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COLLOIDS IN IRON ORE SEDIMENTATION

with special reference to

A PISOLITIC HEMATITE DEPOSIT ON BLACK ISLAND, MANITOBA.

by

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LOCATION MAP

SCALE, 12.5 MILES = 1 INCH



FIG. 1.

BLACK ISLAND MAP AREA

Scale, 3.125 miles = 1 inch



FIG. 2.


ANDESITE


GRANITE


WINNIPEG
SANDSTONE


TRENTON
LIMESTONE

Introduction.

Historical. J.B. Tyrrell noted this occurrence of Manitoba iron ore. In his correlation the rocks of the southern portion of Black Island were placed as Cambro-Silurian in age. The sericite schists were regarded as being probably Huronian in age. Tyrrell noted the stalactitic nature of the hematite. He did not attempt to arrive at a definite conclusion with regard to the origin of the deposit.

Location. Black Island in its relation to the surrounding country may best be realized from Fig. 1. The distance from the mouth of the Red River to Black Island is fifty-four miles. Black Island may be reached from Selkirk, or Victoria Beach by launch. The iron ore deposit in question is located on the east shore of Black Island, being a little north of west from the mouth of the Manigotagan River.

General Stratigraphy. The island lies on the contact between the Ordovician and Pre-Cambrian (Fig. 2.). The Ordovician commonly is at contact with the Pre-Cambrian. Between these horizons, however, there is a sandstone formation which has locally been named Winnipeg Sandstone. This does not generally exceed one hundred feet in thickness and is quite localized. The formation may be of the intercalated type similar to the St. Peter of the central United States. The southern part of Black Island approximating three-fourths in area of the total, is covered by this sandstone. Aside from the outcrops on the island the Winnipeg formation is seen in only one other area on the map as given. This occurs on the southwest corner of the peninsula separating the Manigotagan and Wanipigow River systems. There has been no deposition of limestone on the sandstone insofar as Black Island is concerned, thus the limestone is restricted to the west of the dotted line, Fig. 2. Subsequent to the Ordovician invasion there has been laid down a thin covering of glacial drift. The northern portion of Black Island consists of andesitic and trachytic lavas similar in every respect to the lavas bordering the Wanipigow River eastward. These are pillow lavas that show distinct

flow structure and contain sedimentary inclusions which resemble chert. The iron deposit is part of a true bedded occurrence laid down as such during Pre-Cambrian time. The sediments are exposed along a cliff about three hundred feet long and twelve feet high. They have been profoundly changed by igneous activity and secondary alterations.

General Geology of Eastern Manitoba.

Pre-Cambrian correlation. (Ref.1).

Igneous Division:

Se

Granite.
Gabbro.
Andesite, Trachyte and Rhyolite Porphyries.
Lavas and cherts, interbanded.

Sedimentary Division:

Arkose.
Greywacke.
Quartzite.
Iron Formation.
Chert.
Conglomerate.
Argillite.
Slate.
Shale.

This correlation gives valuable proof that Lawson's Gouthiching Series was older than the Keewatin. In the Rainy Lake district the Gouthiching comprised one main rock type which was essentially a Biotite Schist. In the Rice Lake district, however, there are no less than nine rock types which come under this Gouthiching category. The Rice Lake rocks which most nearly correspond to the Gouthiching type are the sediments which are nearest to igneous contacts and therefore have suffered greatest metamorphism. This vast sedimentary series has been estimated to have a total thickness of fifty thousand feet. Strata originally deposited horizontally are now upturned in a vertical position. The Greywacke and Quartzite have resulted from the metamorphism of more or less pure sandstones. Biotite, garnet and andalusite schists have developed where the

sandstone has given precedence to a clay or silt. The sediments at the base of this series, slate and shale, have been protected by the overlying portions, and consequently did not suffer metamorphism to the same degree. Aside from the above this sedimentary formation may well represent marine deposition. Hence, prior to the vast tectonic upheavals of Pre-Cambrian time, there existed a long period of erosion, during which enormous quantities of sediment were carried by rivers and streams to a hypothetical sea. By virtue of this correlation there can be no possible connection between the cherty iron formation of eastern Manitoba and volcanic activity.

Sedimentary Division.

Shales and slates. These are soft, fissile, greenish-black rocks with good cleavage. They consist essentially of quartz, a little biotite, chlorite and mica. The shales, slates and argillites represent the same unmetamorphosed common ancestor. Proximity to tectonic movements has been the factor which determined the present nature of the rock. Singularly enough, the oldest rocks in the Pre-Cambrian system of eastern Manitoba are the least metamorphosed.

Conglomerate. This rock contains rounded pebbles of granite, chert, greenstone and quartzite. It is one of the puzzling features of correlation. An earlier granite would be essential to the formation of this conglomerate but as the correlation stands this is not implied. Lawson (Ref.2) based his work on the belief that there were two distinct granitic intrusions, Wright (Ref.1) based his correlation on the one granite idea, which, through differentiation, has produced the various white and pink granites found in the area under consideration. There is no evidence at hand which points toward two granites in Eastern Manitoba, outside of the point already referred to.

Chert. The chert bands are of two kinds. One the white variety containing no colored impurity, the other jasper. Where the cherts are not jasper, they are grey, glassy looking rocks, the grains being indistinguishable without magnification.

tion. A few aggregates of calcite, chlorite and sericite were noticed. The bands all stand at high angles producing a linear distribution; the exposed width of the beds being that of their original thickness.

Iron formation. The iron minerals are magnetite and hematite interbedded often with jaspery material. Lenses of rock material of different thickness are often interlaminated with the iron formation. The association of an iron formation, primarily hematitic in its nature, with igneous intrusions, has converted the hematite into magnetite in a manner similar to the east Mesabi Range. There seems to be no way of foretelling whether the hematite was originally laid down as such, or was produced through the agency of secondary alteration of material similar to Taconite or Greenalite. In the Black Island deposit material has been obtained which produced hematite through secondary weathering processes.

Quartzite and Greywacke. The rocks are light grey, massive, medium to coarse grained, they consist of quartz and plagioclase; considerable amounts of calcite, sericite and chlorite are also present. The beds all dip to the north. Their thickness is about ten thousand feet.

Arkose. This formation is localized, particularly, in the vicinity of Bird River. Its importance rests on the knowledge that such rocks are formed by physical disintegration and as such, are terrestrial in origin.

Igneous Division.

