner, 1946), the mineral assemblages are presented in the composition triangle $\text{FeO-SiO}_2\text{-pseudothuringite}$ (Fig. 36b); vapor compositions are not shown.

Mineral assemblages observed in unaltered slaty taconite in Zones 1 and 2 are shown in Figure 37a; the extent of solid solution between different minerals is not known. Stilpnomelane in these assemblages possibly was original or was produced by reaction between chamosite and quartz (Yoder, 1957).

Mineral assemblages of Zone 3 are characterized by the appearance of grunerite and blue-green hornblende at the expense of stilpnomelane, minnesotaite, and some chamosite (Fig. 37b). The diagram is somewhat approximate; grunerite is magnesian and the aluminous amphibole is a calcian hornblende rather than a ferrogedrite. The effects of these complications do not appear serious and can be rigorously ignored if MgO and CaO are considered as perfectly mobile components (Korzhinskii, 1959). The coexistence of chamosite and grunerite in quartz-free rocks is consistent with the persistence of chamosite through Zone 3.

Mineral assemblages in Zone 4 are characterized by garnet, pyroxene, and sparse fayalite and biotite (Grout and Broderick, 1919b; Gundersen and Schwartz, 1962), but data on actual assemblages is scanty. Probable assemblages are shown in Figure 37c for the case where K_2O is available to form biotite; the occurrence of feldspar-bearing pegmatites in Zone 4 suggests that K_2O may be a mobile component in some parts of the iron-formation (Korzhinskii, 1959). In biotite-free assemblages, a grunerite-garnet join is probably present.

In Zone 4, most of the original chamosite-bearing rocks are apparently represented by fayalite- or garnet-bearing assemblages. Highly aluminous assemblages are not observed in the Biwabik Formation, but it is probable that the aluminous chlorites shown in Figure 37c are not stable at the conditions of metamorphism of Zone 4. Other data suggest that the chamosite-quartz join is replaced by the hornblende-cordierite or garnet-cordierite joins (Zappfe, 1912; Ramdohr, 1927). The chamosites themselves probably decompose to such assemblages as cordierite-fayalite-hercynite or magnetite-mullite.

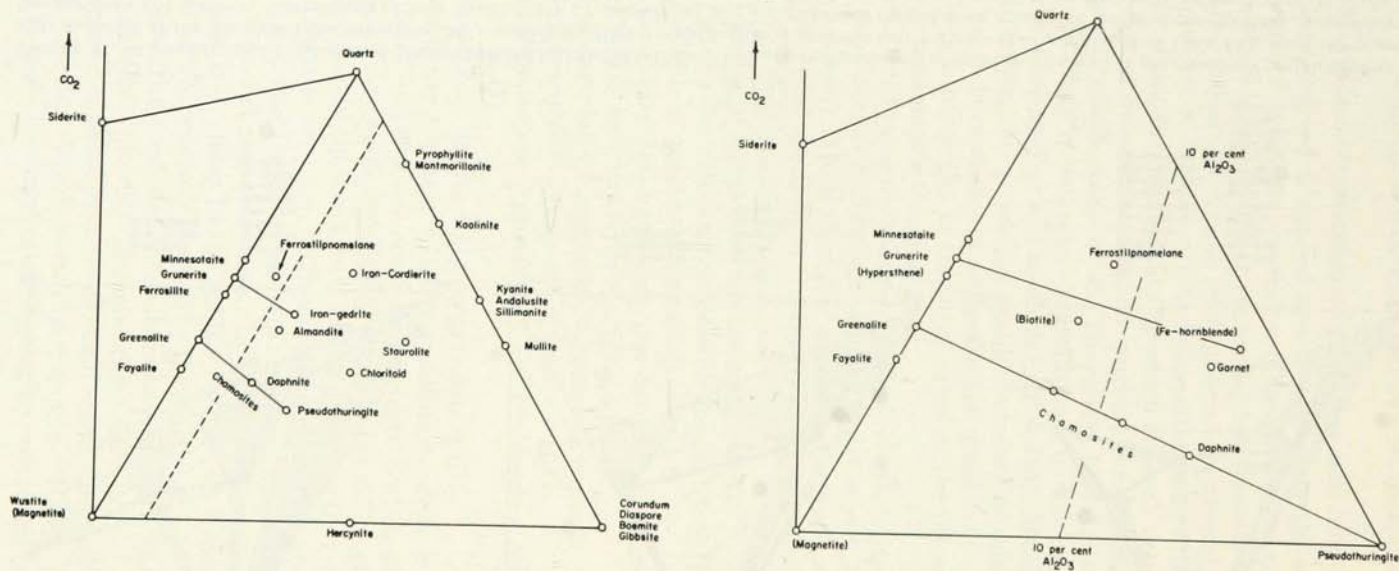


FIGURE 36.—Compositional diagrams of minerals in the system $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2-\text{O}_2$, which are produced during progressive metamorphism of slaty taconite in the Biwabik Iron-formation. A (left) shows the system $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, projected onto the $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ triangle (adapted from Yoder, 1957). The independent CO_2 axis is added to include siderite-bearing assemblages. B (right) is a modified projection of the system onto the triangle $\text{FeO}-\text{Al}_2\text{O}_3$ -pseudotothingite. This diagram is used to discuss mineral assemblages developed in slaty taconite (Fig. 37), in which the Al_2O_3 content is under 10 per cent (dashed line). Vapor compositions are not shown.

