# MINERALOGY AND GENESIS OF THE MAYVILLE IRON ORE OF WISCONSIN

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## I. INTRODUCTION AND ACKNOWLEDGMENTS

This paper presents new mineralogical and chemical data on the Mayville oolitic iron ore of Eastern Wisconsin. These, together

with a brief discussion of its genesis, are the results of a study begun in 1925 and lately resumed in order to confirm and supplement the earlier work.

The first study was carried out at the University of Wisconsin under the direction of Dr. C. K. Leith. In this the senior author had associated with him Drs. C. H. Stockwell, R. H. B. Jones and E. J. Wechter, the primary purpose of the study then being to ascertain the mineralogical distribution of the phosphorus, since the relatively high content of this element greatly restricted utilization of the ore in the blast furnace at Mayville. This step was essential for a later investigation of methods of beneficiation by reduction of the phosphorus to within Bessemer limits. Grateful acknowledgment is herewith made to Dr. C. K. Leith for suggesting the work, to the Youngstown Sheet and Tube Company, Limited, for samples of the run-of-mine ore with analyses, and to all taking part in the initial investigation. Corroboration of many mineral species noted in the optical studies was given by $x$-ray photographs (powder method) made by Drs. C. O. Swanson and C. H. Stockwell.

The restudy of the ore has been completed at Queen's University by the junior author (A.P.B.) as a thesis problem, with facilities not previously available, which have enabled the more accurate determination of doubtful species and the discovery of some other rare minerals not formerly noted. The present report is thus largely of his writing. For the restudy, ore of a slightly different character was used, samples of crushed ore having been obtained from the U. S. Bureau of Mines Experiment Station, Minneapolis, and uncrushed samples from the Geological Museum, University of Wisconsin.

Table I is a compilation of the minerals found in the various samples of the ore examined, the greater number of which make up only a small percentage of the ore as a whole.

TABLE I. MINERALS IN THE MAYVILLE IRON ORE

| | *In Oolites* | *In Matrix* |
|---|---|---|
| Oxides. | Goethite* | Goethite |
| | | Hematite |
| | Hematite (specular and earthy) | Magnetite |
| | | Quartz |
| | Quartz (as nuclei) | Corundum (rare) |
| | | Tridymite   (In volcanic fragment) |
| | Opal | Cristobalite |

Carbonates.

| | |
|---|---|
| Calcite* | Calcite |
| Dolomite | Dolomite |
| Siderite | Siderite |

Silicates.

| | |
|---|---|
| Halloysite* | Orthoclase |
| Leverrierite | Microcline |
| Newtonite | Anorthoclase |
| Chlorite | Perthite |
| Neotocite | Plagioclase |
| | Biotite |
| | Hornblende |
| | Chlorite |
| | Allophane |
| | Stevensite |

Phosphates.

| | |
|---|---|
| Variscite | Collophanite |
| Metavariscite | |
| Evansite | |
| Ceruleolactite | |
| Dahllite | |
| Collophanite | |
| Borickite | |
| Voelckerite | |
| Koninckite | |
| Phosphosiderite | |

Others.

| | |
|---|---|
| Five others unidentified | Pyrite |
| | Pyrrhotite |
| | Gypsum |
| | Fluorite |
| | Northupite |
| | Wapplerite |
| | Hydrocarbon |

* Most common.

## II. OCCURRENCE OF THE MAYVILLE IRON ORE

The Mayville iron ore occurs in several isolated localities in Eastern Wisconsin as lens-like bodies lying unconformably between the Maquoketa (Richmond) shale and the Niagara dolomite. The maximum thickness of ore known is about 55 feet,[1] but at most

[1] Thwaites, Frederik T., Recent Discoveries of "Clinton" Iron Ore in Eastern Wisconsin: *U.S.G.S. Bull.* **540**, p. 338.

exposures of the horizon concerned iron ore is either absent or is represented only by a thin ferruginous dolomite layer.

The age of this ore was long assumed to be Clinton, on account of its lithological and stratigraphic similarity to the Clinton ore of New York. Savage and Ross, however, have shown it to be of Late Maquoketa age,[2] and propose the name *Neda Iron Ore* for the formation.

The ore is a well-stratified deposit of oolitic texture, aptly described by the term "flaxseed ore." Type specimens consist predominantly of hydrous iron oxide and hematite, but calcareous zones, shaly bands and pebbles, and near the top, non-oolitic and pyritic layers are present.[3]

### III. PETROGRAPHY AND MINERALOGY

#### Methods of Study

The texture of the ore and the structure of the oolites is well displayed in both thin and polished sections. Most of the minerals present, however, are masked by the iron oxides, hence their identification was possible only in concentrates prepared by the usual heavy liquid, magnetic[4] elutriation and acid treatment methods of mineral separation. The mineral determinations were made on the basis of optical properties, checked in some cases by *x*-ray diffraction patterns or microchemical tests. The refractive indices and dispersion of several minerals were determined by the Emmons double variation method, but its use was greatly limited by the rarity of some species. A film method of making thin sections,[5] recently described, makes microphotography of the ore easier than is possible with polished sections.

#### The Oolites

Oolitic Structure. The oolites are small oblate spheroids flattened in the plane of the bedding. Their average maximum diameter is 1 millimeter. They consist of numerous concentric shells of differing mineral and chemical composition. In sections the

[2] Savage, T. E., and Ross, C. S., The Age of the Iron Ore in Eastern Wisconsin: *Am. Jour. Sci.*, vol. **41,** 1916, pp. 187–193.

[3] Savage, T. E., and Ross, C. S., *op. cit.*

[4] Magnetic concentrates were made with a Dings Magnetic Concentrator, University of Wisconsin.

[5] Appell, J. E., A Film Method for Studying Textures: *Ec. Geol.*, vol. **29,** 1933, pp. 383–388.

shells are seen as concentric rings of variable colour and width (Plate A, Fig. 1) in many instances surrounding a central nucleus of organic or detrital material.