Lavas. These Keewatin flows may have been the ultimate result of isostatic readjustment produced by an enormous period of sedimentation. Vast outpourings of lava from fissure eruptions seem likely to have played the leading role at numerous places and over large areas. Such a region is typically a plateau country in surface topography as well as in geological structure. The extrusion of lava should not be looked upon as continuous but as intermittent in its period of activity. The intervening periods were of sufficient duration to provide for a temporary drainage system which through mechanical and chemical denudation produced interbedded chert formations. The lavas in relation to the underlying

sediments are concordant. Andesite dykes cut through the sedimentary strata above, serving as flowage channels for the molten rock. At the contact between the lava and sediment there is usually good indication of hybridism. In the vicinity of Bulldog Lake this, is particularly noticeable. The inclusions correspond most closely lithologically to the chert formation. In size, they average about two by one feet. The arrangement of these structures corresponds closely to the direction of flow of the lava. This point of hybridism is one of the salient facts given, to show that sediments were prior to the Keewatin greenstones. The rocks as found today are typically greenish with an abundance of hornblende. They show good pillow structure in many areas, which may or may not be due to submarine extrusion. Granite of at least one period everywhere traverses the older lava.

Plutonism. These are of two types, Granite and Gabbro.

Granites are widely distributed and are the most important type so far as areal distribution is concerned. They show wide diversification in mineral constitution, some being acidic and others basic. The acidic types are represented by the common salmon red variety while the white types are basic. The relationships of these two types cannot be worked out by intrusion of the one into the other, for, they are found to intrude each other. From the nature of all known facts no distinction between Algonian and Laurentian granites in the particular area could be discerned.

Gabbro is confined to two areas that are about eighteen miles apart, the Bird River and Bear River districts. The rock is typically coarse grained but also occurs in more massive fine grained variety. The gabbro occurs in isolated bosses within areas previously mapped as granite. The relative ages of gabbro and granite have not been definitely established. Evidence seems to indicate that the gabbro is older than the granite. The association of copper and nickel sulphides with these gabbro bosses has locally stimulated interest in the exploitation of these discoveries. The country at this period in its history must

have been somewhat similar to the Cordilleran region. Rugged topography was conducive to rapid mechanical erosion with its characteristic peneplanation, but the final resting place of these derived sediments was not destined to be on the parent rock. The area stands today typical of the Laurentian shield devoid of all ancient grandeur. Following the erosional period at the close of the Pre-Cambrian, seas advanced from the south and west covering the marginal parts of the peneplained area, ushering in the Ordovician period.

Ordovician correlation.

The general stratigraphy of the Manitoban Ordovician may be shown by a comparison of the following type sections.

<u>New York and Ontario.</u>		<u>Manitoba.</u>	
Upper Ordovician or Cincinnatian	Ganagoche Richmond Lorraine Utica	Richmond	Stony Mountain - 110'
Middle Ordovician or Champlainian	Gellingwood Franton Black River Lowville Chazy-Stones River-St. Peter.	Champlainian	Upper Mottled Tyndall limestone - 110' Lower Ft. Garry and Carson. Cat Head. Lower Mottled. Winnipeg sandstone, 80 - 100' Black River (possibly)
Lower Ordovician or Canadian	Fort Cassin Beekmantown		

The Canadian has no formation in Manitoba, a fact which indicates that the old Laurentian landmass was not submerged during this period. The greatest thicknesses of sediment were laid down during the Champlainian overlap and consist, principally of limestones and dolomites. The Winnipeg sandstone has been the source of much controversy but may be best correlated with the St. Peter sandstone. The St. Peter extends from Oklahoma to St. Paul and occupies the break between the Canadian and Champlainian submergences. It is a pure quartz sandstone about two

hundred feet in thickness. The rock is believed to have been derived by wind erosion during the emergence period following the Canadian. The Winnipeg sandstone has been recorded by Dowling and Tyrrell (Ref.3) as occurring along the east shore of Lake Winnipeg, on several large islands, and on the western shore. The material is composed of fine white sand in places grading into shale and clay. Its maximum was found to be near Dog Head, and was obtained by soundings. The thickest exposure recorded by Tyrrell was fifty feet of fine white sand at Elk Island. The fossils obtained in the Winnipeg sandstone were; *Lierophyous ottawaensis*, *Rhinidictya mutabilis*, *Escharopora ramosa*, *Strophomena trilobata*, *Orthis testudinaria*, *Cyrtodonta canadensis*, *Aparchites tyrrelli* and *Comularia*. *Lierophyous* and *Cyrtodonta* are Trenton, *Rhinidictya*, *Escharopora*, and *Cyrtodonta* are Black River. From this evidence Dowling was led to suggest that the Winnipeg sandstone represents a passage from Black River to Trenton. The St. Peter sandstone has in part ~~been~~ been derived from Pre-Cambrian and in part from Potsdam (Ref.4). Absence of Cambrian sediments in Manitoba clearly indicates that the Winnipeg sandstone could have been derived only from Pre-Cambrian rocks. It is suggested that the material was carried down from the north by Pre-Cambrian drainage systems and deposited as a shore facies during the transgression of the Champlainian sea. The progressive overlap produced the Trenton limestones which now lie above the Winnipeg sandstone. Insofar as the St. Peter is concerned, the only difficulty encountered seems to be the lack of outcrops lying between St. Paul and Lake Winnipeg. The St. Peter sandstone if extended northward appears to coincide with the Black River formation. In conclusion it may be suggested, that the Winnipeg sandstone represents a northerly continuation of the St. Peter. The proof of this, however, is purely a problem of palaeontology. The relationships of the Winnipeg sandstone may be better appreciated from Fig.5., which is a cross-section along the line AB as taken from Fig.2.

Cretaceous.

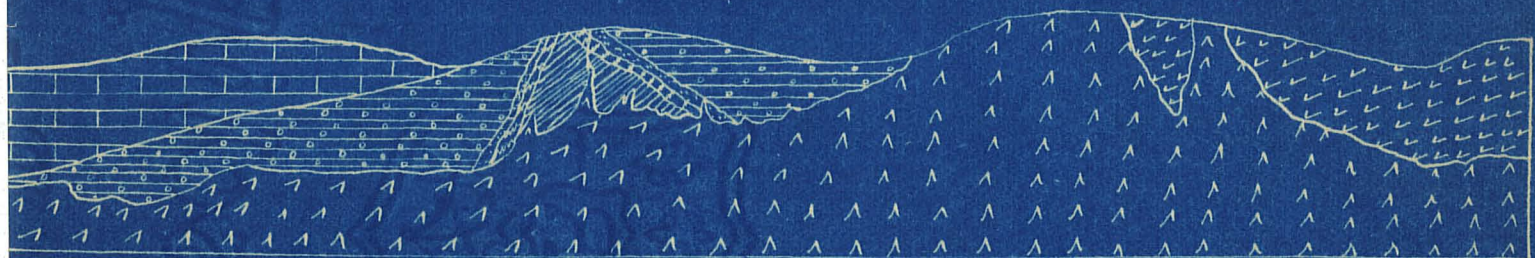
Despite the fact that Cretaceous outcrops are absent in the Black Island area, this discussion would not be complete without reference to this period. Cretaceous horizons are found at Swan Lake to the west and have been determined to be one hundred and fifty feet higher than the Pre-Cambrian peneplane¹⁷ as it occurs at Lake Winnipeg. This is a significant fact in that it may show, that the Cretaceous sea came much further eastward than its present location would indicate. It is therefore, logical, to believe that Cretaceous formations may have covered this area until Tertiary or even later times. Some of the iron and calcium of the deposit on Black Island may have had their source in these sediments.

