GEOCHEMICAL INVESTIGATIONS OF LACUSTRINE FERROMANGANESE CONCRETIONS

GEOCHEMICAL INVESTIGATIONS
OF
FERROMANGANESE CONCRETIONS
FROM
THREE CANADIAN LAKES

by

ARTHUR GEORGE TROUP, B.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
February 1969

MASTER OF SCIENCE (1969)
(Geology)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: Geochemical Investigations of Ferromanganese Concretions from Three Canadian Lakes

AUTHOR: Arthur George Troup, B.Sc.
(McMaster University)

SUPERVISORS: Dr. R. C. Harriss
Dr. J. R. Kramer

NUMBER OF PAGES: vi, 82

SCOPE AND CONTENTS:

Observations on the geological environment of formation and data concerning the mineralogy, petrography and chemistry of lacustrine ferromanganese concretions are presented. Implications of these data with respect to concretion formation are discussed, and a model for concretion genesis is suggested.

ABSTRACT

Ferromanganese concretions from Grand Lake and Ship Harbour Lake in Nova Scotia and Mosque Lake in Ontario were examined.

Concretions were found in water greater than two feet in depth, in areas immediately adjacent to deep portions of holomictic lakes, and were always associated with a thin layer of fresh-water algal growth occurring immediately above the sediment-water interface. Concretions develop around a nucleus and are discoidal in appearance. X-ray diffraction studies show the ferromanganese portions of the concretions to be amorphous. Petrographic and electron probe studies of the ferromanganese portions of the concretions reveal chemical banding with an inverse variation in Fe and Mn concentrations across the banding. Bulk chemical analyses indicate that the Fe/Mn ratios of concretions from a given collection site are similar, whereas Fe/Mn ratios of concretions collected from similar depths in different lakes are different. Trace element abundances are variable between concretions collected from different lakes, but all trace element analyses are two to three orders of magnitude less than those of oceanic nodules.

It is suggested that the supply of iron and manganese for concretion formation is provided by diffusion of iron and manganese ions into an oxidizing epilimnion from an anaerobic hypolimnion during the summer stratification and fall turnover periods.

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. R. C. Harriss for suggesting and supervising this problem.

Thanks are extended to Dr. J. R. Kramer who had the difficult task of assuming responsibility for a partially-completed thesis, to Dr. R. H. McNutt for advice and assistance with analytical techniques, and to Dr. H. P. Schwarcz for advice and stimulating discussion. The help of the following technicians and students is appreciated: J. Grootenboer and L. Falkiner in preparation of polished sections; H. Walker with the electron probe; F. Tebay in the x-ray diffraction work; J. Whorwood with the photographic work; P. J. Lee with statistical computations; M. V. White and J. D. Macdougall during field work and G. Langille with the biological literature. Special thanks are extended to Miss D. K. Church for constructively criticizing the manuscript.

The research was supported in part by a research grant from the Geological Survey of Canada.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

List of Tables

List of Plates

List of Figures

List of Maps

CHAPTER I

GEOCHEMICAL INVESTIGATION OF LACUSTRINE FERROMANGANESE CONCRETIONS

INTRODUCTION:

This thesis presents the results of a detailed field and laboratory study on freshwater ferromanganese concretions from several lakes in eastern Canada. Although extensive investigations have been conducted on oceanic ferromanganese concretions, literature on lacustrine concretions is scarce. Possibly the earliest paper reporting lacustrine concretions is by Honeyman (1881) who discusses "lacustrine hematite concretions" collected from Grand Lake, Nova Scotia. In more recent studies, Kindle (1932, 1935, 1936), Ljunggren (1953, 1955a, 1955b), Gorham and Swaine (1963) and Manheim (1965) have considered physical characteristics, mineralogy and chemistry of freshwater ferromanganese precipitates from various localities. The results of these investigations may be summarized as follows:

(1) The physical features of freshwater ferromanganese precipitates are highly variable, ranging from

---

Throughout the remainder of this report the term concretion will be used in referring to the ferromanganese oxide covering plus the enclosed nucleus, while the term ferromanganese precipitate will be used in referring only to the ferromanganese oxide portions of the concretions.

thin crusts described by Gorham and Swaine (1963) in the English Lake District and by Ljunggren (1953) in northern Sweden to nodular and disk-shaped concretions studied by Kindle (1935) in Nova Scotia lakes.

(2) Ljunggren (1955) was the only investigator to consider the mineralogy of freshwater ferromanganese precipitates in detail. X-ray diffraction analyses of various Swedish lake and stream concretions suggested the presence of the minerals goethite, δ-MnO_2, and manganous manganite.

(3) Chemical analyses have been reported for ferromanganese concretions from a wide variety of geological and hydrological environments. The most noteworthy characteristic of published analyses is the large variation in the iron and manganese concentrations. Price (1967), in a review of the chemistry of natural ferromanganese precipitates, states that "in lacustrine nodules iron takes preference over manganese". The work of Kindle (1935, 1936) and the present study show that this is not true for concretions from Nova Scotia lakes.

(4) Lacustrine ferromanganese concretions have a widespread distribution. They have been observed in small lakes in Nova Scotia, Ontario, Sweden, Northern England, New York, New Hampshire, Vermont and Michigan and in three of the Great Lakes - Lake Michigan, Lake Ontario and

Lake Erie. To date there have been no reports of ferromanganese concretion occurrences in freshwater lakes in subtropical or tropical regions.

The present study was designed to obtain detailed information on the geological environment, mineralogy, petrographic characteristics and chemistry of ferromanganese concretions from Grand Lake and Ship Harbour Lake, Nova Scotia and Mosque Lake, Ontario.

CHAPTER II

PHYSICAL AND GEOLOGICAL ENVIRONMENT OF THE CONCRETION COLLECTION LOCALITIES

Concretions were collected from Grand Lake (Lake Shubenicadie) and Ship Harbour Lake (Lake Charlotte) in Nova Scotia and Mosque Lake in Ontario. Details regarding the location and physical features of these lakes are outlined in Table 1. Descriptions of the concretion sites are given in Table 2.

Grand Lake:

Grand Lake is situated in the N.N.E. striking Shubenicadie valley. The major surface input enters at the extreme southern end of the lake and the Shubenicadie River drains the lake from the east side, two miles south of the concretion collection sites. A terminal moraine surrounds most of the north quarter of the lake, which overlies shales and sandstones of Carboniferous age. The southern three quarters of the lake overlies Cambrian shales and sandstones.

Concretions were found at four locations (map 1) in the part of the lake overlying Carboniferous sediments.

TABLE 1

General Features of Lakes

Lake	Location	Length	Width Av.	Inlet	Outlet
Grand Lake	20 miles due north of Halifax, N.S.	9 miles	1 mile	8 miles south of concretion location	2 miles south of concretion location
Ship Harbour Lake	32 miles N 70° E of Halifax, N.S.	12 miles	1 mile	12 miles N.W. of concretion location	1¼ miles N.E. of concretion location
Mosque Lake	60 miles N.N.W. of Kingston, Ont.	1½ miles	3/4 miles	nil.	3/4 miles south of concretion site.

TABLE 2

General Features of Concretion Sites

Lake	No. of Sites	Under-lying Bedrock	Bottom Sediment	Collection Depth	Benthonic Vegetation		Location of ferromanganese ppt.
					Type	Thickness of zone of occurrence	
Grand Lake	4	Carboniferous shales and sandstones	Coarse-grained sand	2-6 feet	Algae Aquatic Grass	5 cm.	2.5 cm. zone above substrate
Ship Harbour Lake	1	Cambrian shales and sandstones	Coarse-grained sand	2-5 feet	Algae Aquatic Grass	5 cm.	3 cm. zone above substrate
Mosque Lake	1	Grenville gneisses	Coarse-grained sand	2-6 feet	Algae	0.5 cm.	at sediment-water interface

Aerial photographs of the area reveal a strongly-developed lineation, possibly bedding, striking 160° in the sediments. A line striking 160° can be drawn through the four concretion sites, introducing the possibility that structural controls such as underlying manganiferous sediments may be partially influencing concretion formation. However, no such sediments have been reported in this area.

The northern part of the lake is relatively shallow, averaging less than 15 feet in depth (Kindle, 1935). However, a relatively deep channel (greater than 35 feet in depth) extends into this end of the lake, passing between collection sites one and four and continuing as far north as site three.

In all locations investigated, ferromanganese concretions occur where bottom sediment consists of coarse sand with pebbles and cobbles suitable for nuclei. The ferromanganese oxide portion of concretions always occurs in the first 2.5 cm. of water above the sediment-water interface. Concretions are very abundant at depths of 2½ to 4½ feet where in some areas they cover up to 10% of the bottom. In shallower water only a ferromanganese stain occurs on rocks and pebbles and in water deeper than five feet concretions are less abundant, possibly because at greater depths there are far fewer pebbles large enough to serve as nuclei.

In all four concretion locations living organic matter, essentially aquatic grasses and fresh water algae, is abundant in a 5 cm. zone immediately above the sediment-water interface. Fresh water algae cover as much as 10% of the exposed concretion surfaces; however, algal growth is also present on pebbles and rocks having no ferromanganese precipitate.

