A STUDY OF GRAPHITIC SLATES FROM NORTHERN MICHIGAN

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ABSTRACT

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by James F. Olmsted

Several occurrences of so called graphitic "slates" have been observed in the Precambrian of Northern Michigan. In all cases they are related with upper Precambrian or upper Huronian iron formations. This study was undertaken to further determine the nature of these "slates" as well as to better understand their origin.

It has been determined from published analyses and polished and thin sections studies that the "slates" are composed of pyrite, carbonaceous material, clay minerals, sericite and chert. The pyrite composes from 10% to 40% of the rock, and carbon (mostly graphite) about 10%, although in some cases, carbon may be as high as 80%. The high carbon and pyrite content suggests a reducing marine environment.

The Wauseca member of the Dunn Creek slates has been studied most intensively as it appears to be representative of several other similar graphitic "slates." The rock has actually been determined to be an argillite, as the metamorphism in most cases has not proceeded to the extent where slaty cleavage is dominant. The Wauseca member has suffered penecontemporaneous deformation as well as

dynamic metamorphism. Slump structures of several types have been identified.

The pyrite of the Wauseca member, as well as from other areas, is finely divided and is most frequently found in the form of spheres and other irregular shapes. Several rather unusual etch patterns have also been observed. Average size of the pyrite bodies is 3.24 microns which is in the range of many bacterial organisms. The close association of graphite with the pyrite and a comparison of these rocks to the Precambrian shales of Mount Isa, Australia leads to the suggestion that there is some biogenic relationship in the origin of the pyrite and the graphite.

The continual relationship between these rocks and carbonate iron formation bears out the similarity of conditions necessary for deposition of both rock types, i.e., restricted marine environment of low oxidation potential. Several samples which are closely associated with iron formations are peculiarly lacking in iron minerals but are extremely high in carbon content. This leads to the suggestion that although biological activity may have been responsible for deposition of pyrite. It also, under more extreme conditions may have inhibited pyrite deposition.

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FROM NORTHERN MICHIGAN

by

James F. Olmsted

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He also wishes to acknowledge Mr. Jack Olson of the Inland Steel Corporation for providing several drill core samples of the Wauseca member from the Iron River - Crystal Falls district, and Dr. C. E. Dutton of the U. S. Geological Survey, Madison, Wisconsin for information on the location of many outcrops in the Florence district, Wisconsin.

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INTRODUCTION

General

This study has been undertaken in an attempt to gain information concerning the origin and nature of the so-called "graphitic slates" of Northern Michigan. Attention is called to them because of their nature as well as their relationship to surrounding rocks and the bearing they may have upon the understanding of the environment of iron deposition. Highly carbonaceous rocks are not rare in Paleozoic and younger rocks but their paucity of occurrence in Precambrian terranes is notable.

The close association which the "graphitic slates" have with iron formations is not at all surprising when one considers that iron in the form of pyrite is commonly found to make up as much as twenty percent of the rock. An interesting observation has been made that in several occurrences, iron minerals appear to be lacking, yet, the close association with iron formations remains. The presence of graphitic material is strongly suggestive of an organic association. Further, a comparison of the entire assemblage with rock of known organic association gives strong evidence that some life form has played an important role in the formation of these rocks.

Only recently have the graphitic slates been studied to any degree despite the close association to many areas where iron formations have been exploited commercially. United States Geological Survey monographs thirty-six (Clemments and Smyth, 1899) and fifty-two (Van Hise and Leith, 1911) only mention the presence of highly graphitic

slates in several areas and little descriptive discussion was devoted to them. Since World War II, the United States Geological Survey has devoted considerable effort toward working out both the structure and stratigraphy of several iron bearing areas, particularly the Iron River-Crystal Falls district. This has been accomplished through the use of magnetometer surveys, drill core studies, and detailed field mapping. From these studies, two papers by James (1951 and 1954) have evolved in which the lithology of the rock types and the environments of deposition have been thoroughly discussed. James (1958) has also devoted much attention to this district in a later paper concerned primarily with the stratigraphic succession of Northern Michigan. Nanz (1952) has provided several chemical analyses of these and other similar rock types, but does not discuss in any detail the environmental factors bearing on these particular rocks.

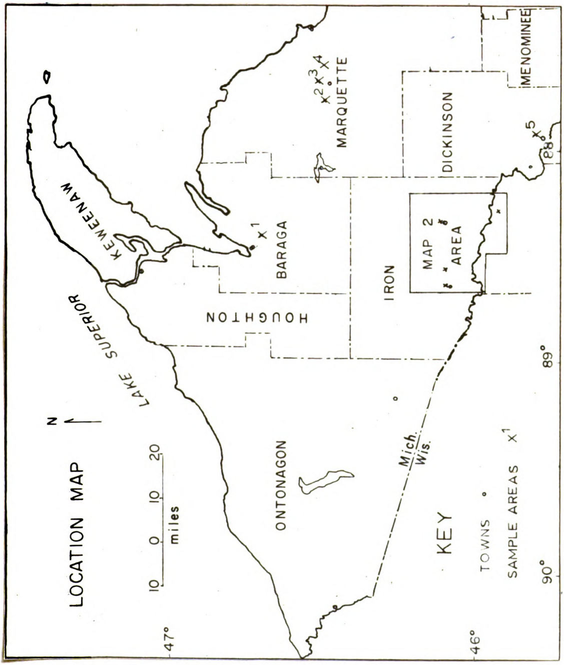
Tyler (1957) has studied a highly carbonaceous rock type which occurs about six miles north of Iron River. This occurrence which is referred to as the Morrison Creek "coal" in some cases contains as much as eighty percent carbonaceous material, but it is very low in iron content. Tyler (1957) has assigned a biogenic relationsip to the origin of this unusual concentration of carbonaceous material. It may be noted here also that highly pyritic rocks are in close association with the "coal." Even though there is much to suggest that the carbon in graphite bearing rocks to some extent can be attributed to the life forms present in the water during their deposition; there has been little enthusiasm for such an explanation. This can be readily understood when one considers that life may not have been necessary for the formation of such rocks, but may have been only contingent to the

process. Yet, the fact remains that such high contents of carbon are somewhat difficult to explain by inorganic processes even though the remainder of the rock could be formed in this manner.

Grunner (1922) has speculated that many structures found in the iron formations of Minnesota may have been developed by organisms or may be due to their influence during deposition. Several of these show indications of growth structures and for the most part are composed of highly graphitic material. Many of these forms closely resemble oolites found in other similar rock types and may well be assigned inorganic origins. Regardless of other possibilities, the inference remains that primitive organisms played some part in the formation of these and other similar rock types.

Distribution

There are several known occurrences of highly graphitic rocks throughout the Lake Superior region. Some of the occurrences in Northern Michigan include horizons within the Michigamme slates of the Marquette and Menominee districts (Van Hise and Leith, 1911). The Iron River - Crystal Falls district probably contains the most continous occurrence of highly graphitic rock in Michigan. Beds of highly graphitic and pyritic rocks are known to occur south of L'Anse in the Taylor mine area. Other sporadic occurrences are known throughout Northern Michigan such as that found north of Iron River. Each of these areas is noted on Map 1. It may be noted here that in each case the graphitic rocks of Upper Huronian or according to current United States Geological Survey terminology, either Middle or Upper Animikie in age. In no case, to the writer's knowledge, are any highly graphitic rocks


LOCATION MAP
10 0 10 20
miles
N
LAKE SUPERIOR
KEWEENAW
HOUGHTON
BARAGA
MARQUETTE
ONTONAGON
IRON
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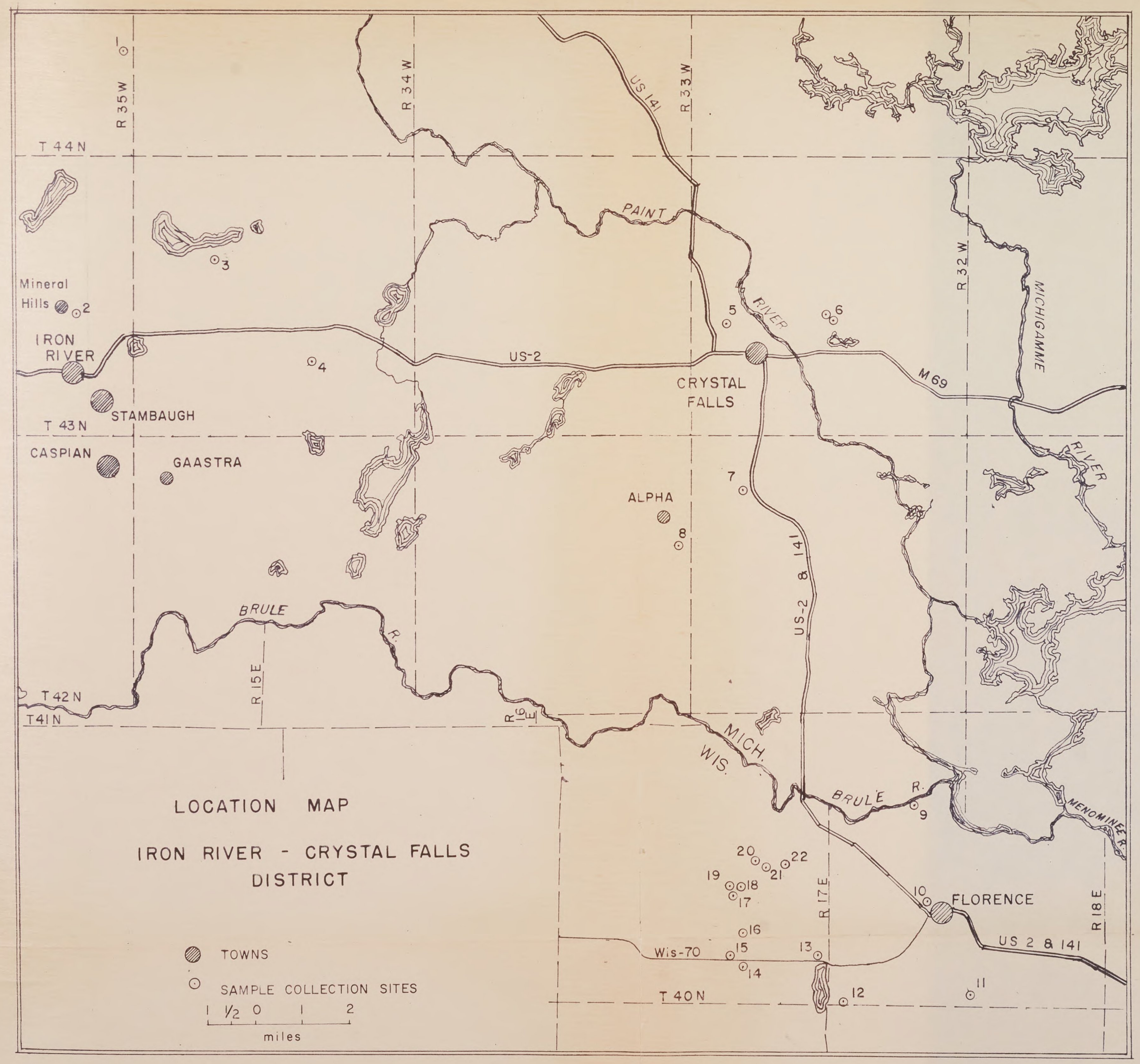
MENOMINEE
MAP 2 AREA
Mich.
Wis.
KEY
TOWNS
SAMPLE AREAS x1
47°
46°
90°
89°
88°


