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Geology and Origin of the
Iron Ore Deposits of the Zenith Mine
Vermilion District, Minnesota

Jerome F. Machamer



UNIVERSITY OF MINNESOTA

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**GEOLOGY AND ORIGIN
OF THE
IRON ORE DEPOSITS
OF THE
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VERMILION DISTRICT, MINNESOTA**

by

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FOREWORD

The Zenith mine, closed in 1962, was one of the major producers of iron ore in the Vermilion district. It yielded approximately 21 million long tons of the total of slightly more than 100 million tons produced in the district since 1884. Nearly all the production was from underground mines. The last operating mine, the Pioneer, closed in April, 1967.

This report, adapted from a thesis submitted to the Graduate School of The Pennsylvania State University, provides a modern study of the iron ores of the Vermilion district, and contributes to a better understanding of their occurrence and origin.

P.K. Sims,
Director

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GEOLOGY AND ORIGIN OF THE IRON ORE DEPOSITS OF THE ZENITH MINE VERMILION DISTRICT, MINNESOTA

by Jerome F. Machamer

ABSTRACT

The Zenith mine, at Ely in the Vermilion iron district of Minnesota, yielded about 21 million tons of high grade iron ore before closing in 1962. The ore that was mined consisted of massive crystalline hematite, brecciated and cemented by a later generation of crystalline hematite. The deposits are steeply dipping tabular bodies enclosed within walls of low-rank metabasalts of the Precambrian Ely Greenstone; they occupy the stratigraphic position of and grade upward into a jaspilitic iron-formation. Geologic and petrographic relations indicate that the deposits are post-metamorphic in age.

One of the ore bodies has a mineralogic zoning characterized by a magnetite zone incorporated within and surrounded by a hausmannite zone. Near the bottom of the deposit both the cementing hematite and the early brecciated hematite give way to carbonate minerals.

Two zones of alteration can be recognized in the greenstone wall rocks: an outer zone composed entirely of chlorite and an inner zone in which the rocks are stained by hematite. The inner zone has a mineralogic zoning; dominant kaolinite grades outward into dominant $2M_1$ muscovite. The altered zones contain substantially more iron than the unaltered country rock.

The composition of some of the carbonate minerals indicates that they were deposited at a temperature near 400°C . The mineralogic relations indicate that during much of the period of ore deposition the fugacities of oxygen and sulphur fluctuated around the equilibrium values for the coexistence of hematite, magnetite, and pyrite, and that the fugacity of CO_2 was on the order of 10^3 atmospheres. The kaolinitic alteration adjacent to the deposits indicates that the altering fluid may have been acid, and it is postulated that the acidity resulted from a relatively high concentration of CO_2 in the fluid.

It is concluded (1) that the deposits were formed by the replacement of the silica in the iron-formation by hematite, (2) that the iron probably was transported in large part as free ferrous ions in an acid hydrothermal fluid, (3) that deposition and replacement was largely restricted to the jaspilite because of its brecciation, and (4) that two of the principal causes of ore deposition were an increase in pH of the fluid resulting from the escape of CO_2 in the brecciated zone and oxidation of the iron to the ferric state. The oxygen may have been derived either from the dissociation of unstable oxidized agents introduced with the ore fluid or by the downward diffusion of atmospheric oxygen through ground water. The source of the metals and the fluid is unknown; gross spatial relations suggest that possibly both the metals and the fluid were derived from depth, in an environment of more intense metamorphism.

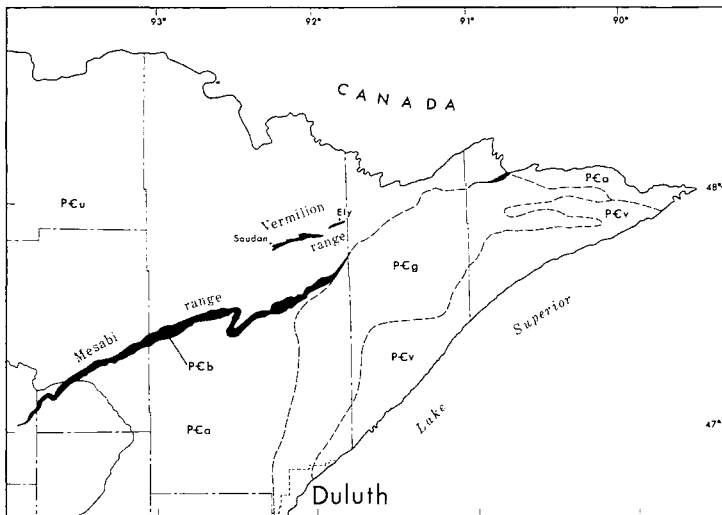
INTRODUCTION

The iron ores of the Vermilion district, in northern Minnesota, consist of hard massive hematite, fractured to a greater or lesser extent and occurring in an equally hard jaspilitic iron-formation. The deposits in the Zenith mine differ somewhat from the other deposits of the district in that the ores on the lower levels contain appreciable quantities of carbonate minerals, magnetite, and pyrite.

The origin of the deposits has been the subject of considerable debate, and the principal objective of this investigation was to attempt to resolve the differing viewpoints. The Zenith mine was chosen for study because (1) it was thought that a detailed knowledge of the mineralogic variations within the mine might yield some new clues to the nature of the ore-forming process, (2) the conclusions might be applicable to other iron ore deposits in the Lake Superior region, and (3) no thorough study available to the public had been made since 1906.

Location and History

The Zenith mine is at Ely, in N½ SE¼ sec. 27, T. 63 N., R. 12 W., northern St. Louis County, Minnesota. It is one of the major mines in the Vermilion district or iron range (fig.1), which generally includes the area from latitude 47°45' to 48°00' north and from longitude 91°30' to 92°15' west.



EXPLANATION

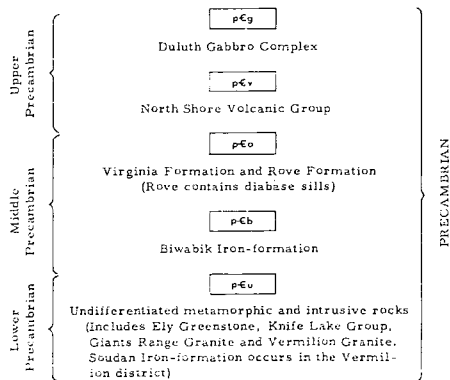


Figure 1. Generalized geologic map of northeastern Minnesota, showing location of the Vermilion district.

Iron-bearing rocks in the Vermilion district were first noted in 1866 near Tower, about 20 miles west of Ely (Eames, 1866). Systematic exploration for iron ore in the vicinity of Tower was begun in 1875, and led to the opening of the Soudan mine in 1884. Iron ore was discovered near the present site of Ely in 1883, and the first shipments -- from the Chandler mine -- were made in 1888. Subsequent exploration and development led to the discovery of additional deposits to the east of the Chandler mine. Eventually five mines were opened on what proved to be an essentially continuous ore body about one and one-half miles long; from west to east these are the Chandler, Pioneer, Zenith, Sibley, and Savoy mines (fig. 2). The Pioneer mine was opened in 1888, the Zenith in 1892, and the Sibley and Savoy in 1899. Other small mines and prospects were discovered in other parts of the range in later years, but none of these have been significant producers. The last active mine, the Pioneer, was closed in April, 1967.

The Zenith mine has been operated by several firms. The principal ones were the Oliver Iron Mining Company, from 1899 to 1919, the Vermilion Mining Company (Pickands, Mather & Company, Agents), from 1920 until 1958, and the Zenith Mining Company (North Range Mining Company, Agents), from 1959 until 1962. The mine was closed in the fall of 1962 because of near exhaustion of marketable ore. Total production of the mine from 1899 to 1962 was approximately 21 million long tons of iron ore.

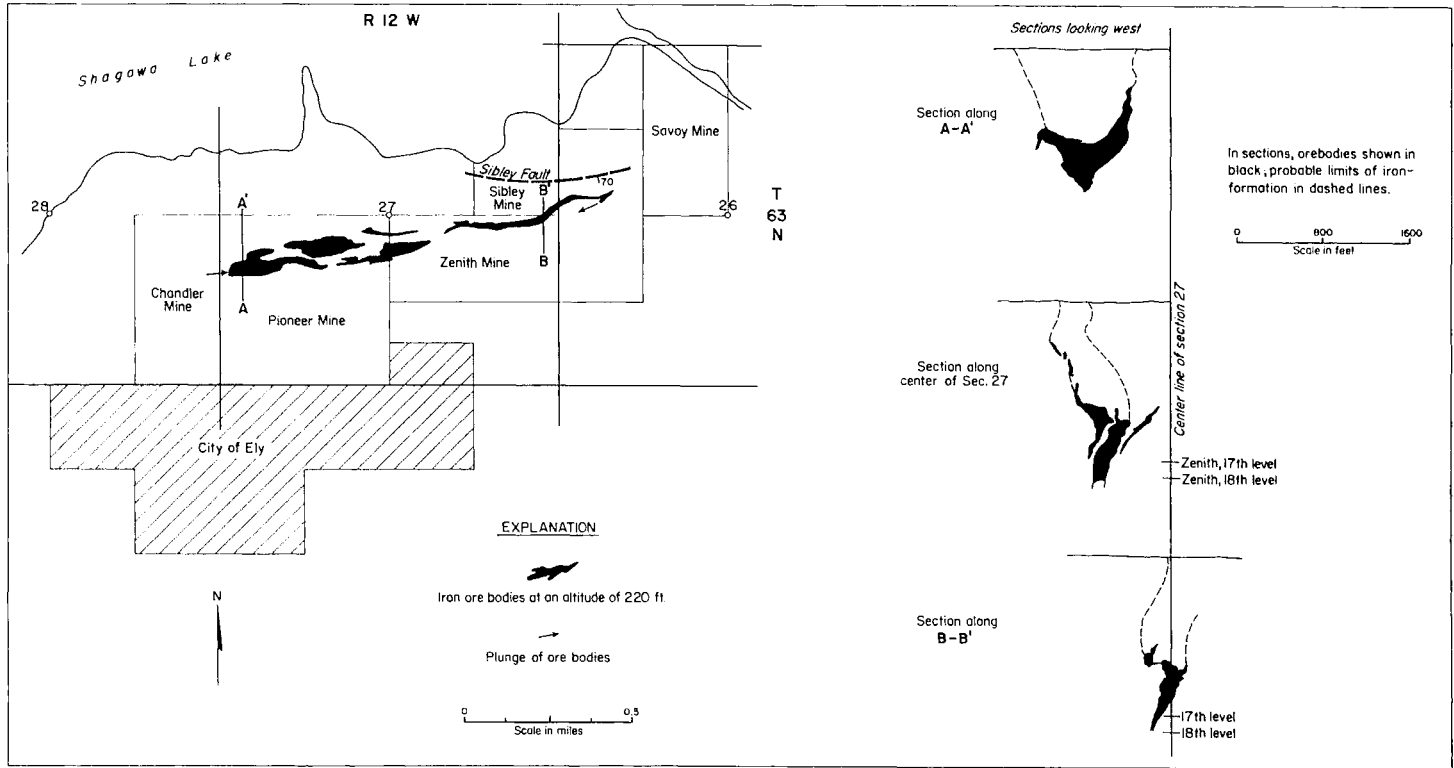
Method of Investigation

The accessible mine openings in the Zenith mine were mapped at a scale of one inch equals fifty feet in a period of nine weeks during the summer of 1961; rock and ore specimens were collected during the study. Detailed mineral relations were studied by means of polished and thin sections of the ores and the surrounding country rocks; the standard optical techniques for mineral identification were supplemented by X-ray diffraction and electron probe analysis; compositional changes of minerals and rocks were determined by chemical analysis.

Acknowledgments

This report is modified from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Pennsylvania State University. The study was done under the direction of Professor John D. Ridge, who provided guidance and assistance in all phases of the work. H.L. Barnes, R.F. Schmalz, R. Scholten, and H.D. Wright gave invaluable assistance. J.W. Greig and Charles Kropp of the Department of Metallurgy aided in the preparation of polished specimens. J.L. Haas contributed much data for some of the thermodynamic calculations. P.K. Sims of the Minnesota Geological Survey critically reviewed the manuscript.

The writer is indebted to the North Range Mining Company, Negaunee, Michigan, and especially to Robert Archibald, Richard Mitchell, and William Jackson for access to the mine property and for the use of mine facilities. A.D. Chisholm of Pickands, Mather & Company provided access to company files on the Zenith mine. Donald Berkner of the Oliver Iron Mining Division, U.S. Steel Corporation, provided general information and maps of the entire Ely area and



Source: United States Steel Corporation; Zenith Mining Company

Figure 2. Map and sections of mines and ore bodies in the Ely area

gave permission for access to the Pioneer mine workings. Finally, W.P. Wolff of Hibbing, Minnesota and J.F. Wolff and H.M. Roberts of Duluth, Minnesota gave much information about the older parts of the mines near Ely, which now are caved.

The study was supported by grants from the Society of the Sigma Xi and the Scientific Research Society of America. The Department of Geology and Geophysics, The Pennsylvania State University, provided much of the equipment necessary for the work, and some of the thin sections. The Experiment Station of the College of Mineral Industries performed approximately 50 partial chemical analyses, and identified one mineral by means of the electron probe. Finally, the writer is indebted to his parents, Mr. and Mrs. Jerome E. Machamer of Duluth, Minnesota, who provided most of the financial support for the study.

GENERAL GEOLOGY OF THE VERMILION DISTRICT

Rock Units

The oldest rocks exposed in the Vermilion district are metamorphosed basalts and mafic intrusives that are included within the Ely Greenstone (fig. 3). These rocks form a belt approximately 7 miles wide and 40 miles long that extends from Tower northeastward beyond Ely. Intercalated within the upper part of the greenstone are discrete lenses and stringers of a banded siliceous iron-formation, known as the Soudan Iron-formation. The Ely Greenstone and included Soudan Iron-formation are overlain unconformably by metamorphosed graywackes and conglomerates of the Knife Lake Group. All the rocks have been folded into a complex doubly-plunging anticlinorium, the axis of which is approximately parallel to and bisects the greenstone belt. The rocks of the Soudan Iron-formation and the Knife Lake Group are present in minor synclines within the belt of greenstone (Clements, 1903). All of the rocks are early Precambrian in age, as defined by Goldich and others (1961).

Intrusive into the greenstone and younger rocks, and bounding the greenstone belt, are the Vermilion Granite on the north and the Giants Range Granite on the south (Grout and others, 1932). Both of these granitic masses have been dated at about 2.5 billion years by Goldich and others (1961). The Duluth Gabbro Complex intrudes both the Giants Range Granite and the Ely Greenstone a short distance to the east of the district. The age of the Duluth Gabbro Complex and related volcanic rocks is 1.1 billion years (Goldich and others, 1961).

Character of Iron Ores

The iron ores of the Vermilion district are associated with the Soudan Iron-formation, and apparently are replacements of this rock. They are massive, hard, blue hematite ores having very little porosity. The majority of the production was lump ore with a guaranteed analysis of 60 percent iron when dried at 212°F., and with very little chemically combined water. In contrast, the natural ores of the Mesabi and Cuyuna districts are residual accumulations of hematite and hydrated iron oxides which are generally fine-grained, soft, and earthy. Although the structural setting of the iron ore deposits in Michigan and Wisconsin is similar to that of those in the Vermilion district, the Michigan and Wisconsin ores are also soft and earthy, and have a relatively high water content.