Ship Harbour Lake:

Ship Harbour Lake overlies Cambrian sandstones and shales, and rhodochrosite-bearing slate bands with associated magnetite bodies are known in the area. A 300-foot-wide manganiferous band, striking 75°, is located 2,000 feet south of the concretion collection site, and two small streamlets draining this area empty into the lake just a few hundred feet from the site.

Concretions were collected from only one location in a small, shallow island bay, in the southern end of the lake (map 2). Concretions are reported to be abundant in other portions of the lake (Beals, 1967; J. Kidson, personal communication, 1967), but a thorough search for these occurrences was not conducted.

Concretions are found resting on a coarse sandy substrate having many small pebbles suitable for nuclei. Concretions are abundant between the depths of 2½ to 3½ feet, and in one area at a depth of five feet a ferromanganese pavement, 2.5 to 5.0 cm. thick covers the bottom sand around the edges of a large boulder. As in Grand Lake, living organic matter, essentially short aquatic grasses and fresh water algae, is abundant in a 5 cm. zone immediately above the sediment-water interface.

Mosque Lake:

Mosque Lake is a small lake overlying Grenville province biotitic gneisses. It is fed from local bogs and ponds and is drained by a small un-named stream which exits from the south shore.

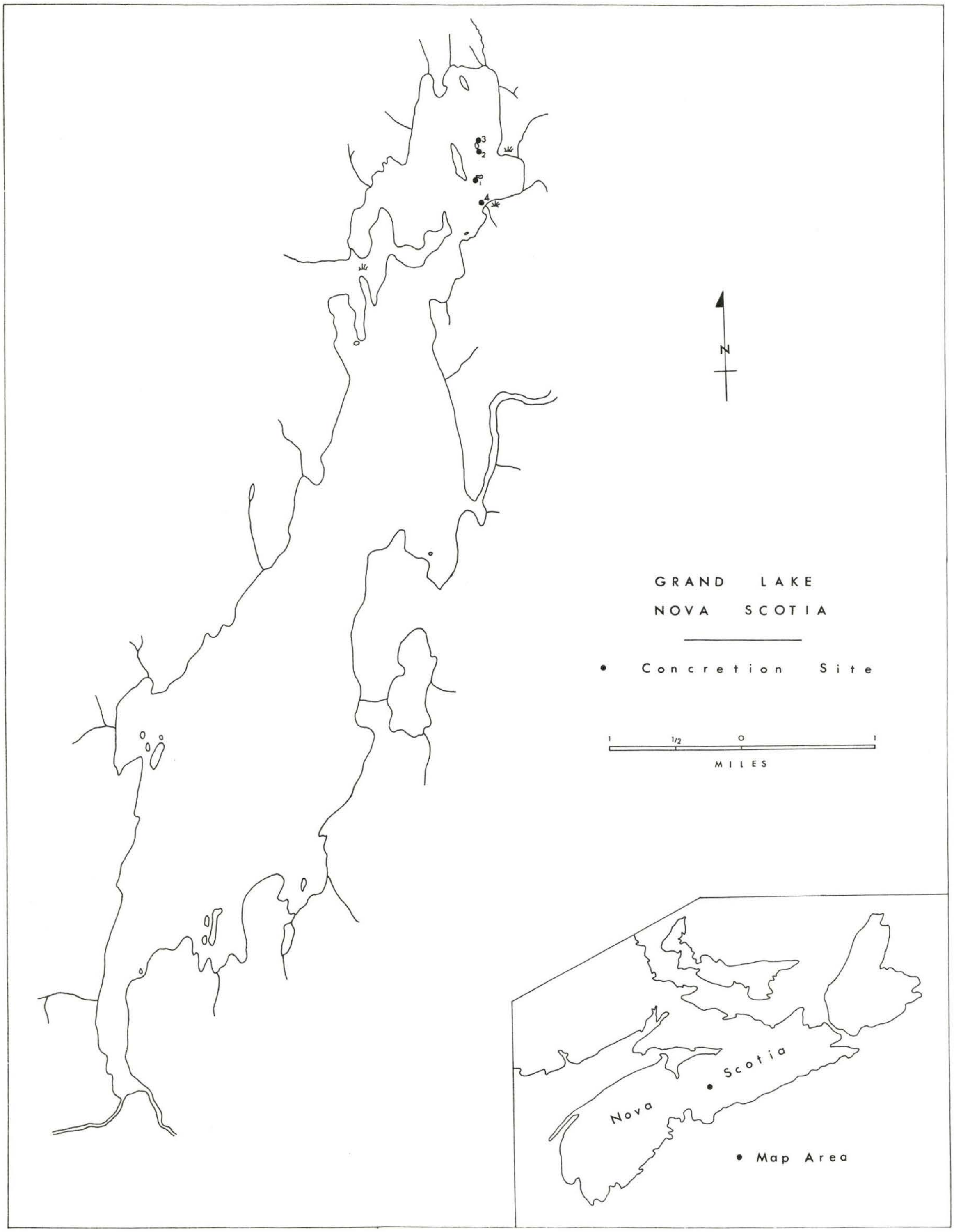
Concretions were found in only one location in a small bay on the north shore of the lake (map 3). A small bog is located onshore immediately adjacent to the concretion site; however, no open channelway exists between the bog and the lake. A deep channel which is 40 feet deep less than 150' south of the concretion collection site, extends into this section of the lake. Concretions were collected from between depths of two to six feet but continued to occur in deeper water.

The ferromanganese precipitate occurs where bottom sediment consists of coarse sand. Between 35 and 45 feet offshore, in two to four feet of water, the precipitate forms small disk-shaped concretions around pebbles of between 1.5 and 4 cm. in width, while larger pebbles and cobbles have only a ferromanganese stain at the interface. Further offshore in deeper water, a narrow ferromanganese oxide rim occurs around pebbles and cobbles immediately above the sediment-water interface. When the lake was visited on October 7, 1967, all shallow water concretions were covered with approximately 1.5 cm. of loose sand. However, when the lake was revisited on June 28, 1968, these concretions were covered with less than 0.5 cm. of loose sand and many were exposed at the interface.

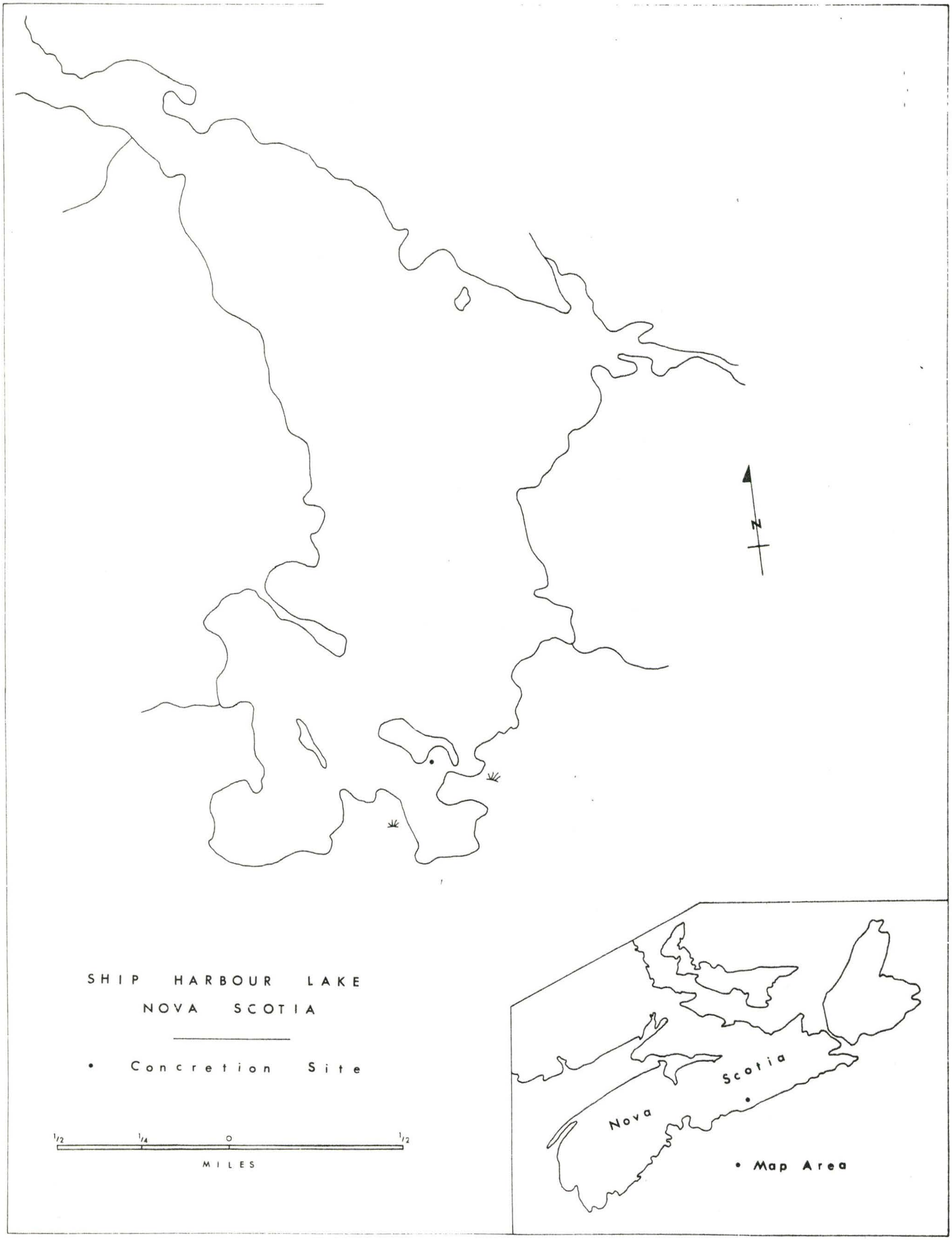
Plant life was not abundant in the site when the lake was visited in October. However, during the spring investigation in late June, a thin zone (less than 0.5 cm. in thickness) of algal growth was found on the surface of rocks, pebbles and concretions in the collection area.