Pleistocene.

Glacial till averaging ten feet in thickness has been deposited on top of the Winnipeg sandstone. The area, in question, has more or less escaped the intense glacial erosion of the east and west. This accounts for the exposures of Winnipeg sandstone, which, are remnants of the Pre-glacial regolith not destroyed by erosion.

Geology and Origin of the Black Island Iron Formation.

The Black Island iron formation is Pre-Cambrian and has been deposited prior to the granitic invasion. Quartz veins have produced secondary silicification to a marked degree, and are likely to be derived from underlying granite. These sediments are a considerable distance from the main series eastward and do not give definite evidence as to their exact age. It is for this reason, that one would not be justified in correlating them with the older sedimentary formation. They may have been formed by weathering of the Keewatin andesite. The formation, as exposed, was seen to consist of chert, sericite schist, breccia and marine clay. If we regard the formation as part of the older series then the source of supply is lost in the antiquity of the strata. The Keewatin andesite



GEOLOGICAL CROSS SECTION

B


 ANDESITE


 GRANITE


 HEMATITE
& CALCITE


 SERICITE
SCHIST


 CHERT


 WINNIPEG
SANDSTONE


 TRENTON
LIMESTONE

FIG. 3.

on the other hand, would not be a hypothetical source. The order of deposition turns, on the point of the sericite schist, which is now dipping almost vertically. The schist indicates that the sediments have been tilted into a steeply inclined anticlinorium, the roof of which has subsequently been removed. The other beds possess no criteria for determination of dip. The strata were originally deposited in a horizontal position. The order of deposition is as follows: (a) Marine clay. (b) Sericite schist. (impure sandstone) (c) Chert.

Chert. There are two main ideas which have been put forward to explain the origin of chert. Firstly, hypotheses that seek to explain the origin through segregation by organic means. Secondly, hypotheses to explain the material of the chert as a direct chemical precipitate. Chert bands in Pre-Cambrian areas cannot readily be explained on the organic hypothesis. There are no evidences of life in the rocks.

W.A. Farr (Ref.5) has presented the most comprehensive ideas on chert thus far published. His views, in part, are as follows: "Silica is derived by weathering. It is transported by streams as colloid. Peneplaned landmasses favor chemical denudation. Streams draining such areas, carry greater amounts of silica. Landmasses of high relief favor mechanical denudation, thus increasing the amount of clayey material transported to the sea. The colloidal silica is precipitated, on reaching the sea, by alkali salts functioning as electrolytes."

Apart from these two theories, the volcanic origin recently revived by Samson, (Ref.6) should be mentioned. In Newfoundland, chert associated with pillow lavas, pointed to consanguinity of origin. By way of contrast, the Black Island cherts are not associated with any igneous formation; neither can we look upon the cherts of the older sedimentary series as being connected with any igneous activity. A sedimentary theory of origin, then, is the only logical position in connection with the origin of these cherts. The Black Island rocks of this type are principally silica with minor amounts of ferric oxide. The chert outcrops in a band four feet in thickness on either side of the sericite schist formation.

A few nodules or horizons of chert occur along with green marine clay. The chert beds represent proximity to a river, draining an area not particularly high in relief. Since original deposition the silicic acid has dehydrated and passed over into cryptocrystalline chert, a process which may have been hastened by igneous activity.

Sericite Schist. These rocks are the dominant type. They contain about ninety percent quartz and about ten percent sericite. As such, they are sedimentary in origin. Primarily they constituted impure sands, that were converted into sandstone and later into sericite schists. The sericitization seems likely to have been the result of granite intrusion, which set up sufficient pressure and temperature to convert the argillaceous impurity of the sandstone into sericite.

Breccia. This material is scattered along the contact between the iron formation and sericite schist. The fragments are both angular and rounded pebbles of chert and quartz. The cementing material is green marine clay and calcite. Quartz fragments indicate that the breccia was formed during the igneous intrusion of granite quartz epophyses. The granite intrusion, then, was attended by brecciation of chert, sericite schist and marine clay. The quartz veins, in addition, were broken into angular fragments which subsequently were laid down in a loosely compacted mass. The interstices between the fragments were occupied by marine clay. On exposure this clay was oxidized to hematite and dehydrated. This produced shrinkage cracks between the clay and fragments. These cracks were later occupied by calcite, which was brought in and precipitated from solution (See Fig. 5).

Marine clay. This greenish colored rock, is material which readily undergoes oxidation to hematite. It contains quartz crystals imbedded in an isotropic medium. The four elements contained are Aluminum, Iron, Silicon and Magnesium. The clay is scattered throughout the iron formation in isolated nodules, which are generally seen in protected places. The ferrous iron strongly suggests marine deposition. Pisolitic hematite is considered to be the result of secondary

changes, which this rock has undergone. The material may be compared, to some extent, with Greenalite from the Lake Superior district. In no way may it be considered as an igneous rock. In this regard it differs from Greenalite. It is much less compact, of a lighter shade of green and lacks the characteristic granular structure. Its origin is considered under the section on chemistry.

Structural Relations of the Sedimentary Series.

Horizontally laid deposits of green clay, impure sandstone and chert constituted a differentiation of river-laid materials deposited in Pre-Cambrian seas. Fluctuation of level in this sea produced, by overlapping and relapping, a transitional and vertical series of the above mentioned materials. The oldest member of the sedimentary series, as exposed along Black Island, is the clay. On top of the clay are gradually exposed schist and chert. During the eruption of Pre-Cambrian rocks, these strata were tilted in a vertical manner by underthrust. This exposed the older beds of marine clay and brought about the necessary condition for secondary decomposition.

Petrology.

The study, in thin sections, of the ore and accompanying rocks has supplied exact information regarding the composition of the sericite schist, in particular.

Combined microscopic and chemical analyses have been the means employed in identifying the material of the marine clay.

Chert Band (Slide X₁), taken from extreme left of the exposure (Fig. 3).

The essential mineral of this rock is quartz. The quartz mass shows definite cracking and secondary crystallization of infiltrated quartz. Hematite is present in well defined rows, and constitutes about ten percent of the rock. These bands are cut across by the secondary quartz veins. The chert also has undergone sericification but to a much lesser extent than the sericite schist. Materials necessary for sericite formation evidently were lacking due to the greater amount of iron present. The rock, as determined, is a lower

The rock, as determined, is a jasper variety of chert.

Sericite Schist (Slide Y₂), taken right of orebody (Fig.3).