LOCATION MAP
IRON RIVER - CRYSTAL FALLS
DISTRICT
TOWNS
SAMPLE COLLECTION SITES
1/2 0 1 2
miles
R 35 W
R 34 W
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R 32 W
T 44 N
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T 42 N
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R 15 E
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R 17 E
R 18 E
US 141
PAINT
RIVER
US-2
M 69
MICHIGAMME
RIVER
US-2 & 141
BRULE
R.
MICH.
WIS.
BRULE R.
MENOMINEE R.
US 2 & 141
Wis-70
Mineral Hills
IRON RIVER
STAMBAUGH
CASPIAN
GAASTRA
CRYSTAL FALLS
ALPHA
FLORENCE
1
2
3
4
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found in the Lower or Middle Huronian assemblages.

The sample areas are shown on the accompanying map. As can be seen, there are three general locations. The area which has been most frequently referred to in this study is the Iron River - Crystal Falls district and is shown in some detail on Map 2. The second is called the Taylor mine area and the third rather broad area includes the Marquette iron mining district.

The samples from the north side of the Iron River - Crystal Falls basin were all obtained from drill cores; the remaining ones are from test pits and outcrops. Because the rapidly weathering pyrite may have been removed in part, there is some doubt as to the usefulness of samples obtained from outcrops. Several samples which are of very low specific gravity were collected from surface outcrops, but in no case were any such samples found in drill cores. Samples of this type were collected from both the Florence and Taylor mine areas. In both cases this rock type is associated with cherty iron formation. Thirty samples were collected in the field, many of which upon later investigation were found to be of limited value.

Samples were collected from three areas in the Marquette district. One of these is a graphitic slate which is associated with the Bijiki iron formation. The other two, in general, are from the lower Michigamme slates. These samples are all good slates showing the typical slaty fracture cleavage. The pyrite and graphite content vary in these samples with the pyrite usually occurring in well-defined bands. Weathering effect does not appear to be intensive.

One sample was collected from the Morrison Creek area which has been cited above. This sample is not the type described by Tyler as "coal" but is strikingly similar to that found in the cores of the

Iron River _ Crystal Falls area. Its stratigraphic relationship to the Iron River - Crystal Falls district is not known, but some speculation as to their similarity could be made.

Although the samples from the Iron River - Crystal Falls area are not necessarily representative of all the other samples, they are representative of most and extensive treatment has been given to them. Much of the structure and stratigraphy of other areas is either extremely complicated or, as in the case of the Taylor Mine area, not well known. For these reasons, the Iron River - Crystal Falls district has been used more or less as a type area and the others may be compared to it, furthermore, this area has been extensively studied and is well described.

Stratigraphy of the Iron River - Crystal Falls District

As previously mentioned, the majority of the samples were collected from the Iron River - Crystal Falls district. As shown on the map, this area covers the southern half of Iron County and extends southeastwardly into Florence County, Wisconsin. The district is generally a three-cornered basin with apices at Iron River on the west, Crystal Falls on the northeast and Florence, Wisconsin on the southeast (Dutton, 1949).

The basin is outlined for the most part by the Badwater greenstone which is a thick succession of altered submarine lava flows which ranges in thickness from several feet to several miles (James, 1958). In the area east of Crystal Falls the greenstone is absent and, therefore, the succession within the basin lies directly on top of the earlier slates (James, 1958).

Above the Badwater greenstone is a thick succession of slates and greywackes known as the Paint River group. They are outlined below.

TABLE 1

Paint River Group	Fortune Lakes Slate
	Stambaugh Formation (overlapped by Fortune Lakes slates)
	Hiawatha Greywacke (slate south of Alpha)
	Unconformity
	Riverton Iron Formation
	Dunn Creek Slate (upper 50' - 100', Wauseca Member)
	Badwater Greenstone

The Dunn Creek slate consists of about 800' of greywacke and slate similar in physical appearance to much of the Michigamme slate (Pettijohn, 1946). The upper 50 to 100 feet has been named the Wauseca member which is the primary concern of this study. It has been described by James (1951, 1958) as a black pyritic, graphitic slate. The type area is at the Wauseca mine located in Mineral Hills just north of Iron River. Due to its nature, it is very weakly resistant rock and seldom outcrops, but is commonly encountered in mines and test pits throughout the district (James, 1951). Descriptions will be deferred at this point and a complete discussion taken up later. It may be pointed out here, though, that the Wauseca member has been subdivided into two units, the upper laminated and the lower conglomeratic or "speckled grey." The "speckled grey" is consistant and distinctive enough to be recognized throughout the district and is often referred to as a marker unit (James, 1958).

Above the Wauseca member and apparently conformable to it is the Riverton iron formation. It is typical of the Precambrian iron

formations in the Lake Superior region, being originally composed mainly of chert and siderite. Its thickness ranges from 100 to 600 feet, the variation being due presumably to the nature of sedimentation (James, 1958).

The upper three formations are of little interest here so their description has not been included. These other formations were deposited above a somewhat important unconformity and they are all for the most part clastic in nature.

Structure of the Iron River - Crystal Falls District

The detailed structure of the district is extremely complex and at this time is not completely known. Only a general consideration will be presented here which is believed to be sufficient to fit the argument that will be presented later. As shown on the U.S.G.S. Map #MF 225, the district has now been determined to be a three-cornered basin (Dutton, 1949). Each of the corners are intensely folded into tight anticlines and synclines. Pettijohn (1952) noted that in the Paint River outcrop area there are four anticlines and synclines within a distance of two thousand feet. Both Pettijohn (1952) and Dutton (1949) have expressed the observation that there is little or no evidence of faulting in their respective map areas and that the rocks acted as incompetent bodies in most cases. Some faulting has been recognized by Dutton (Personal Communication, 1961) in the area near the southern corner of the basin. The structure in this part of the district is somewhat confusing. Due to the incompleteness of intensive study it has not been, as yet, satisfactorily resolved. The faulting has complicated the picture such that some doubt exists as to the numbers

of iron formations present in this area, although, it is strongly felt that there may be two or possibly three (Dutton, Personal Communication, 1961).

In the Iron River corner of the district the folds are generally east trending with a westerly plunge, but several are doubly plunging. In several examples, the limbs of folds are nearly sheared out and several folds are overturned (Dutton, 1949). From the data presented on Map MF 225, none of the structures extend over a great distance. Folds converge with the elimination of one structure giving away to the beginning of another larger one.

The troughs of synclines are the areas of concentration of the iron ore. The concentrations are probably due to thickening as well as trapping of the oxidized ore by the less permeable footwall formations (Clemments and Smyth, 1899). Also, it has been pointed out that in these areas thickening of the footwall strata has given rise to many erroneous thickness measurements of the Wauseca member. Several authors (Dutton, 1949 and James, 1951) have stated that the Wauseca member has behaved almost plastically in its deformation.

Upon examination of the samples, many features are seen that can be related to the deformation of the rock. This in turn has been superimposed upon what appears to be movement that took place during or immediately subsequent to deposition. James (1958) has suggested that the lower "speckled grey" phase of the Wauseca member may have been the result of slumping. Evidence that is believed to support this will be given later in a more appropriate section.

Physical and Chemical Environment of Deposition

It long has been accepted that black shales are deposited under reducing conditions. Many authors have discussed such environments and the facters involved in their existance. Most of the literature is concerned with Paleozoic or later sediments and it is readily accepted that bacteria of both aerobic and anerobic types play some part in their formation. In the case of Precambrian rocks, organisms frequently have been suggested as a means of formation (Grunner, 1922 and James, 1951), but undisputable proof of such origin is difficult to find.

James (1954) has thoroughly discussed the pyrite bearing black slates of the Iron River - Crystal Falls district and has outlined the environment necessary for its deposition. Garrels (1960) has gone into great detail to derive diagrams in terms of oxidation reduction potential (Eh) and hydrogen ion concentration (pH) to show the stability fields of several minerals in these terms. Pettijohn (1949) has summarized the work of several authors in his discussion of euxinic environments and black shale deposition. Strøm (1939) has studied several Norwegian fjords in which the dissolved gasses at the bottom are dominantly hydrogen sulfide. These articles have been used as a guide in the following discussion of environmental conditions, both physical and chemical, which may have existed at the time of deposition of these black slates.

Numerous writers have pointed out that barred or restricted marine basins are conducive to stagnation and the resultant depletion of the oxygen from the deeper water. In his discussion of Norwegian

fjords, Strøm has shown how layering of the water will cut off the circulation to the lower levels, thus likewise, cut off the oxygen supply. In order to create conditions suitable for the primary deposition of pyrite there must be a lowering of the oxidation reduction potential to a point of at least zero on the scale and more probably even into the reducing range. Therefore, there must be material to oxidize, thus, consuming the available oxygen. Such conceivably could be accomplished by two means.