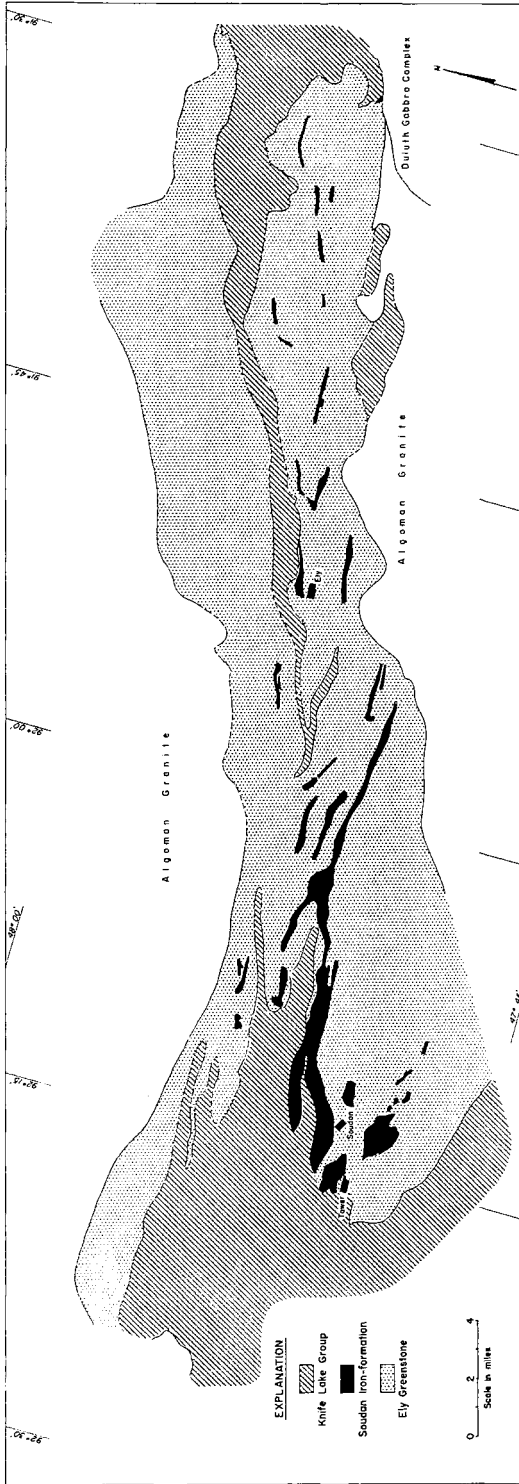


Figure 3. Generalized geologic map of the Vermilion district and adjacent areas..

The only other lump ores produced in the Lake Superior region are obtained from the Marquette Range in Michigan; they are mined from deposits of schistose specular hematite that occur in metamorphosed rocks of Middle Precambrian age (James, 1955; 1958; Goldich and others, 1961).

Much of the ore produced from the mines at Ely consisted of breccia fragments of massive blue hematite cemented in varying degrees by a second generation of finely crystalline hematite. Some of this material has been termed "soft ore" by the miners, although it should properly be called "loosely cemented ore" as the fragments themselves consist of the same hard hematite. In the lower levels of the Zenith mine and those mines farther to the east, the hematite that forms the cement for the breccia fragments gradually gives way to carbonate minerals, also, the amount of magnetite increases markedly and manganese minerals appear in the ore. In addition, the amount of pyrite in the ore increases with depth, a fact common to all the mines at Ely. Typical analyses of ores mined from the Vermilion district are given in Table 1.

Review of Previous Studies

The first discussion of the origin of the Vermilion iron ores was that of Irving (1886), who considered that the bodies of crystalline hematite were formed by the concentration of iron released during the silicification of a carbonate-bearing iron-formation. N.H. Winchell and H.V. Winchell (1891) postulated that the iron ores were the result of the direct chemical precipitation of iron leached from the basic lava flows of the Ely Greenstone.

The Soudan deposits were studied by Smyth and Finlay (1895), who concluded that the deposits were formed by water percolating downward along

Table 1. Typical analyses of iron ores from the Vermilion district

	Zenith ¹ 1924	Zenith Lump ² 1937	Oliver 41 Lump ³ 1961	Zenith Lump ³ 1961
Fe	61.82	64.22	62.71	62.70
P	0.041	0.057	0.079	0.105
SiO ₂	7.05	4.83	5.72	4.25
Mn	0.07	0.05	0.09	0.23
Al ₂ O ₃	2.74	1.81	2.59	2.40
CaO	0.20	0.14	0.19	0.79
MgO	0.12	0.11	0.29	0.38
S	0.012	0.008	0.029	0.027
Ignition loss	1.33	0.94	1.18	1.69

All figures are average analyses of cargo loadings for the year shown. The headings refer to the grade name of the ore and the date of shipments.

Sources:

1. Pickands, Mather & Company, Cleveland, Ohio.
2. "Lake Superior Iron Ore," The Lake Superior Iron Ore Association, Cleveland, Ohio, 1938.
3. "Iron Ore, 1961," The American Iron Ore Association, Cleveland, Ohio, 1962.

plunging structural troughs. This theory called upon a complex intermingling of waters, in which water charged with carbon dioxide through contact with carbonate-bearing iron formation leached silica and iron carbonate from the iron formation, and was later mixed with oxygen-bearing waters which caused the precipitation of the hematite. The theory was first developed by Irving and Van Hise (1892) for the deposits of the Gogebic range in Michigan and Wisconsin, and later was reiterated by Clements (1903), Abbott (1906), and Van Hise and Leith (1911). Both Abbott and Clements concluded that the main period of ore formation was after the deformation and metamorphism of the region, whereas Van Hise and Leith considered that it took place before metamorphism, the massive character of the ores being the result of compaction and recrystallization during the metamorphism.

In 1926 Gruner pointed out that the presence of large vugs in the walls of the iron deposits in the Soudan Formation indicated that the deposits themselves had not been metamorphosed, for the vugs would have been closed by the soft "paint rock" surrounding them had they existed before the metamorphism. He also pointed out several other facts that were difficult to explain by theory of Van Hise, such as the absence of limonitic material, the difficulty of dissolving quartz, the unleached nature of outcrops of the Soudan Formation, and the upward interfingering of ore and unleached iron-formation. Instead, Gruner suggested that hematite and carbonate from rising hydrothermal solutions replaced the quartz; later, the carbonates were dissolved. In support of his position, he cited several other occurrences of hypogene hematite. Gruner elaborated on this idea in 1930, citing more field evidence and the results of some experiments to support his conclusions. Leith restated the Van Hise theory in 1931, and pointed out that surface waters have been very effective in leaching silica and quartz under some conditions, that the structural position of many deposits favored the hypothesis of downward moving water, and that most of the deposits in the Lake Superior region are associated with modern or Precambrian erosion surfaces. In 1932 Gruner outlined his position once again, citing additional evidence, in particular, the expansion with depth of the cross-sectional area of the deposits at Ely. Finally, Gruner (1937) modified his hypothesis to state that heated meteoric waters might have been the principal agent for the removal of silica. Gruner's hypothesis has received rather wide acceptance since 1937 (Roberts and Bartley, 1943b; Klinger, 1956), although the hypothesis of Van Hise also has received some support (Royce, 1938; 1942).

OCCURRENCE OF CARBONATE IN ORE BODIES IN THE LAKE SUPERIOR REGION

The occurrence of large quantities of carbonate minerals in iron ores of the Lake Superior region has generally been thought to be rare, although the mines adjoining the Zenith to the east bottomed in carbonate material (Abbott, 1906; Reid, 1956). Carbonate impurities forced the closing of the large Chapin mine in Iron Mountain, Michigan (according to J.F. Wolff, personal communication, 1961) and the Penn mines east of Iron Mountain (Royce, J., 1960), both on the Menominee range, and similar contamination was recently recognized on the Gogebic range (Royce, J., 1960). Veins of carbonate minerals are also present in

specimens of lump ores collected by the author from the Marquette range.

The origin of the large bodies of siderite and hematite in the Michipicoten district of Ontario has been ascribed by some authors to metasomatic activity (Morrison, 1948; Tanton, 1948), although more recently it has been suggested that they are of sedimentary origin (Goodwin, 1962). Similar siderite deposits in northeastern Minnesota are stated to be of undoubted metasomatic origin (Goldich and others, 1961). The hematite-goethite deposits associated with carbonate rocks at Steep Rock Lake in the Atikokan district of Ontario have variously been considered to be of hypogene (Roberts and Bartley, 1943a) or supergene origin (Joliffe, 1955).

There is much evidence that many of the iron ore deposits in northern Michigan have resulted from the replacement of silicate and/or carbonate minerals by iron oxide minerals (Van Hise and Leith, 1911; Boyum, 1962; Roberts, H.M., personal communication, 1961). Replacement features have been noted at depths greater than 3,500 feet below the present land surface (1,800 feet below sea level). Thus it would appear that a better understanding of the deposits in the Zenith mine might assist in the interpretation of many aspects of the geology of iron ore deposits in the entire Lake Superior region.

DESCRIPTION OF THE ZENITH MINE WORKINGS

Access to the Zenith mine workings (1961) was through No. 3 shaft, which is some 1,200 feet south of the ore bodies. The shaft is vertical and about 1,800 feet deep. The altitude of the collar is about 1,400 feet above sea level; the lowest level is at an altitude of 254 feet below sea level. In 1961, the operating levels were at intervals of 100 feet, except for the lowest level, the 18th, which is 150 feet below the 17th level. Mining was carried on by the method of sub-level caving, with the sub-levels driven at intervals of 20 feet. In this report, locations within the mine property are specified by the use of a coordinate system, the center of which is the center of Section 27.

In 1961 active mining was in progress on the 17th (altitude: 104 feet), and the 18th levels. Two ore bodies were being mined: the West ore body, which is continuous with the main ore body in the Pioneer mine, and the Central ore body, which continues eastward into the Sibley and Savoy mines (fig. 2). The two ore bodies were continuous above the 12th level of the Zenith mine, but it is not known if they connect below that level. A narrow ore body, known as the Northwest seam ore body, which lies to the north of the West ore body, was mined above the 15th level; it is also present as the North ore body in the Pioneer mine, and vestiges of it occur on the main 17th level haulage drift. (see pls. 1 and 3).

Nearly all the workings above the 17th level, and some on the level itself, were caved and thus inaccessible in 1961. Information on these areas was obtained from mine maps and logs of drill holes. Nevertheless, sufficient openings were accessible at the time of this study to give a reasonably good three-dimensional picture of the geological relations in the mine, and to enable me to thoroughly sample the deposit.

GEOLOGY OF THE MINE AREA

Topography

The mines in the Ely area are located between the city and Shagawa Lake, which is about one-half mile north of Ely (fig. 3). The city itself is situated on a prominent hill having a maximum altitude of approximately 1,515 feet above sea level; the ground slopes toward the lake, which has an altitude of about 1,355 feet. Although the original landscape has been destroyed by subsidence over the mine workings, early maps of the area indicate that a slight depression occurred over the western part of the ore bodies, surrounded by a natural amphitheater that opened to the northeast. The topography over the central and eastern parts of the ore bodies was generally irregular, and lower than the hill to the south.

The area has been glaciated, and the hill on which the city is located is underlain by greenstone, which was more resistant to the abrasive action of the glaciers than the surrounding rocks. Neither the orebodies themselves nor the host rock iron-formation cropped out at the surface. The absence of outcrops can be accounted for by extreme brecciation of both the ore and the enclosing iron-formation.

Rock Types

Ely Greenstone

General description

The Ely Greenstone is the name given by Clements (1903) to the low-rank metamorphosed mafic intrusive and extrusive rocks that are widely exposed in the Vermilion district. The rocks are the oldest rocks exposed in the district, their aggregate thickness is unknown.

The greenstone is dominantly massive, although a variety of original structures, including pillow (ellipsoidal), amygdaloidal, and spherulitic, have been inherited from the original mafic volcanic rocks. A well-developed schistosity locally obscures the original structures. The common original textures are either diabasic or porphyritic. Not uncommonly, the original textures have been largely destroyed, and the present texture can be described as a "confused aggregate" (Schwartz, 1924, p. 97).

The common minerals of the greenstone, in approximate decreasing abundance, are plagioclase (generally extensively altered), chlorite, hornblende, epidote, calcite, and magnetite; less abundant minerals are leucoxene, quartz, actinolite, augite, sericite, kaolinite, limonite, and pyrite. Calcite is present both as secondary grains dispersed through the rock and as veins cutting it.

Exposures of the greenstone within the mine workings — mainly in the crosscuts from the No. 3 shaft to the ore bodies and in the drifts from the central to the west ore bodies — indicate that individual units within the greenstone can be distinguished by variations in color and structure; however, no effort was made in this study to establish a stratigraphic succession, for the mine workings do not provide sufficient exposures to determine the continuity of

units. Within the workings, the greenstone ranges in color from light green to greenish-black, but is dominantly dark in color. In general, it is uniformly fine-grained, although in some places it is mottled, suggestive of original porphyritic and diabasic textures. The rock is locally schistose, distorted pillow structures are present in the main haulageways about midway between the No. 3 shaft and the ore bodies. A few lenses of chert or jasper occur near the ore bodies, and the greenstone enclosing these lenses commonly shows a color banding and is very fissile, suggesting a sedimentary or pyroclastic origin. The same is true of some of the greenstone forming the hanging wall of the ore bodies.

Mineralogy

The normal greenstone (that is far removed from the ore bodies) contains actinolitic hornblende (Winchell, 1951, p. 431-437), colorless epidote (pistacite of Winchell), pale green nearly isotropic chlorite, quartz, and untwinned albite (biaxial (+), large $2V$). The actinolite has the following optical properties: pleochroic from colorless to pale green, biaxial (-), $2V =$ about 80° , birefringence $=$ about 0.025, extinction angle $=$ about 20° , optically positive elongation. Also, sphene is common, together with lesser amounts of calcite and pyrite. Texturally, the rock is an extremely complex intergrowth, with many grains tending to merge into one another rather than showing sharp grain boundaries. Actinolite occurs in irregular blades ranging up to 1 mm. in length, commonly with shredded or feathery ends and containing inclusions of other minerals. Chlorite occurs in patches of different sizes, and either is surrounded by or enclosed within blades of actinolite. Epidote is in small idioblastic grains from 0.05 to 0.1 mm. in diameter, which are commonly associated with irregular clumps of sphene. Quartz and albite are commonly interstitial as grains up to 0.1 mm. in diameter; albite occurs as laths up to 0.5 mm. in length. Calcite occurs in small irregular grains and as veins associated with quartz and oligoclase. The calcite veins contain inclusions of the other minerals in the rock, and in some veins the quartz is penetrated by minute needles of actinolite. Quartz in veins containing irregular grains of pyrite has perfectly straight extinction. The specimens examined show no preferred orientation of metamorphic minerals such as actinolite and chlorite although the orientation of albite laths in one specimen suggests a remnant trachytic texture.

The greenstone from the immediate vicinity of the ore bodies, on the other hand, is composed almost entirely of chlorite, fine-grained muscovite, and quartz. The rocks differ in appearance from the normal greenstone mainly in having a somewhat more pronounced cleavage. They could have been derived by the metamorphism of pelitic sediments (Turner and Verhoogen, 1960), or they may be the products of a wallrock alteration of the normal greenstone. If these rocks were sediments, however, many of their sedimentary features should be preserved, just as original igneous features are preserved in the normal greenstone. The absence of sedimentary features in the greenstone adjacent to the ore bodies, and the lack of evidence that the area has been subjected to a retrograde metamorphism which could have destroyed such features, supports the contention that these rocks were normal greenstone which was altered in

connection with the formation of the ore deposits, and do not represent a different rock type, accordingly they will be discussed separately in a later section.

Carbonate and Quartz-carbonate Veins in Greenstone

Veins composed largely of quartz and carbonate minerals cut the greenstone in the mine area. The veins can be divided for descriptive purposes into three groups that may also represent genetic groupings. The first group, composed largely of calcite, is characterized by hematite, either in the vein or staining the rocks surrounding the vein; veins of this type occur principally in the vicinity of the ore bodies and are sparse in the greenstone far removed from the ore. The second group, also composed primarily of calcite, occurs as lenses and segregations a few inches thick in the greenstone. The veins are commonly deformed or bent, and apparently have formed as metamorphic segregations. The third group occurs in a zone 500 to 600 feet south of the central ore body on the 17th level and from 570 to 615 feet south of the ore body on the 18th level (plates 1 and 2); the veins are composed of coarse anhedral quartz with strong undulose extinction, mylonitic quartz, and coarse and fine-grained calcite, which is commonly moderately twinned but only rarely has bent twin planes. Most of the calcite is paragenetically later than the quartz, as shown by the more intense internal deformation of the quartz; optically continuous inclusions of quartz in the calcite suggest that the quartz has been partially replaced by calcite. Associated with the quartz are vermicular chlorite and wedge-shaped crystals of axinite ($\text{HCa}_2 [\text{Mn,Fe}] \text{BA}1_2 \text{Si}_4 \text{O}_{16}$). Undulose extinction in the latter suggests that it crystallized about the same time as the quartz. The veins in this zone are straight, as much as two feet thick, and have the same orientation as the carbonate veins in the ore bodies. No veins of the second group are present in this zone, and the greenstone from this zone is more massive and uniform than normal greenstone.

Soudan Iron-formation

Soudan Iron-formation refers to the very hard iron-rich dense cherts and jaspilites that occur in the Ely Greenstone. It occurs in belts, which range from a few feet to several miles in length, and is well exposed at the Soudan mine, northeast of the village of Tower. At one time the Soudan Iron-formation was thought to have been an essentially continuous sedimentary unit, whose spotty distribution could be related to variable depths of erosion combined with extreme infolding within the greenstone (Clements, 1903). The lenselike and discontinuous nature of the iron-formation, particularly near the Soudan mine, indicates, however, that it probably was deposited as a series of separate and discrete lenses within the volcanic rocks. The position of the lenses in relation to the major structures suggests that the Soudan Iron-formation is restricted to the upper part of the greenstone, but this suggestion has not been proved.