The purpose of the visit on June 28, 1968, immediately after five consecutive days of rainfall, was to investigate the possibility of underwater springs entering the lake in the concretion locality. Temperature profiles were taken at a number of locations in the lake including the concretion site. This investigation showed the lake to be stratified. The water temperature at a distance of 300 feet from shore was constant at $64^{\circ}F$ above a depth of 18 feet, between the depths of 18 feet and 22 feet the temperature dropped to $42^{\circ}F$, and between 22 feet and 105 feet

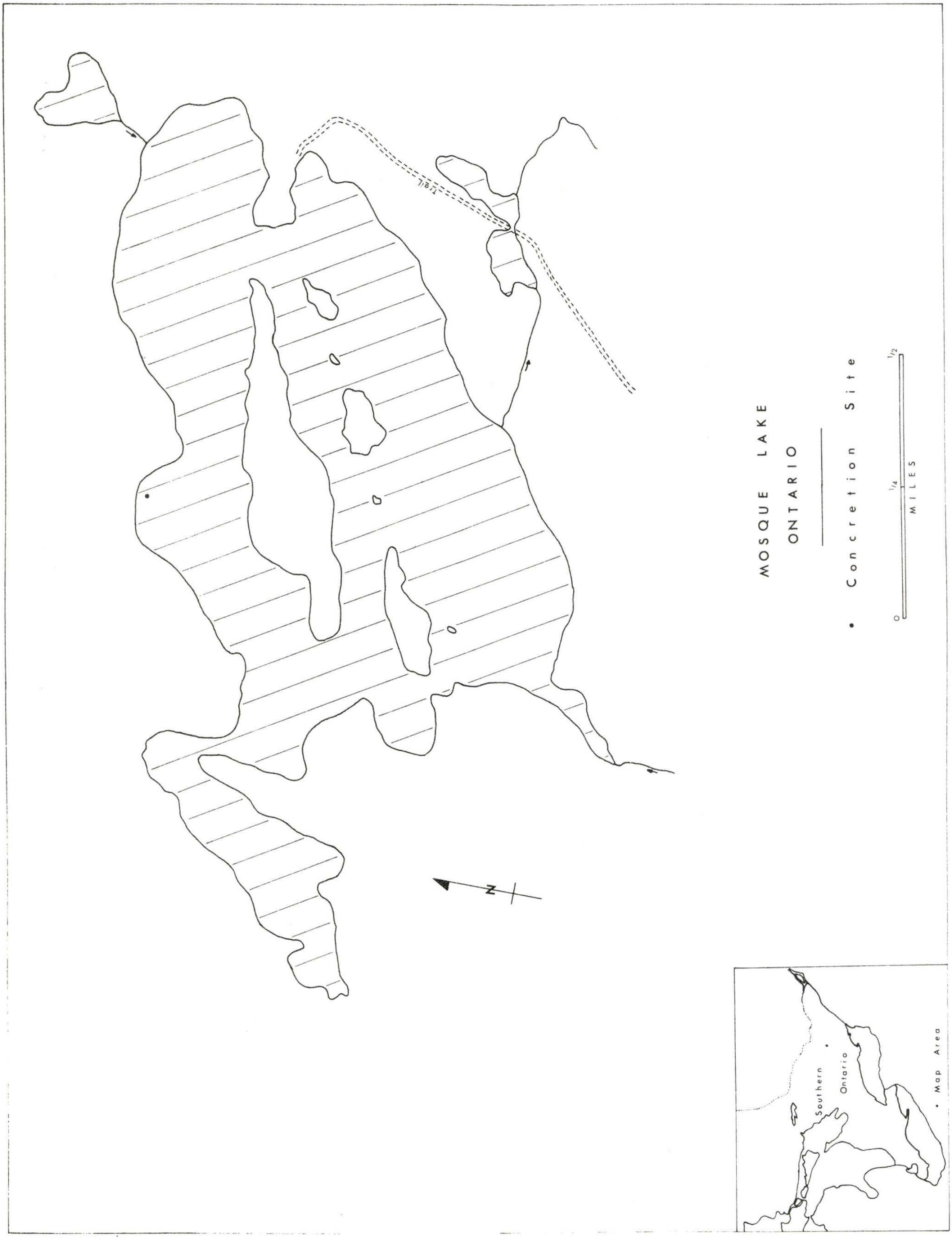
MAP 1


3
2
1
4
N
GRAND LAKE
NOVA SCOTIA
• Concretion Site
1
1/2
0
1
MILES
Nova Scotia
• Map Area

MAP 2


N
SHIP HARBOUR LAKE
NOVA SCOTIA
• Concretion Site
1/2
1/4
0
1/2
MILES
Nova
Scotia
• Map Area

MAP 3


MOSQUE LAKE
ONTARIO
• Concretion Site
0
1/4
1/2
MILES
Trail
N
Southern
Ontario
• Map Area

(the deepest point at which a reading was taken) the temperature slowly dropped to 40.5°F. Within the concretion site the water temperature was constant at 64°F, thus giving no indication of an influx of ground water.

Unfortunately, no springs were located from which ground water temperatures could be determined. However, it has been shown that at this time of the year ground water entering lakes is at a lower temperature than the epilimnon of the lake (Ruttner, 1963; Wasmund, 1927, 1928; Elster, 1939).

Conclusions:

The foregoing observations show that the ferromanganese oxide portion of lacustrine concretions occurs only in a narrow zone, usually immediately above, but occasionally just below the sediment-water interface. The thickness of this zone varies from 0.5 to 3.0 cm. between lakes, and corresponds very closely with the thickness of a zone of abundant benthonic vegetation covering the bottom sediments.

In all concretion sites visited the substrate within the site consisted of a coarse-grained sand; in no cases were concretions found occurring above a clay substrate. It may be that pebbles large enough to serve as nuclei are associated only with the coarse-grained fraction of the sediment, however, further investigation of this phenomenon is required.

In both Grand Lake and Mosque Lake concretions occur at depths of greater than two feet, in areas immediately adjacent to deep portions of the lake in which a hypolimnion would be developed during summer stratification. This introduces the possibility that proximity to deep water may be an important factor in concretion development. In Ship Harbour Lake concretions occur in a partially enclosed bay, far from deep portions of the lake. However, Kindle (1932) suggests that this occurrence results from concentration of ions through evaporation of the water within the shallow constricted bay.

Thermal investigations of Mosque Lake reveal no indication of the existence of underwater springs entering the lake in the vicinity of the concretion site. Since the investigations were carried out at a time when such springs should have been most active, the possibility that concretions here result from a discharge of manganese and iron-rich ground water into the more oxidizing lake water is apparently negated.

CHAPTER III

PHYSICAL CHARACTERISTICS OF THE CONCRETIONS

Grand Lake:

All Grand Lake concretions have a pebble or cobble nucleus which may consist of a slate, sandstone or granite fragment. No preference with regard to rock type is observed, however, rock fragments of less than 2.0 cm. in diameter do not have a ferromanganese oxide crust, and pebbles of less than 4.0 cm. in diameter seldom have more than a ferromanganese stain.

Some Grand Lake concretions are illustrated in Plate I. The ferromanganese oxide rim forms around a nucleus in a plane parallel to the bottom sediments. The rim commences at the sediment-water interface, but attains its maximum width (up to 3.0 cm.) approximately 1.2 cm. above the interface. The thickness of the oxide rims is always less than 2.5 cm. Occasionally on smaller nuclei the oxide covering extends over the entire upper surface

---

For the sake of clarity, concretion width will be defined as the maximum distance between the outermost edge of the nucleus and the outermost edge of the ferromanganese oxide rim, measured in a plane parallel to the sediment-water interface. Thickness will be defined as the maximum distance between the lowermost surface of the ferromanganese oxide crust and the uppermost surface of this crust, measured in a plane perpendicular to the sediment-water interface.

of the pebble, however, this portion of the crust is seldom more than 0.2 cm. in thickness. The upper surfaces of large nuclei, beyond a distance of 2.5 cm. above the sediment-water interface, may be entirely free of any oxide covering, and at most have only a ferromanganese stain.

The majority of the nuclei in Grand Lake consist of slate fragments several centimeters across but only 0.5 to 1.5 cm. thick. About such rock fragments the ferromanganese oxide crust has grown concavely outwards and upwards above the level of the nucleus, giving the concretion a saucer-like appearance. However, some concretions exhibit a downward growth and others are observed resting on edge, suggesting disturbance possibly by wave action during violent storms.