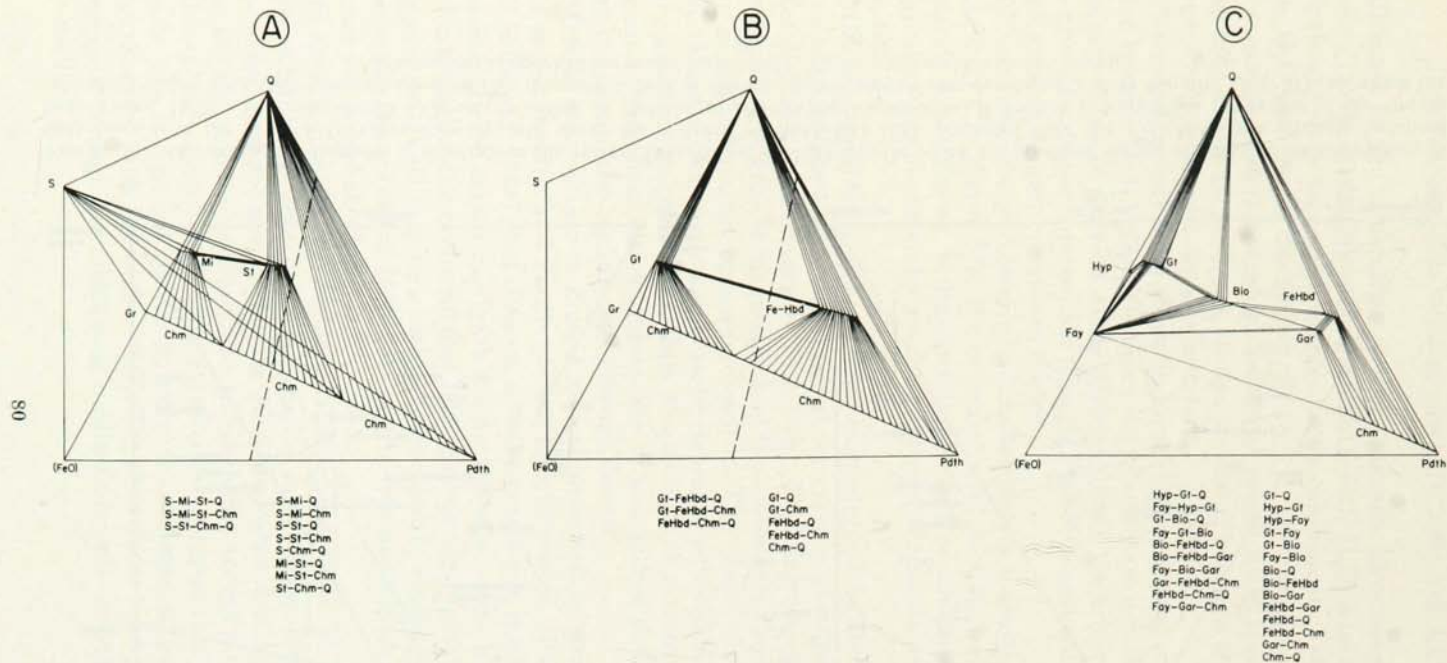


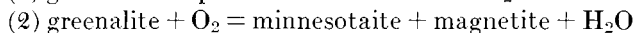
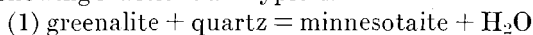
FIGURE 37.—Compositional diagrams of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2\text{-O}_2$, showing mineral assemblages present in progressively metamorphosed slaty taconite of the Biwabik Iron-formation. All assemblages shown coexist with magnetite and with a vapor composed of H_2O , CO_2 , and O_2 (vapor compositions not shown). Assemblages of four solid phases (+ magnetite) are invariant and coexist with a vapor of specified composition. Assemblages of three solid phases (+ magnetite) are univariant, and two solid phases (+ magnetite) constitute a divariant assemblage. Unaltered slaty taconite is characterized by siderite-bearing assemblages (A, left). Grunerite-bearing assemblages (B, middle) characterize the moderately metamorphosed taconite in Zone 3. Assemblages shown for the highly metamorphosed slaty taconite of Zone 4 (C, right) are largely schematic; there are no detailed data.

MINERALOGICAL ISOGRADS IN THE BIWABIK IRON-FORMATION

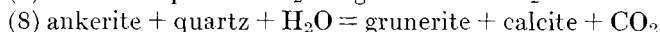
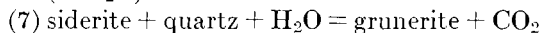
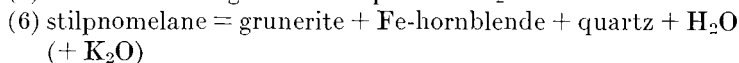
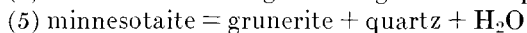
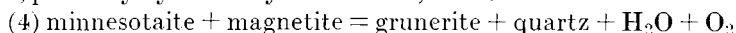
The term isograd is applied here to designate the appearance or disappearance of a specific mineral with progressive metamorphism; these changes are believed related to increasing temperature toward the contact of the Duluth Gabbro. A close relation between mineralogical changes and a restricted set of factors such as temperature and total pressure is difficult to establish, for the reactions by which minerals develop or decompose are dependent on additional factors such as the occurrence and chemical potentials of volatile components (Thompson, 1955; Greenwood, 1962).

A great variety of balanced equations may be written arbitrarily for reactions between various iron minerals (Miles, 1946; Mueller, 1960; Kranck, 1961). However, the variability and uncertainty of mineral compositions and the general occurrence of magnetite and quartz as possible participants makes such a procedure of doubtful value in the present study; a more schematic treatment is therefore used.

The unaltered taconite in Zones 1 and 2 is characterized by the development of minnesotaite and stilpnomelane, at least in part, from earlier greenalite and chlorite. These changes, which do not appear to be related to thermal effects of the Duluth Gabbro, may be expressed in several ways; the following reactions are typical:

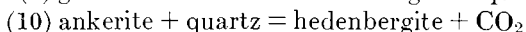
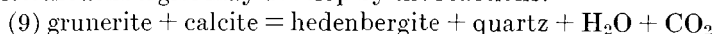


In both silicate and carbonate iron-formation, grunerite develops in Zone 3, probably by a variety of reactions, such as:

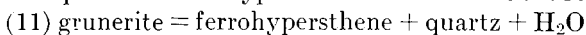


Reactions 7 and 8, which occur in carbonate-bearing rocks, do not take into account varying Fe/(Fe + Mg) ratios in the different phases. Siderite has approximately the same ratio as the grunerite that apparently forms from it. Ankerites are more magnesian than coexisting grunerite (Fig. 32); additional iron could be obtained from associated magnetite.

Mineralogical changes characteristic of Zone 4 are the development of hedenbergite and, closer to the gabbro contact, of ferrohpersthene and fayalite. Hedenbergite may develop by the reactions:



Development of ferrohpersthene could reflect the reaction:



Reaction 11 could be complicated slightly by variations in composition of

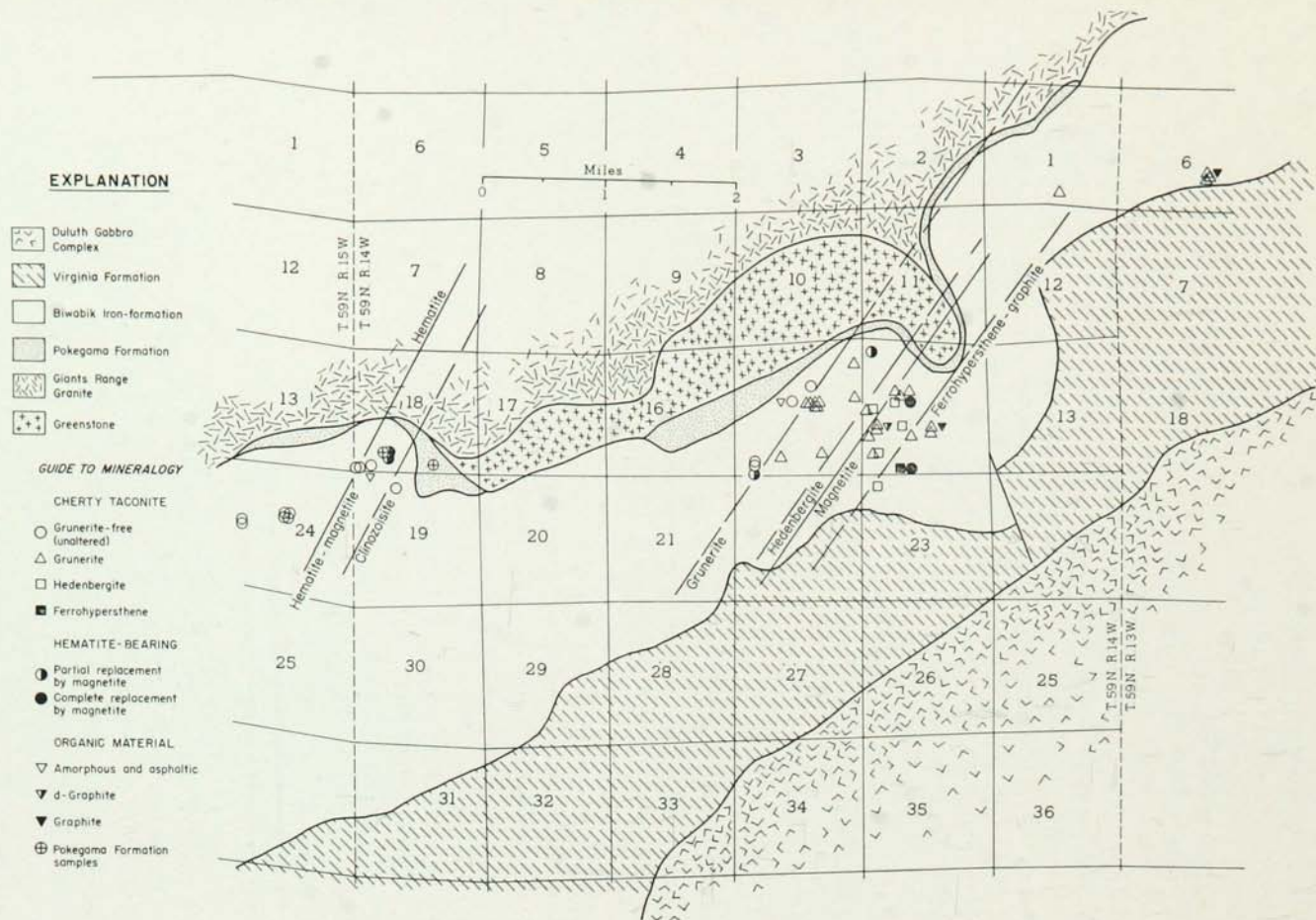
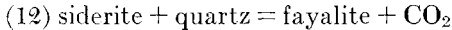