Organic debris is material that finds its way to the bottom of basins in a state capable of being oxidized. Any inorganic material that is introduced into a depositional basin is normally in an oxidized state and therefore is not usually capable of being further oxidized. The other alternative is the oxidation of material that may be introduced in a lower valence state through hydrothermal or volcanic emanations. Very likely, the change in organic matter takes place through the action of anerobic bacteria or is at least aided by their activity. Thus, there are two possible alternatives to which we might ascribe the deposition of primary iron sulfides. The former alternative has been used in part in the formulation of the disputed source bed concept (Walpole, 1958 and 1960; and Knight, 1957).

The presence of carbon in abundance is not readily explained, at least, by use of a hypothesis involving volcanic emanations. It appears that the reduction of carbonates to their respective elements by purely chemical means would require conditions more extreme than those normally found in any sedimentary environment. The reduction of more complex organic material to simpler molecules is typical of the activity of bacteria. The final step of reducing these substances to free carbon or graphite would probably require the more severe

conditions provided by the subsequent metamorphism of the rocks.

One of the objectives of this work is to discover evidence as to which of the above mechanisms was most prevalent in the origin of both the graphitic material and the pyrite. Love and Zimmerman (1961) have shown that the Precambrian Mount Isa shale of Australia contains a great deal of syngenetic pyrite and they have shown that its formation is involved with living organisms. These rocks, from description and photographs, appear to be somewhat similar to the rocks of this nature found in the Iron River - Crystal Falls district. The similarity is very suggestive of an organic relationship in the origin of these black slates.

As is shown in Fig. 1, the oxidation potential of the water must be near or below zero in order to precipitate pyrite. These conditions are what James (1954) has referred to as the sulfide facies. The Riverton iron formation immediately above the Wauseca member is in the field of carbonate deposition. Near the top of the Wauseca member, one sample was found showing primary pyrite and siderite in close association. There is also abundant carbonaceous material, This is in agreement with Garrel's (1960) diagrams which show that only slight variations are necessary in Eh in the change from sulfide to carbonate deposition. Evidently, the fields overlap to some degree. James (1954) depicts the lower most part of the basin as that of sulfide deposition; this is in agreement with Strøm (1939) and many others who have studied such deposits. The conditions necessary for the deposition of pyrite through inorganic processes should also be necessary for biogenic deposition. This will be discussed in greater detail in a later section.

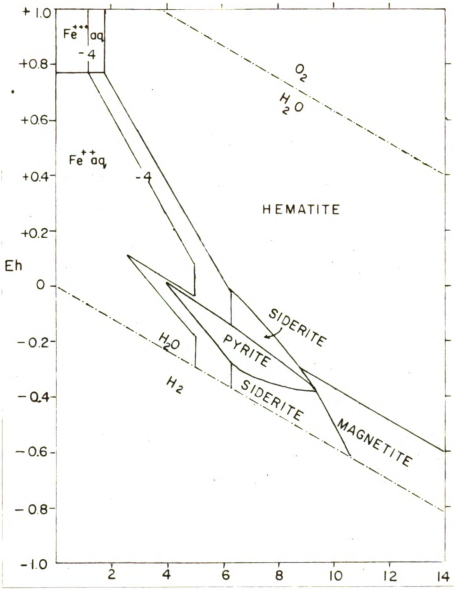

Fig. 1

Other than carbonaceous material and pyrite, the remainder of the rock is probably composed of silica and argillaceous material. Chemical analyses of several samples cited in the literature show that silica ranges in content from thirty-five to forty-five percent. Little of this can be seen in thin sections as the rocks for the most part are a dense opaque black, but where thin sections can be used most of the

non-opaque material is extremely fine-grained quartz. Alumina is relatively abundant, showing the presence of some clay minerals which undoubtably make up the remainder of the mineralogic composition.

Of those samples which are high in pyrite, the total of the oxides that are most likely to occur in silicate are in the range of 50% to 60%. Considering that all of the K_2O is in clay minerals, their average amount can be estimated. From such estimates the clay minerals make up from 20% to 30% of the rock; the remaining silicate is then some form of quartz (probably deposited as chert).

Methods used

As originally proposed, this study was undertaken to discover evidence relating to the origin of the graphitic slates and their somewhat anomalous high content of carbon. To achieve this, several methods of study were outlined which included petrographic analysis and chemical methods which appeared applicable. Neither of these in the exact sense of their meaning were found useful.

It was found that only in a few isolated cases were thin sections of any use. The high contents of carbonaceous material and pyrite rendered the sections opaque. To the writer's knowledge, there is no suitable method for removing such material as graphite from a thin section. Polished sections were then turned to as an alternative means of descriptive study. These have proven to be valuable in the description and elucidation of many of the factors which have been applied to the final conclusions.

During the study, it was found that the pyrite may have some bearing upon the solution to the problem of origin of the graphite.

After a search of the literature for methods of studying the pyrite, it was found that a comparison to the Mount Isa shales of Australia might be instructive. The theory that the pyrite may have some relationship to living organisms, as postulated by Love and Zimmerman (1961), was investigated. Several attempts were made to isolate organisms by methods outlined by the above authors from the pyrite but were unsuccessful. A comparison of shapes and sizes of the pyrite spheres to those of Mount Isa was resorted to, to show the striking similarities which the two rock types possess.

It was hoped that a trace element analysis would be instructive to the understanding of the environmental conditions under which deposition of the graphitic rocks took place. There are several comparative methods which are being used which appear to show marine versus non-marine deposition. Unfortunately, it has been impossible to complete these studies at this time. It is hoped that a trace element study can be completed in the near future.

Several x-ray powder photographs were made which have been very helpful in understanding the present state of the graphite. Some of these have been included in the appendix section.

An attempt was also made to isolate any organic material from the rock by methods outlined by Tyler (1957). The results of this experiment were apparently negative, which seems to have some bearing upon the failure to isolate any organisms from the pyrite.

No complete chemical analyses were made due to the complexity of such work. As an alternative, several chemical analyses were obtained from literature,four of which have been included in Appendix B. These have been instructive as to the mineral assemblage present as

well as bringing out the fact of the very high iron and carbon content of the rock. This has made a basis for the discussion of the conditions of deposition in relation to the conditions of the iron formation itself.

ROCK DESCRIPTIONS AND PETROLOGY

General Considerations

For descriptive purposes, two types of graphitic slates have been defined. This division is based upon the pyrite content of the rock which is manifested in the color and specific gravity. The first is the highly pyritic type which is almost entirely limited to the Wauseca member. A somewhat similar pyritic slate is found in association with the Bijiki iron formation north of Champion Station as well as some lenses of black slate which occur within the lower Michigamme. The second type recognized is non-pyritic. This is primarily found near the southern extremity of the Iron River - Crystal Falls district which has been called the Florence district and at the Taylor Mine area. Both the pyritic and non-pyritic slate can be further subdivided into distinct groups depending upon the internal structure of the rock. The subdivisions are as follow:

TABLE 2

Pyritic	Bedded - often brecciated and folded
	Massive - containing numerous conglomeratic fragments
Non-pyritic	Bedded
	Massive

Although the actual composition of the bedded and massive types is similar, the subdivision is necessary to describe the different histories that may have effected each during and immediately subsequent to

deposition. Several structures show evidence of submarine slumping which introduces what is thought to be important evidence upon the question of primary or a secondary origin of the pyrite. Similar structure is found in the non-pyritic type, which indicates some similarity of environment for both.

Wauseca Member

The Wauseca member is high in pyrite and has a specific gravity ranging from 2.5 - 3.1. Color varies somewhat from a light grey to black, often modified by the typical brassy color of pyrite. Due to the abundance of pyrite, the rock is much harder than the more graphitic types and somewhat more brittle. Most of the samples found in the Wauseca member have a conchoidal or hackley fracture but some (in particular, the well-laminated) were found to split along bedding planes.

There are two specific types of structures found in the Wauseca member: the lower massive and somewhat conglomeratic "speckled grey" which has a rather wide distribution (James, 1958) (Plate 1); and the upper laminated (Plate 3). The "speckled grey" is a massive homogeneous rock containing irregular fragments of what appears to be an earlier laminated slate. Commonly, the fragments are oriented with respect to their longest axes suggesting the bedding direction. The fragments are frequently darker in color than the matrix and in some cases much harder. This was found to be due to quartz or chert which in some instances made up most of the fragments. Others are almost entirely clay minerals and quartz with enough graphite to give the dark color. Commonly, fragments can be seen that are almost wholly pyrite.

Under high magnification, the matrix material appears to consist

of submicroscopic matter which according to the chemical analyses is probably clay minerals, quartz and carbonaceous material. In addition, well-defined blebs of pyrite can be seen which show random shapes, some being angular while others are well-rounded (Plate V). It is frequently impossible to see any relationship between the pyrite and the enclosing material. This form of pyrite will be discussed further in a later section.

The laminated type (Plate III) commonly referred to as being stratigraphically above the "speckled grey" (James, 1958) is noticeably devoid of fragments although some brecciation is found. The individual laminae are recognized by differences in pyrite, carbon content, as well as by textural differences. Under the microscope, the highly pyritic laminae appear similar to the speckled grey, whereas, the dark layers show much less pyrite and are often entirely black. The boundaries of the layers are sharp, but frequently show irregularities which might be caused by contemporaneous deformation. The laminae have thicknesses ranging from 1 to 4 mm., but in some cases are as much as a centimeter thick.

In some of the samples from the Wauseca member a rather well developed foliation may be found and in each case the pyrite appears to be recrystallized. The pyrite is then usually found in small veinlets and irregular blebs rather than having an even distribution throughout (Plate VI). When the rock is broken along a cleavage plane, the broken surface usually has a glossy sheen similar to that of graphite and has the characteristic graphite streak. Under the microscope, this type appears similar to the speckled grey, but the large veins and cubes of pyrite often contain a darker yellow, softer

mineral believed to be chalcopyrite, showing the presence of copper. It may be interpreted that this foliated slate has been subjected to a higher degree of metamorphism due to folding. The possibility that mineralizing solutions accompanied the folding is indicated by the chalcopyrite. The alternative is recognized that copper may have been included in minor amounts in the original sediments.