Various "abnormal" types of oolites are described under the discussion of Nuclei.

MINERALOGY. A surprisingly large number of minerals occur in the oolites, including a variety of uncommon species. Those present in sufficient quantity to permit their determination are described below. They are referred to those known minerals with which their properties agree most closely, and are listed in order of abundance.

Indices of refraction, where given to the third decimal place are correct to $\pm 0.001$.

### Goethite ($Fe_2O_3 \cdot H_2O$)

On vertically-illuminated polished sections of the ore the predominance of this mineral gives a dull grey colour to the oolites. Its presence was confirmed by $x$-ray powder photographs.

### Calcite, Dolomite, Siderite

Calcite in the oolites is invisible in thin sections, but was identified by its optical properties in oil immersion mounts of oolitic material. Dolomite is much less abundant than calcite, and siderite was found only in two or three mounts of oolitic material.

### Halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$)

Halloysite makes up the bulk of the insoluble residue left after treatment of the oolites with strong HCl and $HNO_3$. Under a binocular microscope this mineral appears white and finely-granular like unglazed porcelain. It is in fragile spheroidal shells, forming the framework, at it were, of the oolites. Under the microscope the halloysite is white, with irregular fracture and a rough fracture pattern on its surface. It is very difficult to free the mineral completely of iron by the acid treatment; most of the grains retain a pale brownish colour. The intimately-held iron makes the material slightly anisotropic and raises the index of refraction and the dispersion. Besides this impure halloysite, occasional rose to orange-red grains of what appears to be stained halloysite are seen. It was suspected that the colour might be due to manganese, but a spectrographic examination[6] of a small amount of the material revealed the presence of only Al and Si plus minor amounts of Mg and Fe. Optical measurements on the purest halloysite gave $N_D = 1.540 - 1.550$, $N_{(F-C)} = 0.007 - 0.010$. Its determination was verified by $x$-ray and chemical methods.

### Leverrierite ($Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$?)

Leverrierite forms a small part of the insoluble residue. It was positively identified from $x$-ray photographs. The mineral most closely resembling leverrierite optically gave:

$$N_g = 1.586, N_m = 1.585, N_p = 1.537.$$

$$N_g - N_p = 0.049.$$

[6] For this examination the authors are indebted to Mr. G. A. Harcourt at Queen's University.

These figures were obtained by recording the approximate indices of a large number of grains throughout the study. The mineral is present as vermicular aggregates or warped laths, colourless or yellow to brownish. Many grains show incomplete extinction.

Leverrierite and related minerals have a rather wide range of indices. Some grains that otherwise resemble the leverrierite just described have different optical constants. A basal flake showed $2V = 0° \pm$, $N_g = N_m = 1.515$. This index increased
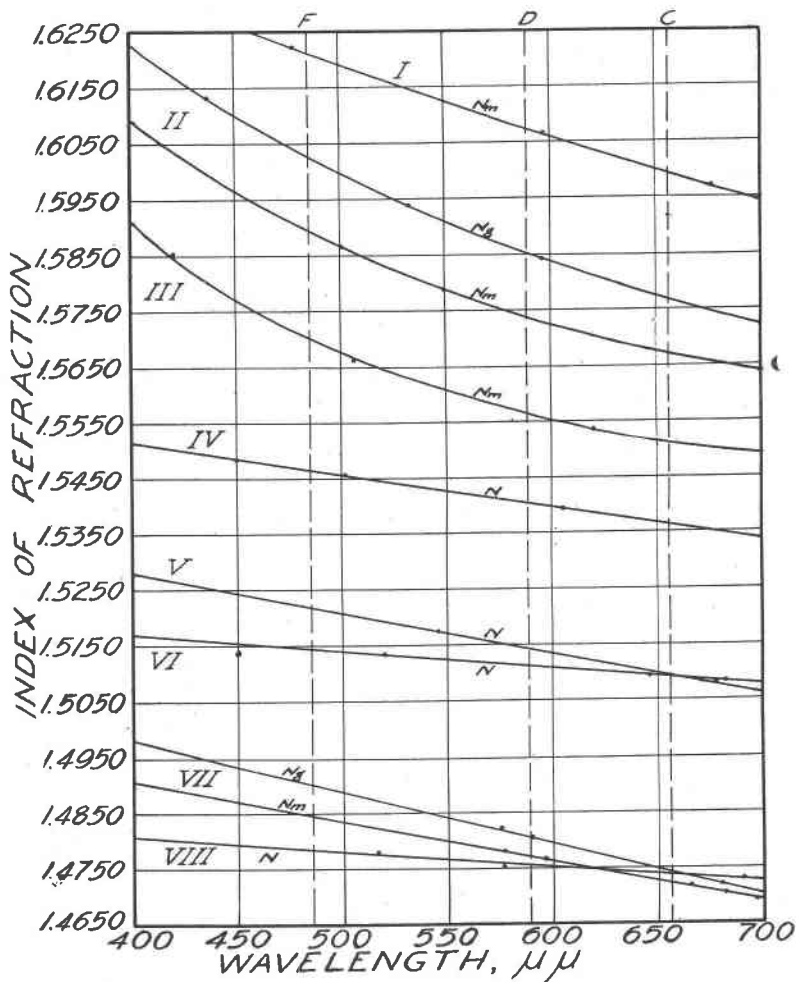


FIG. 1. Chromatic dispersion of some minerals of the Mayville ore. I. Chlorite, II. Variscite, III. Leverrierite, IV. Halloysite, V. Northupite, VI. Stevensite, VII. Tridymite, VIII. Allophanite.

appreciably after several hours immersion in the index liquid.[7] Another lath-like individual gave $N_m = 1.5558$, $N_{(F-C)} = 0.0187$ (Fig. 1).