The ferromanganese oxide portion of the concretions is usually dull black in colour but occasionally a thin, dark red-brown film, often displaying a metallic luster, covers part or all of the surface. While broken concretion surfaces are always black, narrow concentric bands displaying a metallic luster are often seen within the concretions.

Ship Harbour Lake:

The Ship Harbour Lake concretions (Plate I) are similar in colour and texture to the Grand Lake concretions, but do not exhibit the saucer-like shape. On many of the concretions the ferromanganese oxide completely encloses the pebble nucleus giving the concretion a nodular or lenticular appearance.

Nodular and lenticular-shaped concretions forming about a fragment of another concretion are also found at this site. The nodules are invariably less than 3.0 cm. in diameter, while lenticular concretions without a pebble nucleus are found up to 7.5 cm. in diameter, but seldom are greater than 1.5 cm. in thickness. The maximum diameter is invariably attained 0.5 cm. above the interface, suggesting growth occurs most rapidly at or only slightly above the interface.

Oxide rims occurring about pebbles and cobbles are between 0.5 and 3.0 cm. in thickness and up to 4.0 cm. in width. The maximum thickness occurs at the sediment-water interface giving the concretions a dome-like appearance which somewhat resembles the cap of a mushroom. In this respect these concretions are quite distinct from those at Grand Lake, and this may indicate a somewhat different mode of precipitation.

Mosque Lake:

Mosque Lake concretions consist of a ferromanganese

TABLE 3

General Characteristics of Concretions

Lake	Nucleus		Oxide Rim				
	Minimum size	Rock type	Shape	Maximum width	Maximum thickness	Dist. above interface of max. thickness	Colour
Grand Lake	3.5 cm.	Slate Sandstone Granite	Concave up	3.0 cm.	2.5 cm.	12 - 15 mm.	Black
Ship Harbour Lake	2.0 cm.	Sandstone Granite	Convex up	3.5 cm.	2.5 cm.	5 mm.	Black
Mosque Lake	2.0 cm.	Sandstone Granite	Planar	2.0 cm.	0.5 cm.		Red-Brown

PLATE I

Ferromanganese concretions. Samples 1 and 2 are nodules from Ship Harbour Lake, Samples 3 and 4 are upper and lower surfaces respectively of typical Ship Harbour Lake concretions. Specimen 5 displays the upper surface of an unusual form of Grand Lake precipitate. Samples 6 and 7 exhibit upper and lower surfaces respectively of typical Grand Lake concretions. Specimen 7 is unusual in having an oxide crust over the entire lower surface, most do not. Samples 8 and 9 represent typical upper and lower surfaces of Mosque Lake concretions. Samples are pictured two thirds their actual size.

PLATE I


5


6


7


3


9


8


4


2


1

oxide rim 0.2 to 0.5 cm. in thickness and up to 0.5 cm. in width about a pebble or cobble nucleus. Nuclei consist of granitic and sandstone pebbles greater than 2.0 cm. in diameter. Generally both the upper and lower surfaces of the nuclei are free of oxide crust or stain.

In a few cases cobbles are found exhibiting several oxide rims oriented at slightly different angles, suggesting the body has been disturbed at various times in its history as a nucleus for concretion development. In such cases oxide rims oriented at an oblique angle to the present position of the sediment-water interface do not extend below the oxide rim presently situated at the interface. Also, when oblique rims extend to distances of 1 cm. or more above the interface they are broken and discontinuous indicating that they are being removed by abrasive forces.

Mosque Lake concretions are dark red-brown in colour. The upper and lower surfaces often display a metallic luster but the outer edge is always dull in appearance, possibly due to the removal of the lustrous surface by the abrasive action of bottom sand on the exposed outer edge.

Conclusions:

The foregoing observations show that there exists a minimum size for pebbles which may act as nuclei for concretion development. This minimum size varies with the concretion site and possibly is a function of the degree of agitation in the particular site. Small pebbles will be constantly disturbed by wave and current action so that any ferromanganese oxide covering will quickly be brought into contact with the reducing substrate where it will be dissolved.

It is seen that concretion width is very often greater than concretion thickness suggesting that concretion growth occurs most rapidly in a plane parallel to the sediment-water interface. The distance above the interface at which the maximum width is attained is a function of the individual concretion site; however, maximum width always occurs within the zone of abundant benthonic vegetation and may be controlled by a pH gradient existing between the surface of the substrate where decay of dead organic matter is occurring and the uppermost region of living plant material where photosynthesis is most active.

In Mosque Lake pebbles occasionally display several oxide bands indicating periodic disturbance of the nucleus, possibly by violent storm turbulence. In such cases rims oriented obliquely to the interface are discontinuous below the interface where conditions are sufficiently reducing to dissolve the ferromanganese oxides. Where the bands are tilted up some distance above the interface, they are being removed by abrasion. This indicates that active precipitation of the ferromanganese oxide occurs only in a narrow zone in close proximity to the sediment-water interface.

CHAPTER IV

INTERNAL STRUCTURE OF THE CONCRETIONS

Grand Lake:

Polished cross section of concretion samples from Grand Lake were prepared and were studied by reflected light methods using a Zeiss Ultraphot II microscope. Magnifications of up to 1500X were used in studying the samples; however, magnifications of 80X to 200X were found to be most satisfactory. At higher magnification a sharply focused image could not be obtained due to relief resulting from the porous nature of the ferromanganese precipitate. Additional information on polished section preparation is given in the appendix.

Under inclined white light concretions are found to consist of alternating concentric black and red oxide bands. Subsequent electron probe studies indicate these correspond to manganese and iron-rich bands respectively. Under direct monochromatic light the iron-rich oxide bands appear white in colour while the manganese-rich oxide appears grey (Plate II). Although many bands are continuous about the concretion rim, many are discontinuous and irregular indicating that they have been broken during

PLATE II

Photomicrograph of a cross section of a concretion sample from Grand Lake, Nova Scotia. White bands having high relief are Fe-rich and grey bands are Mn-rich. The area shown is 625 x 500 microns.

precipitation. The distance between the centres of any two adjacent similar bands and between centres of subsequent similar bands is extremely variable, ranging from 0.05 mm. to 0.25 mm.

Dark field illumination was also used in studying the polished concretion sections. In this process the specimen is illuminated by inclined light such that smooth, flat surfaces reflect light out of the field of view and appear dark while irregular surfaces which tend to scatter light appear light. The observations indicate that the manganese-rich oxide portions of the concretions have a much higher porosity than the iron-rich oxide bands.

Ship Harbour Lake:

Polished sections of Ship Harbour Lake concretions could not be made due to polishing problems arising from enclosed sand grains. However, in broken cross section the concretions appear very similar to Grand Lake concretions, with the exception that they are more porous. Also, in Ship Harbour Lake concretions but not in Grand Lake concretions, large quantities of diatom tests are contained within the ferromanganese oxide. In many samples certain layers are so enriched in diatom tests that they appear in hand specimen as concentric white bands, which are conformable with the concentric oxide banding of the

PLATE III

Cross section of a Ship Harbour Lake precipitate (black), developed about a siltstone nucleus (grey). Note diatom rich band (white) within the precipitate. Actual diameter of sample is 3.5 cm.

concretions (Plate III).

Mosque Lake:

Examination of broken cross sections of Mosque Lake concretions reveals each ferromanganese oxide rim to be composed of several individual oxide bands up to 2 mm. in thickness, which can be distinguished by colour differences. The manganese-rich oxide is homogenous in colour while the iron-rich oxide varies in colour from yellow to dark red-brown. The contact between the manganese-rich and iron-rich oxides is always sharp and often a metallic luster is displayed at the contact. Individual concretion rims seldom have more than three or four oxide bands but samples having up to five bands are known.

On one large cobble the remains of nine ferromanganese oxide rims were visible. These rims were sectioned and examined to determine the number of oxide bands in each. The results of this investigation are shown in Table 4. The rim occurring furthest from the sediment-water interface is the oldest and is designated rim 1. Rims occurring progressively closer to the interface are numbered successively. Seven of the nine rims are found to commence with red iron-rich oxide bands.

TABLE 4

Sequence of oxide bands within a number of rims developed about one nucleus in Mosque Lake.

Rim Number	Rim Width	Oxide Sequence from nucleus outwards
1	0.4 cm.	Red - Black
2	0.4 cm.	Red - Black - Red - Black
3	0.2 cm.	Red - Black
4	0.2 cm.	Red - Black
5	0.2 cm.	Red - Black
6	0.2 cm.	Black - Red - Black
7	0.2 cm.	Red - Black
8	0.2 cm.	Red - Black
9	0.6 cm.	Black - Red - Black - Red - Black

Conclusions:

The foregoing investigations show concretion rims to consist of alternating black manganese-rich and red iron-rich oxide bands. Dark field illumination studies show the manganese-rich oxide to have a much higher porosity than the iron-rich oxide. The oxide bands are broken and discontinuous possibly as a result of abrasive forces acting during precipitation.

Large quantities of diatom tests are observed in Ship Harbour Lake concretions. These were first reported by Kindle (1932, 1935) who was able to identify 52 different species within the concretions. Kindle (1932) suggested that diatoms might be responsible for precipitation of the ferromanganese oxide, but discarded this opinion (Kindle, 1935) when he found diatoms were present only in shallow water concretions.