FIGURE 38.—Geologic map of part of the Mesabi range near Mesaba (R.14W. and R.15W.), showing generalized mineralogical isograds determined in the present study. Changes shown in Zone 2 are: H/(H + M), partial reduction of hematite to magnetite; Cz, formation of clinozoisite from chloritic material in the Pokegama Formation. Changes shown in Zone 3 are: Gt, formation of grunerite; Hd, formation of hedenbergite; M, complete reduction of hematite to magnetite; FeHyp, formation of ferrohysterthene; G, development of crystalline graphite (in organic matter).

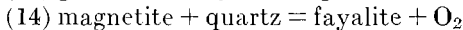
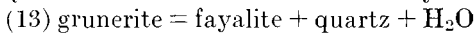
the amphibole; cummingtonite could form with ferrohypersthene (see above, p. 67).

Formation of fayalite by reaction between siderite and quartz has been proposed by several investigators (Gruner, 1946; James and Clayton, 1962):



However, experimental studies by the writer (French, 1964a; French and Rosenberg, 1965) indicate that the nature of this reaction is unstable, and the present study indicates that siderite is depleted by reaction to form grunerite (reaction 7) before the appearance of fayalite in the taconite.

Fayalite in the Biwabik Formation may form from the reactions:



Neither reaction will occur outside the P_{O_2} limits within which fayalite is stable (Eugster, 1959). The reverse of reaction 13 — that is, formation of grunerite at fayalite-quartz contacts — has been observed naturally (Bowen and Schairer, 1935; Gundersen and Schwartz, 1962).

Figure 38 shows the approximate location of several mineralogical isograds in the metamorphosed Biwabik Iron-formation. The lines are based largely on the writer's mineralogical studies and on additional data kindly supplied by the Erie Mining Company.

Two isograds occur within Zone 2, at a distance of 3 to 4 miles from the gabbro contact; they correspond to the incipient reduction of hematite to magnetite and the development of clinozoisite. The changes have been observed only in 18:59-14, and the trend of the lines is uncertain.

The line that marks the appearance of grunerite passes diagonally through 15:59-14; it is probably the most accurately located isograd, for it is bracketed at several points by samples of grunerite-free and grunerite-bearing taconite. The other isograds are drawn parallel to it.

Pyroxenes were not observed in the taconite in 15:59-14 and seem restricted to 14:59-14. The hedenbergite isograd, which designates the outer margin of Zone 4, has been drawn from only a few points and is approximate. Within Zone 4, other mineralogical changes include the disappearance of hematite, ankerite, and siderite.

Ferrohypersthene seems to occur closer to the gabbro than does hedenbergite; an approximate isograd is shown in Figure 38. The complete transformation of organic matter into crystalline graphite seems to occur at approximately the same location (Fig. 34).

Scattered observations on sulfide minerals in the taconite of the Biwabik Formation (Fig. 23) suggest that a transformation from pyrite to pyrrhotite possibly occurs with metamorphism, but the data are too meager to establish a definite boundary. Apparently, pyrrhotite is the stable mineral in highly metamorphosed taconite (Gundersen and Schwartz, 1962, p. 78). Direct comparison of the occurrences noted in the present study (Fig. 23) is not possible. The pyrrhotite observed occurs in coarse-grained, heden-

bergite-bearing veinlets in metamorphosed taconite. By contrast, most pyrite was noted in acid-insoluble residues of samples of the Intermediate slate, prepared for study of the organic matter (Table 10). Pyrite was not seen in samples from Zone 4; any pyrrhotite originally present would not have survived the acid treatment.

More data would be needed to establish the existence of a "pyrrhotite isograd" on the Mesabi range. James (1955, p. 1475) notes that pyrite in the sulfide facies persists at the highest grade of regional metamorphism; however, some pyrrhotite reported in contact-metamorphosed iron-formation (Ramdohr, 1927) possibly developed from pyrite.

The major isograds are strikingly compressed; it is possible to pass from unaltered taconite in 15:59-14 to its highly metamorphosed equivalent within 2 miles. The isograds, in particular the grunerite isograd, do not parallel the present contact of the gabbro and appear to diverge from it toward the east. Insufficient data are available to locate the isograds farther east; if the diverging trend is maintained, the system of metamorphic zones based on distance from the gabbro contact would probably not be applicable east of 59-14.

CONDITIONS DURING METAMORPHISM

GENERAL DISCUSSION

Any attempt to use mineralogical data from the Biwabik Iron-formation to evaluate temperature, pressure, and the partial pressures of volatile gas species during metamorphism is hampered by the large uncertainty in relations between such quantities as total load pressure (P_t), total gas pressure (P_{gas}), and the partial pressures of various volatile components ($P_{\text{H}_2\text{O}}$, P_{CO_2} , P_{O_2} , etc.). The conclusions reached will be conditioned by any assumptions made about these quantities.

It is reasonable to postulate that the mineral assemblages in the highly metamorphosed taconite coexisted with a vapor phase composed chiefly of CO_2 and H_2O , which contained minor amounts of CH_4 , H_2 , and CO and trace quantities of O_2 and S_2 . A significant $P_{\text{H}_2\text{O}}$ is indicated by the preservation of iron amphiboles in the highly metamorphosed taconite, although exact values cannot be specified. The only indication of P_{CO_2} is the occurrence of calcite in highly metamorphosed taconite; a value of P_{CO_2} in excess of 10 bars would probably be sufficient to stabilize calcite at temperatures below $1,000^\circ\text{C}$ (Harker and Tuttle, 1955).

The value of P_{O_2} during metamorphism apparently remained within the stability field of magnetite + quartz in the majority of the Biwabik Formation — that is, between the hematite-magnetite and quartz-fayalite-magnetite buffers (Eugster, 1959). Hematite in unmetamorphosed taconite is reduced to magnetite near the contact. In the highly metamorphosed taconite, magnetite and quartz apparently coexist without reaction in most of the stratigraphic section (Gundersen and Schwartz, 1962, p. 115); fayalite has developed in slaty taconite in a restricted stratigraphic interval.