In addition to fine-grained quartz, the Soudan Iron-formation contains hematite, magnetite, iron-silicate minerals, pyrite, and some carbonates. The most striking rocks in the formation are the jaspilites, composed of distinct

alternating layers of blue hematite and white or red quartz, but more commonly the layering is rather diffuse, and the quartz layers are colored by the other minerals present. Different facies, similar to those described by James (1954), can be recognized in the formation: quartz-silicate-pyrite facies, quartz-magnetite facies, and quartz-hematite-(magnetite) facies. Commonly the layers, particularly in the jaspilites, are cut by quartz and hematite veins (Clements, 1903).

Layering is present throughout the Soudan Iron-formation and is continuous, even where the individual layers are only a few hundredths of an inch thick. Although the layering is fantastically contorted in some places, it is generally not deformed and is parallel to contacts with the enclosing greenstone. This suggests that the rock was originally a chemically precipitated sediment which has not undergone any great chemical changes since it was formed. Had the rock developed from a cherty iron carbonate, as postulated by Clements (1903), it would seem unlikely that the delicate layered structure would be so well preserved. A crude stratigraphic sequence may exist in the Soudan area, grading upwards from pyritic chert through lean jasper into jaspilite (Klinger, 1960), but this may be local and related to the development of the iron ore deposits at Soudan; the detailed work necessary to establish a sequence has not been done in other areas.

Several authors have commented on the presence of a clastic member within the Soudan Iron-formation (Clements, 1903; Reid, 1956), but nothing resembling the published descriptions was found in the Zenith mine. The fissile pyritic greenstone that forms parts of the hanging wall of the Zenith deposits was probably a tuffaceous or clastic sediment, and is unlike the material described by Clements and Reid.

The main body of iron-formation which capped the ore deposits in the Ely area is no longer accessible for examination, and is exposed at only a few places in the caved ground above the deposits. The greater part of the capping material has been reported to be a jaspilite composed of alternating layers of hematite and fine-grained quartz (Abbott, 1906; Reid, 1956). Specimens collected from the surface, from mine dumps, and from material slumped into the workings from above tend to confirm this, although some specimens are better described as lean jasper or red pyritic chert.

Small bodies of cherty material occur in the greenstone both to the north and the south of the ore bodies. Layers of greenish-white chert as much as 20 feet thick that contain considerable pyrite occur about 100 feet south of the central ore body on both the 17th and 18th levels. These layers are characterized by well developed conformable bedding, and are probably continuous, or at least occur in a continuous zone between the two levels. Very thin stringers of similar material, separated by greenstone layers, are present in two zones between the central and west ore bodies on the 17th level. The other occurrences are small and consist of reddish chert. On the 18th level west drift, about 160 feet east of the line between the pioneer and Zenith mines, minute stringers of this reddish chert show distinct cross cutting relations to larger chert bodies, indicating that at least some of this chert has been introduced as vein material.

The material from the zone south of the central ore body is composed primarily of fine-grained quartz or a dolomitic carbonate (MgCO_3 35%, $[\text{Mn,Fe}] \text{CO}_3$ 15%, CaCO_3 50%) having lesser amounts of pyrite, iron oxides, and chlorite. Chlorite occurs in stringers and layers, and locally is disseminated through the chert. Pyrite occurs as cubes in the chlorite layers and as beds or layers composed of small anhedral grains. All these rocks are extensively veined by carbonate minerals, and some are composed almost entirely of these minerals. The carbonate veins are of at least two different ages. Carbonate minerals of the earlier stage are highly twinned, whereas those of the second stage are generally untwinned. The rocks made up largely of carbonate consist of euhedral grains having long diagonal dimensions that average 0.15 mm. These grains commonly show a compositional zoning, which can be detected optically by the change in refractive indices, and show no evidence of internal or external deformation. Small patches of quartz and chert are scattered throughout the rocks, and the carbonates are euhedral towards these patches. There are also two stages of quartz veins; grains of the earlier stage have extreme undulose extinction whereas those of the later stage have nearly straight extinction. Both quartz and carbonate veins carry euhedral, unfractured grains of pyrite, together with some chalcopyrite. Hematite and magnetite, where present, are associated with the carbonates; hematite occurs as minute crystals disseminated throughout small areas of the carbonate, and magnetite occurs as layers bordered by carbonate and cut by carbonate veins in a quartz-magnetite-pyrite jaspilite. In this latter rock, the magnetite grains are bordered by hematite rims, although the accompanying pyrite is unaltered.

The specimens collected from mine dumps, from caved material in the mine, and from outcrops in the caved area over the mine workings are all composed of hematite and chert, or fine-grained quartz. The material is either a jasper, consisting of fine quartz with disseminated hematite, or a jaspilite composed of alternating layers of red jasper and blue crystalline hematite. The rock is generally veined, and many veins are probably syngenetic; however some of the veins contain very large grains with straight extinction. Some of the quartz veins have associated crystalline hematite; hematite also occurs in carbonate-hematite veins, hematite-chlorite veins, and hematite-apatite veins, as well as in monomineralic veins. The carbonate veins do not have matching walls, indicating some replacement of the quartz, and apparently carbonates themselves have been replaced by hematite.

Graphitic Schist

A layer of graphitic schist about one-foot thick, which contains numerous pyrite nodules, forms the footwall (north wall) of the eastern extremity of the central ore body on the 18th level, where it was penetrated in two mine openings about 250 feet apart. Similar material was found at approximately the same stratigraphic position in the Sibley mine and in wide zones in some parts of the Pioneer mine (Reid, 1956). The complete mineral composition of the rock is unknown, for the rock disintegrates readily and it was not possible to cut thin sections.

Stratigraphic Position of the Ore Bodies

Throughout most of the vertical range of the ore bodies in the Zenith mine and adjoining mines both the hanging walls and footwalls of the deposits are greenstone or its altered equivalents. The ore bodies grade upward through an irregular transition zone into Soudan Iron-formation, and in the upper levels of the mines occur in the iron-formation along the footwall contact with the greenstone (Abbott, 1906). Furthermore, horizons of jaspilite are found within the ore bodies at several places. The orientation of the ore bodies and banding within the ore bodies is similar to or parallel to the orientation of chert lenses and layers in the greenstone. These features support the interpretation that the deposits are conformable bodies that occupy the position of the Soudan Iron-formation. The stringers of altered greenstone that cross the ore bodies in some places are apparently mafic dikes that were intruded into the iron-formation, whereas those that are essentially parallel to the contacts probably represent tuffaceous material incorporated within the chert.

Structural Geology

Major Structures

General Relations

The major structural feature in the area of the mines near Ely has been considered to be a doubly-plunging syncline, called the Ely trough, which has an axial plane that strikes about N. 70° E. The eastern half of the syncline is thought to be overturned and the north limb in the central and eastern parts of the fold to be cut off by a fault. This interpretation is based on the synclinal shape of the ore bodies in both plan and section (fig. 2) in the Chandler and Pioneer mines, and on the fact that the layering in the jaspilite and in the ore in the Chandler mine also has a synclinal pattern (R. S. Archibald, oral communication, 1962). The north ore body of the Pioneer mine, which continues into the upper levels of the Zenith mine where it is called the Northwest Seam ore body, is thought to represent the easternmost extension of the north limb of the fold.

Several facts — including the lack of symmetry, the absence of evidence that the north limb is cut off by a fault, and the presence of narrow stringers of jaspilite or ore several hundred feet beneath the bottom of commercial ore in both the Sibley and Savoy mines (J. F. Wolff, oral communication, 1961; Reid, 1956) — seem to contradict a synclinal theory. Considering the lenslike nature of the bodies of Soudan Iron-formation, it is possible that the entire body of ore and jaspilite at Ely is simply a large lens of Soudan Iron-formation containing interlayers of tuffs and flows, which is tilted into a near vertical position. A plausible explanation for the apparent absence of a north limb for the syncline is a lensing out of the iron-formation on the north flank, such that it never extended further east than the Northwest Seam ore body in the Zenith mine. These various interpretations have been widely debated by persons familiar with all the mine workings at Ely (Royce, Stephen, and Leith, C. K., private reports

for Pickands Mather & Company). In any event, mine workings and diamond drill holes show conclusively that there is no major fault immediately north of the ore bodies.

The ore bodies that were exploited in the Zenith mine were essentially tabular, although there is a large roll in the south contact in the eastern part of the mine extending into the Sibley mine, which resulted in a great thinning and virtual offset of the ore body beneath the 13th level (pl. 3). In the central part of the Zenith mine, between the 12th and 13th levels, the ore body was too narrow to mine, and for operating purposes was thus divided into the West and the Central ore bodies. Mining operations do not reveal whether there is any connection between the two ore bodies beneath the 12th level.

Whether the major structure and the associated minor structures resulted from folding or from lenticular and irregularly distributed original jaspilite bodies is not yet known. It is clear, however, that the ore bodies, or at least those east of the Pioneer mine, were not developed in a structural trough with an impervious bottom, as postulated previously by several writers (Clements, 1903; Abbott, 1906; Van Hise and Leith, 1911).

Faults

Only one major fault, the Sibley fault, is known in the Ely area (fig. 3). It is not exposed in the workings of the Zenith mine, but was exposed in the Sibley and Savoy mines and has been intersected by several diamond drill holes. The fault lies about 600 feet north of the central ore body, strikes approximately east, and dips about 70° S. where exposed. The rocks forming the footwall belong to the Knife Lake Group; the Ely Greenstone forms the hanging wall. Nothing is known about the actual direction of movement along the fault, but the sense of the apparent displacement is that of a reverse fault.

Minor Structures

Brecciation

One of the major characteristics of the ore in the Zenith mine and other mines in the Ely area is a pronounced brecciation of most all the material in the ore bodies, and commonly also of the wallrock immediately adjacent to the ore bodies. Also, specimens of iron-formation that were obtained in the study are highly fractured, and earlier reports state that most of the jaspilite capping was fractured or brecciated (Clements, 1903; Abbott, 1906).

Well-developed slickensides occur at several places in the rocks near or along the contact between the ore and the country rock, indicating that there was considerable movement along the contact zone. The directions of movement indicated by the slickensides are not consistent, however, and generally the individual fracture zones have only small lateral continuity. Although the area occupied by the ore bodies obviously has been a zone of structural adjustment, the lack of continuity and consistency among the various subsidiary fractures indicates that the ore bodies are not localized along a fault zone.

Cleavage

The greenstone exposed in the mine workings has two cleavages, which can be observed in the same exposures. The dominant cleavage is virtually parallel to the ore bodies, ranging in strike from N. 70° E. to N. 80° W. and in dip from 70° to 90° S. The subordinate cleavage varies with the attitude of the ore bodies; the strike of the cleavage is approximately 20° more northeasterly than that of the dominant cleavage, ranging from N. 80° E. to N. 50° E.; the angle of dip is the same as that of the dominant cleavage. These cleavages are somewhat better developed in the rocks adjacent to the ore bodies; this fact could reflect a greater deformation of these rocks or it could be a consequence of compositional differences.

On a regional scale, the cleavage in the greenstone is generally parallel to the trend of the major anticlinorium, and to the lenses of Soudan Iron-formation within the greenstone. On the presumption that it is an axial plane cleavage, the two cleavages are interpreted to have resulted from a reorientation of the stresses causing the major deformation. This reorientation might in turn be partly responsible for the brecciation of the ore bodies and the jaspilite.

Joints and Veins

Both the ore bodies and the surrounding greenstone are highly jointed, and some of the joints contain well-defined carbonate or quartz-carbonate veins. The ore bodies have two well-defined joint sets: one set strikes essentially north and dips vertically; the other set strikes approximately east and dips approximately 10° N. (fig. 4). The two joint sets are also present in the greenstone. The greenstone, however, contains several additional joint sets (fig. 5) and veins.

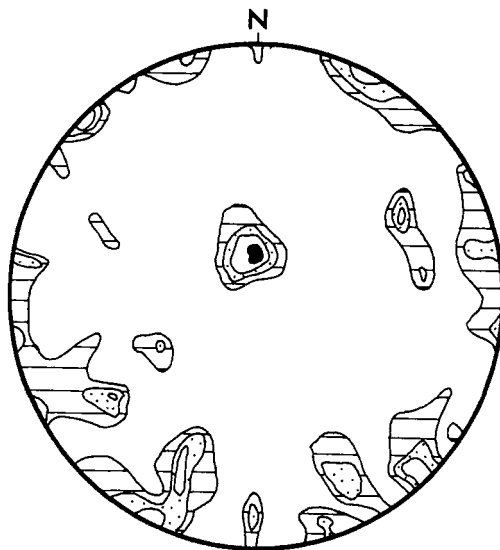


Figure 4. Orientation of poles to joints in ore bodies. Contours at 2, 4, 8, and 16 percent. Plotted on the upper hemisphere, Schmidt equal-area net. Based on 95 measurements.

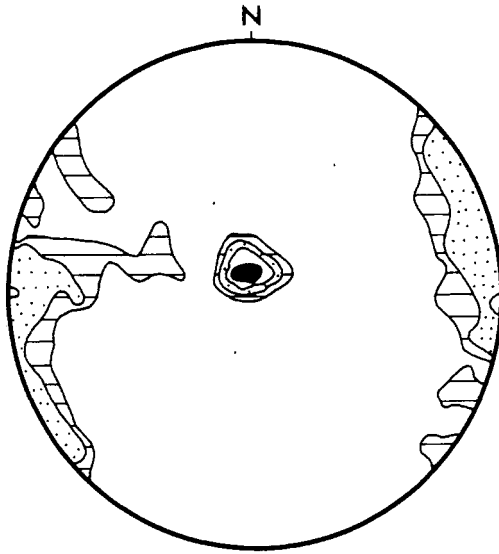


Figure 5. Orientation of poles to joints in greenstone. Contours at 2, 3, 4, and 6 percent. Plotted on the upper hemisphere, Schmidt equal-area net. Based on 92 measurements.

Possibly the difference in jointing between the greenstone and the ore bodies is simply a result of differences in the relative competency of the two rock types. This possibility seems unlikely, however, as some of the joint sets are present in both the greenstone and the ore. An alternative suggestion is that the joint sets that appear to be present only in the greenstone were developed before the formation of the ore.

The sub-horizontal veins, which contain quartz and carbonate (see p. 12), are found only in the ore bodies (fig. 6) and in the greenstone (fig. 7) some 500 to 600 feet south of the central ore body. Sub-horizontal joints are common in the ore bodies but not in the adjacent greenstone. The joints might have developed as a result of sheeting, in response to the erosion of the overlying rock column, but this hypothesis can hardly explain the vein fillings in the joints or the restriction of the veins to certain well-defined zones. If the true movement on the Sibley fault was principally reverse, then the horizontal veins could well be gash fractures resulting from the same forces that caused the movement along the fault itself. Movement in response to such forces would tend to take place along discontinuities in the rock, such as lithologic contacts, thus explaining the restriction of the veins to the ore bodies and the massive greenstone. The veins are not present in the more schistose greenstone because in these rocks the movement was not concentrated along lithologic contacts, but was distributed throughout the rock and taken up along the cleavage planes.

If the horizontal joints and veins did actually form in this manner, then the Sibley fault must have been an active structural feature during and after the

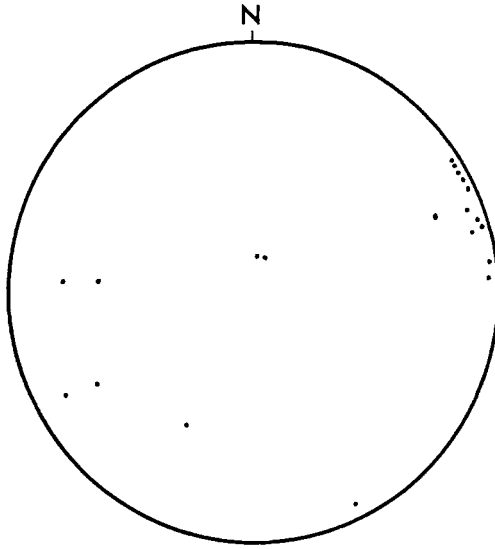


Figure 6. Orientation of poles to veins in ore bodies. Plotted on upper hemisphere, Schmidt equal-area net. 20 measurements.