This formation usually contains chert fragments, and is stained by hematite. It is well slickensided and jointed. The joints strike N.15°W., and dip N.25°E. Hematite is found all along these joint planes. As seen in the slide the essential mineral is quartz, the grains of which are not so fine as those of the jasper. The sericite is arranged along planes of schistosity producing a rock which is light greyish in color, and very misleading in the hand specimens. Hematite is also present, but in insufficient quantity to produce a rock similar to the jasper (Fig.7). The chief point of variation, between these two rocks, lies in the sericite-hematite ratio. In the chert, the amount of potassium and aluminum was small. Consequently there has been little development of sericite. In the schist, the amount has been sufficient to produce considerable quantity of sericite. In the schist, the iron has remained in the uncombined condition. Percolating solutions have carried this iron along the joint planes, which have been discolored by hematite.

Breccia (Slide Y₃), taken from zone of brecciation between the schist and iron formations.

Fragments of chert and quartz are cemented by marine clay and calcite. The clay is altered to secondary hematite. The clay matrix gives evidence of leaching and concentration of iron. In this process, oolites, are formed. The quartz and chert fragments were apparently cemented by the wet clay-like material which shrank on dehydration. This left cracks which were later filled by secondary calcite. The calcite has traversed all available space, and frequently crystallizes in amygdaloidal cavities.(Fig.6).

Marine Clay (Slide Y₄), nodules within the orebody.

This material contains many inclusions of quartz. It readily undergoes alteration, which is marked by a change from ferrous to ferric iron. All stages in the decomposition of the clay may be observed in various sections. The undecom-

posed specimens are traversed by filamentous structures (Fig.4), which are strongly suggestive of organic casts. Material occurs in the white areas of the photograph, which are lighter than the surrounding olive colored substance. The plants, if such, may have contained an amount of magnesium, which, on their decay, concentrated this element in these particular areas. Professor Buller, of the Department of Botany, University of Manitoba, was unable to say definitely that these structures indicated algae remains. Professor Lowe, of the same Department, stated, "That these structures strongly suggested organic casts." Apart from the quartz and a little sericite all the material is isotropic. This fact indicates one or other of two modes of origin: (1) A supercooled glass. (2) A colloidal precipitate. As number (1) is obviously to be disregarded we look upon the isotropism as due, to particles too small to be resolved under crossed nicols. Such particles would be colloidal in size. The marine clay is shown in both Figs. 4 and 5. The filamentous structures, referred to above, are the thin lines shown on the right of Fig.5. The structures of Fig.4 are much larger.

Pisolitic Hematite (Slide Y3). From the Hematite formation, (Fig.3).

The hematite occurs either as stalactites or as pisolites. The stalactites probably were produced under the action of gravity, which had the effect of joining the ~~matrix~~ pisolites one above the other. The pisolites show typical globular structure, but in cross-section they are isotropic. In reflected light they exhibit a characteristic banded structure. Alternate bands of the iron oxide are respectively crystalline and amorphous. The crystalline bands are black, and grow radially toward the centre of the pisolite. The amorphous bands appear to be red hematite. The interstices between the pisolites and stalactite are filled with calcite. Between the calcite and the pisolite there is usually a very thin layer of unaltered, marine clay. The structure of the pisolite is illustrated in Fig.8.

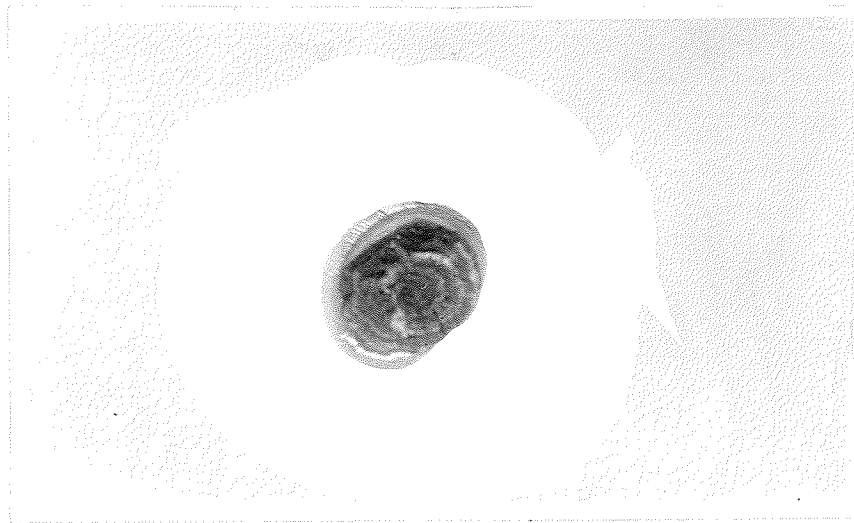


Fig. 8. Magnified 10 diameters. Reflected light.

The above figure represents a cross-section of Black Island pisolite. The characteristic banded appearance mentioned on page 17 is quite apparent. The black bands are amorphous red hematite while the interstitial portions of the pisolite between these bands consist of black, crystalline hematite. The pisolites contain a small percentage of silica and water in addition to the oxide of iron.

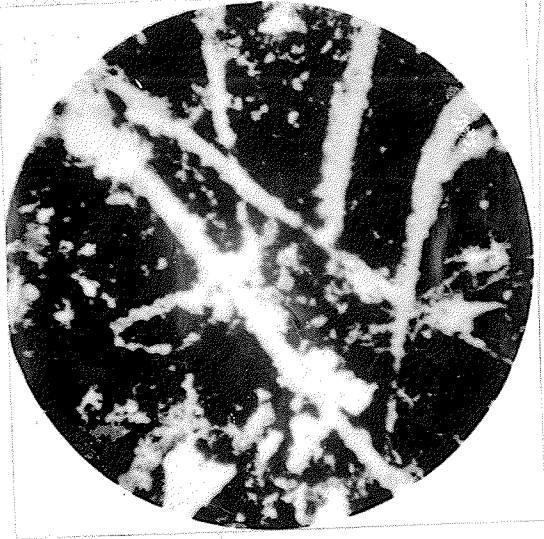


Fig. 4. +nicols.
Probable organic structures
in
Black Island marine clay.

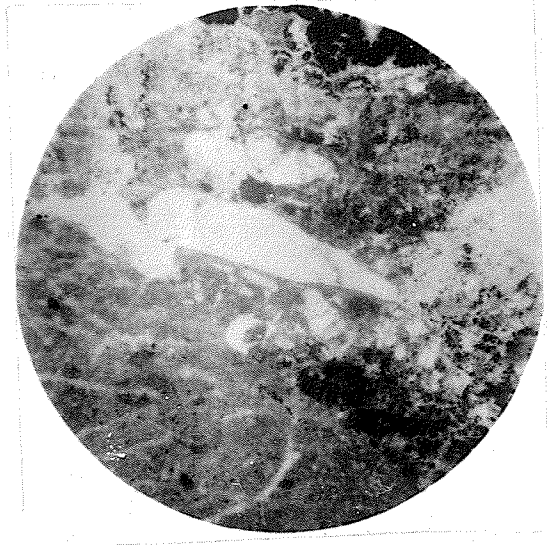


Fig. 5. +nicols.
Calcite and pisolitic hematite
showing shrinkage crack between
the iron and calcite. The cal-
cite is later than the iron ore.