Between 500° and 900°C , the hematite-magnetite buffer specifies values of f_{O_2} between 10^{-18} and 10^{-7} bars, and the quartz-fayalite-magnetite buffer corresponds to values of f_{O_2} between 10^{-25} and 10^{-13} bars (Eugster and Wones, 1962). If the QFM buffer is accepted as the lower limit of possible values of f_{O_2} during metamorphism, values of the ratios $f_{\text{CO}_2}/f_{\text{CO}}$ and $f_{\text{H}_2\text{O}}/f_{\text{H}_2}$ will be in excess of 15 (Eugster and Wones, 1962, Fig. 3; French and Eugster, 1965, Fig. 1); higher values of f_{O_2} will increase the ratios.

However, considerable uncertainty is still present about the relation among P_{gas} , $P_{\text{H}_2\text{O}}$, and P_{CO_2} . In many previous studies it has been tacitly assumed that $P_{\text{gas}} = P_{\text{H}_2\text{O}} + P_{\text{CO}_2}$. However, equilibrium calculations in the system C-H-O (French and Eugster, 1965) have indicated that methane, CH_4 , may be a significant component of the gas phase under moderately reducing conditions that may be attained in geological environments, and the assumption may be seriously in error for the more reduced graphite-

and fayalite-bearing metamorphosed slaty taconite. Further, no definite limits on the ratio P_{H_2O}/P_{CO_2} can be specified. The relation between these two partial pressures is particularly important, since many of the reactions by which amphiboles and pyroxenes develop during metamorphism involve both these species. In such reactions, the reaction temperature is strongly dependent upon the composition of the vapor phase (Greenwood, 1962, and oral communication, 1963).

FORMATION OF WOLLASTONITE

The mineral wollastonite ($CaSiO_3$) occurs in a calcite marble at the top of the Biwabik Iron-formation in the area of highly metamorphosed taconite (Gundersen and Schwartz, 1962, p. 100). Formation of the mineral from calcite and quartz has been studied experimentally (Harker and Tuttle, 1956), and its occurrence may be used to estimate temperatures adjacent to the Duluth Gabbro Complex during metamorphism.

Approximate temperatures and pressures developed have been estimated in connection with temperature determinations made on the Mesabi range by oxygen-isotope methods (James and Clayton, 1962). The probable thickness of the overlying Duluth Gabbro Complex (8–12 km.) would produce a lithostatic pressure of between 2 and 4 kb. Assuming a value of P_{CO_2} between 500 and 1,000 bars, the occurrence of wollastonite indicates a minimum temperature of 600°C adjacent to the gabbro contact (James and Clayton, 1962, p. 227).

Even assuming that P_{gas} is not less than half of P_t (i.e., $P_{gas} = 1-2$ kb.), it is probable that P_{CO_2} is less than P_{gas} ; a large discrepancy between P_t and P_{CO_2} would allow wollastonite to form at lower temperatures (see Thompson, 1955; Greenwood, 1961). At extremely low values of P_{CO_2} , wollastonite could form by reaction of calcite and quartz at temperatures as low as 400°C (Burnham, 1959, p. 916). For values of P_{CO_2} of 500 to 1,000 bars, a minimum temperature of 600°C is probable.

The occurrence of wollastonite in the highly metamorphosed Biwabik Formation thus establishes a fairly definite minimum temperature of 400°C and indicates a probable minimum temperature of 600°C near the contact of the gabbro. Since the occurrence of wollastonite indicates only that the temperature required for reaction was attained, these estimates are only minimum values.

At higher temperatures, wollastonite and calcite react to form the mineral spurrite ($2Ca_2SiO_4 \cdot CaCO_3$). The univariant P_{CO_2} - T curve for this reaction (Tuttle and Harker, 1957; Burnham, 1959) thus establishes maximum temperatures for the stable coexistence of wollastonite + calcite at a fixed value of P_{CO_2} . At values of P_{CO_2} below 200 bars, spurrite may form between 700° and 900°C. Spurrite has not been reported from the marble unit of the Biwabik Formation near the Duluth Gabbro, but study of this unit has not been sufficiently thorough to establish that it is absent or that wollastonite and calcite do coexist without reaction. Occurrence of spur-

rite would indicate relatively low values of P_{CO_2} during metamorphism (Burnham, 1959).

EVIDENCE FROM THE IRON CARBONATES

Temperatures attained in Zone 3, between 1 and 3 miles from the gabbro contact, are less certain. The Biwabik Formation in this zone contains grunerite and iron-bearing carbonates; the mineralogy is virtually identical to that produced by moderate regional metamorphism of iron-formation. James (1955, p. 1477) has noted that, in northern Michigan "the key mineral of the intermediate-intensity metamorphism of the iron-formation rocks is grunerite. The appearance of this mineral probably slightly precedes that of garnet in the argillaceous rocks." James's estimates of the "garnet isograd" in that area (1955, p. 1485) suggest a temperature of 300°–350°C for the development of grunerite.

Experimental studies of siderite stability (French, 1964a; French and Rosenberg, 1965) considered only relations in the system Fe-C-O and are therefore not directly applicable to the metamorphosed Biwabik Iron-formation. During metamorphism, siderite apparently reacts with available silica and water to form grunerite; similar behavior is observed in many other areas of metamorphosed iron-formation (Irving and Van Hise, 1892; Van Hise and Bayley, 1897; Allen and Barrett, 1915; Gustafson, 1933; Tilley, 1938; James, 1955).

The equilibrium siderite + magnetite + graphite + vapor determines maximum stability temperatures of siderite in equilibrium with vapor. For conditions where $P_{\text{gas}} = P_{\text{CO}_2} + P_{\text{CO}}$, these temperatures lie between 455° and 465°C for values of $P_{\text{CO}_2} + P_{\text{CO}}$ between 500 and 2,000 bars. Because of the steepness of the univariant curve, the effect of conditions where $P_t < P_{\text{CO}_2}$ is not extreme (French, 1964a). From these data, it is estimated that reaction of siderite and quartz to form grunerite occurred at temperatures below 450°C; a probable maximum temperature for this reaction is 400°C.

Calcites from grunerite-ankerite-calcite assemblages in Zone 3 contain less than 1 mole per cent MgCO_3 and as much as 9 to 11 mole per cent FeCO_3 (Fig. 32). Experimental studies of the solvus between siderite and calcite (Rosenberg, 1960, 1963) indicate that a calcite of this composition would coexist with a calcian siderite at approximately 400°C. Because the calcites examined coexist with grunerite and ankerite instead of with siderite, this inferred temperature is only approximate.

Data from the carbonate minerals in the moderately metamorphosed taconite in Zone 3 suggest that grunerite develops from siderite and ankerite at temperatures not in excess of 400°C; it is probable that temperatures of 300° to 400°C were attained in this zone during metamorphism.

SIGNIFICANCE OF FAYALITE IN METAMORPHOSED IRON-FORMATION

The iron olivine fayalite (Fe_2SiO_4) is of particular interest in the study of metamorphosed iron-formations because it is stable only within a

narrow range of P_{O_2} values between the quartz-fayalite-magnetite and quartz-fayalite-iron buffers (Eugster, 1959). The occurrence of fayalite or of the more oxidized equivalent assemblage magnetite-quartz allows an estimation of values of P_{O_2} during metamorphism.

No fayalite-bearing rocks (eulysites) have been described from areas of regional metamorphism where intrusive igneous rocks are generally absent (Tilley, 1938; James, 1955; Mueller, 1960; Kranck, 1961). By contrast, numerous eulysites, including many of the classic Swedish deposits, are clearly related to igneous intrusions (Von Eckermann, 1922, 1936; Geijer, 1925; Ramdohr, 1927; Miles, 1943, 1946; Freitsch, 1957; Sarap, 1957). A few fayalite occurrences are of uncertain association (Tilley, 1936).