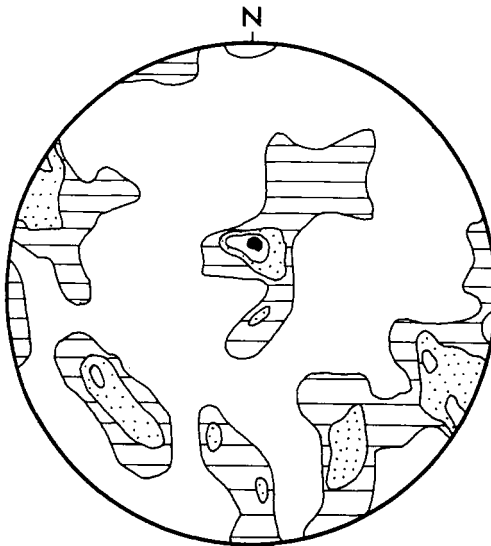


Figure 7. Orientation of poles to veins in greenstone. Contours at 2, 4, 6, and 8 percent. Plotted on upper hemisphere, Schmidt equal-area net. Based on 47 measurements.

formation of the ore bodies. In this manner one might account for the several stages of brecciation of the ore bodies, as well as the movement in the wall rocks adjoining the ore.

Age of Mineralization

The hematite that constitutes the ore bodies formed subsequently to the regional deformation of the rocks within the belt of Ely Greenstone. A preferred orientation, which would be expected if it had been deformed in the same manner as the surrounding rocks, both in hand specimens and in polished sections, is lacking. In the same way, the carbonate and quartz-carbonate veins that are associated with the hematite do not show evidence of extreme internal deformation. On the other hand, the brecciation of the ore bodies and the other indications of movement along the walls of the ore bodies, together with the presence of undulatory extinction in quartz and twinned carbonates in some of the relatively late veins cutting the ore, indicate that differential movement continued during and after the formation of the ore.

Whether the deformation that produced the brecciation was associated with the last major orogeny that affected the area – about 2.5 billion years ago (Goldich and others, 1961) – or with some later activity is not known. Specimens of sericite schist associated with the ore bodies in the Soudan mine have a potassium-argon age of 2.53 billion years, but sericite from later pyrite veins in the Soudan mine gives an age of 1.6 billion years (Goldich and others, 1961).

ECONOMIC GEOLOGY

The ore bodies at Ely are composed principally of massive hematite, which has been brecciated and cemented by a later generation of hematite or by later carbonate minerals. They are tabular in shape, enclosed within walls of Ely Greenstone, and grade upwards into fractured and brecciated jaspilite. The lower limits of the ore bodies, where they have been reached by mining operations, are determined either by a decrease in width or by a decrease in iron content resulting from mineralogical changes in the ore.

The iron-bearing materials exclusive of the original iron-formation in the Zenith mine can be grouped into 5 types: (1) massive hematite, (2) brecciated massive hematite having a hematite cement, (3) brecciated massive hematite having a carbonate cement, (4) brecciated carbonate minerals cemented by a later carbonate, and (5) massive magnetite containing variable amounts of carbonate minerals and pyrite. All five types of ore are found in the Central ore body, but the West ore body is composed almost entirely of brecciated hematite cemented by hematite. The carbonate-bearing material is common only in the Central ore body. This material was first recognized on the eastern end of the 15th level; it increases in abundance with depth, and forms the major part of the Central ore body on the 18th level.

In addition to hematite, magnetite, hausmannite, and pyrite occur in the ore in significant amounts. Trace amounts of goethite, pyrrhotite, chalcopyrite, covellite, chalcocite, and native copper have also been found. Gangue minerals other than the carbonates are present in very small quantities, and include quartz, chlorite, kaolinite, apatite and some very poorly crystalline phosphates of uncertain composition, topaz, tourmaline, and gypsum. The carbonate minerals include both calcite and dolomite (which contains variable amounts of ferrous iron in solid solution); in general the early carbonates are dolomite-rich whereas the later carbonates are calcite.

The distribution of the iron and manganese minerals within the Central ore body follows a well developed zonal pattern; hausmannite appears abruptly in the central part of the ore body just above the 17th level, and just below the hausmannite zone magnetite becomes the principal iron mineral.

Two alteration zones can be distinguished in the greenstone surrounding the ore bodies; an outer zone in which the rock is composed largely of chlorite, and an inner zone in which the rocks are colored red by the presence of significant amounts of hematite. Some of the rocks immediately adjacent to the ore bodies are composed almost entirely of hematite and kaolinite, and these rocks are separated from the common hematite-chlorite rocks of the inner zone by rocks composed of fine-grained muscovite and hematite. The most significant chemical change from the unaltered to the altered greenstone is a pronounced increase in iron content.

Both magnetite and hematite were formed throughout the period of ore deposition, but at any given time and place the first mineral to be deposited was magnetite. Pyrite and pyrrhotite also formed throughout the period of ore deposition; pyrrhotite was the first of these to be deposited. The majority of the hausmannite was deposited in the late stages of ore formation.

Form and General Relations of Ore Bodies

The deposits in the Zenith mine are tabular bodies enclosed within walls of Ely Greenstone or its altered equivalents. Contacts of the ore bodies with the greenstone are sharp or are marked by a narrow brecciated zone containing fragments of ore and greenstone. The ore bodies were followed laterally during mining until the thickness diminished to less than a minable width; in no cases were they followed to the actual termination of the ore. Vertically, the ore bodies grade upward through an irregular transitional contact into jaspilite (Abbott, 1906). The jaspilite at the contact itself is commonly a mass of loose, sugary chert grains (J.F. Wolff, personal communications, 1961). Both the ore bodies and the jaspilite above them are extensively brecciated, although characteristics of the jaspilite such as banding commonly can be traced into the ore (Abbott, 1906). The lower mining limits of the ore bodies in the Sibley and Savoy mines were determined in part by a decrease in the thickness of the ore, and in part by a decrease in the grade of ore caused by an increase in the carbonate content. The lower limits of the Central ore body in the Zenith mine were determined solely by a mineralogical change, which was marked by a

decrease in the hematite content of the ore and a corresponding increase in the carbonate, magnetite, and pyrite content. The material could not be profitably mined either because of low iron content or high sulfur content, and therefore was not followed further. A true bottoming of the ore is unknown.

Thin lenses that carry large amounts of hematite occur sporadically within the greenstone in the vicinity of the ore bodies, and at places these approach ore grade. These lenses are composed of chlorite and hematite in varying proportions, and are surrounded by brown or red altered greenstone in which the hematite content diminishes gradually away from the lens. The bodies are essentially parallel to the main ore bodies, and were formed through the replacement of the greenstone by hematite along minor fractures or shear zones.

Types of Ore and their Distribution

The iron-bearing material in the Zenith mine, exclusive of the pyritic and hematitic cherts and the jaspilite, can be grouped texturally and mineralogically into five different types:

Type 1, very dense, uniform, hard blue material composed almost entirely of crystalline hematite.

Type 2, composed of fragments of type 1 cemented by a secondary crystalline hematite, which commonly has minute vugs lined with hematite crystals.

Type 3, same as type 2, except the cementing material is composed dominantly of carbonate minerals.

Type 4, composed largely of carbonate minerals that vary in color from light red or gray to dusky red; also contains some fragments of type 1 material and earlier carbonate minerals.

Type 5, composed principally of magnetite, with variable amounts of carbonate minerals and pyrite.

The various types generally grade into one another over distances of about one foot; however, types 4 and 5 on the 18th level merge more imperceptibly over much greater distances. The great bulk of the ore that was mined was material of types 1 and 2, but includes some of type 3. The remainder of the iron-bearing material was not merchantable because of its low iron or high sulfur content.

With the exception of type 5, some of each of the types is layered. In type 1, and in type 2 where not destroyed by brecciation, this layering is produced by textural differences, the layers of massive hematite alternating with layers of more porous hematite. In type 3, the layering may be of the same nature, or the ore may be composed of alternating layers of massive hematite and carbonates. The layering in type 4 is caused by rather subtle color differences in the carbonates and by a few discontinuous layers of massive hematite. Where the layering could be readily distinguished within the mine, the layers were essentially parallel to the walls of the deposit.

All five types of iron-bearing material are present in the Central ore body. On the 17th level, the east and west ends of the ore body largely consist of types

3 and 4 material, whereas type 2 material predominates in the center of the ore body. No ore of type 1 was seen in place during my study, but several large chunks which reportedly came from about 40 feet above the 17th level were seen in the mine workings. On the 18th level, the central and eastern parts of the ore body are predominantly type 4 material, with some areas of types 2 and 3. The western part of the ore body has not been thoroughly explored on this level, but apparently consists of type 5 material, with some type 4 on the very western end.

The West ore body is much more uniform than the Central ore body, and on the 17th level consists entirely of type 2 material. A small patch of type 3 material occurs between the 15th and 16th levels in the east end of the ore body, and some material of this type occurs on the north side of the Pioneer ore body just across the property line. On the 18th level, the ore body consists of a stringer of very hard type 2 material on the south side, with a triangular shaped area of softer type 2 material, together with some type 4 material on the north side.

Carbonate-bearing material was first encountered on the 15th level, in the extreme eastern end of the Central ore body. On the 16th level this material forms patches in the eastern half of the ore body, and on the 17th level it occurs throughout the entire length of the ore body.

Noticeable concentrations of pyrite, which may be accompanied by magnetite, are present at places in both the hanging and footwalls of the ore bodies. Although generally confined to the greenstone wall rocks, large amounts of pyrite are also disseminated through the altered greenstone within the ore bodies and in some of the type 2 iron-bearing material.

Carbonate veins are very common in the Central ore body and sparse in the West ore body. They also occur to a much lesser extent in the greenstone. One specimen of carbonate material from a vug contains native copper intimately intergrown with carbonate crystals. Quartz veins are rare in the ore bodies, but are common in the greenstone.

Mineralogy of the Ore Deposits

Hematite

Hematite (Fe_2O_3) is by far the most abundant mineral in the deposits, and the only mineral of economic importance. It constitutes from 85 to 95 per cent of the material that was considered to be ore (types 1 and 2), and is abundant in most of the other iron-bearing material.

Hematite occurs in a variety of different forms. The most common is that found in the massive ore (type 1, or the fragments in types 2 and 3), where it occurs as an aggregate of irregular interlocking grains. These grains are rather uniform in size and shape; the average long dimension of the grains ranges from 0.05 to 0.1 mm.

In type 2 ore, the secondary hematite commonly has a reticulated pattern similar to a boxwork; the interstices may be empty, or they may be filled,

generally with carbonate mineral. The cementing hematite may also form a feathery network of very fine stringers. These types of hematite are found also in some of the massive fragments, and both types grade into the massive hematite. It is the alternation of these with the massive hematite that causes the layering in types 1 and 2 material.

Where the majority of the cementing material consists of carbonate minerals, hematite occurs as minute crystals scattered throughout the carbonate, and commonly as euhedral crystals extending from the edges of the fragments into the carbonate matrix. These crystals have about the same range in length as the grains in the massive hematite, but their average length is only 0.03 to 0.04 mm. Small patches of botryoidal hematite also occur in the cementing material, as well as in the massive fragments. These patches usually have a center filled by a carbonate mineral or by chlorite.

Where hematite occurs in the altered greenstone it is present in minute veins and in minute crystals disseminated through the rock. Rare clumps made up of grains 0.03 to 0.05 mm. long are present, but most of the material is finer grained.

Magnetite

Magnetite (Fe_3O_4) occurs sparsely in all the ore, and in large amounts in the type 5 material. In type 5 material it forms irregular grains or clumps of grains, which range in length from 0.1 mm. down to the limit of resolution of the microscope, occurring in a matrix of carbonate minerals and rarely chlorite. In the other types of iron-bearing material, magnetite occurs as remnants in the center of hematite grains and crystals. Generally, these remnant grains are found only in the fragments of massive hematite, but some of the hematite crystals in the carbonate cementing material have centers of magnetite, particularly near the type 5 material.

Goethite

Crystals of goethite (HFeO_2) with a maximum length of perhaps 0.5 mm. were found lining minute vugs in a vein of sideritic carbonate in the western end of the Central ore body on the 18th level. They are associated with siderite crystals of about the same size. Both minerals were identified by their X-ray diffraction patterns, and the identification of goethite was confirmed by its brown color, yellow-brown streak, striated prismatic crystals, and adamantine luster.

It is possible that very small amounts of goethite occur in the hematite ore. No goethite was observed in any of the polished or thin sections, but it could have been overlooked.

Hausmannite

Hausmannite (Mn_3O_4) is present in variable amounts in a zone surrounding the type 5 material in the Central ore body. Identification of the mineral was

established by X-ray techniques at the University of Minnesota (Royce, J., private company report). The mineral occurs both in the fragments of massive hematite and in the material cementing the fragments, but is far more abundant in the latter. In the massive hematite, hausmannite occurs in the same form as the hematite itself, whereas in the cementing material it occurs in irregular clumps or in clusters of radiating needles that reach a length of 5 to 6 mm. The amount present varies from specimen to specimen, and ranges to as much as 15 per cent. In general, it decreases in abundance away from the center of the zone.

Pyrite and Pyrrhotite(?)

Pyrite and a metallic mineral thought to be pyrrhotite are always closely associated, and are discussed together. The mineral thought to be pyrrhotite occurs as small (0.01 mm. or smaller in diameter) pinkish-cream, anisotropic, metallic grains within some pyrite grains.

Pyrite occurs principally as layers in chert in the altered greenstone that forms the walls of the deposits, in the lenses and stringers of altered greenstone within the ore bodies, and in the type 5 material. It also occurs very sparsely in the massive hematite ore and in the carbonate minerals in types 3 and 4 material. The pyrite in the layers within chert ranges in diameter from a maximum of about 1 cm. to a fraction of a millimeter. The smaller grains are generally rounded, whereas the larger grains tend to be subhedral and transect the layering. Because the larger grains transect the layering, it is thought that they might have been formed by recrystallization of the smaller grains. The same is generally true of the pyrite that occurs in the fissile greenstone near the hanging and footwalls of the deposit. These rocks are commonly layered; the fine pyrite is probably primary, and the coarse pyrite probably formed by the recrystallization of the fine pyrite. Features such as strain shadows of quartz around the euhedral grains and schistosity or cleavage which bends around the larger grains suggest that this pyrite formed before or during the major metamorphism.

The pyrite that occurs in the stringers of altered greenstone within the ore bodies and in some of the altered greenstone adjacent to the ore is rather different from that just described. It tends to occur in isolated anhedral to euhedral grains, or clumps of grains that reach a length of 4 mm. Very commonly these grains are extensively fractured and cut by veinlets of chlorite or carbonate. The edges of these veinlets are extremely irregular, suggesting that the pyrite has been partially replaced by the veining material. The same is true for the pyrite that occurs in the massive hematite and in type 5 material, but in these cases the vein filling is either hematite or magnetite. Pyrite also occurs as remnant grains inside larger grains of hematite and/or magnetite in the ore material. The pyrite that occurs in the carbonate in type 3 and 4 material may be fractured and veined by the carbonate, or it may occur in small unfractured euhedral crystals.

Copper Minerals

Chalcopyrite (CuFeS_2) is present in very small amounts in the Zenith mine, and associated with it are minute grains of minerals whose optical properties resemble those of chalcocite and covellite. The latter two minerals are sparse and were noted in only one polished specimen. Chalcopyrite occurs as very thin films along minor fractures in the greenstone, commonly in the vicinity of the ore bodies, and as fillings in parallel fractures that cut the chert layers in the pyritic cherts south of the Central ore body. It is associated also with pyrite in the altered greenstone adjacent to the ore bodies and with the pyrite in the carbonate in types 3 and 4 material. In the latter occurrences, the chalcopyrite occurs as small irregular grains with the pyrite and as veinlets cutting it. One specimen of native copper was found as a skeleton crystal intergrown with a manganese calcite lining a vug in the Central ore body.

Carbonate Minerals

Carbonate minerals occur in late veins that cut the ore bodies and the greenstone, as the cementing agent in type 3 material, and as the principal constituent of type 4 material. Carbonates also occur as an interstitial gangue material cementing fragments of massive hematite, as microscopic veinlets cutting all types of ore and the adjacent altered greenstone, and as the dominant mineral in the pyritic chert south of the Central ore body on the 17th level.

Most of the specimens of iron-bearing material of all types that contain carbonate minerals show several stages of crystallization of carbonate. On the basis of veining relations, four or five different stages of carbonate minerals are recognized; a still earlier generation of carbonate forms the cementing matrix of massive ore fragments or forms the fragments themselves. In addition, many carbonate grains have a compositional zoning, indicated by a change of refractive index within an optically continuous grain, and others show perthite-like intergrowths, which may have resulted from the exsolution of distinct carbonate phases. Because of this petrographic complexity, no attempt was made to correlate in detail the stages of carbonate formation.