Non-Pyritic, Highly Graphitic Type

The non-pyritic slate commonly occurs in the southern extension of the Iron River - Crystal Falls district as well as the Taylor Mine area. The color is very dark bluish-grey to black and the streak of the rock is graphitic and shiny. Due to the high content of carbon and lack of pyrite, the specific gravity is much lower than that found in the Wauseca member. The fracture of the rock is irregular and hackley in most instances, but where bedding is more evident it will cleave along the bedding planes. In one outcrop a definite slaty cleavage was noted; such occurrences are apparently rare and not characteristic of the rock. Due to the high content of graphite, the rock is soft and readily scratched by a sharp point. Nevertheless, it is a very tough rock and is not easily broken by a blow of a hammer.

Commonly seen structures are bedding or laminations, and small rounded blebs surrounded by lighter grey weathered material which may be the alteration product of original pyrite. Small veinlets of quartz can often be seen. These have been interpreted as products of metamorphism. When inspected under a hand lens, the surface of the rock appears spongy, which may be the result of weathering. In some samples, folding of the laminae can be seen. This can be on a large scale

involving bedding up to a centimeter thick and again on a scale so small that a hand lens or low power microscope is necessary to see it.

The explanation of the lack of the pyrite in these samples is somewhat of a problem. In each case, the outcrops are in close association with iron formations, yet, they are notably low in iron. There appear to be three choices of explanation: first, the iron may never have been deposited; second, it may have been removed during the metamorphism; and three, weathering may have been responsible for its removal. None of these are totally satisfactory as an all-inclusive explanation.

Under the microscope, it appears as an extremely fine-grained rock. For the most part, it appears to consist of a randomly oriented, flaky aggregate. Generally, bedding can be recognized and is usually somewhat contorted. Some larger fragments are commonly seen which appear to be composed of material similar to the remainder of the rock. These are usually randomly distributed and fairly rare. A few flecks of highly birefringent material is present. In a few cases, small fragments or blebs of pyrite can be seen.

Minor Structures

As previously discussed, the environment of deposition of black shales is presumed to be in a restricted basin. This is well supported by the presence of sulfide minerals as well as large amounts of carbon. The shape of such a basin would have a great influence upon the final characteristics of the material being deposited. The slope of the sides of the basin would control any movement of the sediments subsequent to deposition. That such penecontemporaneous slumping has taken place

becomes apparent upon close inspection of the rock.

The angle of slope necessary for submarine slumping is variable depending upon the nature of the material composing the sediments (Pettijohn, 1957). In some cases where sediments are high in water content, slumping may occur on a slope of only a few degrees. The mechanisms which cause such slumping may also be variable. The weight of overlying sediments higher on the slope is a possible cause. A sudden shock or earthquake is frequently considered as the cause for such slumping. Regardless of the cause, it will be made evident that slumping or contemporaneous deformation has taken place in the formation of many of the rocks of the Wauseca member.

One problem that is somewhat difficult is the determination of origin of deformational structure found in many of the samples. Several authors (Dutton, 1949 and Pettijohn, 1946, 1952) have discussed the structure of the Iron River - Crystal Falls district and it is evident that extensive folding has taken place. Many of the structures found in the samples appear to be related to tectonic folding, but several are also randomly oriented and irregular in shape. The later type appear to be a result of some type of slumping or movement contemporaneous or nearly so with deposition.

Tectonic folding would result in oriented drag folding along the limbs of structures. Such minor folds are oriented with respect to the deformational forces and consequently show a relationship to the major structure as would the cleavage which may result (Pettijohn, 1957). Unfortunately, none of the samples were oriented in the field and in many cases the structure is not well known so the relationship of minor to major structure cannot be determined. Few of the samples show any

fracture cleavage, but in isolated cases a regular pattern of veining can be seen. The typical structure that is associated with such veining and cleavage is regular and continues over a reasonable distance (two to three inches). In contrast to these regular structures, several seem to have little or no continuity within a small area. This type of structure consists of folding of beds in a random manner, folding of a group of beds with no translation of the folding into adjacent beds and folding of beds around fragments (Pettijohn, 1957).

Both types of structures cited above can be recognized in many of the samples. There is no need here to prove the existance of tectonic deformation, as this has been readily demonstrated in numerous instances. The problem at hand is that of showing that contemporaneous movement or slumping has taken place and is responsible for many of the structures found. Some of the criteria frequently used for this determination is cited below.

1- Notable variations in thickness of the contorted zone (Miller, 1922)

2- A very irregular upper surface of the folded zone and a rather regular under surface (Miller, 1922)

3- Bulging of immediately overlying strata over little anticlinal folds (Miller, 1922)

4- The distinct evidence of the filling of the depressions on the upper surface of the corrugated zone before the general layers of overlying materials were laid down (Miller, 1922)

5- Discontinuity of the structures (Pettijohn, 1957)

6- Breaking or crumpling of beds giving the effect of a pseudoconglomerate (Pettijohn, 1957).

Many of the above noted criteria are present in the Wauseca member and much of the structure is interpreted to be due to slumping, sliding and flowing contemporaneous with deposition.

Some of the mechanisms of slumping and flowing have been noted. Highly plastic materials as these sediments are presumed to have been at the time of deposition, would be susceptible to movement from minor effects. The rocks containing high amounts of pyrite, which was probably forming during the early stages of burial, were probably sediments of rather high density. Such heavy material would be subject to movement or slumping with the slightest disturbance. Some of the sediments in which chert was being precipitated along with large amounts of pyrite may have been subject to early lithification. These deposits may have been included in later slumping which caused their brecciation or fragmentation. In many examples the results of such brecciation can be seen and included with what was originally more plastic material. It is difficult to determine if any such flow features are present in the graphitic material from other areas. In some cases where bedding is evident in the highly graphitic rock,folding can be seen. Criteria for contemporaneous deformation is evident here, also, but is difficult to show positively. This is due to a lack of contrast between the beds and the very frequently massive nature of the rock.

In the cases where bedding can be observed in the highly graphitic rocks, several structures can be seen. Stringers of material from the finer grained beds have been squeezed into the surrounding more coarse beds. Small folds in a particular bed are not represented in adjacent beds and folds in adjacent beds have no relationship to one another. All of these characteristics are presumed to be typical of contemporaneous deformation.

The presence of abundant fragments in the lower part of the Wauseca member as described by James (1958) is again evidence of

slumping or submarine flow. Pettijohn (1957) has stated that, "If the solid/fluid ratio exceeds some critical value, Newtonian flow ceases and the deposit is not graded." This appears to be the case with the "speckled grey" which shows fragments of several different sizes in no particular gradational pattern. Thus, the suspension must have been viscous enough to prevent normal settling according to Stoke's law. Another factor that is readily noticeable is the orientation of the fragments into a lineation which probably represents some sort of "bedding" parallel to the direction of flow.

James (1958) has stated that, "The fragments in the massive type are of the same rock type as the matrix." This conclusion deserves some comment. For the most part, these fragments are of a darker color than the matrix and the pyrite in them is much more coarse. Upon close examination, it was found that the fragments were high in chert and clay minerals (some of which appear to be chlorite).

Two samples of the less pyritic and graphitic material from below the Wauseca member were examined and found to be similar in color and nature to the fragments. They are more like the Dunn Creek slates, in fact, one sample is from an area mapped as the Dunn Creek formation.

The above descriptions make evident a complex history which may have some implication on the environment of deposition of the Wauseca member. Again, reconsider the stratigraphy of the member.

The lower, primarily clastic Dunn Creek formation shows many variations in conditions. Pettijohn (1946) has mapped much of this formation on the east side of the basin south of Crystal Falls. He notes pyritic beds as well as some carbonate iron formation. At the horizon immediately below the Wauseca member, the Dunn Creek formation

consists of a black slate composed of some pyrite, chert, and argillaceous material along with small amounts of carbonaceous material. The only difference here between the Dunn Creek itself and the Wauseca appears to be the higher content of clastic material in the Dunn Creek in comparison to the amount of carbonaceous matter and pyrite.

The lower part of the Wauseca member is a massive sometimes rather choatic assemblage composed of fragments of black slate enclosed in a typical highly pyritic matrix. The fragments are frequently surrounded by a swirl of the matrix material which suggests that the particle was rolling or twisting as the slurry moved along the slope. The upper part of the member is well laminated and frequently shows disturbance of the beds. In some examples, the upper bedded material shows little or no effects of disturbance. There are few fragments included, but those which were observed were surrounded by the bedded material which appeared to flow around them. A sharp transition to the overlying iron formation is generally typical of the upper part of the member (James, 1951).

In some cases, brecciation of the upper part of the member was observed. This disturbance must have been subsequent to lithification of at least part of the rock. The matrix material as well as the fragments here are frequently similar to cherty iron formation, but large amounts of pyrite as well as graphite are present. The above observations suggest a sequence of events that might have been somewhat as follows.

The inflow of clastic material gradually decreased during the later stages of the Dunn Creek deposition so that with the beginning of the deposition of the Wauseca member, only small amounts of clay

minerals were being introduced, thus causing the relatively high carbon and pyrite content. As the lower part of the Wauseca member was deposited in a highly viscous state, some movement due to its weight would begin to take place. If there were any interbedding at all, some of the lower more clastic material would be included to some degree in the slump.