In the Lake Superior region, fayalite is found only at the contacts of the Duluth Gabbro Complex with iron-formation on the Mesabi and Gunflint ranges (Zappfe, 1912; Grout and Broderick, 1919b; Gundersen and Schwartz, 1962); it is not observed elsewhere in the region (James, 1955).

The restriction of fayalite to igneous contacts may reflect conditions that are more reducing than those in regionally metamorphosed rocks, in which magnetite and quartz coexist (Eugster, 1959). Ramdohr (1927) provides geological evidence for such an interpretation by describing progressive reduction of hematite-bearing iron-formation within the contact aureole of the Brocken granite. As the granite is approached, hematite-chert rocks are reduced to magnetite-quartz rocks, and then further altered to fayalite-quartz and fayalite-magnetite assemblages.

In the highly metamorphosed iron-formation on the Mesabi range, the development of fayalite appears to be restricted to a zone about a hundred feet thick in the Lower Slaty and Upper Cherty members of the Biwabik Formation (Gundersen and Schwartz, 1962, p. 115). Elsewhere in the formation, even closer to the gabbro, magnetite and quartz coexist.

These relations suggest that the formation of fayalite during metamorphism was not the result of a general reduction near the gabbro (e.g., by introduction of hydrogen and water) (Eugster, 1959). Gundersen and Schwartz (1962, pp. 115–116) have proposed that fayalite formed only in layers rich in organic material and graphite, in which a more reducing atmosphere could be maintained. A similar mechanism has been suggested by Zen (1963), and is in agreement with the observed preservation of differences in P_{O_2} in metamorphic rocks over very short distances (James, 1955; Kranck, 1961; Zen, 1963).

Study of the organic matter in the Biwabik Formation by the writer (see above, p. 72) indicates that crystalline graphite occurs in the iron-formation near the contact of the gabbro. Some of the metamorphosed slaty taconite contains the assemblage quartz-fayalite-magnetite-graphite (Gundersen and Schwartz, 1962, pp. 31–34).

The writer's preliminary investigations on the univariant equilibrium quartz-fayalite-magnetite-graphite-vapor (French, 1964a) are somewhat inconclusive. Direct application of the results to the assemblages in the

Biwabik Formation is also hampered by the fact that the olivine in the metamorphosed taconite is slightly magnesian, about Fa_{90} (Gundersen and Schwartz, 1962, pp. 76, 95–96).

The steepness of the univariant QFMGV curve (French, 1964a, Fig. 25) reduces the effect on the temperature of large uncertainties in the value of $P_{\text{CO}_2} + P_{\text{CO}}$. If this value was between 500 and 2,000 bars, the experimental curve suggests temperatures of $780^\circ\text{--}810^\circ\text{C}$ for formation of fayalite near the gabbro contact.

Although these temperatures are not geologically unreasonable, they must be regarded with caution because of unexplained discrepancies in the determination of the QFMGV curve. Temperatures of 750° to 850°C would suffice to produce spurrite in the calc-silicate marble under conditions of low P_{CO_2} (Burnham, 1959); a search should be made for the mineral.

SUMMARY AND CONCLUSIONS

A detailed mineralogical study of progressively metamorphosed sedimentary iron-formation was carried out in an attempt to apply experimentally determined data on the stability of siderite, FeCO_3 , to natural assemblages.

The Biwabik Iron-formation, on the Mesabi range in northern Minnesota, extends for about 120 miles in a generally east-northeast direction. The formation is the middle member of the threefold Animikie Group of Middle Precambrian age; it overlies the clastic Pokegama Formation conformably and is in turn overlain conformably by the thick argillites of the Virginia Formation. At the eastern end of the Mesabi range, the Animikie Group has been metamorphosed by the intrusion of the Duluth Gabbro Complex; mineralogical changes along the strike of the formations appear to be related to the gabbro.

Intensive economic development of the soft iron ores and, more recently, of the taconite on the Mesabi range has resulted in intense geological study of the area over a period of more than sixty years. The geological relations are uncomplicated and well known; detailed sampling is facilitated by numerous open-pit mines and drill cores.

Along the strike of the Biwabik Iron-formation, four zones, related to distance from the gabbro, are distinguished on the basis of the mineralogy of the taconite. Zone 1 corresponds to unaltered iron-formation, and Zone 2 to transitional material; Zone 3 designates moderately metamorphosed taconite, and Zone 4, nearest the gabbro contact, is characterized by highly metamorphosed and recrystallized taconite.

The unaltered taconite of Zone 1 is a mineralogically complex chemical sediment that has been affected by considerable postdepositional alteration. Two fundamental kinds of taconite are distinguished: *cherty taconite*, characterized by a granule texture and a high percentage of quartz, and *slaty taconite*, characterized by fine laminations which reflect differences in mineralogical composition, by a general absence of granules, and by a low percentage of quartz.

Unaltered cherty taconite is composed of quartz, hematite, magnetite, siderite, ankerite, talc, and the iron silicates greenalite, minnesotaite, and stilpnomelane. Only greenalite, quartz, hematite, and magnetite are regarded as definitely primary; the other minerals exhibit secondary textures. In unaltered slaty taconite, chamosite, siderite, quartz, magnetite, and possibly some minnesotaite and stilpnomelane are considered primary. The conditions under which the secondary minerals developed are uncertain; the writer favors the view that the mineralogy of unaltered taconite in

Zone 1 reflects a distinct period of low-grade metamorphism before the intrusion of the Duluth Gabbro Complex.

The mineralogy of the transitional taconite in Zone 2 is virtually the same as that in Zone 1. Considerable replacement by silica and ankerite is observed, but these changes are not definitely related to the Duluth Gabbro.

Development of the iron amphibole grunerite, $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, characterizes the moderately metamorphosed taconite of Zone 3. The appearance of grunerite coincides with the disappearance from the taconite of such pre-metamorphic minerals as greenalite, stilpnomelane, minnesotaite, siderite, and ankerite; none of these minerals is observed to persist through Zone 3. Some chamosite-rich slaty taconite persists unaltered through Zone 3.

In Zone 3, grunerite is clearly a prograde mineral, and may be observed in the process of formation in both silicate- and carbonate-rich taconite; the "grunerite isograd" probably represents a variety of complicated chemical reactions. The appearance of calcite in Zone 3 is related to production of grunerite from the assemblage ankerite-quartz. No siderite-grunerite assemblages were observed; the disappearance of siderite in Zone 3, however, probably reflects reaction with quartz to form grunerite.

The taconite in Zone 4, within 1.7 miles from the present Duluth Gabbro contact, is characterized by complete recrystallization, by the development of a metamorphic fabric, and by an increase in the grain size of quartz. Iron pyroxenes, iron amphiboles, and rare fayalite are characteristic of this zone. Quartz and magnetite are the only original components of unaltered taconite that remain stable in Zone 4; calcite is the only carbonate observed. The taconite in Zone 4 contains numerous small lenses of coarse-grained minerals that apparently originated by replacement. Near the gabbro contact, larger veins and "pegmatites" have been reported (Gundersen and Schwartz, 1962).

A special study made of a hematite-bearing unit — "Red Basal taconite" — indicates that original hematite is reduced to magnetite near the gabbro contact. Definite partial reduction and replacement of hematite by magnetite is observed in Zone 2, about 3.5 miles from the gabbro contact. Within 1.5 miles of the contact, no hematite remains in this unit, and magnetite is the only oxide observed.