Many of the carbonate minerals occur as subhedral to euhedral grains. The grains generally show little sign of deformation although some are extensively twinned and rarely the twin planes are slightly bent. This observation provides a means for determining the relative ages of the carbonates within a particular specimen. Where more than one stage of carbonate minerals is apparent, based on the varying degree of internal deformation, oriented remnants of the earlier carbonate in the later one can be seen. Other features such as optically continuous grains that extend from a carbonate vein into an earlier carbonate also indicate that the carbonate minerals have been extensively reworked. Again, where the relative ages of the minerals could be determined, the earlier carbonates are generally colored some shade of red and contain abundant minute hematite crystals, whereas the later ones tend to be white or light pink and devoid of hematite. It has been noted earlier that some of the carbonate veins in the greenstone also contain small amounts of hematite, or are bordered by narrow selvages of red-stained rock.

The carbonate minerals vary widely in composition (tbl. 2). Compositions of selected specimens were determined by a method established by Rosenberg (1960), using variations in the index of refraction of the ordinary ray and the (211) lattice spacing. Some of the specimens were then analyzed for manganese by spectrographic techniques, to check the analyses obtained by Rosenberg's method and to gain some idea of the total manganese content; iron was not determined by this method because many of the carbonates contain minute hematite crystals which could not be separated. The compositions seem to agree very well, except for two specimens of manganiferous calcite which contain more than 10 per cent MnCO_3 , which is greater than the total $(\text{Fe,Mn})\text{CO}_3$ indicated by the Rosenberg method. In general, the analyzed carbonates fall into two compositional groups, one being essentially calcite with limited amounts of Mg, Fe, and Mn in solid solution and the other being essentially a dolomite, with a constant amount of Ca and variable amounts of Fe, Mg, and Mn. In addition, a very few of the specimens are siderite with small amounts of Ca, Mg, and Mn in solid solution.

In a general way, the composition of the carbonate minerals varies systematically with their relative age. Where possible, they were divided into early and late carbonates on the basis of veining relationships or on their position in layered veins; those carbonates that formed the bulk of the type 4 material were also considered early carbonates. In nearly every case, the early carbonates as here defined are dolomites, whereas the late carbonates are calcite solid solutions. Most of the hausmannite in the deposit is associated with late veins and breccia cement, but the manganese content of "early" carbonates is not appreciably different from that of the "late" carbonates. In addition, there does not appear to be any regular spatial variation in the composition of the carbonates.

Table 2. Composition of single-phase carbonate minerals from the Zenith mine, in mole percentages of end-member components.

	CaCO_3	MgCO_3	$(\text{Fe,Mn})\text{CO}_3$	MnCO_3 ¹
Early carbonate minerals	52	30	18	
(type 4 material)	51	38	11	
	51	29	21	
	52	44	4	3.4
	50	46	4	
	50	40	10	2.5
	55	24	21	7.3
	49	45	6	1.8
	53	35	12	6.3
	50	30	20	5.0
	55	22	23	6.8
	51	31	18	
	55	24	21	

	CaCO ₃	MgCO ₃	(Fe,Mn)CO ₃	MnCO ₃ ¹
Early vein carbonate	50	45	5	2.0
minerals (earlier of two phases)	52	42	6	
	51	38	11	4.6
	50	35	15	
	49	36	15	2.5
	53	33	14	
	52	27	21	
Late vein carbonates (later of two phases) and carbonates from single phase veins	50	35	15	
	96	4	0	
	51	38	11	
	94	2	4	4.4 ²
	50	44	6	
	97	2	1	0.97
	6	16	78	4.6
	89	2	9	
	52	44	4	
	96	4	0	1.7 ²
	97	3	0	1.3 ²
	97	3	0	
	93	4	3	
	96	3	1	
	98	0	2	
	98	2	0	
	96	3	1	0.98
	95	5	0	
	51	40	9	2.5
	100	0	0	
51	34	15		
92	3	5	11.7	
85	3	12	13.6	
95	4	1	1.7 ²	
93	3	4		
8	7	85	3.9	
94	3	3		
95	2	3		
95	4	1		
96	3	1		

¹Spectrographic analyses, Mineral Constitution Laboratories, College of Mineral Industries, Pennsylvania State University. N. Suhr, analyst.

²The apparent discrepancy in the composition of these samples is probably due to the possible 2 per cent error in the method used to determine the bulk composition of the carbonates.

Quartz

Quartz is not common in the ore bodies themselves, although it occurs in veins, in the cherty material in the greenstone, and in the jaspilite capping the ore bodies. That quartz which does occur within the ore bodies generally is associated with the carbonate material in types 3 and 4 ore, where it forms small irregular grains. Petrographic relations suggest that these are remnants of grains that have been largely replaced by the carbonate minerals. Quartz also occurs in some of the carbonate veins that cut the ore bodies, as small remnant grains, and as small euhedral crystals that coat the walls of the veins. Most of this quartz has straight extinction, although the small size of the grains makes it difficult to determine. Very rarely, minute grains of quartz are present in the fragments of type 1 ore, and a few small quartz veins cut the ore. These veins are composed of large anhedral grains with varying degrees of undulose extinction and smaller subhedral to euhedral grains, which usually have straight extinction. Small amounts of carbonates are also present in these veins, mainly along later fractures.

Layer Silicates

Minerals of the chlorite group occur sparsely throughout the ore bodies. The optical properties and crystallographic habit of the minerals differ widely; most are very fine-grained, many appear to be partly altered or stained by hematite, and more than one chlorite commonly is present in a single specimen. As a consequence, no attempt was made to determine the compositional range of the chlorites; also, the identification of some chlorite is questionable. Chlorite occurs (1) as small remnant grains in the massive hematite fragments, (2) associated with the carbonate minerals in types 3 and 4 material, and (3) with the carbonate and quartz-carbonate veins cutting the ore bodies and the greenstone. Chlorite also is found in minute veins, associated with crystalline hematite, and as vermicular intergrowths in some of the quartz.

Chlorite is the main constituent of the rock bodies within the ore bodies. The material generally is extremely fine-grained, but some of it has a porphyroblastic texture. The chlorite in the porphyroblasts is generally pleochroic from colorless to light green, whereas that in the matrix is non-pleochroic and darker green. The contrast in optical properties indicates that the two chlorites differ in composition.

Where chlorite is associated with ore, particularly along the borders of the ore bodies and in the rock seams within it, other layer silicates may be present. These are difficult to identify. The birefringence and general indices of refraction, however, indicate that a part of this material probably is kaolinite, whereas almost certainly a part is fine-grained muscovite. Kaolinite also occurs in small amounts throughout the ore bodies as patches of white to greenish-white material along fractures and between breccia fragments.

Apatite, Topaz, and Tourmaline

Apatite, topaz, and tourmaline are treated as a group, as none is abundant and all involve some of the volatile elements or oxides. Calcium phosphates are

most common occurring both as the mineral apatite and as aggregates of poorly crystalline rounded grains of indefinite composition, which were identified by the electron probe. These phosphates occur most commonly in the fringes of the ore bodies and in the lenses of hematite-bearing altered greenstone that are near the ore bodies. The well crystallized apatite commonly forms minute tabular or rounded grains associated with hematite crystals in late cross-cutting fractures. The poorly crystallized material occurs in minute clumps and veinlets in greenstone that has been impregnated with hematite along tiny fractures or in pervasively altered greenstone. The phosphate minerals are always associated with iron minerals that appear to have been introduced into the rock.

Topaz and tourmaline have each been found in only one specimen. The topaz occurs in small rounded and wedge-shaped grains associated with a small quartz vein that cuts the east end of the Central ore body. Some of the grains are along fractures which also carry hematite and calcite, but the larger ones form discrete grains in the vein. The tourmaline is colorless to bluish-green, and occurs in prismatic grains associated with quartz-pyrite veinlets and chloritic lenses in a thin layer of pyritic chert. The euhedral texture and association with quartz veins suggests that the tourmaline was introduced into the rock.

Gypsum

Acicular and lathlike crystals of gypsum as much as 3 mm. long were found in specimens from the south side of the Central ore body on the 17th level. Other specimens from the immediate vicinity have traces of malachite. Both of these minerals occur along fractures in the ore and are associated with a limonitic coating on the walls of fractures. The area in which these specimens were found had been open to the atmosphere for about 10 years at the time the specimens were collected, and the ore in this area contains large amounts of pyrite. It seems likely, therefore, that these minerals formed subsequent to the opening of the mine workings.

Mineral Distribution and Zoning

The distribution of magnetite, pyrite, and hausmannite in the western part of the Central ore body defines a zonal arrangement in both lateral and vertical dimensions. Although magnetite occurs in small amounts throughout most of the ore body, it is sufficiently abundant to deflect a compass needle only in the area of the type 5 material, which is below the 17th level, and in some of the other mineralized material that immediately adjoins the type 5 material. This area is the magnetite zone, and is also the only place within the main body of mineralized material where pyrite occurs in abundance and with any degree of regularity. Hausmannite occurs within the magnetite zone and in a small area surrounding the magnetite zone; this small area is the hausmannite zone.

The limits of the zones cannot be exactly outlined because of the lack of accessible mine openings, but the zones are nevertheless well defined. Although magnetite is present in most of the specimens studied, it is abundant only within the magnetite zone. With three known exceptions, hausmannite occurs only within the limits of the hausmannite zone; it is common inside these limits and ab-

sent outside of them. The three exceptions are widely scattered, but all are within the Central ore body. Neither magnetic material nor hausmannite were observed in the West ore body.

In a larger sense, the entire Central ore body and parts of the West ore body on the 17th level and below can be regarded as being within a carbonate zone. Types 3 and 4 material were first reported from the eastern end of the Central ore body on the 15th level; the volume of this material was greatly enlarged on the 16th level, and the material encompassed is present throughout the Central ore body on the 17th level. Specimens in the mine office collection indicate that type 3 material also occurred on the 14th level and similar material can be found on the dumps of the Sibley and Savoy mines. Possibly type 4 material also is more widespread, and it may have been reported previously only as routine iron-formation. The limits of such a carbonate zone are therefore poorly defined, and it is possible that carbonate material was so widespread that a carbonate zone as such does not exist.

Wall Rock Alteration

A halo of altered greenstone, which can be divided into two principal zones, surrounds the ore deposits in the Zenith mine. The outer zone differs substantially in mineralogy and chemical composition from the unaltered greenstone, but cannot be distinguished megascopically from it. The inner zone, immediately adjacent to the ore bodies differs markedly in both color and physical properties from the unaltered rock.

Outer zone

The rocks of the outer zone differ from the normal greenstone in lacking an amphibole mineral or epidote. The width of the zone is unknown as the rocks are megascopically indistinguishable from the normal greenstone, but to judge from available chemical analyses it appears to exceed 100 feet.

The principal mineral in the rocks of the outer zone is a chlorite, accompanied by lesser amounts of fine-grained muscovite, quartz, and albite. The quartz and albite occur as scattered small rounded grains commonly having ragged indistinct edges. The quartz appears to be partially replaced by chlorite and the albite by muscovite. Leucoxene is ubiquitous but sparse, and generally forms aggregates that are parallel to the schistosity.

The rocks in the outer zone have a schistose structure, and contain both megascopic and microscopic veins of quartz, chlorite, and carbonate minerals as well as scattered euhedral grains of carbonate minerals. The veins of different mineralogy show no consistent paragenetic sequence; however, the last recognizable event was a carbonate metasomatism that affected all the previously-formed veins and commonly also the rock itself. The quartz and carbonates in these veins show varying degrees of internal deformation; minerals of the later stages are generally clear and have no twinning or undulatory extinction.

Some of the carbonate and quartz-carbonate veins in the outer zone contain small amounts of hematite, and the rock immediately adjacent to the

vein is stained red. These veins are not restricted to the altered zone, for similar veins occur in the normal greenstone 300 or more feet from the ore body. Also, lenslike patches of rock that are heavily stained or impregnated with hematite are present in the outer zone, and are similar to the more highly altered material of the inner zone. These patches are as much as 20 feet thick, grade outward into the normal rock of the outer zone, and locally contain as much as 50 per cent crystalline hematite in the center. They occur on both the north and south sides of the West ore body, and on the north side of the Central ore body. Finally, small amounts of pyrite and chalcopyrite occur in the veins in the outer zone and rarely as thin coatings along cleavage planes and other small fractures throughout the outer zone.

Inner Zone

The inner zone is as much as 40 feet thick in the accessible workings, and consists of rocks that are generally brown or red in color, although some are black to pale green and pink. Probably the zone was much thicker in some of the upper levels. The rocks commonly have a slight schistosity or cleavage, but locally are very soft and lack any visible internal structure. Contacts of the altered zone with the ore bodies are either sharp or marked by slight brecciation and slickenside striae whereas contacts with the outer zone are transitional. The rock generally is impregnated with hematite, which imparts a pronounced red color to it. The transition to the outer zone is marked by a gradual decrease in the amount of hematite; in the outer margins of the zone hematite is present only along cleavage planes and small-scale fractures.

The principal mineral in the rocks of the inner zone is chlorite, and at least two distinct members of the chlorite group are present. X-ray diffraction studies indicate that all the chlorites are iron-rich, with the intensities of the (001) and (003) reflections less than those of the (002) and (004) reflections (Brindley and Robinson, 1951). Kaolinite and fine-grained muscovite ($2M_1$ polytype) are present in many specimens, and occur intermixed with the chlorite as discrete local patches or, in the case of kaolinite, as the major mineral. In addition, two of the specimens studied contain vermicular books and irregular grains of a mineral that has many of the optical properties of an illite (hydromuscovite of Rogers and Kerr, 1942; low relief, $n >$ balsam, moderate birefringence). Less abundant minerals are quartz, both as veins and primary grains, carbonate minerals, commonly as veinings; apatite; zeolites (identification uncertain); and rare grains of talc and zircon. The opaque minerals include leucoxene, which is uniformly distributed through the rocks as a primary mineral of the original greenstone, and pyrite, which is present in euhedral crystals and in irregular seams and clumps, as well as the more abundant hematite. Hematite forms small grains and overgrowths scattered through the rock, stringers and veins associated with kaolinite or carbonate minerals, and discrete veins.

Petrographic relations indicate that the rocks within the inner zone had a complex history. Following the development of the initial chlorites and other layer silicates, the rocks were brecciated or otherwise fractured, impregnated by hematite, and cut by veins of quartz, hematite, carbonates, and

chlorite. The complexity of the events is indicated by the fact that some specimens show two or more stages of veining by carbonates, hematite, or chlorite. In general, however, impregnation by hematite preceded the veining. Replacement was more significant than fracture filling in developing the veins, for the veins tend to be irregular in width and commonly contain remnants of the pre-existing rocks. In this regard, most of the carbonate veins contain hematite, which appears to have replaced the carbonate minerals, and most of the quartz appears to be replaced by chlorite.

The intensity of the hematite staining in the inner zone decreases away from the ore bodies, and this decrease is commonly accompanied at many places by a mineralogical change. The principal layer silicate in the outer part of the inner zone is always a chlorite. The minerals occurring adjacent to the ore are kaolinite and chlorite and, slightly further out, muscovite; the muscovite-bearing rocks are always separated from the ore by a thin layer of either kaolinitic or chloritic rocks.

Chemical Changes Accompanying Alteration

Analyses of the altered rocks from both the inner and outer zones reveal that they are significantly enriched in iron over the normal greenstone (tbl. 3). An average of three analyses of normal greenstone gives a content of 10.4 per cent FeO (Schwartz, 1924), whereas altered rocks from within 50 feet of the ore bodies contain an average of 20.4 per cent FeO (percentages given are total iron, recalculated to FeO for comparison). The iron content of the altered rocks diminishes gradually away from the ore bodies, and at distances of more than 100 feet from the ore bodies approaches that of the normal greenstone. The ratio of ferrous to total iron increases away from the ore bodies, and then decreases in the normal greenstone.

Complete chemical analyses of the altered rocks are not available, and therefore the total chemical changes accompanying the alteration cannot be treated quantitatively. Some idea of the changes involved can be gained, however, by comparing the mineralogy of the altered and unaltered rocks. Those rocks of the inner zone composed largely of kaolinite must have undergone a removal of SiO_2 and an addition of Al_2O_3 , as the percentages of these oxides in kaolinite differ markedly from the analysis of the average greenstone. Likewise, the presence of any significant amount of muscovite implies the addition of K_2O . Much of the CaO and MgO released by the destruction of the amphiboles and epidote may have gone into carbonate minerals, but some may have been removed from the rock. There is probably some MgO in the chlorite also, but the X-ray diffraction studies indicate that the chlorites throughout the altered zones are iron-rich. Finally, the abundance of layer silicates indicates that water has been added to the rocks in significant amounts.