Examination of a Mosque Lake cobble exhibiting nine ferromanganese oxide rims shows seven out of the nine rims to commence with an iron-rich oxide layer, indicating that disturbance of the cobble has occurred most often shortly before or during the period of deposition of the iron-rich oxide.

CHAPTER V

MINERALOGY

Techniques:

Polished sections of two concretions from Grand Lake sites 1 and 2 were examined by reflecting microscope methods, under magnifications of up to 1500X.

Eight powdered samples from the three lakes were placed in powder press mounts and examined by x-ray diffraction strip chart recording techniques. The samples were irradiated with both unfiltered and manganese filtered iron x-radiation using a 1^{o} divergence slit, a 0.003 inch receiving slit and a 1^{o} scatter slit.

Three powdered Ship Harbour Lake samples were examined by x-ray diffraction powder camera methods. The samples were irradiated with manganese filtered iron x-radiation and were exposed for periods of 23, 35 and 62 hours respectively. During all x-ray diffraction work settings of 30 Kv and 16.5 mA were maintained.

Results:

In samples examined optically, no crystalline structures were identified in the ferromanganese rims.

TABLE 5

"d" Spacings for Lines Obtained from Samples Examined by Powder Camera Methods

SAMPLE I 23 hr. Exp. d(A)	Suspected Mineral	SAMPLE II 35 hr. Exp. d(A)	Suspected Mineral	SAMPLE III 62 hr. Exp. d(A)	Suspected Mineral
		4.25	Q	4.25	Q
		4.13	?		
		4.03	?		
		3.68	O	3.68	O
		3.34	Q		
		3.19	O	3.19	O
		2.457	Q		
		2.283	Q		
		2.237	Q		
		2.229	Q		
		1.980	Q		
		1.816	Q		
		1.672	Q		
		1.542	Q		
		1.452	Q		
		1.384	Q		
		1.375	Q		
		1.289	Q		
		1.256	Q		
		1.230	Q		
		1.200	Q		
		1.827	Q		
		1.153	Q		
		1.0815	Q		
		1.0475	Q		
		1.0430	Q		
		1.0143	Q		
		1.0120	?O		
		0.9895	Q		
		0.9870	Q		
		0.9782	Q		
		0.9760	Q		

Q - alpha quartz line.

O - oligoclase line.

? - unknown.

TABLE 6

"d" Spacings for Various Manganese and Iron Minerals and Suspected Contaminant Minerals.

Todorokite d(A)	δ-MnO$_2$ d(A)	Ramsdellite d(A)	γ-MnO$_2$ d(A)	Goethite d(A)	Lepidocrocite d(A)	α-SiO$_2$ d(A)	Oligoclase d(A)
9.60	7.27	4.08	4.02	5.02	6.25	4.26	6.4
				4.20		3.343	4.5
7.17	3.60	3.10	2.53	3.36	3.29	2.458	4.07
				2.68		2.282	3.67
4.76	2.44	2.53	2.41	2.57	2.47	2.237	3.47
				2.47		2.128	3.18
4.42	1.412	2.43	2.10	2.43	2.36	1.980	2.90
				2.24		1.817	2.80
2.45		2.32	1.62	2.17	2.09	1.672	2.59
				2.09		1.659	2.52
2.39		2.13	1.38	2.00	1.932	1.541	2.43
				1.915		1.453	2.37
2.34		2.04		1.798	1.847	1.382	2.29
				1.715		1.375	2.10
2.22		1.88		1.685	1.732	1.372	2.07
				1.656		1.288	2.01
1.42		1.82		1.598	1.566	1.256	1.95
				1.559		1.228	1.87
1.39		1.64		1.503	1.522	1.1997	1.83
				1.448		1.1973	1.81
		1.60		1.388	1.452	1.1838	1.77
				1.357		1.1530	1.74
		1.53		1.315	1.433	1.0816	1.70
						1.0477	1.66
		1.46			1.369	1.0437	1.56
						1.0346	1.49
					1.218	1.0149	1.45
						0.9896	1.42
					1.190	0.9872	1.38
						0.9781	1.36
						0.9762	1.33
						0.9607	1.32
							1.17
							1.16
							1.13
							1.11
							1.06
							1.04
							1.03
							1.01
							0.987

In the strip chart recording traces, peaks were obtained from only two Ship Harbour Lake samples. In both instances the peaks were identified as alpha quartz peaks. (Quartz and minor feldspar grains are the main constituents of the underlying sand in Ship Harbour Lake.)

The powder camera mount exposed for only 23 hours was underexposed and no lines could be determined. The sample exposed for 35 hours gave a total of 32 lines. All but two of these were identified as alpha quartz and oligoclase feldspar lines (Table 5). The remaining two lines were not identified. The sample exposed for 62 hours gave three lines which were identified as alpha quartz and oligoclase feldspar lines.

Conclusions:

The above results indicate that most of the iron and manganese precipitate is in an x-ray amorphous state. Differential thermal analysis of Swedish concretions (Ljunggren, 1955b) has shown most of the iron and manganese to be in the form of hydrated amorphous oxides. This may be the case for the ferromanganese precipitates of the present study as well.

CHAPTER VI

CONCRETION CHEMISTRY

INTERNAL DISTRIBUTION OF ELEMENTS

An Ms-64 Acton electron probe (see Haughton, 1967, for details of the instrument) was employed to investigate the distribution and inter-relationship of various elements within individual concretions. Polished cross-sectional surfaces cut from concretions from Grand Lake sites 1 and 2 were studied. The technique described by Burns and Fuerstenau (1966) was followed closely during the study.

Probe Operating Conditions:

Throughout the analysis, the probe was operated at 26 kilovolts and 50 nanoamperes. The spectrometer was evacuated during use and secondary x-radiation was diffracted by means of a quartz $112\bar{0}$ crystal.

Analytical Techniques:

(a) Wavelength scanning between the angles of 120° and 200° was carried out at a number of locations on the specimens in order to determine which elements were present in detectable quantities.

(b) Electron beam scanning was carried out on various areas of the sample surfaces. This operation has been described by Burns and Fuerstenau (1966):

> "The electron beam focused to a diameter less than one micron, is swept in a regular manner across a square area of sample while a synchronous oscilloscope display indicates the two-dimensional intensity distribution of back scatter electrons or a selected characteristic x-radiation."

Photographs of the oscilloscope display were taken for back scatter electron, Mn $K\beta_1$, Fe $K\alpha_1$, $A\ell$ $K\alpha_1$, and Si $K\alpha_1$ x-radiation.

(c) X-ray intensity profiling for the elements Mn and Fe was carried out while the specimen was traversed under a stationary beam. A preliminary traverse across a nine-millimeter section of concretion was run at a relatively rapid traverse rate of 500 microns per minute. A second traverse was conducted at a rate of 10 microns per minute across a 300 micron section of concretion which had previously been investigated by electron beam scanning.

(d) X-ray intensity point counting was conducted over a 120 micron section of the second traverse route described in (c) above. Ten second counts of Mn $K\beta_1$ and Fe $K\alpha_1$ secondary x-radiation were carried out at five micron intervals along the traverse. Five countings were performed at each point and the average of these results was recorded.

(e) X-ray intensity point counting for Fe $K\alpha_1$ x-radiation was performed on a sample of pyrite in an attempt to quantify the iron results. Unfortunately, no suitable manganese standard was available.

Results:

In all wavelength scanning operatings only four peaks were detected. These corresponded to the Fe $K\alpha_1$, $K\alpha_2$ and $K\beta_1$ peaks and the Mn $K\beta_1$ peak. In spite of the relatively high Zn content indicated by bulk chemical analyses, (Table 8) the Zn, as well as traces of Cu, Pb, Ni, Co and Hg were below the limit of detectability.

Electron beam scanning photographs are shown in Figures I, II and III. Figures I and II display back scatter electron and Fe and Mn x-radiation photographs for representative 300 micron square areas of samples from Grand Lake sites 1 and 2 respectively. These samples have essentially the same characteristics. Figure III displays a 75 micron square area of a Grand Lake concretion in which $A\ell$ and Si as well as Mn and Fe x-radiation photographs have been taken.

Back scatter and x-ray photographs show manganese

FIGURE I

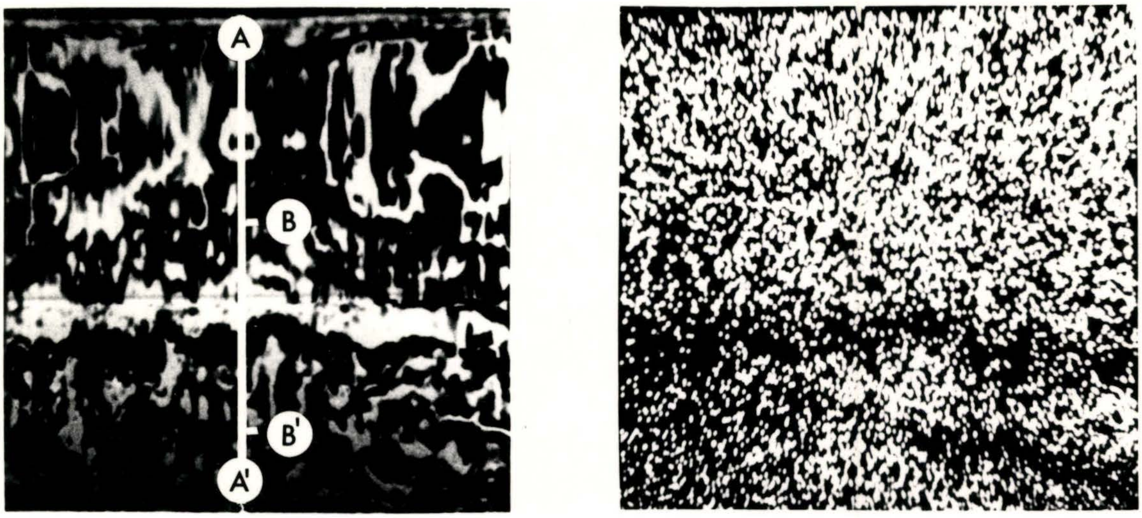
B. S. E.