Fig. 6. x-nicols.
Black Island Breccia. The fine lines
probably are organic casts. The
white crystals are quartz. The black
material is pisolitic hematite.

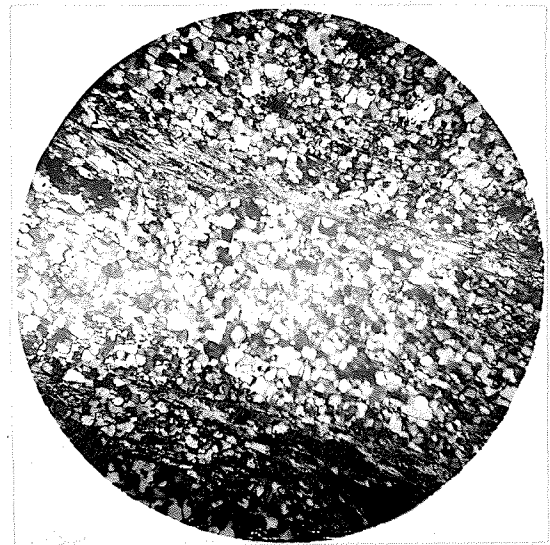


Fig. 7. x-nicols.
Black Island Sericite Schist.
Consisting of ninety percent
quartz, and ten percent seri-
cite. The rock, as such, is
sedimentary in origin.

CHEMISTRY.Chamosite ore of Schmiedefeld (Beck and Weed). (Ref.7).

SiO ₂	18.65%	(Calculated theoretical composition of Chamosite).
Al ₂ O ₃	8.48	
Fe ₂ O ₃	3.73	SiO ₂ 39.00%
FeO.....	45.13	Al ₂ O ₃ 13.00
MgO.....	1.68	Fe ₂ O ₃ 6.00
CaO.....	0.84	FeO..... 42.00
P ₂ O ₅	0.44	H ₂ O..... <u>10.00</u>
CO ₂	13.00	100.00%
SiO ₂	1.63	
H ₂ O.....	<u>6.44</u>	
	100.00%	

Glauconite taken from the expedition of HMS. Challenger. (Beck and Weed).Ref.7.

SiO ₂	56.62	50.85	51.80	55.17	27.74
Al ₂ O ₃	12.54	8.92	8.67	8.12	13.02
Fe ₂ O ₃	15.63	24.40	24.21	21.59	39.93
FeO	1.16	1.66	1.54	1.55	1.76
MnO	trace	trace	trace	trace	trace
CaO	1.69	1.26	1.27	1.34	1.19
MgO	2.49	3.15	3.04	2.84	4.62
K ₂ O	2.52	4.21	3.85	3.38	0.95
Na ₂ O	0.90	0.25	0.25	0.27	0.62
H ₂ O	<u>6.04</u>	<u>5.55</u>	<u>5.68</u>	<u>5.76</u>	<u>10.85</u>
Total	100.41	100.25	100.32	100.39	100.68

Chamosite from Newfoundland. (Ref. 8).

SiO ₂	21.68	25.50
Al ₂ O ₃	21.05	25.56
TiO ₂		
Fe ₂ O ₃	11.05	6.50
FeO.....	30.17	32.62
CaO.....	1.41	0.00
MgO.....	2.95	3.16
MnO.....	0.00	0.31
Na ₂ O.....	0.39	0.00
K ₂ O.....	0.22	0.00
H ₂ O.....	<u>11.13</u>	<u>10.55</u>
Totals.....	100.01	99.80

Grossenite Lake Superior. (Ref. 9).

	<u>sol.</u>	<u>insol.</u>	<u>sol.</u>	<u>insol.</u>	<u>sol.</u>	<u>insol.</u>
SiO ₂	13.45	48.45	19.30	36.56	23.11	13.61
Al ₂ O ₃	0.37		0.61		0.56	
Fe ₂ O ₃	15.00	0.64	13.81	0.76	6.44	2.60
FeO.....	10.26		17.57		30.93	
MgO.....	2.33		3.22		5.35	
CaO.....	0.28					
Na ₂ O.....						
K ₂ O.....						
H ₂ O ⁻	2.50		2.58		1.34	
H ₂ O.....	4.17		5.74		6.13	
TiO ₂						
CO ₂	2.04					
P ₂ O ₅						

Range in composition of Glauconite. (Ref.10).

SiO ₂	40.00%	to	53.61%
Al ₂ O ₃	6.62	to	13.00
Fe ₂ O ₃	15.16	to	25.43
FeO.....	1.32	to	10.17
MgO.....	6.95	to	2.97
CaO.....	0.57	to	1.97
Na ₂ O.....	0.42	to	2.16
K ₂ O.....	3.49	to	9.54
H ₂ O.....	4.93	to	10.32

Range in composition of Greenalite.

SiO ₂	46.12%	to	61.90%
Al ₂ O ₃	0.57	to	1.09
Fe ₂ O ₃	5.01	to	15.00
FeO.....	16.28	to	30.93
MgO.....	2.53	to	5.35
CaO.....	0.05	to	0.28
H ₂ O ⁻	0.75	to	2.50
H ₂ O.....	4.17	to	6.41

Thuringite. (Ref.11).

SiO ₂	23.60%
Al ₂ O ₃	17.29
Fe ₂ O ₃	13.50
FeO.....	36.30
H ₂ O.....	10.20

Theoretical formula deduced:-



The analyses given in the foregoing pages show how materials vary from the analyses of marine clay from Black Island as given below.

Marine Clay. from Black Island.