Discussion of Wall Rock Alteration

The pattern of alteration surrounding the ore bodies in the Zenith mine is similar to that which surrounds some of the porphyry copper and other hydrothermal deposits (see, for example, Schwartz, 1959; Burnham, 1962). The

Table 3. Iron content of altered and unaltered Ely Greenstone

Sample Location	Total Iron ¹ (as FeO)	Actual FeO ¹	Actual FeO Total Iron
Within 50 feet of ore bodies	16.1%	13.7%	.85
	21.5	19.45	.91
	23.8	21.41	.90
	16.6	15.50	.93
	21.3	18.65	.88
	<u>23.0</u>	<u>20.81</u>	<u>.79</u>
Average	20.4		.876
From 50 to 100 feet from ore bodies	22.1	19.71	.89
	12.7	11.91	.94
	20.1	18.30	.91
	18.4	<u>16.85</u>	<u>.92</u>
	Average	18.3	
More than 100 feet from ore bodies	16.7	14.92	.89
	16.1	14.82	.92
	11.2	11.00	.98
	13.9	11.44	.82
	11.4	<u>10.48</u>	<u>.92</u>
Average	13.9		.906
Average greenstone ²	10.4	7.3	.70

¹Analyses by C.O. Ingamells, Mineral Constitution Laboratories, College of Mineral Industries, Pennsylvania State University.

²Data from Schwartz (1924).

general pattern of hydrothermal alteration is characterized by the following mineralogic zones, proceeding from the unaltered country rock towards the vein: an epidote-chlorite zone, a montmorillonite zone, a kaolinite zone, a muscovite zone, and a biotite zone. Individual patterns differ, depending upon factors such as the rock types and nature of the mineralization, and the inner zones may not be present in less intense altered areas. With respect to the Zenith mine, the epidote-chlorite zone is represented by the unaltered greenstone, the montmorillonite zone is either absent or, more likely, is represented by the chlorite rocks of the outer zone, and the kaolinite zone is represented by the inner part of the inner zone of alteration. The muscovite zone is only rarely represented.

Montmorillonite is either absent from the altered rocks or present in such small amounts that it was not detected by optical or X-ray examinations. Considering the addition of iron to the altered rocks and the oxidation state of the iron, however, it seems likely that the chlorite rocks (outer zone, and the outer part of the inner zone) are equivalent to the montmorillonite zone of the typical alteration halo. X-ray diffraction studies indicate that the chlorites are iron-rich, and chemical analyses indicate that most of the iron is in the ferrous state. The montmorillonites and chlorites are similar structurally, but the

montmorillonite lattice has only a limited capacity for divalent ions, and the iron in iron-bearing montmorillonites (nontronite) is largely in the ferric state, whereas the exact opposite is true for the chlorites (Brindley, G. W., personal communication; Deer, Howie and Zussman, 1962). It is reasonable to expect, then, that the abundance of ferrous iron would favor the development of chlorite in preference to montmorillonite, and thus account for a chlorite rather than a montmorillonite zone.

The only other discrepancy between the more common case of hydrothermal alteration and that at the Zenith mine is the reversal of the kaolinite and muscovite zones. A layer of sericite schist as much as 30 feet thick reportedly bordered the Northwest seam ore body (Reid, 1956), but this area is no longer accessible; the relations there might have been more similar to the idealized sequence. It should also be noted that the wall rock alteration at the Zenith mine is nearly identical to that at the Soudan mine (Schwartz and Reid, 1955), except that kaolinite is less abundant at the Soudan mine and a nearly pure sericite rock borders the ore bodies in some places.

Mineral Paragenesis

The paragenetic sequence of the minerals that form the ore bodies in the Zenith mine could not be established in detail because of the variations between the specimens studied, but the gross pattern is known. The first major event apparently was the replacement of the larger bodies of Soudan Iron-formation — together with some of the surrounding greenstone — by the iron oxides and carbonate minerals that now form fragments in the brecciated material. Fragments of massive hematite thus formed contain remnant grains of carbonate minerals in addition to quartz and layer silicates, indicating that at least some of the carbonate deposition preceded or was contemporaneous with the deposition of the iron oxides. The material was then brecciated and cemented either by hematite or a combination of hematite and carbonates, and in turn was again fractured and veined by hematite, carbonate minerals, and quartz in all combinations. As the wall rock alteration was accompanied by and characterized by a marked increase in the iron content of the altered rocks, it most likely developed concurrently with the ore bodies.

At any point in space and time, the first iron oxide to be deposited apparently was magnetite; later it was oxidized to or surrounded by hematite, for most all specimens studied contain some remnant magnetite. The oxidation did not take place as a single event, however, but was contemporaneous with the deposition of the iron, for each successive stage of carbonate veins carry euhedral crystals of hematite with magnetite cores. The amount of hematite formed in the successive carbonate veins decreased with time, however, and the last veins contain little or no hematite.

Some pyrite also was forming during most of the period of mineralization. Unquestionably some of the pyrite in and around the deposit is an original primary mineral in the iron-formation, but the fact that pyrite is enclosed by and encloses hematite, is fractured and veined by hematite, and occurs in discrete grains in late carbonate veins indicates that a part was formed at later

stages. Much of this pyrite contains small cores or remnants of pyrrhotite, corroborating the concept of progressive oxidation accompanying the deposition of iron, as shown by the magnetite-hematite relations. The rare copper sulfides apparently postdate the iron sulfides with which they are immediately associated, and the one known occurrence of native copper is associated with a late calcite vein.

Hausmannite formed with massive hematite both in the early stages and in the later carbonate veins and cementing material. It increases in abundance relative to hematite in the late veins, however, and appears to have been deposited mainly after the majority of the hematite.

Quartz was deposited with carbonate during several stages of carbonate-vein formation, and also crystallized in late quartz veins that occur in the Central ore body. Most of this quartz occurs as scattered remnant grains in the carbonate minerals, but even in the quartz veins themselves it shows evidence of being partially replaced by carbonates.

The extent to which these processes represent discrete events is unknown, but the several stages of carbonate veins and the variations in the amount of crystal deformation from one stage to the next indicate that the period of mineralization coincided with a period of tectonic activity, and that fracturing probably was more or less continuous. It is also likely that the main mineralization and the deposition of carbonates and iron oxides were also continuous and virtually contemporaneous, proceeding to varying degrees of completion at various places in the deposits as old channelways were closed by the deposition of minerals and new ones were opened by repeated fracturing.

Genesis of the Deposits

General Mode of Origin

The hematite deposits in the Zenith mine were formed by the post-metamorphic replacement of the iron-formation, and perhaps some of the surrounding greenstone, by iron oxides. That the deposits formed after the last period of regional deformation and metamorphism is shown by the association of the deposits with such obviously post-metamorphic features as the altered wall rocks, the loosely-cemented jaspilite immediately above the deposits, and the undeformed hematite-carbonate veins in the rocks surrounding the deposits. Furthermore, there is absolutely no indication of any preferred orientation in the hematite, although such orientation would be expected and has developed in metamorphosed hematite deposits and hematite-bearing rocks in Michigan (Van Hise and Leith, 1911). Finally, there is the evidence from the Soudan mine to indicate that the deposits there, and by association the other deposits, of the Vermillion range, are post-metamorphic (Gruner, 1926; Klinger, 1960).

The replacement origin of the deposits was recognized in most of the earlier investigations (Clements, 1903; Abbott, 1906; Van Hise and Leith, 1911). The average jaspilite at the Soudan mine contains 34.1 per cent iron and 50.8 per cent silica (Klinger, 1956), which is equal to 32.6 per cent Fe_2O_3 by volume

and 67.4 per cent SiO_2 . Assuming that the composition of the jaspilite at Ely is similar to that of the jaspilite at Soudan, the comparison of these figures with the approximate composition of type 1 ore in place (90 per cent Fe_2O_3 by volume, 7 per cent SiO_2 , and 3 per cent porosity) indicates that approximately 57 per cent of the present volume of the massive ore is occupied by hematite that was introduced into the deposits. The volume relationships could be explained by a slumping and resultant compaction of the ores, although there are no features suggestive of slumping in the ore or adjacent wall rock, nor are there large voids within or above the deposits. There are, on the other hand, many features still present in the ore such as banding, lenses of unreplaced iron-formation, and stringers of altered greenstone which would have been destroyed had any significant slumping occurred.

The fundamental question is whether the replacement of the gangue minerals in the iron-formation was primarily a supergene or a hypogene process. It is well known that under certain environmental conditions ground waters can dissolve and transport large quantities of iron, silica, and carbonates, and it is equally well known that hydrothermal solutions can do so also, although the conditions and mechanisms are not as well understood. The arguments cited by Gruner (1926) in support of the hydrothermal hypothesis all apply, although the lack of alteration of the bulk of the iron-formation at the surface might be simply a structural effect. Mineral zoning is characteristically associated with hypogene deposits, but in the case of the Zenith mine it might be caused by decreasing circulation of ground water, and hence decreasing extent of oxidation, with depth. Some features of the wall rock alteration, notably the development of kaolinite adjacent to the deposits, could be attributed to either hypogene or supergene processes.

The overall association, however, is more suggestive of hypogene than of supergene deposition. The following factors support a dominant hypogene origin: (1) the association of the iron oxides and the ore bodies with carbonate minerals of probable hypogene origin; (2) the similarity of the wall rock alteration, particularly the zoning, to that surrounding many unquestioned hydrothermal deposits, and the accompanying introduction of iron into the altered wall rocks; (3) the evidence that the deposition of iron and the oxidation of magnetite to hematite were virtually contemporaneous processes; (4) the mineral zoning, which brings together elements which generally are separated by supergene processes (Mason, 1958); and (5) the occurrence of hausmannite, which apparently is always a hypogene mineral (Hewett and Fleischer, 1960). The hypothesis is further substantiated by data on the composition of some of the carbonate minerals and the presence of $2M_1$ muscovite in the alteration halo, which indicate that the temperature of the ore solutions was in the range of $200^\circ\text{-}400^\circ\text{C}$. The large scale removal of quartz can be more readily understood under these conditions, due to the increase in solubility of quartz at higher temperatures (Kennedy, 1950). It may be that some of the "soft" ore which occurred in the upper levels of the mine resulted from the partial or complete leaching of the cementing carbonates by surface waters, as suggested by Gruner (1926), but this idea is not pertinent to the main argument.

Nature of the Material Replaced

The question might be raised as to the nature of the material that was replaced by the iron oxides. It has always been implied that the host rock for the ore deposits was a jaspilitic iron-formation (Van Hise and Leith, 1911; Gruner, 1926; Royce, 1938; Reid, 1956). Jaspilitic iron-formation definitely is the host for the ore at the Soudan mine and for the upper part at least of the Ely deposits. Some of the type 4 material in the Zenith mine has a well developed color and compositional layering, however, which suggests that this material may be a remnant of a primary carbonate facies of the iron-formation. If this material is an original sediment, then it is possible that the bulk of the material replaced by the iron oxides was a carbonate mineral and not a variety of quartz, and therefore that stratigraphic and mineralogic variations within the iron-formation were the principal controls for localization of the ore deposits.

Whether or not the layered type 4 material is a primary sediment and, if so, whether it constituted the bulk of the replaced material, cannot be directly determined. The carbonate grains in the type 4 material are generally untwinned, indicating that they have not undergone any significant deformation since they were formed. There is abundant evidence, however, that these grains have been recrystallized or reworked, and thus the absence of twinning in the carbonates does not necessarily mean that they are not primary. These rocks do contain a few quartz grains, which apparently are remnants of grains largely replaced by the carbonates, but this fact does not prove that the original rock was a chert. The remnant grains of quartz, carbonate, and chlorite in the massive hematite do not give any clue either, as they are not sufficiently abundant to give a reasonable sample of the original rock.

Carbonate-bearing facies of iron formations are common throughout the Lake Superior region (Clements, 1903; Van Hise and Leith, 1911; James, 1954; Goodwin, 1962), although the minerals commonly associated with them are chert, iron silicates, magnetite, and iron sulfides. Rocks composed of hematite, chert, and carbonates are found in the region (James, 1954; White, 1954), but no rocks composed solely of hematite and carbonate have been reported to my knowledge. On a broader scale, jaspery or jaspilitic iron-formations similar in all respects to the common variety of the Soudan Iron-formation occur in areas of metamorphosed basalts throughout the Canadian Shield (Geological Survey of Canada, 1957), but no mention is made of carbonate-hematite rocks.

For the reasons given and for lack of evidence to the contrary, it is assumed that the bulk of the material replaced by iron oxides was chert or fine-grained quartz, although it is possible that some of the type 4 material may well be a primary sediment or have developed by the oxidation and recrystallization of a primary carbonate sediment.

Control of Ore Localization

It appears that the ore deposits in the Zenith mine were localized by fracturing and brecciation of the original iron-formation. In many places the contact between the ore and the greenstone is marked by a breccia consisting of

fragments of hematite and of the altered greenstone. As pointed out by Abbott (1906), the fracturing of this soft material would hardly have produced angular fragments, and some of the brecciation must therefore have preceded the alteration of the fragments, and thus deposition of the ore. This fracturing and brecciation would facilitate both the influx of solutions and the rate of reaction, and the deposits thus formed would tend to be localized in the areas of greatest deformation. It should be pointed out, however, that if the majority of the material that was replaced was a carbonate iron-formation, the primary control of ore localization could well have been as much lithologic as structural.

Physical Conditions of Ore Deposition

Temperature

The range of temperatures under which the deposits formed can be estimated by the composition of some of the carbonate minerals, and by the stability range of $2M_1$ muscovite. The phase relations in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$ were determined by Rosenberg (1960) for temperatures above 400°C . (fig. 8). The diagram shows the compositions of carbonate minerals that can exist in a stable condition, and the range in composition of the minerals which can coexist in equilibrium at the temperatures shown. The phase

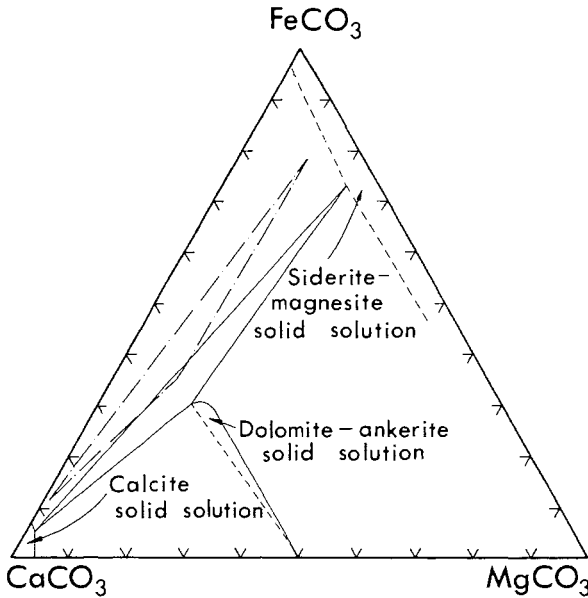


Figure 8. *Subsolidus phase relations in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$, after Rosenberg (1960). Three areas of single-phase solid solutions (calcite, dolomite-ankerite, and siderite-magnesite) are shown. Solid and dashed lines show observed and inferred boundaries at 400°C . and sufficient pressure to prevent dissociation; the three-phase triangle at 500°C . is shown by dot-dash lines.*

relations are not significantly changed by the addition of as much as 10 weight per cent MnCO_3 , and therefore the application to the carbonates in the Zenith mine is justified, as only two of the analyzed specimens have more than 10 per cent MnCO_3 , and these were both from the same sample.

The practical application of these data requires coexisting equilibrium mineral pairs. If there is evidence that the mineral pair was formed contemporaneously at equilibrium, then their compositions can be interpreted by Rosenberg's diagram both to show whether they were in equilibrium and to determine at what temperature they were formed. In general, the petrographic relations between the carbonates in the Zenith mine are so complex that it is difficult to determine which of the carbonate phases might have formed contemporaneously and to transfer the information from a thin section to a hand specimen for sampling. The compositions of carbonates that might be construed as having formed in equilibrium with each other are plotted on Figure 9, the members of each pair being connected by a tie line. The compositions plotted are, for the most part, two obviously different carbonates from the same vein. The pair labeled 110 probably represents the closest approach to equilibrium; in this pair the sideritic member existed as separate and discrete grains scattered uniformly through a vein composed largely of the other member of the pair.