Mn

Fe

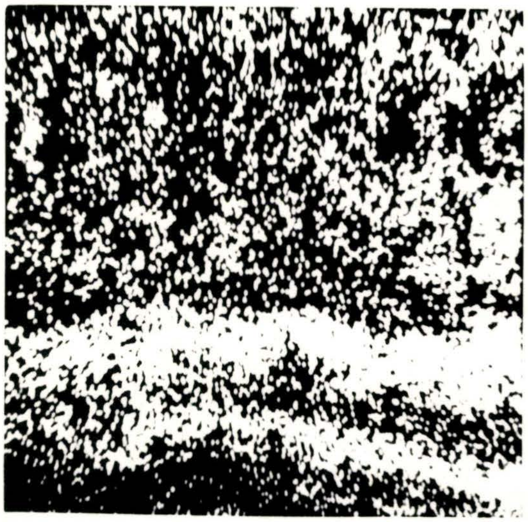
Electron beam scanning photographs of back-scattered electron (B.S.E.), Mn $K\beta_1$ radiation and Fe $K\alpha_1$ radiation from a 300 x 300 micron section of a concretion from Grand Lake site 1.

FIGURE II



B. S. E.

Mn

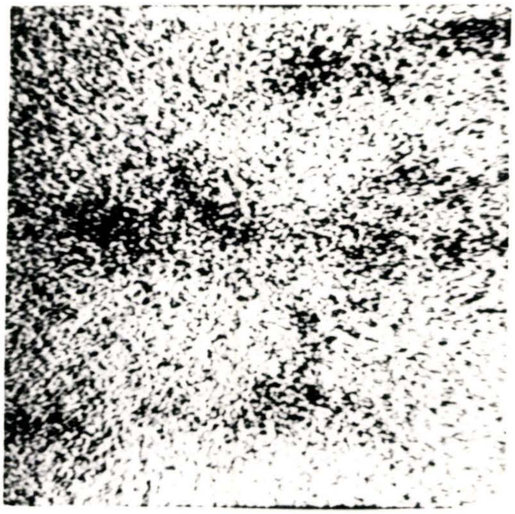


Fe

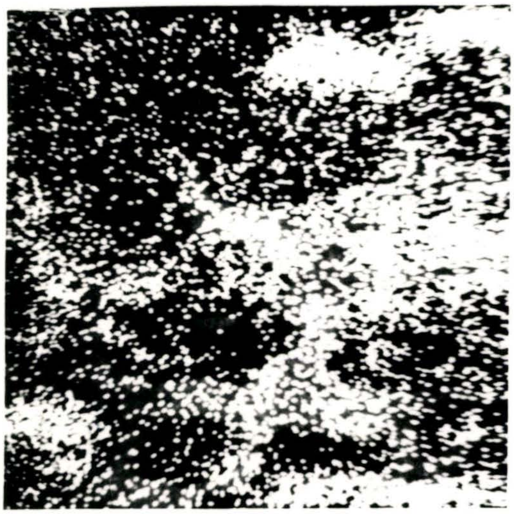
Electron beam scanning photograph of back-scattered electron, Mn $K\beta_1$, and Fe $K\alpha_1$ radiation from a 300 x 300 micron section of a concretion from Grand Lake, site 2. The x-ray intensity profiling path, A-A', and the x-ray intensity point counting path, B-B', are shown.

FIGURE III

B.S.E.

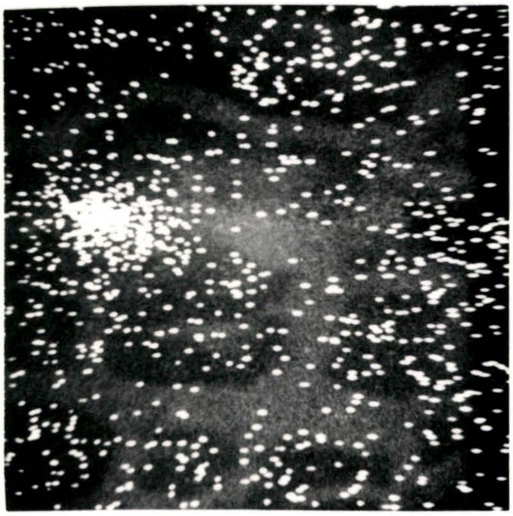


Mn



Fe

Al



Si

Electron beam scanning photographs of back-scattered electrons (B.S.E.) and selected characteristic K-Radiation from a 70 x 70 micron section of a concretion from Grand Lake, site 1.

concentrations to be inversely related to iron concentrations. Iron is concentrated in relatively narrow concentric bands which correspond to areas of high reflectivity in back scatter electron photographs. Both Aℓ and Si are somewhat irregularly distributed; however, both elements tend to show maximum concentrations in the Mn-rich portions of the sample. Whether or not this is significant is difficult to assess.

The preliminary x-ray intensity profiles for the elements Mn and Fe are shown in Figure IV. The concretion composition varies greatly; however, no periodicity is observed in the chemical variation. The detailed intensity profiles are shown in Figure V, for a traverse along the line A-A' across the area shown in the back scatter electron photograph of Figure II. The intensity profile results are in good agreement with the secondary x-radiation photographs shown in Figure II. Two very intense Fe peaks with corresponding low values in the Mn curve are found in the position of the two Fe rich bands shown in the photographs.

The x-ray intensity point counting traverse route B-B' is shown in Figure II. The results are given in Table 7 and in Figure VI these data are presented in the form of a plot of Fe intensity - vs - Mn intensity. Although there is considerable scatter (possibly due to variation

FIGURE IV

Intensity profiles obtained from a specimen traverse across a 9 mm. cross section of a concretion from Grand Lake, site 1.

FIGURE IV

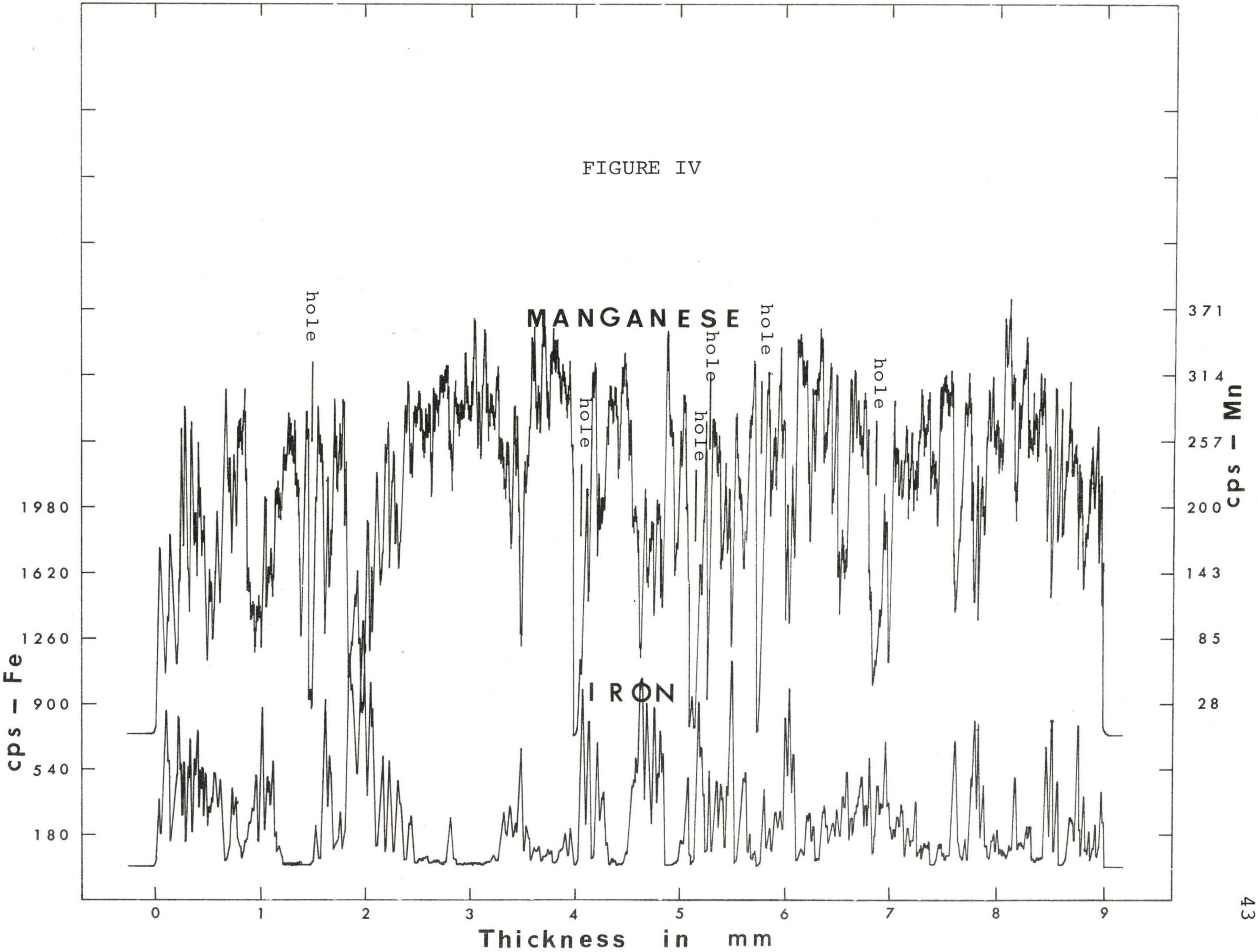

MANGANESE
IRON
hole
hole
hole
hole
hole
hole
cps – Fe
1980
1620
1260
900
540
180
cps – Mn
371
314
257
200
143
85
28
0
1
2
3
4
5
6
7
8
9
Thickness in mm