Metamorphism of the Pokegama and Virginia formations by the Duluth Gabbro Complex has been established by earlier investigators; detailed mineralogical studies could not be carried out by the writer because of the difficulty of obtaining samples. In Zone 2, both stilpnomelane and clinzoisite are observed to form in the Pokegama Formation from chlorite-bearing particles and matrix material. The appearance of clinzoisite is probably related to the intrusion of the Duluth Gabbro.

Compositions in terms of the Fe, Mg, and Ca end-members were determined for about 65 carbonates from the Biwabik Iron-formation, using determinations of n_0 and $d(211)$. Analyses indicate that the amount of

Mn in the carbonates is low enough to prevent significant errors in determining compositions.

Siderites from the unaltered taconite have compositions approximating $\text{Ca}_3\text{Fe}_{7.5}\text{Mg}_{2.0}$; ankerite compositions from the same zone are quite uniform at approximately $\text{Ca}_{5.3}\text{Fe}_{2.4}\text{Mg}_{2.3}$, and contain 50 to 55 mole per cent of the ferrodolomite, $\text{CaFe}(\text{CO}_3)_2$, end-member. Calcites occurring in metamorphosed taconite are distinctly iron-rich and magnesium-poor, approximating $\text{Ca}_{8.9}\text{Fe}_{1.0}\text{Mg}_{1.1}$.

No definite progressive change in the compositions of siderite and ankerite is observed along the strike of the Biwabik Formation; there is no indication of progressive removal of the iron from the carbonate during metamorphism. Calcites from the metamorphosed taconite show a progressive increase in Ca toward the gabbro and are virtually pure CaCO_3 near the contact.

The compositions of cummingtonite-grunerite amphiboles, sampled along the strike of the Biwabik Formation, were determined approximately by measurement of n_{γ} . A general enrichment in the Mg end-member toward the contact is evident; grunerite (containing more than 70 mole per cent $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$) does not occur within a mile of the gabbro.

Considerable variation in grunerite composition may reflect the nature of coexisting phases. Determinations of coexisting carbonates and grunerite in metamorphosed taconite indicate that grunerites coexisting with both ankerite and calcite are more magnesian than those coexisting with calcite alone. Although these variations agree with predictions made from the Phase Rule, it is not definitely established that the phases in question are at equilibrium, and definite conclusions are not yet warranted.

Studies of the acid-insoluble residues from the organic-rich Intermediate slate indicate that a progressive increase in crystallinity of the organic matter occurs with metamorphism. X-ray diffraction patterns of organic material from unmetamorphosed taconite are either amorphous or exhibit a broad peak characteristic of asphaltic compounds. Adjacent to the gabbro, the organic material has been transformed into both disordered graphite (d-graphite) and into completely crystalline graphite.

The present study indicates that metamorphism of the Biwabik Iron-formation by the Duluth Gabbro Complex was largely isochemical and was characterized by a progressive loss of water and CO_2 from the iron-formation. There is no evidence that the premetamorphic iron-formation consisted only of quartz and magnetite, or that the present mineralogy has resulted from large-scale introduction of material into the iron-formation through "pegmatites" and other veins, as proposed by Gundersen and Schwartz (1962). Grunerite in Zone 3, where large intrusive veins are absent, is clearly a prograde mineral.

Mineralogical data in the present study serve to locate approximately the following mineralogical isograds:

partial reduction of hematite to magnetite

appearance of clinozoisite (in the Pokegama Formation)
appearance of grunerite
appearance of hedenbergite
disappearance of hematite
appearance of ferrohypersthene
appearance of graphite (in the organic matter)

The isograds are extremely compressed; the transition between unaltered and highly metamorphosed taconite takes place within a horizontal distance of approximately two miles. The grunerite isograd, which is most accurately located, is not parallel to the present gabbro contact and diverges from it toward the east.

A schematic presentation of the mineral assemblages that develop in cherty taconite as a result of metamorphism is constructed, using the system $\text{FeO-SiO}_2\text{-H}_2\text{O-CO}_2$. Analogous diagrams are constructed for slaty taconite, using the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2\text{-O}_2$. The diagrams are consistent with known data on mineral assemblages, although such data are scanty, particularly in the highly metamorphosed taconite of Zone 4.

The use of mineralogical data to determine conditions during metamorphism is hampered by the uncertain relations between T , P_t , P_{gas} , $P_{\text{H}_2\text{O}}$, and P_{CO_2} . Values of P_{O_2} within the stability field of magnetite + quartz are indicated; such values correspond to a vapor phase composed dominantly of H_2O and CO_2 . The occurrence of fayalite in a restricted stratigraphic interval in the iron-formation near the gabbro contact apparently has resulted from the local maintenance of anomalously low P_{O_2} values by organic matter (now graphite) in these layers; the partial pressure of methane, CH_4 , could have been significant under these relatively reduced conditions.

The occurrence of wollastonite near the gabbro contact establishes a probable minimum temperature of 600°C during metamorphism; the absence of spurrite has not been established, and a maximum temperature cannot be fixed. Experimental studies on the univariant equilibrium quartz + fayalite + magnetite + graphite + vapor (QFMGV) have yielded indefinite results, but suggest that temperatures as high as 800°C could have been reached.

Temperatures of 300° to 400°C are suggested for the development of grunerite in Zone 3 on the basis of the disappearance of siderite and the iron content of the associated calcite.

REFERENCES AND INDEX

REFERENCES

- Allen, R. C., and L. P. Barrett, 1915, Contributions to the Precambrian Geology of northern Michigan and Wisconsin, *in* Geology of the Marenisco Range: Mich. Geol. Survey Pub. 18, pp. 65-85.
- Bayley, W. S., 1893, Actinolite-magnetite schists from the Mesabi iron range in northeastern Minnesota: *Am. Jour. Science*, 146: 176-180.
- Blake, R. L., 1958, A study of iron silicate minerals in iron-formations of the Lake Superior region, with emphasis on the Cuyuna district: Minnesota: Univ. Minn., Ph.D. thesis.
- , 1965, Iron phyllosilicates of the Cuyuna district in Minnesota: *Am. Mineralogist*, 50: 148-169.
- Bowen, N. L., and J. F. Schairer, 1935, Grunerite from Rockport, Massachusetts and a series of synthetic fluor-amphiboles: *Am. Mineralogist*, 20: 543-551.
- Broderick, T. M., 1919, Detail stratigraphy of the Biwabik iron-bearing formation, East Mesabi district, Minnesota: *Econ. Geol.*, 14: 441-451.
- Brown, G., ed., 1961, The X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), 544 pp.
- Burnham, C. W., 1959, Contact metamorphism of magnesium limestones at Crestmore, Calif.: *Geol. Soc. Am. Bull.*, 70: 879-920.
- Choquette, P. W., 1955, A petrographic study of the "State College" siliceous oölite: *Jour. Geol.*, 63: 337-347.
- Deer, W. A., R. A. Howie, and J. Zussman, 1963, Rock-forming minerals (5 vols.): New York, Wiley.
- Dolence, J., 1961, The Pokegama quartzite in the Mesabi range: Univ. Minn., M.S. thesis.
- Elftmann, A. H., 1894, Preliminary report of field work during 1893 in northeastern Minnesota: *Minnesota Geol. and Nat. Hist. Survey*, 22nd Ann. Rept., pp. 141-180.
- Eugster, H. P., 1959, Reduction and oxidation in metamorphism, in P. H. Abelson, ed., *Researches in geochemistry*: New York, Wiley, pp. 397-426.
- , and D. R. Wones, 1958, Phase relations of hydrous silicates with intermediate Mg/Fe ratios: *Ann. Rept. Director Geophys. Lab., Carnegie Inst. of Washington*, v. 57, pp. 193-194.
- , 1962, Stability relations of the ferruginous biotite, annite: *Jour. Petrology*, 3: 82-125.
- Flaschen, S. S., and E. F. Osborn, 1957, Studies of the system iron oxide-silica-water at low oxygen partial pressures: *Econ. Geol.*, 52: 923-943.
- Ford, W. E., 1917, Studies in the calcite group: *Trans. Conn. Acad. Arts Science*, 22: 211-248.
- French, B. M., 1964a, Stability of siderite, FeCO₃, and progressive metamorphism of iron formations: Johns Hopkins Univ., Ph.D. thesis.
- , 1964b, Graphitization of organic material in a progressively metamorphosed Precambrian iron formation: *Science*, 146: 917-918.
- , and H. P. Eugster, 1965, Experimental control of oxygen fugacities by graphite-gas equilibria: *Jour. Geophys. Res.*, 70: 1529-1539.
- , and P. E. Rosenberg, 1965, Siderite (FeCO₃): Thermal decomposition in equilibrium with graphite: *Science*, 147: 1283-1284.
- Frietsch, R., 1957, Studier över skarnbildningen i Grythyttfältet (English summary): *Geol. Fören. Stockh. Förh.*, 79: 133-160.
- Geijer, P., 1925, Eulytic iron ore in northern Sweden: *Sverig. Geol. Unders. Afh.*, ser. C, no. 324, 15 pp.
- Goldich, S. S., and others, 1961, The Precambrian geology and geochronology of Minnesota: *Minn. Geol. Survey Bull.* 41, 193 pp.
- Goldsmith, J. R., and others, 1962, Studies in the system CaCO₃-MgCO₃-FeCO₃: 1. Phase relations; 2. A method for major-element spectrochemical analysis; 3. Compositions of some ferroan dolomites: *Jour. Geol.*, 70: 659-688.