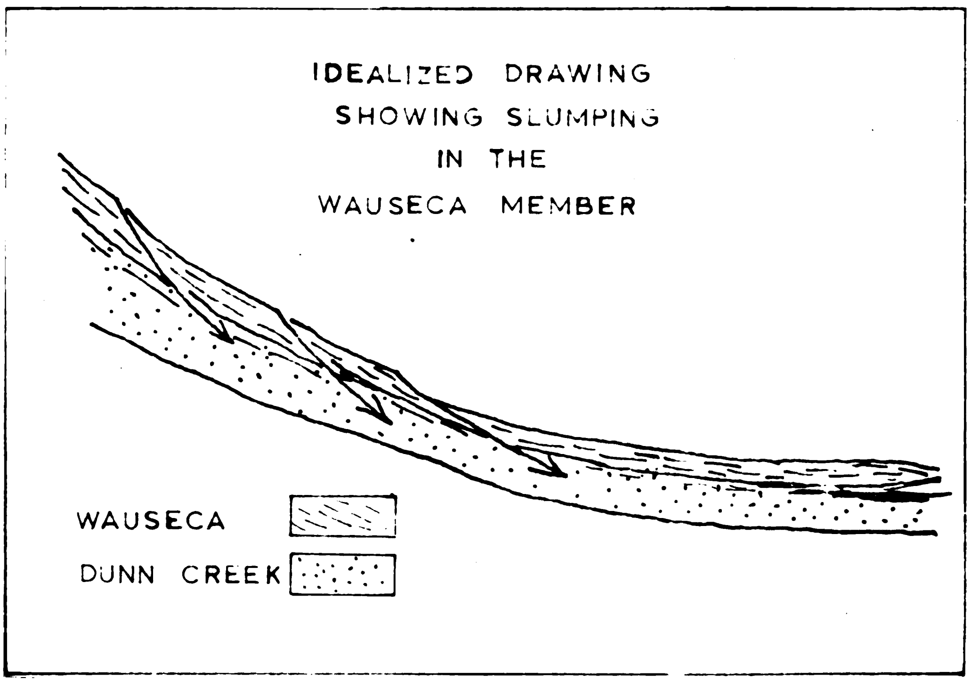

Fig. 2.—— The lower stipled represents the Dunn Creek and the upper is the Wauseca. Some interbedding is possible. The right side of the figure shows how the Wauseca may have flowed across the basin completely destroying the bedding, thus, forming the massive "speckled grey" phase of the Wauseca.

The first slumping would take place toward the center of the basin due to overlying weight. With less support, the sediments higher on the slope would be included in the slumping. The reverse of this could also be true with initial slumping higher on the slope due to a greater angle of the slope. In either case, enough mixing took place to give a resultant rock which has included fragments from the underlying beds. At no time did the material become fluid enough so that differential settling velocities were active.

As material was added to the lower part of the basin, the slumping decreased to a minor amount so that only distortion of the bedding resulted as opposed to the previous total destruction of any bedding. Thus, as we go up in the column, very subtle changes take place at least in some areas and more regular bedding becomes apparent. In the areas where, as James (1958) describes, there is no bedded phase, rapid slumping may have continued. In other areas bedding became dominant in the upper part of the formation.

The fact that in all cases where any bedding is disturbed, the bedding being shown by changes in pyrite content, the highly pyritic beds are distorted and folded as well, giving good evidence for the syngenetic origin of the pyrite. This fact the writer believes is well displayed in each case and is the basis for much of the reasoning in the following section.

ORIGIN OF THE PYRITE AND GRAPHITE

The previous discussion makes evident the primary nature of the pyrite. The presence of large amounts of graphite as well as primary pyrite is important criteria as to the environment of deposition. The many primary sedimentary structures and the low amounts of clastic material in these sediments also indicate the conditions under which deposition occurred. Further evidence as to the origin of these graphitic "slates" can be obtained from examination of the rock under high magnification.

Several factors have been established which demonstrate the primary nature of the pyrite. The shape and size of the individual grains are believed to be significant (Love and Zimmerman, 1961). The distribution of the pyrite in relationship to bedding and structure has been used as criteria for the primary nature of such deposits (Love and Zimmerman, 1961). The lack of any other sulfides* makes a hydrothermal origin for the pyrite unlikely. The lack of other sulfides also makes the theory of volcanic emanations into the depositional basin less likely. An analysis for such trace elements as chlorine, fluorine and other volcanic associates might provide valuable information concerning such deposition.

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*Some chalcopyrite was determined to be present in secondary or recrystallized pyrite in association with veining and fissures.

Evidence for a suitable environment for the preservation of organic material during deposition can be obtained by considering the pyrite. The stability fields of pyrite and siderite are shown in Fig. 3. This diagram shows only those ranges which might be encountered under normal marine conditions. A third parameter which controls the size of the stability fields is the concentration or more specifically, the activity of the components. Referring to Fig. 1, note the line marked with a (-4) which parallels the hematite field. This notes the increase of the stability fields when the activity of iron is changed from 10^{-6} to 10^{-4}. It may be noted that this increase has its major effect outside of the range of marine environments. Also, note, that with very small concentrations of both iron and sulfur, pyrite remains within the range indicated.

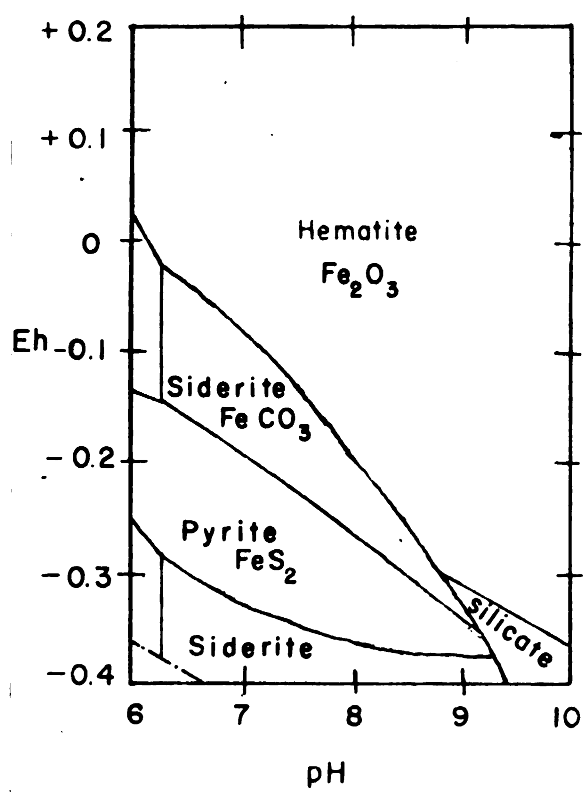

Fig. 3.-- Modified after Garrels (1960).

From this data, the conclusion may be drawn that it would be normal for pyrite to occur in rocks deposited under conditions suitable for the preservation of organic materials. The actual process by which pyrite was found is difficult to explain, but based upon the presence or organic material a suggestion may be made that the association is more than incidental. Even though some organic activity may be responsible for the formation of the pyrite, the anerobic conditions would also be necessary for pyrite to be preserved. Further evidence for such a relationship can be found in the nature of the presently existing carbon.

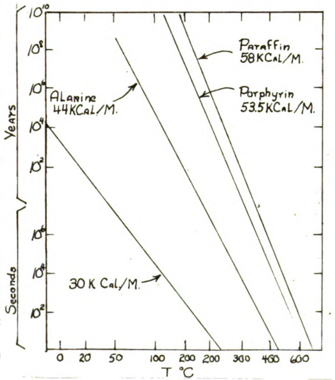

Fig. 4.-- After Ableson (1959).

The poorly crystalline nature of much of the graphite appears to be evidence of organic origin of this material. See Plate VIII. Ableson (1959) has discussed the association of organic material and carbon in rocks and the stability of such organic compounds. As shown in Fig. 4, many organic compounds are stable to high temperatures, but with great periods of time even the most stable compounds are broken down at much lower temperatures. The kinetics of the reactions which reduce organic materials to carbon indicate that temperatures encountered in deep burial are sufficient to yield free carbon in a period of time consistant with the age of these rocks. Tyler (1957) has pointed out that the severity of metamorphism other than that caused by folding in the Morrison Creek area is not great. From evidence presented by the several authors who have worked in the Iron River - Crystal Falls district, the metamorphism there is also of limited extent in so far as temperatures are concerned. Yet, it can readily be imagined that temperatures even as high as 150°C - 200°C may have been reached, thus, providing the driving energy to dissociate many of the organic compounds which may have been originally present in the sediments. Further, it has been shown that where the grade of metamorphism has reached the extent where about 70% of the carbon is present as fixed carbon, very little in the way of organic materials such as spores can be found (Wilson, 1961).

Such evidence as outlined above provides a reasonable basis for believing that gradual decomposition of organic material produced the free carbon. The process by which graphite is produced from amorphous carbon is unknown for geologic environments. Tyler (1957) has pointed out that the Morrison Creek occurrences have been graphitized to about

the same extent as that produced by temperatures of 1250°C in the graphitization of coke. He further notes that there is no evidence of temperatures of this magnitude found in this area. It is also safe to say that the same is true of the entire assemblage which constitutes the sedimentary sequence of the Iron River - Crystal Falls district. Tyler (1957) further concludes that the graphitization of these materials is probably more a function of high pressures and geologic time, rather than of high temperatures. In the light of such processes, causing the gradual reduction of the complex organic materials to simpler compounds, ultimately lead to the production of amorphous carbon and graphite.

Forty-one polished sections were studied in an effort to characterize the nature of the pyrite and its associations with both itself and the surrounding matrix. Several features have been noted which appear significant. Grondijs and Schouten (1937) have, in their study of the Mount Isa ores, classified the pyrite into five types according to size, shape and to some extent its mode of occurrence. These are as follow:

a. Very fine grained "spherical pyrite," grain size 0.025 - 0.005 mm., mostly with concentric zonal structure.

b. Fine grained pyrite in clean cut crystals, idomorphic or idioblastic, grain size 0.02 - 0.005 mm. Variety a may pass into b.

c. Very fine grained pyrite with skeleton-like shapes, mostly smaller than 0.01 mm.

d. Coarse grained pyrite in sphere like aggregates or in spherolitic concretions, grain size, 0.25 - 0.05 mm.

e. Coarse grained aggregates of fragments of crystals. Size 0.5 - 0.05 mm.