FIGURE V

Intensity profiles obtained from a specimen traverse across a 300 micron cross section of a concretion from Grand Lake, site 2. The traverse route, A-A', is shown in Figure II.

FIGURE V

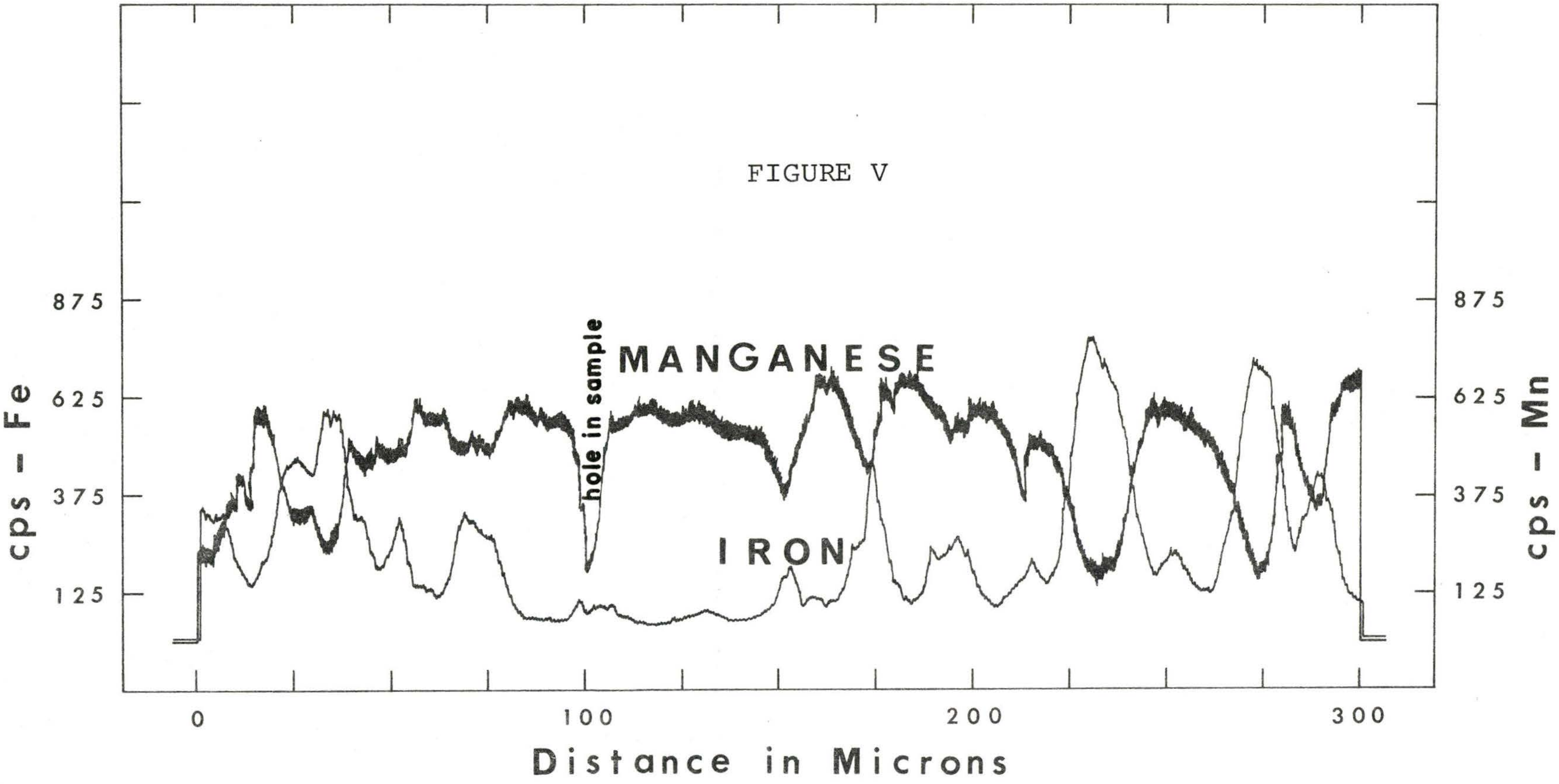
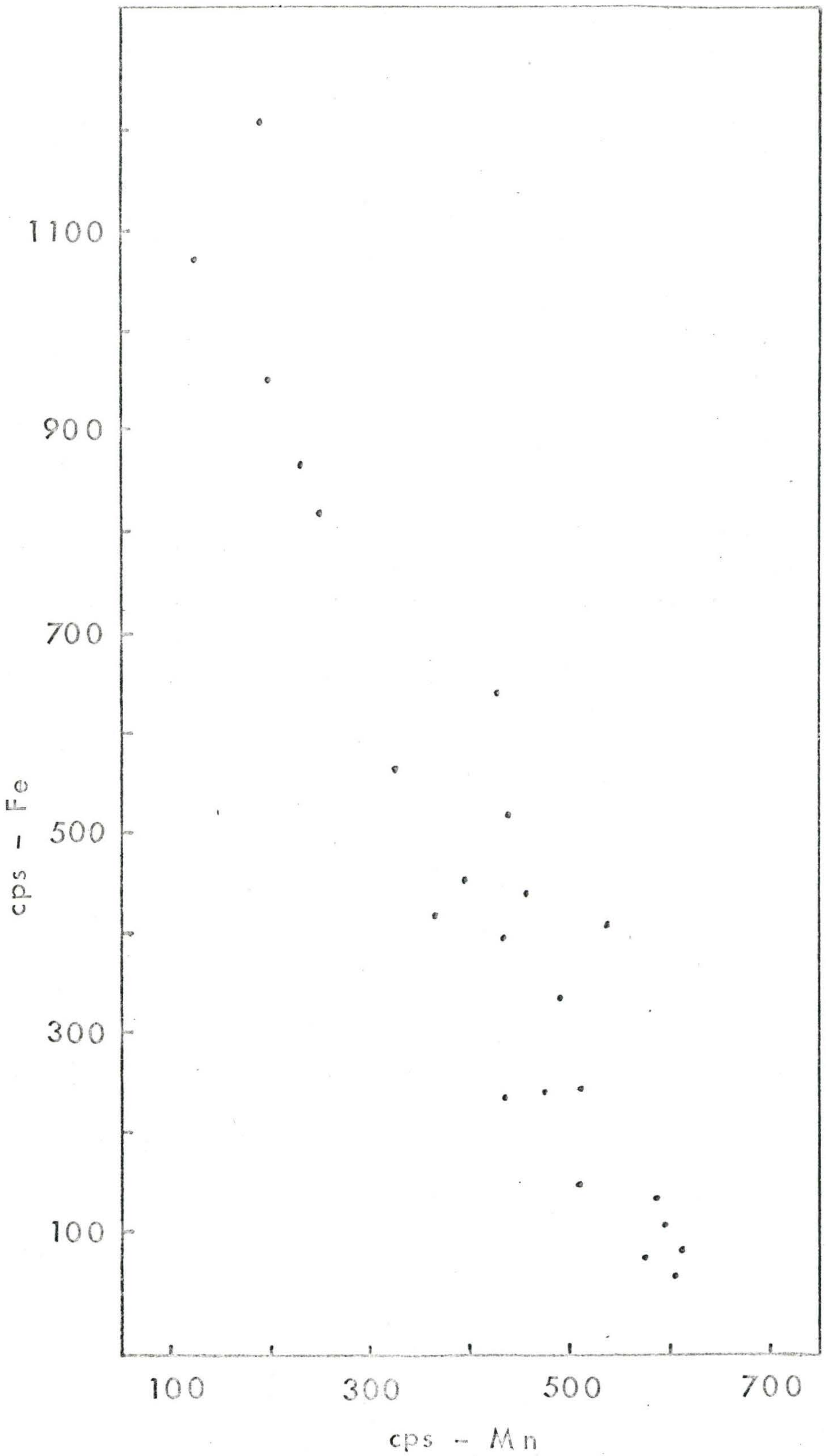

MANGANESE
IRON
hole in sample
cps - Fe
cps - Mn
875
625
375
125
0
100
200
300
Distance in Microns

TABLE 7

Results of an x-ray intensity point count traverse taken across a 110 micron cross section of a concretion from Grand Lake, site 2.