- Graf, D. L., 1961, Crystallographic tables for the rhombohedral carbonates: *Am. Mineralogist*, 46: 1283-1316.
- Grant, U. S., 1900, Contact metamorphism of a basic igneous rock: *Geol. Soc. Am. Bull.*, 11: 503-510.
- Greenwood, H. J., 1961, The system $\text{NaAlSi}_2\text{O}_6\text{-H}_2\text{O-Argon}$: Total pressure and water pressure in metamorphism: *Jour. Geophys. Res.*, 66: 3923-3946.
- , 1962, Metamorphic reactions involving two volatile components: *Ann. Rept. Director Geophys. Lab., Carnegie Inst. of Washington*, 61: 82-85.
- Grout, F. F., 1919, The nature and origin of the Biwabik iron-bearing formation of the Mesabi Range, Minnesota: *Econ. Geol.*, 14: 452-464.
- , and T. M. Broderick, 1919a, Organic structures in the Biwabik iron-bearing formation of the Huronian in Minnesota: *Am. Jour. Science*, 198: 199-205.
- , 1919b, The magnetite deposits of the eastern Mesabi Range, Minnesota: *Minn. Geol. Survey Bull.* 17, 58 pp.
- Grout, F. F., and G. A. Thiel, 1924, Notes on stilpnomelane: *Am. Mineralogist*, 9: 228-231.
- Gruner, J. W., 1922a, Paragenesis of the martite ore bodies and magnetites of the Mesabi Range: *Econ. Geol.*, 17: 1-14.
- , 1922b, The origin of sedimentary iron formation — The Biwabik Formation of the Mesabi Range: *Econ. Geol.*, 17: 407-460.
- , 1924, Contributions to the geology of the Mesabi Range, Minnesota: *Minn. Geol. Survey Bull.* 19, 71 pp.
- , 1936, The structure and composition of greenalite: *Am. Mineralogist*, 21: 449-455.
- , 1937, Composition and structure of stilpnomelane: *Am. Mineralogist*, 22: 912-925.
- , 1944a, The structure of stilpnomelane reexamined: *Am. Mineralogist*, 29: 291-298.
- , 1944b, The composition and structure of minnesotaite — a common iron silicate in iron formations: *Am. Mineralogist*, 29: 363-372.
- , 1946, The mineralogy and geology of the taconites and iron ores of the Mesabi Range, Minnesota: St. Paul, Office of the Commissioner of the Iron Range Resources and Rehabilitation, 127 pp.
- Gundersen, J. N., and G. M. Schwartz, 1962, The geology of the metamorphosed Biwabik iron-formation, Eastern Mesabi district, Minnesota: *Minn. Geol. Survey Bull.* 43, 139 pp.
- Gustafson, J. K., 1933, Metamorphism and hydrothermal alteration of the Homestake gold-bearing formation: *Econ. Geol.*, 28: 123-162.
- Hallimond, A. F., 1924, On stilpnomelane from North Wales: *Mineralog. Mag.*, 20: 193-197.
- Harker, R. I., and O. F. Tuttle, 1955, Studies in the system CaO-MgO-CO_2 . I. Thermal dissociation of calcite, dolomite, and magnesite: *Am. Jour. Science*, 253: 209-224.
- , 1956, Experimental data on the $\text{Pco}_2\text{-T}$ curve for the reaction: Calcite + quartz = wollastonite + CO_2 : *Am. Jour. Science*, 254: 239-256.
- Hoering, T. C., 1962a, The isolation of organic compounds from Precambrian rocks: *Ann. Rept. Director Geophys. Lab., Carnegie Inst. of Washington*, 61: 184-187.
- , 1962b, The stable isotopes of carbon in the carbonate and reduced carbon of Precambrian sediments: *Ann. Rept. Director Geophys. Lab., Carnegie Inst. of Washington*, 61: 190-191.
- Huber, N. K., 1958, The environmental control of sedimentary iron minerals: *Econ. Geol.*, 53: 123-140.
- , and R. M. Garrels, 1953, Relation of pH and oxidation potential to sedimentary iron mineral formation: *Econ. Geol.*, 48: 337-357.
- Hunter, R. E., 1960, Iron sedimentation in the Clinton group of the central Appalachian basin: Johns Hopkins Univ., Ph.D. thesis.
- Hutton, C. O., 1938, The stilpnomelane group of minerals: *Mineralog. Mag.*, 25: 172-206.
- Irving, R. D., and C. R. Van Hise, 1892, The Penokee iron-bearing series of Michigan and Wisconsin: U.S. Geol. Survey Monogr. 19, 534 pp.
- Jaffe, H. W., W. O. J. Groeneveld Meijer, and D. H. Selchow, 1961, Manganoan cumingtonite from Nsuta, Ghana: *Am. Mineralogist*, 46: 642-653.
- James, H. L., 1951, Iron formation and associated rocks in the Iron River district, Michigan: *Geol. Soc. Am. Bull.*, 62: 251-266.
- , 1954, Sedimentary facies of iron formation: *Econ. Geol.*, 29: 253-293.
- , 1955, Zones of regional metamorphism in the Precambrian of northern Michigan: *Geol. Soc. Am. Bull.*, 66: 1455-1488.
- , and R. N. Clayton, 1962, Oxygen isotope fractionation in metamorphosed iron for-