### Variscite ($AlPO_4 \cdot 2H_2O$)

Variscite occurs as small, colourless to very pale pink or yellowish laths with parallel extinction. Measurements of the indices gave:

$$N_g = 1.5857, \; N_m = 1.5737, \; N_p = 1.5570.$$
$$N_g(F-C) = 0.0268.$$
$$N_m(F-C) = 0.0250.$$

Optic sign $(+)$; $Z$ parallel to elongation of laths; $X$ normal to plane of laths. Variscite differs from leverrierite in having lower birefringence, parallel extinction and more regular lath-like grains.

### Metavariscite ($AlPO_4 \cdot 2H_2O$)?

Besides the slightly coloured grains of variscite, a pale green pleochroic mineral in similar lath-like fragments is present in smaller amounts. The optical properties determined for it are: Optic sign $(-)$, $N_g = 1.574$, $N_m = 1.556$, $N_p = 1.543$.

$$N_g - N_p = 0.030.$$

$Z =$ light green, $Y =$ pale yellow green, $X =$ colourless. These properties agree best with the data for metavariscite, but are by no means identical with the figures for that mineral.

### Opal ($SiO_2 \cdot nH_2O$)

Opal in colourless and tinted grains and fragments of spheroidal shells occurs in the insoluble residue from acid treatment of the oolites. It is isotropic with $N_D = 1.540$.

### Dahllite ($7CaO \cdot 2P_2O_5 \cdot CO_2 \cdot \frac{1}{2}H_2O$)

Colourless, fibrous grains and concretionary growths of dahllite are present in some oolites. Elongation of the fibres is negative. Other optical properties are:
Uniaxial negative;

$$N_o = 1.620, \; N_e = 1.605.$$
$$N_o - N_e = 0.015.$$

### Phosphosiderite ($2Fe_2O_3 \cdot 2P_2O_5 \cdot 7H_2O$)

The earlier studies suggested this mineral was one of the principal iron phosphates present, though it was recognized that others might be masked by the abundant hydrous iron oxide, Colourless fragments with a perfect cleavage, indices above and below 1.730, and showing strong dispersion, were considered as phosphosiderite rather than siderite, which they resemble somewhat optically, particularly on a basis of the low ferrous iron content of the ore. Chemical tests further showed that fragments of this mineral or related iron phosphates are quantitatively important in some oolites.

### Collophanite ($3Ca_3P_2O_5 \cdot Ca(CO_3, F_2, SO_4, O) \cdot nH_2O$)

Blue stained, yellowish and colourless collophanite is present in small amounts. The grains are very irregular in outline and surface and have no cleavage. The

[7] See Larsen, E.S., *U.S.G.S. Bull.* **679**, p. 193.

optical character of the mineral is isotropic with $N = 1.568$. Collophanite was also identified microchemically in the matrix of the ore.

### Koninckite ($FePO_4 \cdot 3H_2O$)

A pale olive-yellow to greenish mineral without cleavage is optically similar to koninckite as described by Larsen.[8] Most grains are isotropic with $N = 1.643$. Other fragments are very slightly anisotropic and have $N_m$ a little greater than 1.644. Phosphorus is present as revealed by a microchemical test.

### Borickite ($3CaO \cdot 7Fe_2O_3 \cdot 2P_2O_5 \cdot 24H_2O$)

A wine-red to red-brown isotropic mineral forms some of the oolite shells. It has no cleavage, conchoidal fracture and $N = 1.64–1.67$. These properties together with a microchemical test for phosphorus suggest that the mineral is borickite. The latter has a highly variable index of refraction.

### Voelckerite ($10CaO \cdot 3P_2O_5$)

Colourless, almost isotropic grains of a mineral resembling voelckerite, with $N_g$ slightly less than 1.6345 and $N_p$ slightly greater than 1.630 were found in the first ore studied.

### Evansite ($3Al_2O_3 \cdot P_2O_5 \cdot 18H_2O$)

The mineral identified as evansite lacks colour and cleavage and is isotropic with $N = 1.495$. It is insoluble in HCl or HNO$_3$. Small irregular grains of the mineral have a pearly-white appearance under the microscope.

### Ceruleolactite ($3Al_2O_3 \cdot 2P_2O_5 \cdot 10H_2O$)?

Fibrous, lath-like grains of a pale blue colour seem to be uniaxial positive, with $N_e = 1.587$, $N_o = 1.585$. $E(\|$ elongation$) =$ pale blue, $O =$ very pale blue to colourless. Laths are soluble in HCl since none were seen in the insoluble residue of the oolites. This mineral is very rare in the oolites, but the data obtained strongly suggest that it is ceruleolactite.

### Neotocite ($MnSiO_3 \cdot nH_2O$)?

A grain of a light yellow-brown, isotropic mineral with conchoidal fracture was found in one concentrate of oolitic material. Enclosed by the isotropic portion were small, curving fibres of very low birefringence. These had almost the same refractive index as the isotropic part, which was 1.540. The grain was lost before a microchemical test could be attempted, but its physical and optical properties agree closely with those of neotocite.

Besides the minerals described, a number of others are undoubtedly present in the ore in very small amounts, but the data obtained were insufficient to identify them. The approximately-determined optical properties of some of these suggest the presence of newtonite and planerite. At least four other minerals were seen for which the optical character is even less perfectly known.

Of all the minerals described or mentioned above, borickite, metavariscite and ceruleolactite were not recorded in the original study of the ore. On the other hand newtonite, phosphosiderite and voelckerite were not found during the more recent work. This apparent difference in the mineralogical constitution of the ore is prob-

[8] Larsen, E. S., *op. cit.*, p. 97.

ably related to variation in its chemical composition, as the samples in the two studies were not the same. (See discussion of chemistry of the ore.)

NUCLEI. Most of the oolites in thin and polished section show no central nucleus, but this is in many cases due to the cut of the sections. Four types of nuclei are recognized in the oolites: (a) fossil fragments, (b) mineral or rock fragments, (c) fragments of reworked ore, (d) cruciform nuclei.