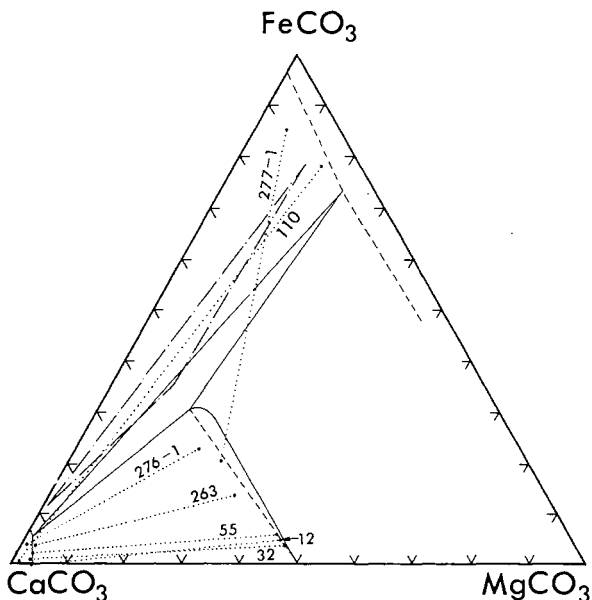


Figure 9. Compositions of carbonate minerals which might be construed as having formed in equilibrium plotted on the subsolidus phase diagram for the system CaCO_3 - MgCO_3 - FeCO_3 . Individual compositions are plotted as dots; the parts are connected by dotted tie lines.

Except for sample 277-1, the compositions of the pairs suggest that they formed at or near equilibrium. The only pair that gives any definitive information about a possible temperature of formation, however, is sample 110. The composition of the calcite member and the fact that the tie line joining the two compositions crosses the three-phase field both indicate that the mineral pair formed at a temperature somewhat less than 400°C., whereas the composition of the sideritic member suggests a temperature of formation somewhat above 400°C. Allowing for plotting errors and the 2 per cent analytical error, this mineral pair probably was formed at a temperature close to but lower than 400°C.

The composition of the sideritic member of sample 277-1 lies on the two-phase boundary at 500°C., suggesting that this carbonate formed at or above this temperature. The carbonate minerals commonly crystallize at compositions that are metastable at the temperatures of their formation; therefore, the composition of a single phase is not as reliable a temperature indicator as a coexisting mineral pair. Nevertheless, the composition of this specimen tends to confirm that the mineral was deposited at a moderately high temperature.

Experimental data on muscovite indicate that the 1M polytype will undergo a phase transition to the 2M₁ polytype somewhere in the range 200° to 350°C. (Yoder and Eugster, 1955). Most minerals at the time of their formation tend to be in equilibrium with their environment, and it is therefore probable that the 2M₁ muscovite formed above the temperature of the transition to the 1M polytype. Similar data indicate that at temperatures of 350° C. and above the assemblage kaolinite-muscovite will tend to react to form the assemblage muscovite-pyrophyllite-boehmite (Hemley, 1959). Thus the presence of both 2M₁ muscovite and kaolinite in the altered rocks close to the ore bodies indicates that the temperatures of alteration were at least 200°C., but probably were not much higher than 350°C.

The carbonates used for temperature determinations were taken from the center of the deposits, and their temperatures of formation presumably approximate the maximum temperature of ore formation. The minimum possible temperature was thus from 200° to 350° C., and the maximum was probably higher than 400° C.; the general temperature range during most of the period of ore deposition was probably from 350° to 400° C.

Pressure

Pressures existing at the time of ore formation cannot be estimated with any degree of accuracy, although the repeated brecciation of the deposits indicates that they were formed at fairly shallow depths. The implication is that the deposits were open to ground water circulation at least part of the time; under these conditions the effective pressure on the ore fluid would be close to the hydrostatic pressure. On the other hand, fluid pressures in hydrothermal wells may greatly exceed the hydrostatic pressure (Fenner, 1936; White and others, 1963).

Chemical Conditions of Ore Deposition

Large amounts of oxide and carbonate minerals and minor amounts of sulfide minerals were introduced into the Zenith deposits, suggesting that the partial pressures (or fugacities) and absolute amounts of oxygen, sulphur, and carbon dioxide were important chemical factors controlling the formation of the assemblages of iron minerals. If the mineralogic relations suggest that two minerals containing the same element, such as magnetite and pyrite, formed in equilibrium with each other, the ratio of the activities (and therefore fugacities) of the gaseous species involved in the reaction can be calculated, provided that data on the reaction temperature and free energies of formation of the reactants and products can be obtained. The general method can be illustrated by considering the mineral pair cited, in the reaction $3\text{FeS}_2 + 2\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{S}_2$, where:

$$\Delta F_{\text{R}}^{\circ} = \Sigma(\Delta F_{\text{f}}^{\circ}) \text{ products} - \Sigma(\Delta F_{\text{f}}^{\circ}) \text{ reactants}^{1/}$$

and

$$\Delta F_{\text{R}}^{\circ} = -RT \ln K, \text{ where } K = \frac{(a_{\text{S}_2})^3}{(a_{\text{O}_2})^2}$$

Absolute values for the fugacities can then be calculated as functions of temperature if there is some independent means of estimating the fugacity of one of the gaseous species. If free energies of solution and ionization for the aqueous species are known for the appropriate temperatures, then the activities of the various species in the solution and the pH of the solution can also be calculated; however the free energy information is not available.

The presence of remnant magnetite in the several stages of hematite indicates that the fugacity of oxygen which prevailed at the time of ore deposition fluctuated around the equilibrium value for the coexistence of magnetite and hematite, although most of the time it exceeded this value. The fugacities of oxygen (f_{O_2}) in equilibrium with various pairs of iron and manganese minerals are shown in Figure 10. The general method used to calculate the curves was to first calculate the change in free energy for the reactions, by the use of free energy functions tabulated in Lewis and Randall (1961). The fugacities of oxygen at various temperatures were then calculated by the method described above.

The presence of hematite and magnetite inclusions in pyrite, and pyrite inclusions in hematite, suggests that these three minerals may have formed in equilibrium with each other, at least in the magnetite zone in the Central ore

^{1/} $\Delta F_{\text{R}}^{\circ}$ = Standard free energy change accompanying a given reaction.

$\Delta F_{\text{f}}^{\circ}$ = Standard free energy change accompanying the formation of a compound from its elements in their standard states.

(a_{X}) = The activity of element or compound X under the conditions of the reaction; in the case of gases, activity is numerically equal to fugacity.

R = The universal gas constant.

T = Temperature in degrees Kelvin.

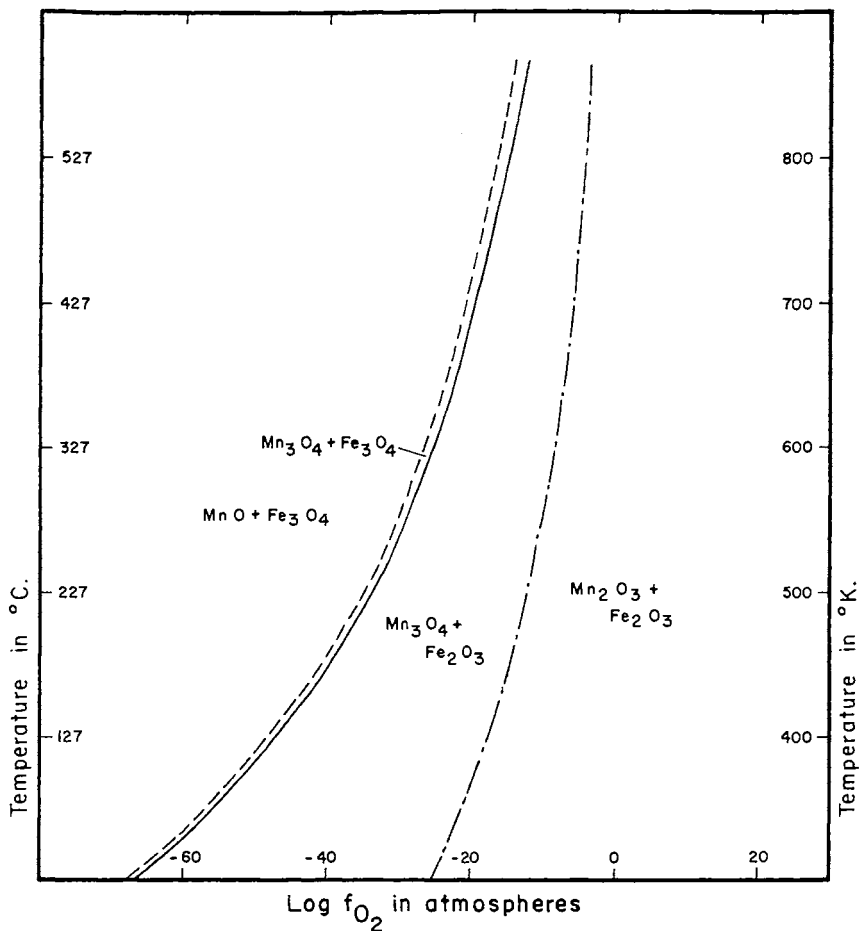


Figure 10. Fugacities of oxygen (f_{O_2}) in equilibrium with various mineral combinations, plotted as a function of temperature. The dashed line represents the mineral combination $MnO-Mn_3O_4$; the solid line $Fe_3O_4-Fe_2O_3$; and the dot-dash line $Mn_3O_4-Mn_2O_3$.

body. The fugacities of sulphur in equilibrium with this mineral combination at 250° and 400° C. were calculated (tbl. 4), using the reactions and equations cited previously, and the equilibrium fugacity of oxygen for the coexistence of magnetite and hematite. The presence of pyrrhotite remnants in pyrite indicates that the initial fugacity of sulphur must have been lower than the equilibrium value for the conversion of pyrrhotite to pyrite, and these values were calculated for the same temperatures, using the same general method (tbl. 4). Thermodynamic data for the sulfides were obtained from Barnes and Kullerud (1961), and for the oxides from unpublished compilations by H. L. Barnes.

Rare late siderite veins are present in the Central ore body, and one of these contains small vugs lined with minute crystals of siderite and goethite.

Table 4. Range of fugacities of oxygen, sulphur, and carbon dioxide at the time of ore deposition, at various possible temperatures of ore deposition all values in atmospheres.

Temperature	250° C.	400° C.
Fugacity of oxygen ¹	10 ^{-31.8}	10 ^{-20.2}
Minimum fugacity of sulphur ²	10 ^{-14.8}	10 ^{-7.4}
Fugacity of sulphur ³	10 ⁻¹⁰	10 ^{-3.7}
Fugacity of carbon dioxide ⁴	10 ^{3.4}	10 ^{4.9}
Maximum fugacity of carbon dioxide ⁵		10 ¹⁰

¹Equilibrium value for the coexistence of magnetite and hematite.

²Based on the presence of remnant pyrrhotite.

³Equilibrium value for the coexistence of magnetite, hematite, and pyrite.

⁴Equilibrium value for the coexistence of magnetite, hematite, and siderite.

⁵Equilibrium value for the coexistence of graphite and water, when the fugacity of water is 1000 atmospheres and that of oxygen is determined by the coexistence of magnetite and hematite.

Assuming that the major difference in the free energies of formation of hematite and goethite is due to the hydration of the hematite, and that the fugacity of oxygen at the time the crystals were formed was close to the equilibrium value for the coexistence of magnetite and hematite, estimated values for the fugacity of carbon dioxide at 250° and 400° C. were calculated from the reaction $2\text{FeCO}_3 + \frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{CO}_2$ (tbl. 4). The thermodynamic data on siderite were estimated from data on the fugacity of carbon dioxide (Majumdar and Roy, 1956) and from experimental data on the breakdown of siderite (French and Eugster, 1962, corrected by J. L. Haas).

Carbon dioxide and methane might also be produced by the reaction of graphite in the graphitic schists with water, according to the reactions $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$ and $\text{C} + 2\text{H}_2\text{O} = \text{CH}_4 + \text{O}_2$. The fugacities of oxygen, carbon dioxide, and methane in equilibrium with graphite and water at 1,000 atmospheres and 400°C. were calculated from data in Wagman and others (1945), and are shown in Figure 11 (see also tbl. 4). In this case, the reaction $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$ can be expressed in terms of oxygen by the use of the equilibrium constant for the dissociation of water to form oxygen and hydrogen.

The values for the fugacity of carbon dioxide calculated from reactions involving siderite would seem to be unreasonably large considering that the pressures under which the deposits were formed were probably not extremely high, but it should be noted that the partial pressure of carbon dioxide may be considerably lower than the fugacity under these conditions (Majumdar and Roy, 1956; Walter, 1963). The uncertainty in the value of the free energy of formation of siderite is large, and an error of 3 Kcal. in the value used will change the calculated value of the fugacity of carbon dioxide by more than one order of magnitude. There is also the possibility that siderite was unstable with respect to hematite at the time that it was formed.

The very high values of the fugacity of carbon dioxide obtained by considering the reaction between graphite and water indicate that the graphite in

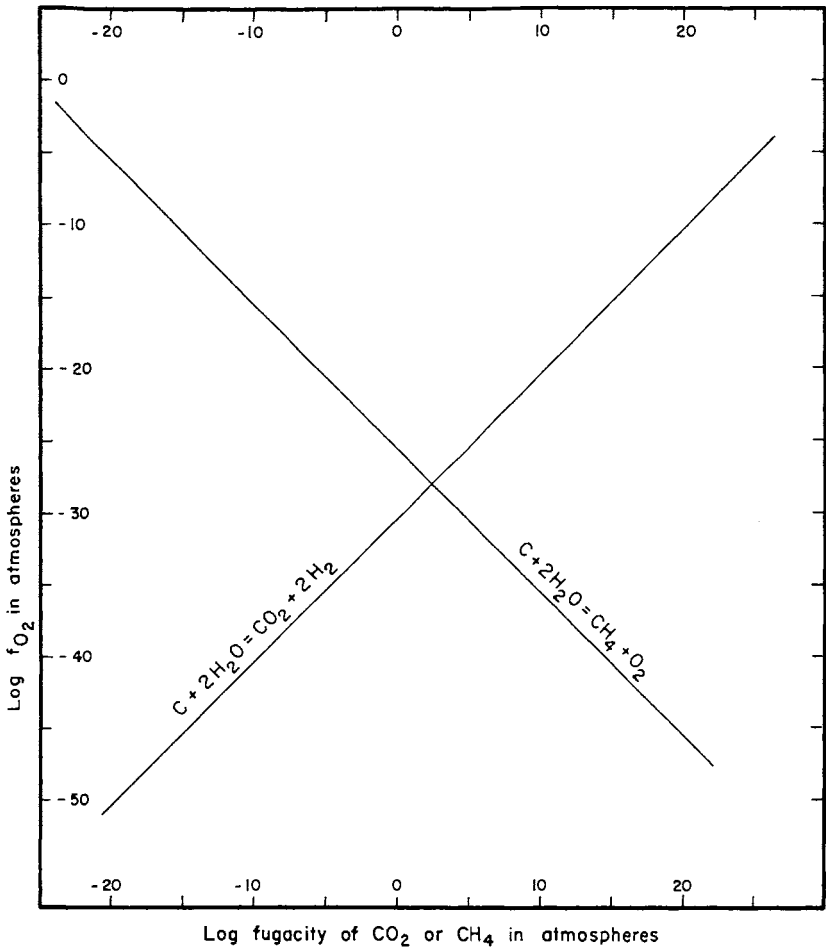


Figure 11. Fugacities of carbon dioxide and methane in equilibrium with water at 1000 atmospheres pressure and graphite at 400°C., plotted as a function of the fugacity of oxygen.

the graphitic schists could not have been in equilibrium with the ore fluid. They do, however, confirm that the fugacity of oxygen must have been near the value determined from the magnetite-hematite relations, and that the pressure of carbon dioxide was relatively high. Had the pressure of CO₂ been otherwise, quantities of methane would have been produced and the deposits would have been in a generally reduced state, rather than the generally oxidized state that characterizes them.

Mechanism of Ore Transport

The nature of the alteration surrounding the Zenith deposits, with kaolinite immediately adjacent to the ore bodies and muscovite bordering the kaolinite, suggests that the fluid in which the iron was transported could have

been weakly to moderately acid (Barnes, in press). The presence of early minerals containing ferrous iron, of late iron carbonate veins, and of large amounts of ferrous iron in the altered wall rocks suggests that a large part of the iron was transported in the ferrous state. The occurrence of iron in oxides, sulfides, carbonates, and silicates would further suggest that much of it was present as free ions in solution, and not as complexed ions. Experimental data on the solubility of magnetite (Holser and Schnee, 1961) support these conclusions in that magnetite is soluble in weakly acid solutions under hydrothermal conditions, largely as uncomplexed ferrous ions. An unknown amount of the iron may have been transported as a molecular (i.e. unionized) solute, but the effect of this possibility cannot be readily assessed.