- mations of the Lake Superior region and in other iron-rich rocks, in A. E. J. Engel, H. L. James, and B. F. Leonard, eds., *Petrologic Studies (Buddington Volume)*: New York, Geol. Soc. Am., pp. 217-239.
- Jolliffe, F., 1935, A study of greenalite: *Am. Mineralogist*, 20: 405-425.
- Kennedy, W. Q., 1936, An occurrence of greenalite-chert in the Ordovician rocks of the southern uplands of Scotland: *Mineralog. Mag.*, 24: 433-436.
- Korzhinskii, D. S., 1959, Physicochemical basis of the analysis of the paragenesis of minerals (English trans.): New York, Consultants Bureau, 142 pp.
- Kranck, S. H., 1961, A study of phase equilibria in a metamorphic iron formation: *Jour. Petrology*, 2: 137-184.
- LaBerge, G. L., 1964, Development of magnetite in iron-formations of the Lake Superior region: *Econ. Geol.*, 59: 1313-1342.
- Leith, C. K., 1903, The Mesabi iron-bearing district of Minnesota: U.S. Geol. Survey Monogr. 43, 316 pp.
- Miles, K. R., 1943, Grunerite in Western Australia: *Am. Mineralogist*, 28: 25-38.
- , 1946, Metamorphism of the jasper bars of Western Australia: *Geol. Soc. London Quart. Jour.*, 102: 115-154.
- Moorhouse, W. W., 1960, Gunflint iron range in the vicinity of Port Arthur: Ontario Dept. Mines, 69 (pt. 7): 1-40.
- Mueller, R. F., 1960, Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron formation: *Am. Jour. Science*, 258: 449-497.
- O'Rourke, J. E., 1961, Paleozoic banded iron-formations: *Econ. Geol.*, 56: 331-361.
- Pettijohn, F. J., 1957, *Sedimentary rocks* (2nd ed.): New York, Harper, 718 pp.
- Quinn, A. W., and H. D. Glass, 1958, Rank of coal and metamorphic grade of rocks of the Narragansett basin of Rhode Island: *Econ. Geol.*, 53: 563-576.
- Ramberg, H., 1952, *The origin of metamorphic and metasomatic rocks*: University of Chicago Press, 317 pp.
- Ramdohr, P., 1927, Die Eisenerzlager des Oberharzer ("Osteröder") Diabaszuges und ihr Verhalten im Bereich des Brockenkontakts: *Neues Jahrb. Mineralogie, Geologie u. Paläontol., Beilage Bd. 55, Abt. A*, pp. 333-392.
- Richarz, S., 1927a, The amphibole grünerite of the Lake Superior region: *Am. Jour. Science*, 214: 150-154.
- , 1927b, Grunerite rocks of the Lake Superior region and their origin: *Jour. Geol.*, 35: 690-707.
- , 1930, A peculiar blue-green amphibole from the metamorphic iron formation of the eastern Mesabi range, Minnesota: *Am. Mineralogist*, 15: 65-68.
- Rosenberg, P. E., 1960, Subsolidus studies in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3\text{-MnCO}_3$: Penn. State Univ., Ph.D. thesis.
- , 1963, Subsolidus relations in the system $\text{CaCO}_3\text{-FeCO}_3$: *Am. Jour. Science*, 261: 683-689.
- Sarap, H., 1957, Studien an den Skarnmineralien der Äsgrube im Eisenerzfeld von Norberg, Mittelschweden (English summary): *Geol. Fören. Stockh. Förl.*, 79: 542-571.
- Schwartz, G. M., ed., 1956, Guidebook for field trips, pt. 1. Precambrian of northeastern Minnesota: Geol. Soc. Am., Minneapolis meeting, 235 pp.
- Smythe, J. A., and K. C. Dunham, 1947, Ankerites and chalybites from the northern Penine orefield and the north-east coalfield: *Mineralog. Mag.*, 28: 53-74.
- Spurr, J. E., 1894, The iron-bearing rocks of the Mesabi range in Minnesota: *Minn. Geol. and Nat. Hist. Survey Bull.* 10, 268 pp.
- Steadman, R., and R. F. Youell, 1958, Mineralogy and crystal structure of greenalite: *Nature (London)*, 181: 45.
- Sundius, N., 1931, Optical properties of manganese-poor grünerites and cummingtonites compared with those of manganiferous members: *Am. Jour. Science*, 221: 330-344.
- Swain, F. M., A. Blumentals, and N. Prokopovich, 1958, Bituminous and other organic substances in Precambrian of Minnesota: *Am. Assoc. Petroleum Geologists Bull.*, 42: 173-189.
- Taylor, R. B., 1964, Geology of the Duluth Gabbro Complex near Duluth, Minnesota: *Minu. Geol. Survey Bull.* 44, 63 pp.
- Thompson, J. B., Jr., 1955, The thermodynamic basis for the mineral facies concept: *Am. Jour. Science*, 253: 65-103.
- Tilley, C. E., 1936, Eulysites and related rock-types from Loch Duich, Ross-shire: *Mineralog. Mag.*, 24: 331-342.

- , 1938, Cummingtonite-bearing rocks from the Lewisian: *Geol. Mag.*, 75:76-81.
- Tuttle, O. F., and R. I. Harker, 1957, Synthesis of spurrite and the reaction: Wollastonite + calcite = spurrite + carbon dioxide: *Am. Jour. Science*, 255:226-234.
- Tyler, S. A., 1949, Development of Lake Superior soft iron ores from metamorphosed iron formation: *Geol. Soc. Am. Bull.*, 60:1101-1124.
- Ubbelohde, A. R., and F. A. Lewis, 1960, Graphite and its crystal compounds: Oxford, Clarendon Press, 217 pp.
- Van Hise, C. R., and W. S. Bayley, 1897, The Marquette iron-bearing district of Michigan: U.S. Geol. Survey Monogr. 38, 608 pp.
- Van Hise, C. R., and C. K. Leith, 1901, The Mesabi district: U.S. Geol. Survey Ann. Rept., 21 (pt. 3): 351-370.
- , 1911, The geology of the Lake Superior region: U.S. Geol. Survey Monogr. 52, 641 pp.
- Von Eckermann, H., 1922, The rocks and contact minerals of the Mansjö Mountain: *Geol. Fören. Stockh. Förh.*, 44:203-410.
- , 1936, The Loos-Hamra region: *Geol. Fören. Stockh. Förh.*, 58:129-143.
- White, D. A., 1954, The stratigraphy and structure of the Mesabi range, Minnesota: *Minn. Geol. Survey Bull.* 38, 92 pp.
- Winchell, H. V., 1893, The Mesabi iron range: *Minn. Geol. and Nat. Hist. Survey*, 20th Ann. Rept., pp. 111-180.
- Winchell, N. H., 1893, Some problems of Mesabi iron ore: *Minn. Geol. and Nat. Hist. Survey*, 21st Ann. Rept., p. 134.
- , and H. V. Winchell, 1891, The iron ores of Minnesota: *Minn. Geol. and Nat. Hist. Survey Bull.* 6, 430 pp.
- Wolff, J. F., 1917, Recent geologic developments on the Mesabi iron range, Minnesota: *Am. Inst. Mining Metall. Petroleum Engineers Trans.*, 56:142-169.
- Yoder, H. S., Jr., 1957, Isograd problems in metamorphosed iron-rich sediments: *Ann. Rept. Director Geophys. Lab., Carnegie Inst. of Washington*, 56:232-237.
- Zappfe, C., 1912, Effects of a basic igneous intrusion on a Lake Superior iron-bearing formation: *Econ. Geol.*, 7:145-178.
- Zen, E., 1960, Metamorphism of Lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont: *Am. Mineralogist*, 45:129-176.
- , 1963, Components, phases, and criteria of chemical equilibrium in rocks: *Am. Jour. Science*, 261:929-942.

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