The fossil fragments have spherulitic or cellular structures. Most of them resemble pieces of corals or Silurian bryozoa. One coral fragment has been identified by Dr. W. H. Twenhofel as Syringopora. Many of the fossil fragments are replaced by iron oxides, except those that are siliceous. Some are similar to spherulites such as Vaughan describes forming the nuclei of calcareous oolites.[9]

Fragments of quartz, and probably of other minerals, and of rock fragments are not abundant as nuclei in the oolites of the Mayville ore as they are in similar deposits such as the Clinton.[10]

The most important class of nuclei are those consisting of reworked fragments. Among these the following types occur.

1. Angular to rounded fragments of iron oxide.

2. Two smaller oolites forming the nucleus of a larger enclosing one. (See Plate A, fig. 2)

3. Fragment of reworked oolitic ore, containing several oolites, as nucleus of a larger oolite.

4. Fragment of a single oolite as nucleus of a larger enclosing one. In some cases the nuclear oolite is eroded at one end only; at the opposite end the bands are conformable with those of the enclosing oolite.

A fifth type, which is really not an oolite at all, is similar to the "fausse ooliths" described by Cayeux[11] from the French oolitic iron ores. It comprises rounded fragments of reworked ore without enclosing concentric bands. One such grain seen in the Mayville ore consisted of numerous siliceous sponge spicules embedded in iron oxide.

The cruciform nuclei form one of the most interesting features of this ore. As far as can be learned, such nuclei have not been de-

[9] Vaughan, T. W., Oceanography and its relations to other earth sciences: *Jour. Washington Acad. Sci.*, vol. **14**, 1924, p. 327.

[10] Smyth, C. H., *N.Y.S.M. Bull.* **207, 208**, 1919, p. 176.

[11] Cayeux, L., Les Minerais de Fer Oolithiques de France, Fasc. II, Minerais de Fer secondaires, **1922**, pp. 909–911.

scribed before from oolitic ores. As the name implies, the cruciform nuclei are small cross-shaped objects. The two arms of the cross are at right angles to one another, and are commonly of unequal lengths. The oolitic shells conform to the outline of the cross for only a short distance outward from the latter. (See Plate A, fig. 3.) One of these crosses, picked from an oolite with a needle, was found to consist of slightly magnetic specular hematite.

## THE MATRIX

The non-oolitic portion of the ore consists largely of pore space, by volume. The bulk of the solid material between the oolites is crystalline hematite, with minor amounts of goethite and probably halloysite and leverrierite. Some of the goethite is crystalline with radiating structure. The hematite forms encrustations around the oolites, its crystals projecting into the interstitial spaces and thereby giving the latter the appearance of vug-like cavities. Calcite and dolomite are present in varying amounts with the iron oxides. The small remaining fraction of the matrix contains several minerals in insignificant quantities, as well as a large part of the total organic and detrital matter of the ore, and occasional small phosphatic nodules. Although only single grains of some of the minerals were found, they were often large enough to permit their determination. A number of the minerals mentioned below are of little importance in the study of the ore on account of their rarity, but are considered of sufficient mineralogical interest to merit description.

### *Northupite*, ($MgO \cdot Na_2O \cdot 2CO_2 \cdot NaCl$)

A fragment of white translucent mineral about $\frac{1}{8}$ inch long proved to have properties closely similar to those given for northupite. On one side of this fragment were rounded solution cavities; on the opposite surface a small isometric crystal projected from the main mass of the mineral. The forms present, as noted with a hand lens, were the cube bevelled by narrow faces of the dodecahedron. The mineral is easily soluble in water, and has a rather bitter, saline taste. It effervesces with dilute HCl. Microchemical tests on the aqueous solution showed the presence of Mg, Ca, Na and Cl, the first-named element giving by far the strongest reaction. Calcium may be explained by the presence of minute included grains of an impurity which, from microscopic observation, is probably calcite.

The optical properites of this mineral are as follows:

Colourless; no cleavage. Isotropic, $N = 1.5145$, $N_{(F-C)} = 0.0122$.

The crystal habit, solubility and dispersion given above differ somewhat from the same properties in northupite, as described by Winchell,[12] but otherwise the

two minerals are very similar. That occurring in the Mayville ore has possibly a slightly different chemical composition.

### *Wapplerite* ($2CaO \cdot As_2O_5 \cdot 8H_2O$)

A single grain of this mineral was found associated with a green chloritic mineral. The arsenic mineral is white and in powdered form under the microscope shows rhomb-shaped grains with angles of 60° and 120°. On such flakes, which seem parallel to a cleavage, an acute bisectrix figure normal to $Z$ is obtained. The extinction angle $X \wedge$ elongation on such fragments is 21°. The indices of refraction are: $N_g = 1.552$, $N_m = 1.537$, $N_p = 1.528$. Microchemical tests on the mineral gave positive results for both As and Ca and negative for P.

### *Chlorite* (Hydrous Mg, Fe, Al, Silicate)

Several grains of green, flaky material from the matrix apparently belong to the chlorite group. The optical properties of that associated with the wapplerite are as follows:

$$(-)2V = 0° \pm ; \; N_m = 1.6074 = N_p \text{ (nearly)}; \; N_m(F-C) = 0.0216, \text{ (see Fig. 1)}.$$
$$X = Y = \text{light green}; \; Z \text{ practically normal to the cleavage } \{001\}.$$

The mineral is insoluble in cold HCl. Microchemical tests on it show Al and Mg to be present. It is possible grains of this mineral are present also in some oolites.

### *Stevensite* ($H_2Mg_3(SiO_3)_4 \cdot H_2O$)

A small lath-like fragment of a white, waxy mineral proved to have properties close to those given for stevensite. In oil immersion mounts the mineral is colourless with very low relief. It has conchoidal fractures but little or no cleavage. Optically is is isotropic with $N = 1.5113$, $N_{(F-C)} = 0.0053$, (see Fig. 1). The mineral is only slightly soluble in HCl or $HNO_3$. The solution gave a slight microchemical reaction for Mg.