Causes of Ore Deposition

The restriction of the large ore bodies to a brecciated zone indicates not only that structural controls were effective in localizing deposition of the ore, but also that the processes responsible for the precipitation of the ore minerals could proceed more readily in a zone of open space than they could elsewhere. The brecciated zone was probably open to ground water circulation at least part of the time, and rising heated solutions entering this zone would probably be cooled and diluted by the ground water. Because of the large amount of open space, the pressure on the rising fluid would decrease. The decrease in solubility and resultant precipitation of the ore minerals might therefore be due to decreasing temperature, decreasing density of the ore fluid, loss of volatile compounds from the ore fluid which acted as complexing agents for the iron in solution, changing pH of the ore fluid, oxidation of soluble divalent cations to their less soluble trivalent states, or to a combination of these processes.

Effect of Oxidation

The mineralogic relations indicate that at any particular stage of mineral deposition, the early minerals contain some ferrous iron, whereas the late minerals contain only ferric iron. This evidence that oxidation was contemporaneous with mineral deposition, coupled with the evidence that a large part of the iron was transported in the ferrous state, suggests that the oxidation itself may have been one of the principal causes of ore deposition.

The mineral distribution and the mineral zoning in the Central ore body can best be explained as a function of the availability of oxygen and the supply of metals. The abundance of magnetite at the bottom of the ore body reflects a diminishing supply of oxygen with depth. Similarly, pyrite is common only in those places where the amount of oxygen available would be limited; in the greater part of the deposit the sulphur was probably oxidized to a higher oxidation state and little if any iron sulfide would have been formed. The absence of gypsum or anhydrite can be accounted for by the increasing solubility of anhydrite with decreasing temperature (Dickson and others, 1963). The limited distribution of hausmannite may well result from a limited amount of available manganese; its close association with magnetite means that nearly all of the manganese was precipitated upon the partial oxidation of manganous to manganic ions.

The hypothesis that one of the principal causes of ore deposition was the oxidation of ferrous and manganous ions to their respective trivalent states requires the supply of large amounts of oxygen, on the order of several million tons. In considering the source of this oxygen, or equivalent amounts of other oxidizing agents, it must be borne in mind that the extent of oxidation in the ore bodies decreases with depth, and decreases away from the ore bodies into the wall rocks. Furthermore, the ratio of ferrous to total iron in the altered wall rocks indicates that there has been very little oxidation of the iron which was introduced into the wall rocks. These facts would suggest that the oxidizing agent, if it were introduced as a component of the ore fluid, was of such a nature that it could react effectively with the ferrous iron only in the brecciated zone, and that the reducing agent produced by the reaction could escape without having any further effect on the ore bodies or the ore fluid. The material which best fits these requirements would be an unstable compound which could dissociate into oxygen and stable volatile products upon entering areas of lower pressure. An example of such a compound might be nitrogen pentoxide, which would dissociate according to a reaction such as $N_2O_5 = NO_2 + NO + O_2$. It is otherwise difficult to understand why the oxidation would affect only the ore bodies and not the wall rocks, and why it would increase in intensity upwards.

The transport of atmospheric oxygen in or through ground water to the site of oxidation and deposition would also produce the observed mineral distribution, although it is very unlikely that there would be sufficient ground-water circulation to provide the requisite amounts of oxygen by simple transport alone. Calculation of the diffusion rate of oxygen through water, assuming a steady state situation at 18°C., a partial pressure of oxygen in the water at the surface of 10^7 atmospheres, and a depth of 3,000 meters, indicates that sufficient oxygen to form one cubic centimeter of hematite from ferrous oxide would diffuse through a column of water one square centimeter in area in 70,000 years (data from International Critical Tables, 1928). Considering that oxygen was continually being consumed at the site of deposition, and that diffusion rates increase with increasing temperature, it would seem possible from a theoretical basis to provide sufficient oxygen and other oxidizing agents to form the deposits in a geologically reasonable period of time, largely by diffusion through the ground water to the site of oxidation.

This argument is in part negated by the fact that many sulfide deposits have been immersed in ground water for millions of years with no observable oxidation or alteration other than that which was the result of processes taking place above the water table; obviously in these cases oxygen has not diffused through the ground water to react with the sulfide minerals. In the case of the sulfide deposits, however, the reactions would take place between components in solution and well crystallized solid compounds, and these reactions are frequently so slow that a metastable situation may persist indefinitely (Garrels, 1959). On the other hand, reactions between solutes are usually very rapid (Garrels, 1959), and this fact lends some support to the proposition that the oxygen might have been provided by downward diffusion through ground water.

From a structural standpoint, most of the deposits of high grade iron ore in the Lake Superior region, except those of the Mesabi and Cuyuna districts,

occur in plunging structural troughs. These are the places that most likely would be occupied by descending ground waters, and this point is the major support of the supergene theory of Van Hise. If the formation of the deposits was completely independent of ground water activity, the deposits should be located in the crests of folds, or similar places where rising waters might be impounded; the brecciated zone in the Zenith mine could have acted in this manner, although the brecciation affects the jaspilite capping as well as the ore bodies (Abbott, 1906). The fact that the high grade iron ore deposits of the region are not, in general, located in such structural crests would also suggest that ground water played some role in their formation.

If the ore fluid emanated from a true magmatic source, it is quite possible that it could contain significant quantities of nitrogen, and that the breakdown of nitrogen pentoxide or similar compounds provided the necessary amounts of oxygen. It is suggested in the final section, however, that the ore fluid was derived from the progressive metamorphism of the greenstone and the iron-formation at greater depths within the earth's crust. Since the greenstone presently exposed contains little, if any, nitrogen, the principal oxidizing agent, if the ore fluid was of metamorphic origin, must have been oxygen from the atmosphere.

Effect of Changing pH

Another major cause of ore deposition may have been a change in pH which would accompany the loss of carbon dioxide from the ore fluid. The nature of the wall rock alteration indicates that the ore fluid could have been moderately acid, and thermodynamic calculations indicate that the fugacity of carbon dioxide at the time of ore deposition was quite high. The ore fluid, therefore, if it were acid, may well have been so because of dissolved carbon dioxide. The loss of this carbon dioxide from the fluid, resulting either from the lower pressures prevailing in the brecciated zone or from the precipitation of carbonates by reaction with CaO and MgO leached from the wall rocks, would increase the pH of the fluid and in turn result in the precipitation of iron and manganese oxides or hydroxides. This situation is the opposite of that which apparently occurs in the formation of hydrothermal sulfide deposits, where the precipitation of the sulfides is accompanied by a decrease in pH resulting from the progressive ionization of hydrogen sulfide, to produce hydrogen ions and bisulfide ions, as sulfide ions are withdrawn from the solution. The relatively small amount of sulphur in the Zenith deposits suggests, however, either that the supply of sulfur was limited or that sulfur did not participate to any great extent in the processes of ore deposition; in the situation under discussion, the behavior of carbon dioxide, which was present in large quantities, probably was the major control on the pH of the ore fluid.

Effect of Decreasing Temperature and Pressure

Certainly a decreasing density of the ore fluid will lower the dissolving power of the fluid and cause the deposition of some of the ore minerals, and it is reasonable to assume that decreasing temperature of the ore fluid will also lower

the solubility of the ore minerals. These effects will not cause complete precipitation, however, whereas changes in oxidation state of the iron and in the pH of the solvent drastically affect the solubilities of iron salts. Lacking direct experimental evidence to the contrary, therefore, it is probable that the principal causes of ore deposition were the changing pH of the ore fluid and progressive oxidation of the iron in the fluid.

Source of the Metals and the Ore Fluid

The metals and the ore fluid could have been derived either from a crystallizing igneous body, as in the classic hydrothermal hypothesis, or from the iron-formation and surrounding greenstone by metamorphic processes. The only known intrusives in the immediate vicinity of the Ely mines include both acidic and basic dikes (Clements, 1903; Reid, 1956), and it has been suggested that the acid dikes were the source of the fluids (W. P. Wolff and J. F. Wolff, written communications, 1964); however, it is possible that both the acidic dikes and the basic dikes (Reid, 1956) predate the period of metamorphism and thus precede the period of ore formation. The nearest large intrusive body is the Giants Range granite; the granite is bordered by a wide contact metamorphic zone (Clements, 1903; Schwartz, 1924), suggesting that the volatile content of the magma was relatively high. Although the nearest outcrop of the granite is more than two miles away, the granite can be considered as a potential source for the ore fluids. The Duluth Gabbro Complex could be considered as a possible source, although it is an unlikely one because the gabbro is several miles from the deposits, and the projected position of the sill-like body is several thousand feet above the deposits. The association between the ore deposits and the known intrusives in the area is therefore questionable, at best.

An alternate hypothesis is that the metals and the ore fluid were derived from the progressive metamorphism of the iron-formation and the surrounding greenstone. The greenstones are composed largely of hydrous minerals and contain about 3 per cent water (Schwartz, 1924); the progressive metamorphism of large volumes of this rock, with the accompanying formation of anhydrous minerals, could conceivably provide ample water to account for the observed metasomatism. Carbonate minerals from both the greenstone and the iron-formation would tend to become decarbonated under the same conditions, and their breakdown would provide the carbon dioxide which was present in the ore fluid. The metals themselves would be provided to the ore fluid by reaction during metamorphism between the fluid and iron-bearing minerals of the iron-formation. As none of the greenstone exposed in the mine workings or on the surface, except near igneous contacts, shows any indication of a higher grade of metamorphism, this process, if it took place at all, must have occurred at depths within the earth greater than those equivalent to anything now exposed in the vicinity.

If such a process has been operative and effective, it would be expected that the iron content of highly metamorphosed iron-formations would be less than that of the equivalent iron-formation in a lower grade metamorphic zone. The studies which have been conducted on the metamorphism of iron-forma-

tions (James, 1955; Gunderson and Schwartz, 1962) show no supporting evidence, although the nature of the studies is such that the effect could have gone unnoticed. Throughout the Lake Superior region, post-metamorphic high grade iron deposits, in which much of the iron appears to have been introduced, are associated with iron-formations of low metamorphic rank. Where the iron-formations are cut by post-metamorphic intrusives, the only effect on the iron-formation is a simple thermal metamorphism, and the areas where post-metamorphic intrusives are most abundant are also the areas of higher grade metamorphism. The distribution of high grade iron deposits is therefore somewhat antipathetically related to the distribution of post-metamorphic intrusives, which suggests that the iron and the ore fluids may well have been derived from some source other than intrusive bodies. The hypothesis that the ore fluids and their metal content were generated by metamorphism is not new, but has been applied to other iron ore deposits (Klinger, 1960; Dorr, 1963), as well as to many sulfide deposits. Since the hypothesis might be very difficult to prove or disprove by field studies, it is suggested that the testing of the hypothesis would be a fertile field for experimental investigation.

SUMMARY AND CONCLUSIONS

The high grade iron ore deposits in the Zenith mine, now largely mined out, are part of a larger group of deposits located north of the city of Ely, Minnesota, in the Vermilion district or range. The deposits, which occupy the stratigraphic position of the jaspilitic Soudan Iron-formation and occur within walls of altered metabasalts (Ely Greenstone), consist largely of massive hematite, brecciated and cemented by secondary hematite. In the lower levels of the mine, both the primary and secondary hematite give way to carbonate material and two more or less concentric mineral zones appear, the outer zone characterized by hausmanite and the inner zone characterized by hausmannite and magnetite. None of these mineralogical variations are present in the other mines in the Ely area.

It has been suggested by various writers that the Ely deposits were formed by:

1. the leaching of silica from the primary iron-formation, resulting in the formation of a residual hematite body which was later compacted, hardened, and fractured by deformation and metamorphism;
2. the post-metamorphic leaching of silica and introduction of iron by downward moving surface water;
3. the post-metamorphic leaching of silica and simultaneous introduction of iron by rising heated waters.

The purpose of this study was to attempt to resolve these differing viewpoints, and to analyze the mineralogical variations to determine the physical and chemical conditions under which the deposits were formed.

The following facts about the deposits were determined in the study.

1. The deposits are surrounded by a halo of altered greenstone, which is 100 or more feet thick. The iron content of the altered greenstone was increased by a factor of two or more.

2. The alteration halo can be divided into three mineralogical zones: an outer zone consisting almost entirely of chlorite, an intermediate zone composed of chlorite and hematite, and an inner zone composed of kaolinite and hematite. The kaolinitic material is spotty in occurrence, and at some places a small amount of rock with $2M_1$ muscovite separates the chloritic and kaolinitic rocks. This situation contrasts with the normal greenstone, which is composed primarily of actinolite, epidote, chlorite, albite, and quartz.
3. The altered greenstone, and lenses of chert within it, have been subjected to an intense carbonate metasomatism; commonly these carbonates have minor amounts of hematite associated with them. The carbonates in the altered greenstone, as well as those in the carbonate-bearing mineralized material, commonly show no sign of deformation since they were formed.
4. The hematite of the ore lacks any preferred orientation.
5. All paragenetic stages of hematite contain remnants of magnetite.
6. A pronounced mineralogic zoning exists within the Central ore body.
7. Very small amounts of phosphorous- and fluorine-bearing minerals occur with some of the hematite.
8. Structural evidence that would indicate compaction of the deposits is lacking.
9. The ore bodies are cut by nearly horizontal veins that also occur in a restricted zone in the greenstone south of the ore bodies. The attitude of these veins is similar to that of gash fractures that would have developed along the south-dipping Sibley fault (north of the ore bodies) if the movement on the fault were in a reverse sense.

These data are interpreted to indicate that (1) the deposits are post-metamorphic, (2) they were formed by the replacement of the silica in the iron-formation by iron oxides, and (3) replacement resulted from rising heated waters. The Sibley fault apparently was an active structural feature before, during, and after the formation of the ore bodies, and the stresses causing movement on the fault may have caused the brecciation of the ore bodies. The brecciation indicates that the ore bodies were formed at a relatively shallow depth.

It is concluded that most of the original material subsequently replaced was a cherty iron-formation and the chert was largely replaced by carbonates. The primary control on localization of the ore bodies probably was brecciation of the original jaspilitic iron-formation.

The composition of some of the carbonate minerals, when compared with the phase relations in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$, indicates that the minerals probably were formed in the temperature range $350^\circ\text{-}400^\circ\text{C}$. The carbonates that were studied are from the central part and are not necessarily representative of the entire deposit. The presence of $2M_1$ muscovite in the altered wall rocks indicates that the minimum temperature of the ore solution probably was above 200°C ., whereas the presence of kaolinite indicates that wall rock temperatures did not rise much above 350°C .

The mineralogic relations suggest that the fugacity of oxygen during ore deposition fluctuated around the equilibrium value for the coexistence of magnetite and hematite, and that in certain areas magnetite, hematite, and pyrite were formed under near equilibrium conditions, whereas siderite and goethite formed near equilibrium in other areas. Based upon these relations and the temperature data, the deposits probably were formed in an environment in which the fugacity of oxygen ranged upward from $10^{-31.8}$ atmospheres, sulphur upward from $10^{-14.8}$ atmospheres, and carbon dioxide up to $10^{4.9}$ atmospheres.

The mineralogic relations also suggest that at least part of the iron was transported in the ferrous state, and that the oxidation to the ferric state was contemporaneous with the deposition of the iron minerals. The presence of kaolinite in the altered rocks adjacent to the ore bodies indicates that the ore fluid may have been, in part, weakly to moderately acid in character; the possible high fugacity of carbon dioxide suggests that any acid character of the solution may have been due to dissolved carbon dioxide. Experimental data indicate that iron is soluble under these conditions, largely as uncomplexed ferrous ions. The precipitation of the iron may well have resulted from an increase in pH of the solution caused by the loss of carbon dioxide and from the oxidation of the ferrous ions to the ferric state. The necessary amounts of oxygen may have been provided by the dissociation of compounds such as nitrogen pentoxide, or by the diffusion of atmospheric oxygen through ground water. All three of these processes are such that they would occur most readily in a brecciated zone filled with ground water, where the ore fluid would undergo a substantial decrease in pressure. As the deposits are restricted to a brecciated zone, it is suggested that these processes contributed to the deposition of the iron oxides.

The metals and the fluid in which they were transported may have been derived from intrusives or more likely from a higher grade metamorphism of the iron-formation and enclosing greenstone at greater depths.

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