Grondijs and Schouten (1937) note that types "a", "b" and "c" belong in the oldest generation of pyrite and are probably primary. Each of the first three types are commonly found in the samples from the Iron River - Crystal Falls district. As can be seen in Plate VI,the typical concentric structure is seldom observed, but a lack of homogeneity is evident. Grondijs and Schouten (1937) compared the Mount Isa pyrite to that of the Meggen, Rammelsberg and Mansfield districts of Germany and concluded, as have many who have studied the German deposits, that both are syngenetic. However, they have pointed out some differences between the German occurrences and the Mount Isa ores. The pyrite in the German occurrences consist either of aggregates of small grains or of radial fibrous structure throughout. The Mount Isa ores as well as the pyrite examined in this study frequently show a massive core surrounded by a concentric ring. It has also been pointed out that the aggregate type noted in the German deposits is present in the Mount Isa deposits (Love and Zimmerman, 1961). This has also been noted in the present study of the Michigan occurrence. Grondijs and Schouten also have pointed out that the common presence of marcasite in the German occurrences is not the case with the Mount Isa ores. Further, they have assigned a later origin to the small amounts of marcasite which have been noted in their work. No marcasite has been encountered in the present study nor has any pyrrhotite been identified such as that which Grondijs and Schouten have determined as the predecessor of marcasite in the Mount Isa ores. As noted above, large clusters of pyrite have been observed in the Wauseca member but Grondijs and Schouten's "type d" is absent as far as can be determined. "Type e" is rather commonly found and is most frequent in the rocks

which more clearly show the effects of metamorphism, ie. show more definite fracture cleavage or foliation. This is undoubtedly the result of recrystallization of earlier pyrite.

Types "a", "b" and "c" are the forms of pyrite that are of the greatest concern in this study. They bear important implications concerning the environment of deposition as well as some of the mechanisms that were active during and immediately subsequent to deposition. There are two alternative theories that may be suggested.. The first is the conclusion drawn by Grondijs and Schouten (1937) and Schouten (1946), that the primary deposition of the pyrite was due to some inorganic process. The second possibility is that a biogenic process is responsible for deposition of both the pyrite and the carbonaceous material.

Referring again to the Mount Isa shales, more intensive work on the pyrite fraction of the rock than that of Grondijs and Schouten (1937) was accomplished by Love and Zimmerman (1961). In their study, intensive work was done to characterize the pyrite more accurately than previously. Several size and shape analyses were made as well as descriptions of the particles and the characteristic structures. In many of their examples, etching proved to reveal a very well-defined concentric structure as was previously described (Grondijs and Schouten, 1937). Further, upon oxidation of the pyrite, numerous small, rounded translucent bodies were freed and these were described as fossil micro-organisms. The size of the bodies was comparable to that of the pyrite spheres and in most cases comparable to the shape of the spheres from which they were removed.

A size analysis of the pyrite from the Wauseca member is comparable

to that of the Mount Isa pyrite spheres. In a count of two hundred spheres from two samples, the average size was 3.24 microns with the mode falling between two and four microns. This consistency of size can be noted throughout all of the samples from the Iron River - Crystal Falls district.

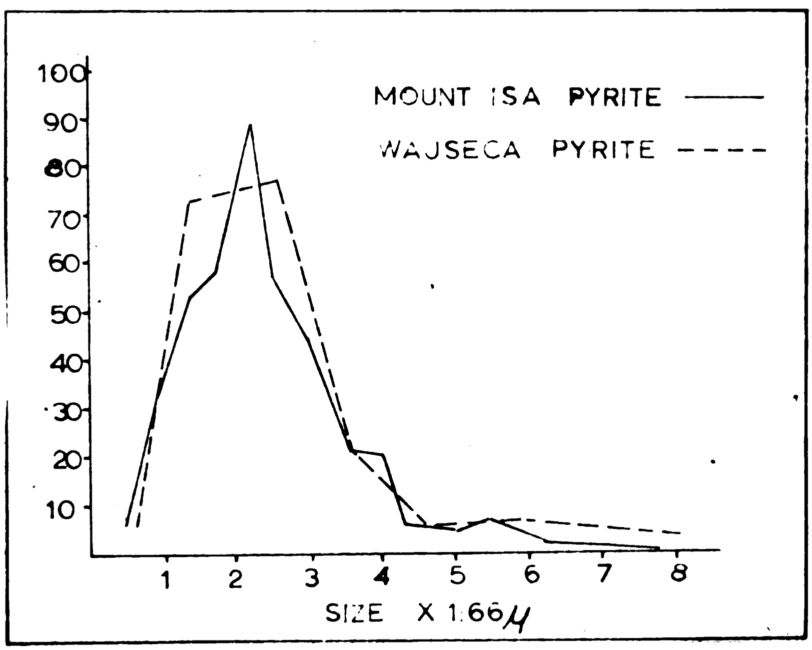

Fig. 5.— Size analysis of pyrite spheres from Mount Isa, Australia and Iron River - Crystal Falls district, Michigan. Size data from Mount Isa pyrite after Love and Zimmerman (1961).

The shape of the pyrite particles ranges from well-rounded to sub-angular and random. There appears to be no variation in shape from one sample to another. Many of the slightly larger, more irregular shaped particles are the result of coalescing of two or more smaller rounded spheres. This can often be seen much better after etching for a short period of time (Plate V).

Two methods were used for etching the pyrite to bring out any structure that may be instructive. Originally, H_2SO_4 was used, but it was found to be too fast and tended to over etch the sample or to completely destroy the pyrite. A solution of H_2SO_4 and $KMnO_4$ was found to be slower and produced much better results.

As previously noted, etching made possible the observation that many of the larger rounded or random shapes were actually clusters of smaller sphere-like particles. On the individual spheres etching brought out a variety of patterns. The very well-defined concentric pattern noted in the Mount Isa pyrite was seen in some examples but more frequently other patterns were observed. Often the entire center of the grain would etch leaving only an outer shell. The reverse of this often was seen where the center remains while most of the outer part is etched away. Often one or two wavy lines were observed in the grain with a slight increase in width of the lines in the center of the grain. In the more angular grains, the wavy lines were often observed as well as a dark line around the inner core parallel or nearly so to the outer edge of the particle.

A definite parallel comparison to the description of the Mount Isa ores given by Love and Zimmerman (1961) or Grondijs and Schouten (1937) would be difficult to make, but there are many similarities. The first and probably most important, is that the spheres and other irregular shapes are definitely hetrogeneous and subject to differential etching. The etch patterns seem to follow some pattern not related to crystal structure. Either the center or the outer part of the fragments will etch away displaying some type of concentric structure.

as noted by Love and Zimmerman (1961), composite grains often occur in the Mount Isa ores,this is also true in the Wauseca member.

Recrystallized pyrite was observed in several of the rock samples, notably those with a more definite foliation as a result of metamorphism. Well-defined cubes were observed in a few cases in addition to the random shape pyrite of that found in vein or deseminated deposits of hydrothermal origin. In one case, excellent pressure shadows composed of feathery quartz were found along the margin of the pyrite (Plate III, Fig.1). It appears that this type of pyrite is closely related to zones of more intense shearing. In such cases, bedding is no longer evident and the matrix material varies in color from black to a dark grey. The pyrite is in small veinlets up to a millimeter in thickness and two or three centimeters long, which parallel the foliation.

Chalcopyrite is commonly associated with the vein-like pyrite in small rounded blebs and along fissures (Plate VI, Fig. 2). It appears to be later than the pyrite, and in most cases replaced it along the cracks and fractures. Some crystalline quartz (as opposed to chert) is commonly found in association with the pyrite either as rounded blebs enclosed in the pyrite or along the edges. Graphite is also found in small rounded blebs within the pyrite and in a massive form around the pyrite (Plate VI, Figs. 1,2). It can be identified easily as it has a tendency to smear over the pyrite during the polishing. No other minerals have been identified with the pyrite other than the gangue or other primary minerals, ie. siderite or chert. The paucity of such minerals as lead or zinc sulfides to some extent attests to the primary nature of the pyrite as well as the lack of

mineralizing solutions associated with deposition or metamorphism. The later pyrite is probably a response of the mineral to the stress pressures and associated heat which caused the folding of the entire basin rather than the result of metasomatism or hydrothermal activity.

In the two areas in the Marquette district where samples were taken, the rock appears to be of slightly higher metamorphic grade in that it can be called slate. The pyrite is in definite beds which are usually at some angle to the foliation. The carbon content appears to be much lower and the typical graphitic streak is not apparent as it is in the samples from the Wauseca member. Most of the pyrite in these samples can be classed with the "type e." It occurs as well-defined cubes and irregular shapes but almost always with euhedral or idoblastic outlines. In a small percentage of cases, spherical and irregular outlined grains can be seen, but these are minor.

As in the examples of the "type e" pyrite in the Wauseca member, these samples from other areas appear to show a definite response to the metamorphic conditions. In each case the quartz that is associated with the pyrite crystals is a coarse crystalline type rather than chert. Pressure shadows of quartz were frequently observed attesting to the dynamic metamorphic intensity. As with the Iron River - Crystal Falls district, intense pressures rather than high temperatures appear to be the major agent of metamorphism.

As previously discussed, the preservation of carbon in rocks is due to the lack of oxygen in the depositional environment, it being one of slightly reducing conditions and near neutral pH values. Further, the evidence suggests that the pyrite has a biogenic associated origin. This is supporting evidence that the carbon was

originally in the form of organic materials.

Several x-ray powder patterns have been run which show that the degree to which the graphite is crystallized is variable. It is not exactly clear what causes this variation, but in most cases those rocks which best show the effects of metamorphism are the samples which also show the sharpest and most lines on the powder pattern. A direct correlation between perfection of crystallinity and degree of metamorphism would seem reasonable but at this point would be premature. Also, those rocks in which the slaty cleavage is best developed may have been more readily sheared because of the presence of well-crystallized graphite.

As shown in Plate VIII, most of the powder patterns show lines of equal or better perfection than the manufactured graphite, but there are examples which are less perfect. In any case the recrystallization has continued to a point where it is unlikely that much evidence of the original remains. Further,any unaltered organic material which might be found in these rocks is most likely material that has contaminated the rock at some time subsequent to the metamorphism. One of the procedures to determine the presence of organic material, used by Tyler (1957) was followed for several samples and negative results were obtained. This is not proof of the absence of such materials but inasmuch as this procedure was the most effective for the Morrison Creek "coal" the absence of organic compounds is suggested.