### *Allophanite* ($Al_2O_3 \cdot SiO_2 \cdot nH_2O$)

A relatively large fragment of colourless mineral, slightly stained, showed a parallel banding of its surface when examined in ordinary light. The grain, however, was isotropic and gave $N = 1.4762$, $N_{(F-C)} = 0.0052$ (see Fig. 1). The banding is considered as possibly derived from the alteration of a plagioclase, or as the imprint of a striated mineral once in contact with this grain. Several other grains without the banding were found during the optical examination of the ore.

The remaining mineral fragments present in small amounts are quartz, feldspars (including orthoclase, microcline, anorthoclase, perthite and plagioclase), bleached biotite, hornblende, magnetite, pyrite, pyrrhotite, fluorite and corundum (sapphire).

The fossil fragments in the matrix are nearly all replaced by hydrous iron oxide. One small piece resembling a brachiopod consisted of gypsum needles with a few grains of calcite.

Another type of organic material in the matrix is a lustrous, black hydrocarbon with conchoidal fracture. It is difficultly fusible, and insoluble in several common organic compounds. This material is probably a variety of mineral coal.

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[12] Winchell, A. N., Elements of Optical Mineralogy, Second Edition, Part II, p. 87, and Part III, p. 178.

The most abundant transported fragments in the ore are rough, angular grains of scoriaceous lava up to $\frac{1}{2}$ inch in diameter. These are largely altered to iron oxide (including much magnetite) but remnants of dirty green to brown glass, dusty with minute inclusions and elongated crystallites, are visible in some of the fragments. The average index of the isotropic glass is 1.53, a value that agrees with those given for glasses of moderately basic composition.[13] Under a binocular microscope some of the lava fragments display flowage lines in well-preserved detail.

One of the freshest-looking of the lava grains, when crushed and examined microscopically, was found to contain two colourless minerals, identified respectively as tridymite and cristobalite. The properties on which these determinations are based are given below.

### *Tridymite*, $SiO_2$

Tridymite is present as wide laths with narrow interbands of glass or of glass and magnetite. The mineral is colourless with negative relief. The laths appear to be normal to the obtuse bisectrix, and have parallel extinction with $Y$‖elongation, $Z$ normal thereto. Fine parallel lines cross the laths at right angles to the elongation; these are apparently twinning lines, as best shown by insertion of a gypsum plate between crossed nicols. Optical constants are:

$$(-)2V, \text{ moderate (estimated)}.$$
$$N_g = 1.4805, \ N_m = 1.4774, \ N_p = 1.4772.$$
$$N_g(F-C) = 0.0181.$$
$$N_m(F-C) = 0.0132.$$
$$N_g - N_p = 0.0033 \text{ (measured directly, } 0.003^+).$$

These figures agree best with those of Mallard[14] measured on a natural prism of tridymite, though $N_g$ and $N_g - N_p$ are higher for the present specimen. The birefringence, however, is closer to that reported in more recent studies of the mineral.

From the above data it appears that the laths of tridymite are sections across basal plates which are separated from each other by films of altered glass.

The grains of tridymite and of the mineral described below together have optical properties similar to those of ptilolite,[15] but are distinguished from the latter by their high fusibility and greater hardness (>ordinary glass). Both minerals, moreover, are unaffected by strong HCl.

### *Cristobalite*, $SiO_2$

The grains identified as cristobalite are colourless with highly conchoidal fracture, and vary from isotropic to slightly birefringent. Some of the latter show two sets of fine multiple twinning bands intersecting at about 90°. The refractive index of the isotropic form is 1.4858; this figure is the same as that given for the isotropic type, metacristobalite.[16]

Tridymite and cristobalite are of interest in this study since this is the first time, to the writers' knowledge, that they have been described from such sediments.

[13] George, W. O., *Jour. Geol.*, vol. **32**, p. 365, 1924.

[14] Quoted by Sosman, R. B., The Properties of Silica, **1927**, p. 600; from *Bull. Soc. Fr. Min.*, (1890) vol. **13**, p. 169.

[15] Winchell, A. N., *Op. cit.*, Part II, p. 395.

[16] Winchell, A. N., *Op. cit.*, Part II, p. 55.

Other detrital fragments in the ore consist of well-rounded to sub-angular quartz and quartz-feldspar grains, shaly pebbles, small pieces of friable sandstone and a few thin slips of what seems to be chlorite schist.

## NODULES

The small nodules already referred to are roughly spherical in shape, with a maximum diameter of about $\frac{1}{4}$ inch. When the enclosing iron oxides are rubbed off, the nodules are seen to have a dirty yellowish colour. They have no recognizable internal structure. Mineralogically they are composed chiefly of dolomite and calcite, with a smaller amount of an earthy, yellow mineral. This material was tested microchemically and was found to contain calcium, phosphorus and sulphur. Optically it is isotropic with $N = 1.602$. These properties identify the mineral as collophanite or a similar species.

The nodules also contain minor quantities of one or two other minerals which were not determined. One of these may be koninckite.

## IV. CHEMICAL STUDY

### VARIATION IN CHEMICAL COMPOSITION OF THE ORE

The following table illustrates the variable chemical constitution of the Mayville ore.

| | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| $Fe_2O_3$ | 79.25[a] | 77.34 | 76.51 | 41.67 | 60.50 | 79.03[a] | 72.34 |
| FeO | | | | | 0.604 | | 0.44 |
| $P_2O_5$ | 1.13 | 2.75 | | 1.53 | 3.33 | 3.05 | 3.73 |
| $SiO_2$ | 6.18 | 8.57 | 10.13 | 15.12 | 6.90 | 5.75 | 5.12 |
| $Al_2O_3$ | 2.49 | 5.00 | 5.21 | 12.74 | 4.72 | | 3.25 |
| MnO | | 3.50 | 3.10 | 2.56 | 0.20 | | |
| CaO | 6.81[b] | 0.55[b] | 0.75[b] | 15.48[b] | 6.70 | 5.71 | 5.98 |
| MgO | 0.14[b] | 6.64[b] | tr.[b] | 8.25[b] | 2.97 | 0.64 | 0.61 |
| S | | | | | 0.048 | | |
| $CO_2$[a] | | | | | 5.86 ⎫ | | 3.60 |
| $H_2O+$ ⎱ | 4.00[c] | 2.65[c] | 4.30[c] | 2.65[c] | 7.06 ⎬ | 5.69 | 4.90 |
| $H_2O-$ ⎰ | | | | | 0.95 ⎭ | | 0.32 |
| Cl | | | | | | 0.003 | |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 99.842 | 99.873 | 100.29 |

[a] Includes FeO.          [b] As carbonate.          [c] Water, etc.