SiO ₂	35.50%	29.49%
Al ₂ O ₃	18.13	18.26
Fe ₂ O ₃	7.84	8.06
FeO.....	12.64	12.67
MgO.....	14.40	17.19
CaO.....	0.00	0.00
K ₂ O.....	0.50	0.50
Na ₂ O.....	0.50	0.70
H ₂ O.....	<u>10.79</u>	<u>12.90</u>
Totals...	100.01	99.77

There has been quite a number of names, applied to substances which apparently are similar to Chamosite and Greenalite. These are as follows; Berthierine, Hoferite, Plinthite, Hisingerite, Melanosiderite, and Montronite. No authentic analyses of these materials are available. Berthierine, Thuringite and Chamosite are probably produced by precipitation of iron in an aluminic-silicate gel. Hoferite, Plinthite and Hisingerite are probably of colloidal origin, and may indeed be mixtures rather than definite compounds. Melanosiderite is regarded by Weinschenk as the ferric analogue of kaolinite, but this view has been criticized by Bergsät (Ref.12). There can be no doubt in the mind of geologists, that there is still a good deal of work to be done on the amorphous iron minerals, despite the concentrated effort of the Lake Superior geologists. The work of Winchell, Leith, Van Hise, Wolff, Grout, Broderick and Gruner has gone a long way toward the true interpretation of the Mesabi and associated ranges. Still one cannot feel that they have yet given the final solution in the matter of the origin of these and similar ores. Just as there are two great divisions of rocks

so there has been put forward two main theories of origin for the Lake Superior iron ore, Igneous and Sedimentary theories. None of the above men have adhered strictly to the Igneous theory, but Van Hise and Leith appeal to both sources and apply them in turn to the areas which, in their estimation, are most justifiable. Winchell, Wolff, Grout, Broderick and Gruner are believers in the Sedimentary theory but diverge somewhat in minor detail. These last three men constitute a younger school of geologists who have been responsible for reviving the whole question of iron ore deposition. The period following the famous work by Van Hise and Leith has been singularly lacking in constructive hypotheses. Advances in colloidal chemistry, however, have made it possible to make valuable additions to the work primarily inaugurated by these well-known Lake Superior geologists.

While working on the problem of the Black Island marine clay there stood out clearly a marked analogy between these deposits and those of Lake Superior. A tentative arrangement is given for the origin of each type, and their compositions compared.

1. The Marine Clays of Black Island.

From the analyses we know that the rock is composed of iron, silicon, aluminum and magnesium. The iron, silicon and aluminum present are not unusual, but the magnesium requires some special explanation for its presence in such large quantity. Three possibilities suggest themselves to account for this abnormal percentage of magnesium. (a) Secretion of magnesium by algae, from oceanic water, and subsequent decay of the algae, thus concentrating their magnesia content in silts on the ocean floor. (b) Magnesium salts contained in the ocean were the chief precipitants of the iron, aluminum and silica from streams carrying these materials. Magnesium was adsorbed by aluminum hydroxide, ferric hydroxide and silicic acid following their precipitation. (c) The amount of magnesium in Archeozoic seas appears to have been much greater than the magnesium percentage in the seas of today. This fact would support the second hypothesis.

Magnesium is carried by rivers in solution, hence it cannot be inferred that the magnesium can be explained through any colloidal theory of origin. A salt such as magnesium sulphate is then considered to have been the chief electrolyte in precipitating iron, aluminum and silica. Silica is carried as negatively charged sol in slightly alkaline solutions. It is also found in neutral solution, but the size of the particle thus carried is as yet undetermined. Such an alkaline solution of silica would be precipitated by a moderate amount of magnesium. Alumina is also a negatively charged sol. Both alumina and silicic acid are peptized by sodium hydroxide, but a greater amount of alkali is required to peptize alumina. Ferric hydroxide is a positively charged sol and, as such, is not soluble in alkaline solution. It is apparent then that a solution carrying silicic acid and alumina as hydrosol, can only transport iron as hydrogel or as suspensoid. Iron may be transported in this way in addition to transportation in the ferrous condition through the medium of underground streams. Ferrous iron is believed to have developed by precipitation of ferric iron in an environment deficient in oxygen. These above introductory facts are incorporated in the theory of origin now following.

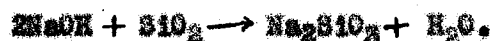
Silicic acid and alumina were carried as hydrosol. Iron carried in the same solution would necessarily be transported as suspensoid or hydrogel. Magnesium salts contained in sea waters were the chief electrolytes which converted the silica and alumina into colloidal gels. Ferric hydroxide was mechanically carried down by the precipitated silica and alumina. Magnesium salts were absorbed in the gel-like mass and carried down to the floor of the ocean constituting a part of the marine clay formation. The exclusion of oxygen reduced the ferric iron to ferrous giving the clay its characteristic greenish color. Algae may have functioned at this time, extracting magnesium from the clay which was later concentrated in specific areas by organic decay. The latter clay, at this period in its life history, consisted of ferrous hydroxide, silicic acid, aluminum hydroxide and adsorbed magnesium salts. Later events saw a withdrawal of seas brought about

by igneous action and tended by exposure of the clays originally laid down in the sea. The ferrous iron was again converted to ferric iron. Aluminum hydroxide silicic acid were dehydrated. The rock consists then of the oxides of ferrous and ferric iron, magnesium, aluminum and silica. From the nature of a deposit of this kind the possibility that of any definite chemical compounds being present is considerably minimized. Crystalline Chamosite and Greenalite from Newfoundland and Lake Superior, although definite compounds, need not have been due to original crystallization. It is possible that such represent an attempt on the part of colloidal precipitates to crystallize. The colloidal state is an unstable condition in nature, a fact, which lends favor to the idea that crystallization of colloidal materials will in all cases be a possibility. Crystallization of colloidal precipitates is a link in the chain to complete the cycle of erosion in nature, an attempt, as it were, to reconstruct the material of the original source from which it was obtained.

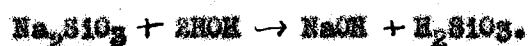
2. The Greenalite of Lake Superior.

Leith and Van Hise, in their work on the origin of Greenalite, used alkaline silica solutions in a number of experiments. The constitution of these solutions has not been satisfactorily proven. It therefore becomes essential in our work to take up this question of the constitution of Water-Glass.

Fundamentally the action of sodium hydroxide on silica has been regarded in chemical literature as a double decomposition proceeding as follows:



Sodium silicate will also undergo hydrolysis in the following manner:



A third fact of introductory importance is the peptizing influence of sodium hydroxide on silicic acid.

Analyses of water-glass solutions are generally given in terms of the oxides of sodium and silica, i.e. $\text{Na}_2\text{O} \cdot x\text{SiO}_2$. The value of x shows all manner of variation

making it quite impossible to call water-glass, sodium silicate. To substantiate this view point the following actual experiments are reproduced.

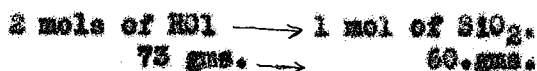
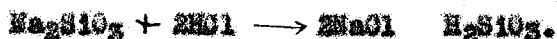
Experiment 1.

A known quantity of HCl was added to ordinary water-glass solution, just sufficient being added to bring about the coagulation of H_2SiO_3 gel. This gel in all cases came down immediately upon the neutralization of the solution. The silicic acid was dehydrated on the waterbath, precipitate was filtered and washed free from chlorides. It was then weighed as SiO_2 .

Practical Data obtained.