The graphite appears to be evenly distributed throughout the rock and shows little or no quantative relationship to the pyrite. Frequently, flecks of strongly anisotropic material can be seen which are tentatively identified as sericite and clay minerals. In

most cases the graphite and the associated minerals are so finely disseminated that little can be seen under the microscope. Rounded bodies which appear to be composed of graphite can be seen frequently, but the graphite is predominately in disseminated form. In most examples, some parallel orientation can be seen which is probably foliation.

As shown in Plate VI, Fig, 2, rounded blebs of graphite can be seen within the massive recrystallized pyrite. The rounded masses are homogeneous and show no structure. They occur as inclusions within the recrystallized pyrite which incorporated them during its recrystallization. The shape of the graphite inclusions again suggests an organic origin of the presently existing graphite.

CONCLUSION

On the basis of the preceeding discussion, several conclusions have been drawn concerning both the environment of deposition and the origin of the rather unusual constituants of the graphitic slates. Few of these conclusions are original, mostly they support previous work, some of which was more general than this particular study. Much of this study has been descriptive and comparative in nature which leads to the fact that the results are somewhat preliminary. Many questions remain unanswered and in at least one case, a new question has arisen which poses an interesting problem.

The environment of deposition plays an important role in many of the conclusions that are to be drawn. The minerals present indicate that the environment must have been one of negative oxidation reduction potential if the pyrite is syngenetic. Thus, the environment would be such that the decomposition of organic material would be negligible. Further, if the pyrite was primary in the rock, a comparison of this environment to presently existing reducing environments appears to be valid.

From the preceeding evidence, it has been concluded that the pyrite is syngenetic and that the graphite which is now found included in the rock is probably all that remains of large quantities of original organic material. The x-ray powder photographs of the graphite show that much of it has been crystallized to a fairly high degree, although some of these show a rather poor crystalline nature. This

variable nature of the graphite is probably the result of either varying intensity of metamorphism or varying effects of metamorphism on slightly different rock types. With the restricted number of samples used in the study it is difficult to see any definite correlation with metamorphism.

The nature of the pyrite in the rock is probably the most interesting factor to come out of the problem. The many similarities to the pyrite found in the Mount Isa shales is very suggestive that both types are the result of similar histories. The writer feels that the conclusion drawn by Love and Zimmerman should not be accepted without reservation for these samples at this time because of some lack of evidence. The isolation of fossil micro-organisms has not been accomplished and until this is done the conclusion must be deferred. Regardless of this, the many similarities of the pyrite from the two areas are striking and inference as to the origin of the pyrite in the Iron River - Crystal Falls district is interesting.

James (1950) has suggested that much of the Wauseca member may have been subjected to marine slumping. Observations made in this study appear to support this with one modification. James has implied a catastropic movement, thus, making at least the lower part of the Wauseca member a well defined marker unit. He has based his reasoning on the fact that the lower part of the Wauseca member is a choatic rock containing numerous fragments in a massive matrix and that little bedding is evident. This is true in many examples but several sections were also observed in which thinly bedded material was either overlain or underlain by typical massive rock (Plate II, Fig. 1). Also the small scale disturbances of the thin beds as shown in Plate I, Fig. 2, suggests smaller scale movements. The total destruction of bedding is

certainly suggestive of more catastrophic slumping, but again could be a function of the state of the material when the disturbance took place. The writer suggests that rather than the occurrence of one or a few large scale slumps, that many smaller scale slumps may have occurred.

One question which remains unanswered is the notable lack of pyrite in several samples from the vicinity of Florence, Wisconsin. As noted earlier, there are several alternatives which may be taken, but none of them appear wholly satisfactory. The massive nature of many of the samples seems to rule out the possibility that weathering has been responsible for removal of any pyrite, although the samples were all taken from surface outcrops.

From the diagram showing the stability fields of pyrite, it can be seen that pyrite could be deposited at extremely low concentrations of both iron and sulfur. The close relation that most of these occurrences have with iron formations is not compatible with the theory that iron was not present in the water at the time of depositon. A lack of sulfur is equally incompatible in that the high amounts of carbon suggest that there was much organic debris in the basin at the time of formation. Organic materials should be an adequate source of sulfur.

This leads to the final alternative that the iron mineral was removed from the rock at the time of metamorphism of the rock. This is not wholly acceptable in that the degree of metamorphism in this area does not appear much greater than other parts of the Iron River - Crystal Falls district. Further, there is much pyrite present in the samples from the Marquette district and these appear to have been

subjected to a high degree of metamorphism.

One other possibility that may be considered is that of an inhibiting action taking place in the environment of the highly graphitic rocks which prevented the precipitation of pyrite. It is notable, also, in the samples collected by Tyler in the Morrison Creek area that iron bearing minerals are negligible, even though the "coal" is surrounded by typical pyritic rock. Such a suggestion would need much investigation and is not offered as a solution to the problem.

Suggestions for Further Study

It has become apparent that the pyrite has provided the best evidence for the understanding of these rocks. Further intensive study with a greater number of samples would be required to provide definite proof of the suggested pyrite-graphite relationship. The comparison of the pyrite to the Mount Isa pyrite has been instructive and in the writer's opinion the pyrite may very likely represent fossil micro-organisms. More work in this light may also have some bearing upon the deposition of siderite and the other iron minerals found in the Lake Superior region.

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APPENDIX A

LIST OF COLLECTION SITES ON MAP 1

1. Taylor mine area
2. Champion Station (Bijiki)
3. Dead River Basin (Michigamme)
4. Hoist Dam Road (Michigamme)
5. Menominee District

LIST OF COLLECTION SITES ON MAP 2

1. Morrison Creek "Coal"— SE¼ of SE¼, Sect. 21*

2. Sherwood Mine

3. Sunset Lake core-- NE¼ of SE¼, Sect. 17, T43N, R34W

4. Bates Fire Tower Core-- SE¼, NE¼, Sect. 27, T43N, R34W

5. Bristol Mine, horizontal core

6. Crystal Falls mine dump and test pits-- SE¼ of NE¼ Sect. 21

7. Dunn Creek slate outcrop-- SW¼ of NW¼, Sect. 8

8. Road cut south of Alpha-- SW¼ of NE¼, Sect. 13.

9. Brule River exposures-- SW¼ of NE¼, Sect. 8

10. Exposures along abandoned RR grade NE of Florence-- NW¼ of SE¼ Sect. 21

11. Road cut south of Commonwealth (slate) SW¼ of SW¼, Sect. 34

12. Ridge east of Keyes Lake; slate low in graphite-- NE¼ of NW¼ Sect. 6.

13. Ridge just north of Keyes Lake-- SE¼ of SE¼, Sect. 25

14. Larson exploration-- NW¼ of NW¼, Sect. 35

15. Roadcut along Wisconsin, Rt. 70-- NE¼ of NE¼, Sect. 34

16. Section SW¼ of NW¼, Sect. 26

17. Section SE¼ of NE¼, Sect. 22

18. Section SW¼ of NW¼, Sect. 23

19. Section SW¼ of NE¼, Sect. 22

20. Creek bed 100 yards north of Brule School-- SE¼ of SW¼, Sect. 14

21. Road Exposure east of Brule School-- SE¼of SE¼, Sect. 14

22. Section SW¼ of SW¼, Sect. 13

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*Ranges and townships are noted in Map 2.

APPENDIX B

TABLE 3

CHEMICAL COMPOSITION*

	1	2	3	4
SiO_2	47.32	58.03	43.80	36.67
TiO_2	0.53	0.64	0.41	0.39
Al_2O_3	7.99	15.00	8.26	6.90
Fe_2O_3	0.24	3.67	2.40	-----
FeO	0.42	5.82	0.91	2.35
Fe#	0.07	0.03	12.01	18.03
MnO	----	0.09	trace	trace
MgO	0.32	1.64	-----	0.65
CaO	0.03	0.26	0.15	0.13
Na_2O	0.03	3.52	0.07	0.26
K_2O	2.19	3.60	2.20	1.81
P_2O_5	trace	0.16	0.03	0.20
H_2O -105°C	13.21	3.46	4.05	1.25
H_2O -105°C	2.11	0.84	0.91	0.55
CO_2	0.06	0.03	0.07	-----
C	22.68	3.27	10.46	7.60
SO_3	0.38	0.14	0.89	2.60
S	2.71	0.04	13.77	20.67

*After Nanz (1953) Journ. of Geol. Vol. 61.
1- Upper footwall, Judson Mine, Crystal Falls, after Nanz
2- Footwall road cut location 14, after Nanz
3- Footwall just below IF furnished by H. L. James after Nanz
4- Laminated footwall after James

#Fe included in pyrite

APPENDIX C

PLATE I

Fig. 1-- Typical massive "speckled grey." Note the suggestion of parallel alignment of the elongated fragments. x 5.2.

Fig. 2-- Highly disturbed bedded type containing several fragments of less pyritic rock. Note swirls of bedded matrix around each fragment. x 5.2.

PLATE I

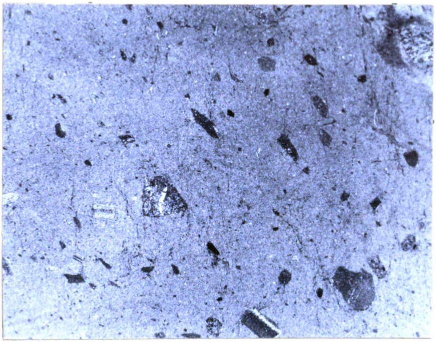


Fig. 1

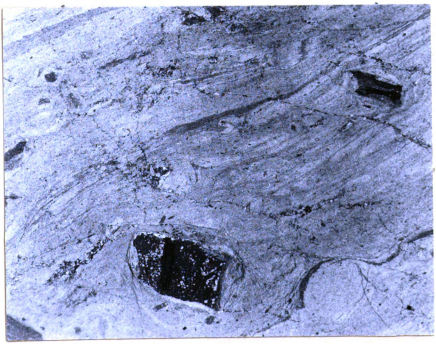


Fig. 2

PLATE II

Fig. 1— Bedded type, probably overlying more massive type showing how beds seem to thin over the fragment and thicken in the depressions on either side. Large fragment at the bottom of the picture is almost wholly pyrite. x 5.2.