I–IV: Analyses compiled by R. D. Salisbury, Geology of Wisconsin, Vol. I, Part
II, 1883, p. 305.
V: Composite analysis of run-of-mine ore used in first study, 1925. By E. J.
Wechter and Mayville Iron Company.
VI: Partial analysis of hand specimen ore used in later study, 1932–33. A. P.
Beavan, analyst.
VII: Partial analysis of sample of crushed ore used in later study. A. P. Beavan,
analyst. (Sample from Bureau of Mines Experiment Station, Minneapolis.)

No attempt is made to recast the analyses into minerals on account of the large number of variables involved. It is apparent from the above figures, however, that the constituents vary independently of one another. Some variation in the kind of minerals present as well as in the relative amounts of each might therefore be expected. This appears to be borne out by the different mineral species found in the two ores studied, which show only a relatively slight chemical dissimilarity.

## COMPOSITION OF THE OOLITES

The composition of the oolites and difference between their composition and that of the ore in which they occur is shown in the

| | VIIa | | Va | |
|---|---|---|---|---|
| | Total | Soluble | Total | Soluble |
| $Fe_2O_3$ | 69.18 | | | |
| FeO | 0.58 | | | |
| $P_2O_5$ | 4.50 | 2.62 | 5.50 | 5.04–5.20 |
| $SiO_2$ | 3.78 | | | |
| $Al_2O_3$ | 4.22 | | | |
| CaO | 6.50 | 6.50 | 7.30 | 7.30 |
| MgO | 0.58 | | | 0.74–0.78 |
| $H_2O+$ | 6.58 | | | |
| $H_2O-$ | 0.38 | | | |
| $CO_2$ | 4.26 | 4.26 | 5.15 | 5.15 |
| Total | 100.56 | | | |

following partial analyses (Va and VIIa) of oolites corresponding respectively to ore analyses V and VII above.

The analyses show that the oolites are higher in lime and phosphorus than the ore as a whole. In ore VII the oolites constitute

75% of the ore by weight. A simple calculation then shows that the matrix contains 1.42% $P_2O_5$. The proportion of oolites in ore V was not determined, but chemical tests indicate that its matrix contains an even smaller amount of phosphorus. In both ores the phosphorus is irregularly distributed in the matrix.

## CHEMICAL COMBINATION AND DISTRIBUTION OF PHOSPHORUS IN THE OOLITES

Calculations based on the phosphorus minerals and their solubility in various acids indicate that the phosphorus in ore V is combined with ferric oxide, lime and alumina in the proportions 68:26:5.5. The approximate corresponding ratios for ore VII are 45:13:42. The marked difference in the proportions of the phosphates is evident in thin sections of the two phases of the ore: in the one first studied concentric shells of dahllite occur in some of the oolites, whereas in the second type no rings of such transparent material are visible.

The distribution of phosphorus in the ore as a whole has already been mentioned. Within the oolites themselves the element is again not uniformly distributed. The ordinary chemical tests for phosphorus were adapted to staining methods for the detection of the element in the manner described by Holmes[17] for the detection of iron. Much difficulty was encountered, however, in developing a method which would retain the phosphorus compound formed, on polished sections. The most satisfactory results were obtained with a recently published test[18] which, by the use of benzidine hydrochloride, gives a deep blue colouration wherever ammonium phosphomolybdate is formed. Staining by this method shows phosphorus only in certain shells of the oolites. It is almost invariably indicated in their outermost spheroids, a fact previously shown in the earlier work by chemical tests. Many of the inner rings also give the blue stain, but this or other staining methods cannot be used to estimate quantitatively the distribution of phosphorus, since phosphatic minerals are not all equally susceptible to the reactions involved.[19] From the study of ore V above, it is estimated that at least 50% of the total phosphorus in the oolites is contained in their outer shells.

[17] Holmes, A., *Petrographic Methods and Calculations*, 2nd Impression, p. 269.

[18] Leitmeier, H., and Feigl, F., Ein rascher und empfindlicher Nachweis der Phosphorsaure: *Min. Pet. Mit.*, Band **39**, pp. 224–240.

[19] Leitmeier, H., and Feigl, F., *Op. cit.*, pp. 229–240.

### V. GENESIS OF THE MAYVILLE IRON ORE

#### ORIGIN OF OOLITIC IRON ORES

A study of the many extensive deposits of oolitic iron ore in the world has lead to the advancement of three theories of origin for those consisting of oolitic limonite[20] and/or hematite. Briefly stated these are:

I. Formation of oolites consisting of various minerals containing iron in the ferrous state, with subsequent alteration under oxidizing conditions to form hydrated ferric oxides or hematite.

II. Deposition of oolitic sediments without important iron content, but later replaced by iron from solutions.

III. Deposition of iron as ferric hydroxide, with later partial dehydration of the iron compound.

At present the first and last conceptions hold most favour among geologists. In the following pages it is endeavoured to show that the Mayville iron ore is of the third type.