10 c.c. of Na_2SiO_3 solution of approximate 8% strength were used.
 5.8 c.c. of HCl were required to coagulate H_2SiO_3 .
 1 c.c. of HCl contains .0305 gms. of HCl.
 5.8 c.c. of HCl contain .17690 gms. of HCl.
 Amount of silica obtained by weight was found to be .6254 gms.
 Therefore .17690 gms of HCl precipitate .6254 of SiO_2 .

Theoretical Data.



Therefore .17690 gms of HCl should precipitate, $\frac{60 \times .17690}{73}$ (SiO₂).
 .1317 gms. of

It can be seen at a glance that, .1317 gms of SiO_2 , the theoretical value is much less than .6254 gms., the amount actually obtained. In a similar experiment .1341 gms. are contrasted with .6644 gms.

Experiment 2.

In this experiment the Na and SiO_2 relationships of the Water-glass solution used above were obtained by analysis.

Practical Data obtained.

5 c.c. of Na_2SiO_3 were taken.
 5 c.c. of HCl were added.
 The amount of NaCl obtained was found to be .2324 gms.
 " " " SiO_2 " " " " " .3538 "
 The calculated amount of Na is .0913 gms.

Theoretical Data.

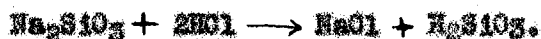
From atomic considerations the ratio of Na to SiO_2 should be 46:60. 46 parts by weight of Na are equivalent to 60 parts by weight of SiO_2 . .0913 gms. of Na, the amount obtained in the experiment, should be combined, then, with ~~.1212~~ ^{.1191} gms. of SiO_2 . Here then .1191 gms. of SiO_2 , the theoretical amount, is contrasted with .3526 gms., the practical amount of SiO_2 in solution, as shown by analysis.

The results of these experiments show that the amount of silica in water-glass is considerable in excess of the amount necessary to satisfy the formula Na_2SiO_3 . The excess silica, or indeed the total silica content, may either be molecularly or colloiddally dispersed. In order to determine this point experiments on ultrafiltration were carried out. It was ascertained that no silica passed through the membrane. Sodium hydroxide did pass through and this was occasioned by a conversion of silica solution to silicic acid gel. By loss of sodium hydroxide its peptizing influence is removed and silicic acid automatically thrown down without the use of any electrolyte whatsoever. The evidence given by this fact is all in favor of colloiddal silica, but is not altogether conclusive. In summarizing it may be stated that, (1) The relative amounts of Na and SiO_2 are not comparable to the formula Na_2SiO_3 . (2) There is always more silica than would theoretically be required from the above formula. (3) Most of the silica of the alkaline solution appears to be carried colloiddally.

Reactions with Water-Glass Solution.

(a) Addition of HCl.

The action has generally been conceded to proceed as follows:

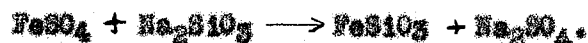


From our work on water-glass solution a slight modification of the above reaction is suggested. Hydrochloric acid when added to the water-glass solution acts upon its alkaline content and in this way produces water. The OH^- ions are

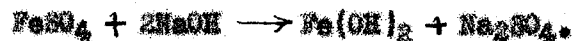
thus removed from the silicic acid which is attended by precipitation.

(b) Addition of FeSO_4 .

As in the case above the action has been thought to be as follows:



FeSO_4 , however, reacts with the alkali of the water-glass solution as follows.



The precipitate is dark green in color and mixed with a variable quantity of silica. This silica which has been precipitated, very probably, owes its origin to removal of OH^- ions which have a stronger tendency towards molecular union with iron than a colloidal union with silicic acid. The products obtained would be ~~likely~~ likely to point toward a definite compound such as FeSiO_3 . In no case, however, were we able to isolate such a substance.

(c) Addition of other salts to water-glass solution.

MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaCl_2 or any other ionizable salt that will combine with OH^- ions will cause a precipitation of H_2SiO_3 . Substances that react to form insoluble hydroxides will produce a mixture of hydroxides and silicic acid. Substances that react to form soluble salts with NaOH will give only a precipitate of H_2SiO_3 .

Greenalite.

Greenalite was first described by the Lake Superior geologists and regarded by them as the source of the hematite deposits. It is argued to have been produced by the action of ferrous salts on water-glass solution and to correspond to the formula, Fe SiO_3 . The variability of analyses of Greenalite given elsewhere in this paper is not in agreement with such a definite formula as FeSiO_3 . It is also apparent that the existence of FeSiO_3 by inorganic preparation is open to question. Where Greenalite crystals are found their composition is, of course, definite. This, rather, indicates a secondary union of a mass essentially consisting of oxides of iron and silica. The application of X-ray photography to such substances as Greenalite will, no doubt, shed much valuable light on the

true relationships of the iron and silica.

Chamosite.

Comparison of the analyses of Chamosite and the Marine Clay of Black Island shows, without doubt, that these two materials are not the same. Chamosite, it will be remembered, is the chief silicate found in the Wabana ore of Newfoundland and the Minette ore of Luxembourg. The material is found crystallized and amorphous in the Wabana beds. Hayes (Ref.13) states, "It seems probable that the crystalline material is the mineral and the amorphous material may not have a constant composition, but may vary within certain limits." His article on the subject also contains this significant statement, "The Chamosite of the spherules must have been in a gelatinous condition, and this may have been the original condition out of which the crystalline Chamosite developed."

Thuringite.

Thuringite from the Minette ores also appears to have peculiarities common to Chamosite and Greenalite. The composition of the gelatinous mass would in all cases determine the type of mineral developed. In cases where a material has not crystallized, it may be suggested that the amorphous mass is a mixture of oxides produced by dehydration of hydroxide gels. It would appear to be a fact that crystals of these substances are unusual features, which fact, would indicate that gelatinous mixtures of iron, aluminum, silicon, etc. are crystallized with difficulty.

SECONDARY ALTERATION.