Fig. 2— Highly disturbed bedded sample showing several differences in textured characteristics. x 5.2.

PLATE II

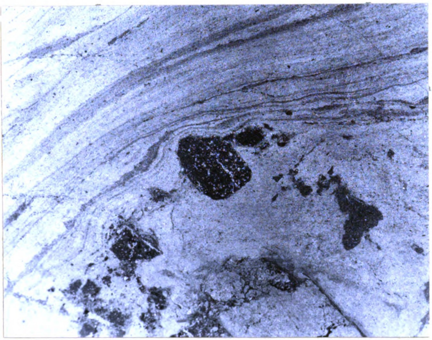


Fig. 1

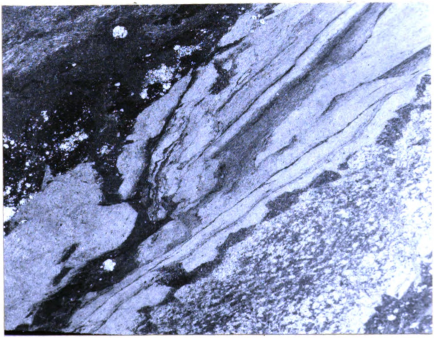


Fig. 2

PLATE III

Fig. 1.-- Well bedded type exhibiting very sharp undisturbed contacts between beds. Large cubes of pyrite have apparently formed from recrystallization of earlier pyrite in those beds where the pyrite is found. Beds containing pyrite are almost wholly composed of quartz. Note several pressure shadows of quartz around several of the crystals. x 5.2.

Fig. 2.-- Bedded pyrite showing some results of deformation. x 5.2.

PLATE III

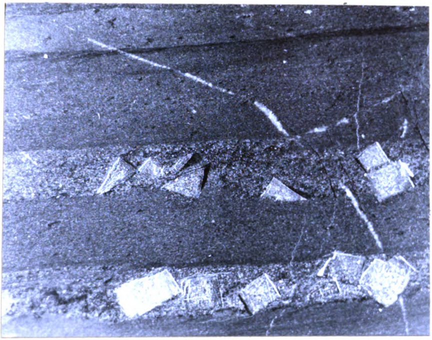


Fig. 1

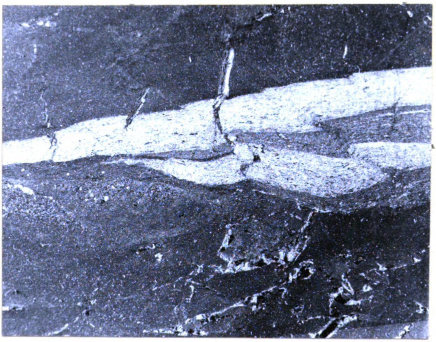


Fig. 2

PLATE IV

Fig. 1.-- Highly graphitic sample showing effects of deformation which is probably penecontemopaneous. Bedding is well shown as a result of variation of texture. x 5.2.

Fig. 2.-- Highly weathered sample which is well bedded. Note numerous small crenulations in the laminae near the bottom of the photo. x 5.2.

PLATE IV

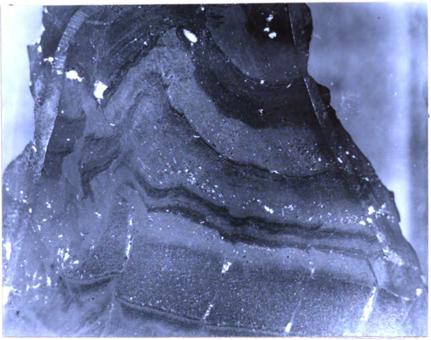


Fig. 1

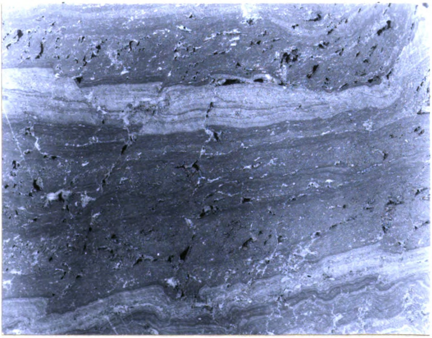


Fig. 2

PLATE V

Fig. 1.-- Unetched fairly well rounded grains. x 1000 oil immersion.

Fig. 2.-- Unetched. Ragged shapes showing heterogeneous nature. x 1000 oil immersion.

Fig. 3.-- Unetched. Shows variation in shapes from well rounded to sub-angular. x900 oil immersion.

Fig. 4.-- Etched sample. Much of this photo was originally a large composite grain. x1000 oil immersion.

Fig. 5. and Fig. 6.-- Slightly etched samples showing several shapes on grain surfaces. x1000 oil immersion.

PLATE V

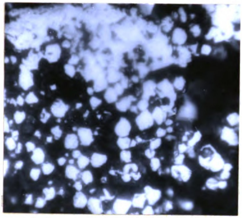


Fig. 1

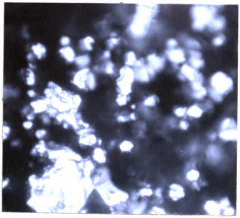


Fig. 2

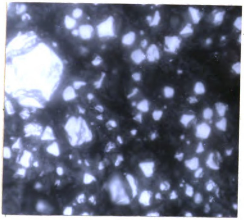


Fig. 3

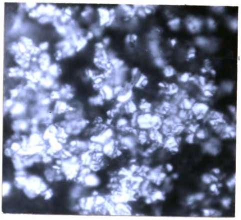
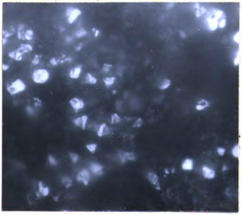


Fig. 4



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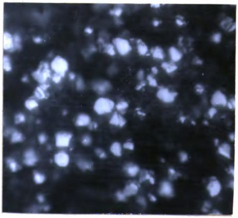

Fig. 6

PLATE VI

Fig. 1.— Metamorphosed slate from Sunset Lake core shows irregular shapes of recrystallized pyrite (light grey). Variable color of the matrix material can also be seen. x 5.2.

Fig. 2.— Same sample as Fig. 1 in polished section. Light grey is pyrite. Medium grey in vein-like replacement is chalcopyrite. Darker grey rounded blebs are graphite. Note how the graphite has smeared out along the surface from the rounded areas. x70.

Fig. 3.— Crystal of pyrite from same sample as Plate III, Fig. 1. Etching has brought out crystallographic structure as opposed to irregular structures found in the much smaller primary spheres. x70.

Fig. 4.— Thin section from the upper part of the Wauseca member. Note outlines of carbonate rhombs which are being replaced by chlorite. Black irregular shapes are pyrite. Light grey ground mass is chert with some finely disseminated graphite included. Uncrossed nicols. x70.

PLATE VI

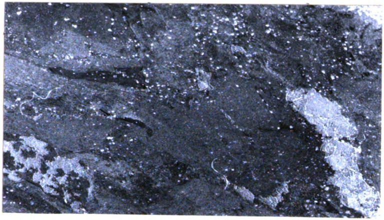

Fig. 1

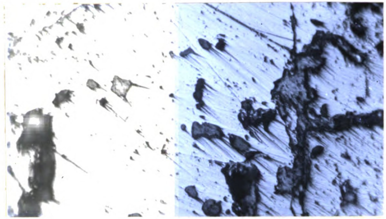

Fig. 2

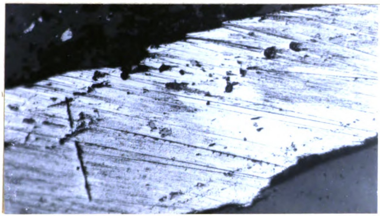

Fig. 3

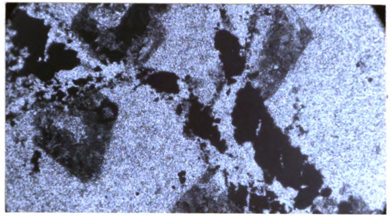

Fig. 4

PLATE VII

Fig. 1.— Thin section showing finely disseminated graphite included in chert. Circular shapes pose an interesting problem. x500 oil immersion.

Fig. 2.— Thin section showing change in content of graphite (white) giving rise to bedding. x70.

Fig. 3.— Highly graphitic sample containing very little pyrite. Some regular shapes are seen but much of the material is in random orientation. x500 oil immersion.

PLATE VII

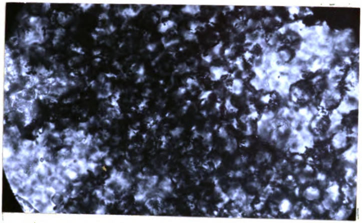

Fig. 1

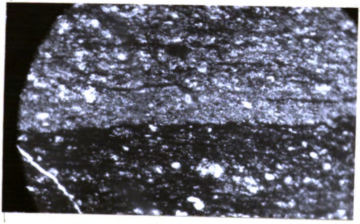

Fig. 2

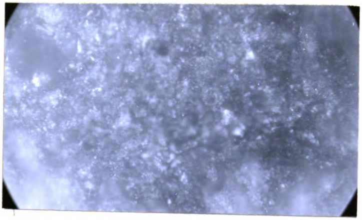

Fig. 3

PLATE VIII

X-ray powder photographs of several samples of purified graphite from graphitic slates.

1- Reference spectographic graphite

2- Graphite from lower Michigamme slate

3- Sunset Lake Core, Wauseca Member

4- Reference same as # 1

5- Highly graphitic sample

6- Wauseca Member from Sherwood Mine

7- Highly graphitic sample from unknown location in the Florence, Wisconsin area.

The first three samples were run for three hours, the last four for two hours.

Note the variation in intensity in the 200 and 201 lines, i.e., second and third lines outside of the intense line in #4.