#### THE MAYVILLE ORE

PRIMARY ORIGIN. No evidence is known to support the view that the Mayville ore belongs to either types I or II of the above classification. Field relations indicative of important mineralogical changes in the ore are not mentioned in the literature regarding the Mayville deposit. In the laboratory the theory of replacement of an original oolitic limestone would seem to be refuted by the presence of "normal" ferruginous oolites of hydrous ferric oxide in calcareous zones in which the matrix consists almost entirely of carbonate grains with a small amount of interstitial iron oxides. The latter, however, do not replace the carbonates. Consideration of this evidence, in conjunction with that of an even more positive nature given below, leaves no reason for believing that the typical Mayville ore formed in any way other than by direct precipitation of ferric hydroxide and aluminosilicates.

MODE OF DEPOSITION. These two substances, ferric hydroxide and hydrated aluminosilicate, are considered to have been deposited from the colloidal state. Apart from the earthy and "amorphous" state of the dominant minerals—a property often, but not necessarily, indicative of colloidal origin—several other features of the ore support the conception of this mode of formation. Chief of these

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[20] Limonite is here used to mean hydrous ferric oxide.

is the concentric structure of the oolites, as held by various authorities.[21] Further, the easy absorption of malachite green by the halloysite of the oolites and the resultant non-pleochroic colour of the mineral is evidence of its amorphous, gel nature according to Grandjean and others.[22] Allophane and opal are likewise mineral gels,[23] and of the phosphate minerals present, variscite, evansite, ceruleolactite, and collophanite have been regarded as of colloidal origin.[24] It is well known that phosphoric acid is adsorbed by many hydrosols, including those of alumina, ferric hydroxide and aluminosilicates.[25]

It was formerly thought that calcareous and limonitic oolites grew by accretion of material as they were rolled on the sea or lake bottom. Much experimental and observed evidence has now accumulated, however, which indicates that most, if not all, sedimentary oolites, form by growth in free suspension.[26] In the Mayville ore the presence of reworked material at first suggests the former origin for the oolites, but the following features seem incompatible with such a mode of formation:

1. Oolites lacking a nucleus.
2. Oolites with two unattached oolites as a nucleus.

There is, nevertheless, abundant evidence that all the oolites of the Mayville ore did not originate in situ. The relatively coarse grains of detrital material, the broken oolites, ore grains and shaly particles, the fragmentary character of some of the fossil remains—all are indicative of shallow water sedimentation of a type characterizing deposition and contemporaneous reworking of similar pre-existing material.

On the other hand, the following observations point equally as clearly to the formation of the oolites in situ in an undisturbed environment:

1. Wide range in grain size of the oolites, indicating lack of sorting.

[21] See Scott, A., The Application of Colloid Chemistry to Mineralogy and Petrology: Fourth Report on Colloid Chemistry and its General and Industrial Applications, *Brit. Assoc. Adv. Sci.*, **1922,** pp. 213–215.

[22] Grandjean, F., *Bull. Soc. fr. Min.*, **1909,** p. 408. Scott, A., *Op. cit.*, pp. 211–212.

[23] Scott, A., *Op. cit.*, pp. 219, 234.

[24] Scott, A., *Op. cit.*, pp. 242–243.

[25] Scott, A., *Op. cit.*, pp. 217–243.

[26] See Bucher, W. H., On Oolites and Spherulites: *Jour. Geol.*, vol. **26,** 1918, pp. 593–609. Pulfrey, W., *Q.J.G.S.*, vol. **LXXXIX,** pp. 416–417. Telfer, L., *Trans. C.I.M.M.*, vol. **XXXVI,** p. 600.

2. Lack of cross-bedding in the ore stratum.[27]

3. Distortion of the banding of one oolite by another in contact with it during growth.

4. Rarely, grains of detrital material (other than nuclei) enclosed in the oolites without distortion of their regular concentric banding.

The obvious conclusion seems to be that both the processes outlined above were active. Thus, while many, perhaps the greater part, of the oolites, formed in situ, others were at the same time washed in from similar deposits previously formed under like conditions of quiet sedimentation.

SOURCE OF MATERIAL OF THE ORE. Significant as they are in the foregoing conception of the conditions of sedimentation, the predominant ore minerals throw no light on the baffling problem of their source. In the present study the only information on this question is that yielded by the clastic grains in the ore.

The most abundant transported material, other than reworked oolitic ore and shaly iron oxide, is the fragmental lava. In view of the important part ascribed to igneous activity in the origin of certain iron formations of the Lake Superior region, the volcanic particles in the Mayville ore at once suggest the possibility of Late Ordovician volcanism to which the deposition of the ore might have been related, directly or indirectly. But as yet no igneous activity of such age is recognized in this part of North America. The very minor amount of material volcanic in origin does not justify the postulation of volcanism to explain the genesis of the deposit under discussion, unusual as that type of deposit is among sediments in general.

The alternative explanation of the lava grains is that they were derived from an older land area composed in part, at least, of volcanic flows. The mineralogy of these fragments, described above, suggests that the flows were dominantly intermediate or basic in composition. It is considered that weathering of such lands supplied the highly ferruginous material now forming the Mayville ore.

The thick pre-Niagaran limestones and dolomites of Wisconsin, all of which contain small amounts of iron and alumina,[28] would

[27] Savage, T. E., and Ross, C. S., *Op. cit.*, p. 192.

[28] Steidtmann, E., Limestones and Marls of Wisconsin: *Wisconsin Geol. and Nat. Hist. Surv., Bull.* 66, 1924, pp. 183–187.

also appear to offer a possible source for a ferruginous, aluminous sediment free from important quantities of detrital material. Again, siliceous and calcareous iron formations, or pre-existing iron ores, may be suggested as the source of the Mayville ore. Neither of these possibilities, however, is supported by evidence of a positive nature; they are, therefore, not considered further.

Assuming, then, that the ancient land area yielding sediments consisted partly of volcanic flows, and further, that no such rocks were formed between Pre-Cambrian and Silurian times, it would appear that over much of this land mass pre-Cambrian rocks were exposed. The present distribution of formations in Wisconsin and adjoining states indicates that the ancient continent, during Late Maquoketa time, lay west and northwest of the area in which the Mayville ore now lies.