Alteration of the marine clay on Black Island has been the cause of such attempts as have been made to determine the commercial possibility of Black Island ore. Secondary changes have removed all but isolated nodules of marine clay and chert. Aluminum and magnesium now present are found in such nodules. The remarkable feature about the secondary alteration has been the development of stalactites and pisolites of ferric oxide. Iron has been dissolved from the marine clay by acidic solutions and reprecipitated by alkalis. The acid waters

were likely produced by oxidation of pyrite contained in the quartz stringers from the granite. The iron would then have been carried in solution as sulphate. The downward percolating solutions precipitated their salt content, no doubt in part owing to evaporation, oxidation and action of alkaline waters. The combined effect of these three processes converted the iron into the hydroxide precipitating it as ferric hydroxide gel. We have here then a case of formation of dispersed systems by condensation. This has been covered in detail by Von Veimarn (Ref.14). He has elaborated the following formula, where

$$a = \frac{N_D}{S_P} \cdot n$$

S_p is the solubility in equivalents per litre of the precipitated substance. N_p is the number of equivalents of the precipitate which must be deposited out of each litre of the solution in order that its concentration shall be reduced to S_p equivalents per litre. n is the viscosity of the solution. a is the dispersion coefficient. $\frac{N_D}{S_P}$ is called the degree of supersaturation. Von Veimarn demonstrated the general validity of the law. He condensed $Ba(CNS_2)_2$ and $MnSO_4$. Varying the concentration from $\frac{N}{20,000}$ to 7N. the Barium sulphate molecules precipitated showed all variation of state from crystal nuclei, small individual crystals, colloidal suspensions or hydrosol, needles, skeletons and star-shaped masses, granules, curdy, flaky and gelatinous precipitates, lastly a gel. Veimarn's work may be applied to the precipitation of ferrous sulphate hydroxide by addition of caustic soda to ferrous sulphate. The solubility of ferric hydroxide is exceedingly small; hence the value of the degree of supersaturation will be correspondingly very great. As seen, as this value becomes increasingly great the precipitate obtained approaches a gel. Von Veimarn, then, has successfully shown that precipitation of iron salts as hydroxides invariably produces a colloidal gel. Provided that precipitation takes place within a confined area, such that the precipitated gel will not be rapidly dispersed, the conditions are proper for development of botryoidal, stalactitic and piscolitic structures. Such forms are characteristically the result of colloidal precipitation. The

ferric hydroxide or ferrous hydroxide, as precipitated in the Black Island occurrence, was composed chiefly of iron with a small percentage of silica. The following variation in composition of Black Island pisolites are quoted:

Fe ₂ O ₃	97.78%	to	98.30%
SiO ₂	1.22	to	6.12
H ₂ O.....	1.00	to	3.58

The analyses for silica gave fairly safe criteria in showing that a certain amount of silica was carried in the same solution with the iron. The silica was precipitated as silicic acid simultaneously with the precipitation of ferric hydroxide. No indication of hydrated compounds could be found to account for the water content of the pisolites. It was attempted to plot a curve, as previously obtained by Fosnjak and Merwin (Ref.15), but the water actually held could not be driven off below 200°C. Higher temperatures could not be attained in our electric thermostat. Occasionally structures, such as are a dominant feature in the Chamosite oolites of Newfoundland, are to be recognized in the Black Island pisolites. In referring to the Chamosite hematite oolites of Newfoundland the following hypothesis in connection with origin is put forward. Hematite oolites may be produced by chemical alteration of originally deposited materials essentially colloidal. Colloidal precipitation of alumina, silicic acid and ferrous hydroxide gives an amorphous mass which may undergo oxidation to produce ferric hydroxide. Dehydration of the hydroxides will subsequently produce the respective oxides. Colloidal material deposited as marine clay, consisting of materials essential to the so called formula assigned to Chamosite, would theoretically undergo the following changes on exposure to weathering. The changes would be dependent on whether the solutions were acidic or basic. If the solutions are basic the principal material to be removed will be silicic acid. Alumina requires a greater concentration of alkali than could be assumed in nature. It is therefore conceded that kaolin will be concentrated in situ along with hematite. If the solution be acidic the components of Chamosite will

all be taken into solution. Aluminum and iron, molecularly dispersed and silicic acid as colloiddally dispersed positive sol. Acid produced by the oxidation of pyrite will carry iron and alumina as sulphates, and silica as peptized silicic acid. Any solution which gives an alkaline reaction will, on meeting a downward percolating acidic solution, produce precipitation of the hydroxides of alumina & ferrous iron along with silicic acid. Surface tension effects produce, more or less, globular shapes which are the beginnings of future colites. Precipitation of ferrous hydroxide in oxidising environment will produce ferric hydroxide, thus forming a surface coating or film around the ferrous hydroxide. This protects the interior of the colite from further oxidation. Such colites having Chamosite nucleii possibly were produced in some such manner. Intermittent supply of material would, in time, produce a structure essentially composed of alternations of iron in ferrous and ferric condition. Local fluctuations in the elemental nature of downward percolating solutions may, in addition, produce a period of deposition of almost pure ferrous hydroxide. In this case the oxidized surface layer would be pure hematite with no admixture of alumina and silica.

RECAPITULATION

A.

The geological history of Eastern Manitoba and its relationship to the deposition of Black Island hematite is as follows:

(a) Original deposition of sediments throughout large areas of Manitoba. The clays of Black Island may be a part of this original series.

(b) Volcanic activity, producing tectonic movements on a vast scale.

(c) Erosion interval with deposition of sediment, now represented by inter-banded chert formations.

(d) Granitic intrusion producing brecciation of Black Island sediments and secondary infiltration of quartz-bearing pyrite.

(e) Exposure of clay producing secondary decomposition processes with production of pisolites.

(f) Infiltration of calcium carbonate-bearing solutions and precipitation. Crystallization of precipitate with shrinkage.

(g) Deposition of Winnipeg sandstone derived by erosion of Pre-Cambrian and laid down as a shore deposit in the advancing Ordovician sea.

(h) Concurrent deposition of Trenton limestone.

(i) Area covered by Cretaceous sediments.

(j) Tertiary erosion of Cretaceous sediments.

(k) Glaciation and deposition of drift concurrent with the deposition of silts and clays of Lake Agassiz.

B.

The salient points arising from the application of colloidal chemistry to iron ore sedimentation are as follows:

(a) Analyses of the water-glass solution show that the relative amounts of the oxides of sodium and silicon are not comparable to the formula Na_2SiO_3 . Silica is always in excess of the amount theoretically required.

(b) No definite formula can be put forward to account satisfactorily for the excess silica in water-glass solution.

(c) The excess silica of the solution must either be present in molecular or colloidal form, or as mixtures of molecular solutions and colloidal dispersoids.

(d) In so far as can be ascertained most of the silica of the solution is carried colloiddally.

(e) It is suggested that silicic acid is carried in rivers and streams as colloid when such are either acidic or basic.

(f) The chemistry of reactions between water-glass and soluble salts is explained in a different way from what has previously been accepted.

C.

The role of colloids in the production of pisolites and oolites.

1. Black Island pisolites have been derived in the following manner:

(a) Marine clay was altered by acidic solutions derived by oxidation of pyrite. Silicon and iron were dissolved.

(b) The silicon and iron were precipitated by alkalies which neutralised the acid solution.

(c) The precipitate obtained was a gel which assumed pisolitic and stalactitic form due to surface tension.

2. Newfoundland oolites may have been the result of the following processes:

(a) Sedimentary beds were leached of their iron and silica content as above.

(b) Surface oxidation of the iron contained in the precipitate produced Fe^{+++} iron which protected the Fe^{++} interior of the oolite.

(c) Intermittent supply of material produced alternate bands of Fe^{++} and Fe^{+++} .

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