These views as to the character and location of the land mass are confirmed by comparison of the detrital material found in the ore with the known types of pre-Cambrian rocks in Wisconsin. The clastic fragments are listed below in order of abundance, together with corresponding rocks from which they were possibly derived.

| | |
|---|---|
| Basic lava grains................... | Basic flows now exposed south of Lake Superior. |
| Grains of quartz, feldspars (or both) hornblende and mica.............. | Pre-Cambrian igneous rocks of Wisconsin. |
| Grains of chlorite schist............. | Crystalline schists of Wisconsin pre-Cambrian Rocks. |
| Grains of sapphire corundum......... | Feldspathoid-bearing rocks in central Wisconsin. |
| Grains of friable sandstone with well-rounded quartz................... | Pre-Silurian sandstones of Wisconsin. |

NATURE OF WEATHERING. Evidence has already been cited, in the reworked character of fragments in the ore, to show that the Mayville deposit was laid down in fairly shallow water. The paucity of clastic fragments and the abundance of meta-colloids in such a formation must therefore bear mutual attestation of chemical decay as the important erosive process, a process promoted undoubtedly by the warm, equable climate prevailing in Late Maquoketa time[29] over a land of low or slight relief and sluggish streams.

[29] Schuchert, C. A., *A Text Book of Geology*, Part II, pp. 232–442.

SECONDARY MINERAL CHANGES. Neither thin nor polished sections of the ore yield much information as to the association of its minerals, on account of the mantle of opaque iron oxides.

The coating of crystalline hematite surrounding the oolites suggests that this mineral has formed through secondary reorganization of iron oxides since consolidation. The large volume of voids between the oolites may represent a concomitant removal of carbonate matrix, since similar hematite coatings are present on some oolites seen in a calcareous band of the ore. Goethite, it would seem, may be either primary or secondary by hydration of hematite, since ferric hydroxide, precipitated in sea water, tends to take the anhydrous form.[30] The oolitic character and predominance of goethite, however, favor a primary origin for this mineral.

Mineral relations observed under a binocular microscope are:

Association of pyrite with a hydrocarbon.
Encrustations of yellow collophanite on the iron oxide minerals.
Encrustations of carbonates on the iron oxide minerals.

The presence of sulphate-bearing minerals (collophanite and gypsum), secondary carbonates and phosphatic nodules all suggest that circulating solutions have influenced the mineral composition of the ore to some extent. Sulphate minerals were formed possibly by such solutions, deriving that radical from the oxidation of pyrite in the ore and acting on primary constituents of the deposit. The consistently phosphorus-rich outer shells of the oolites, a feature that seems difficult to explain as primary, may be due to solution of phosphorus from the matrix and redeposition on the oolites, or to absorption of phosphatic solutions arising in the matrix, by the gel minerals of the spheroids. There is nothing to indicate introduction of phosphorus from outside the ore bed. The rocks adjacent to the ore horizon are themselves almost devoid of phosphorus.[31]

## VI. ECONOMIC ASPECTS OF THE STUDY

As noted in the introduction, the mineralogical study of the Mayville ore was undertaken to ascertain the nature and distribution of the phosphorus minerals preliminary to a study of possible methods of eliminating some or all of these.

The determination that the phosphorus is present as minute

[30] Lindgren, W., *Mineral Deposits* (1928), p. 313.
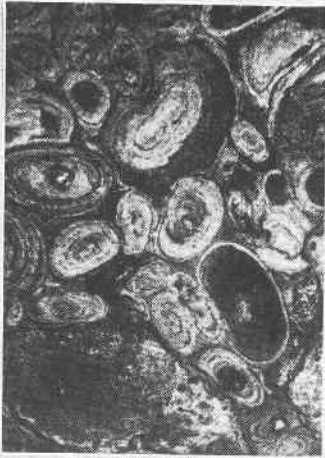[31] Steidtmann, E., *Op. cit.*, pp. 44, 188.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

## EXPLANATION OF PLATE A

Fig. 1. Section of Ore approximately parallel to bedding. Note indentation of one oolite by another, with distortion of banding in the larger. A large "false oolite" of iron oxide occupies the lower left-hand corner. ×27.

Fig. 2. Oolite showing a nucleus consisting of two unattached smaller oolites. ×27.

Fig. 3. Cruciform nucleus. A smaller oolite indents the larger with distortion of its banding. ×84.

Fig. 4. Oolite with nucleus consisting of a broken preexisting oolite. The latter itself has also a nucleus of broken oolite. ×84.

particles of iron, lime and aluminum phosphates, intimately associated and intergrown with iron oxides in the oolites, though concentrated to a major extent in their hard outer shells, suggested that no practical method of effecting a separation of these minerals would be found. Nevertheless some experiments were carried out along lines suggested by the earlier work. In this, the fact that most of the ore being used in the blast furnace in 1925 required nodulizing was taken into consideration. The results of certain experiments are summarized below.

1. Acid treatment of raw and nodulized ore. This method, suggested by microchemical tests on oolites, involved the leaching of ore with nitric and hydrochloric acids of varying concentrations. While 94 per cent of the phosphorus could be removed from the raw ore, and material of Bessemer grade produced from the nodulized product, costs of acid were alone prohibitive.

2. Dephosphorization of raw ore by roasting with sodium carbonate and forming water-soluble phosphate gave interesting results but was not sufficient to make the process appear promising.

3. On account of the intimate association of phosphorus minerals with the iron oxides and slight differences in their magnetic susceptibility (particularly of the iron phosphates and oxides) a magnetic separation of the iron ore minerals from those containing phosphorus was not feasible.

4. The low fusibility of the phosphorus minerals renders any magnetic separation after nodulizing and partial reduction of the iron to magnetite impractical, since the phosphorus-bearing constituents become even more intimately locked up with the iron minerals in the sintered product than in the ore.

The results thus confirm the opinion that elimination of the phosphorus can only be obtained economically by metallurgical methods.