Position	Fe $K\alpha_1$ Count in 10 Sec.	Mn $K\beta_1$ Count in 10 Sec.
1-B	721	5735
2	541	6026
3	1345	5843
4	1070	5919
5	809	6101
6	4071	5358
7	6400	4237
8	5176	4349
9	4498	3895
10	2422	5078
11	4398	4529
12	1454	5087
13	3681	4300
14	2312	4350
15	4160	3643
16	8653	2317
17	12073	1879
18	9497	1993
19	8156	2496
20	3329	4850
21	2364	4749
22	5635	3256
23-B'	10676	1227

FIGURE VI



A plot of the x-ray intensity point count data of Table 7 showing the inverse relationship between manganese and iron.

in sample porosity) the inverse relationship between manganese and iron concentration is readily apparent.

All x-ray intensity countings were repeated five times and maximum variation in number of counts was found to be 8.8%, thus indicating an instrument error of less than 10%. A 22-fold variation exists between the lowest Fe intensity of 54 counts per second (c.p.s.) and the highest of 1,207 c.p.s. while only a five-fold variation exists between the lowest Mn intensity of 123 c.p.s. and the highest of 610 c.p.s. An Fe count of 1,219 c.p.s. was obtained from the pyrite standard.[1]

BULK CHEMICAL ANALYSIS

Partial chemical analysis was carried out on a number of concretion samples for the major elements Fe and Mn, and the minor elements Co, Ni, Cu, Zn, Hg and Pb. A

---

[1] The pyrite standard is known to have a Fe content of very close to 46.6%. Since the maximum Fe count of the Fe-rich portion of the section of concretion examined is very close to that obtained for the standard, it is apparent that this particular band contains on the order of 45% Fe. The Fe-poor portion thus contains approximately 2% Fe. It has been assumed in this comparison that fluorescence, absorption, conductivity and background corrections are similar for the concretion sample and the standard. In actuality, the wide variation in Mn content and in porosity will cause significant but undeterminable variations in absorption, which in turn will significantly affect the apparent concentrations. However, the foregoing figures are of value in that they do give a rough idea of the variability of the Fe (and Mn) concentration.

complete chemical analysis was not attempted since concretions contain a large, variable percentage of enclosed sand grains (on the order of 20% by volume).

Analytical Techniques:

The major elements, Fe and Mn, were determined by x-ray fluorescence techniques (see Appendix for details). Trace elements were determined by Barringer Research Ltd. Standard atomic absorption techniques were employed for all trace elements other than Hg, for which a mercury vapor detector was used.

The final corrected chemical analyses for 11 individual and 6 composite samples of Canadian concretions and one English Lake District specimen are shown in Table 8. Concretion samples are numbered to indicate the lake, the site within that lake and the particular specimen analyzed; for example, number GL-1-W indicates specimen W, collected from site 1 in Grand Lake, Nova Scotia. Duplicate analyses were carried out on four samples in order to determine analytical precision. Duplicate analyses are indicated by the letter A or B following the initial sample number; for example, GL-1-YA is a duplicate analysis of sample GL-1-Y. Composite samples are indicated by the letter 'C' followed by the composite sample number and the number of

TABLE 8

Chemistry of concretions from Grand Lake, Nova Scotia.

Sample No.	Fe/Mn	% Fe	% Mn	Co ppm.	Ni ppm.	Cu ppm.	Zn ppm.	Hg ppm.	Pb ppm.
GL-1-W	0.433	15.5	35.9	220	338	13	1940	50	25
GL-1-X	0.599	20.9	34.9	202	243	12	1575	34	24
GL-1-XA	0.599	20.9	34.9	192	230	8	1500	37	28
GL-1-Y	0.552	18.6	33.7	192	215	10	1575	46	26
GL-1-YA	0.549	18.7	34.0	192	215	10	1575	46	26
GL-1-Z	0.577	19.3	33.4	192	215	10	1340	40	25
GL-1-C1 (10)	0.530	18.1	34.2	192	373	16	1850	64	26
GL-1-C2 (10)	0.549	17.8	32.4	202	272	16	1650	40	28
GL-2-Y	0.468	16.8	35.9						
GL-2-Z	0.434	14.6	33.6	212	373	14	1875	44	13
GL-2-C1 (9)	0.449	14.2	31.7	183	238	11	1575	34	28
GL-2-C1B (9)	0.449	14.2	31.7	192	238	10	1650	50	29
GL-4-Z	0.470	16.3	34.4						
GL-4-C1 (5)	0.457	14.7	32.2	202	316	13	1500	56	19

TABLE 8 (cont'd)

Chemistry of concretions from Ship Harbour Lake (SH), Nova Scotia; Mosque Lake (ML), Ontario; and one concretion #107785 from the English Lake District.

Sample No.	Fe/Mn	% Fe	% Mn	Co ppm.	Ni ppm.	Cu ppm.	Zn ppm.	Hg ppm.	Pb ppm.
SH-1-X	0.458	11.7	25.5	230	125	9	536	50	19
SH-1-Y	0.709	20.0	28.3	230	149	8	500	67	19
SH-1-Z	0.560	15.7	28.1	212	149	8	518	40	28
SH-1-ZA	0.560	15.7	28.1	220	149	8	536	14	10
SH-1-Cl (16)	0.636	16.9	26.5	220	107	6	467	21	28
ML-1-Z	2.52	39.8	15.7						
ML-1-Cl (16)	2.56	40.2	15.7	135	95	10	250	30	24
107785	0.824	20.1	13.5						

Sample #107785 donated by E. Gorham.

concretions composing the sample; for example, number GL-1-C1 (10) indicates composite sample no. 1 composed of 10 concretions from site 1 in Grand Lake, Nova Scotia.

Major Element Abundance:

The two elements Fe and Mn account for from 37.2 to 55.8 weight % of the concretions. If it is assumed that these elements occur as the oxides Fe_2O_3 and MnO_2, they may account for 57.1 to 85.1 weight % of the concretions. Physical examination of the concretions suggests that the variation in major element abundances is most probably due to differences in the amount of sand contaminant present. Thus, it is more meaningful to discuss the Fe/Mn ratio than the absolute weight per cent of these elements when comparing the chemistry of different concretions, since the Fe/Mn ratio will not be greatly altered by variations in the percentage of sand contaminant.

Iron/Manganese Ratio:

As shown in Table 8, the Fe/Mn ratio varies from 0.43 to 2.56 for samples from different Canadian lakes. Probe studies reveal that the Fe/Mn ratio within a single concretion may show even larger fluctuations from on the order of 0.04 to as high as 5. The plot in Figure V illustrates qualitatively the wide variations in the Fe/Mn ratio.

Chemical analyses of 41 concretions from Grand Lake (all sites) give an average Fe/Mn ratio of 0.502 while the Fe/Mn ratio for seven concretions analyzed individually fell within the range of 0.43 to 0.59. Nineteen Ship Harbour Lake concretions have an average Fe/Mn ratio of 0.626. Although only three concretions from this lake were analyzed individually, the Fe/Mn ratio of these was found to range from 0.45 to 0.71, a significantly greater range than displayed by Grand Lake concretions. Seventeen Mosque Lake concretions have an average Fe/Mn ratio of 2.56. Unfortunately only one concretion from this lake was large enough for individual analysis; however, this had an Fe/Mn ratio of 2.52 which is very close to the mean.

From the above analyses it is seen that there is a significant difference in the average Fe/Mn ratio of concretions from different lakes, suggesting that the bulk Fe/Mn ratio for samples within a particular lake is to a large extent determined by the water chemistry of the local watershed. However, the fluctuating Fe/Mn ratio within individual concretions and the relatively large variation in Fe/Mn ratio between concretions collected from an individual site, such as Ship Harbour Lake, suggest that other very localized phenomena may be affecting the Fe/Mn ratio of the ferromanganese precipitates.

Trace Element Abundances:

In this study the trace elements Co, Ni, Cu and Pb are an order of magnitude lower than the values reported for Pacific nodules (Table 9). Zinc is of the same order of magnitude as in Pacific nodules but varies by more than a factor of five between lakes. Nickel varies by a factor of four between lakes. This wide variation in Zn and Ni content suggests that these elements and possibly to a lesser extent other trace element concentrations may be controlled by the water chemistry of the local watershed.

Previous Analyses:

Several previous investigations of the chemistry of lacustrine ferromanganese precipitates have been conducted. Kindle (1933, 1935) reported chemical analyses of three samples collected from two Nova Scotia lakes and one New Hampshire lake; Ljunggren (1953, 1955b) analyzed 14 Swedish lakes and stream samples; Gorham and Swaine (1963) presented analyses of eight oxidate crusts from the English Lake District and Manheim (1965) reported the partial chemistry of several Swedish and Karalian-Finnish lake nodules. These analyses are presented in Table 9 along with the results of the present study and the average chemistry of Pacific nodules as reported by Menard (1964).

TABLE 9

Summary of data available on the chemistry of freshwater ferromanganese precipitates.

		% Fe	% Mn	Co ppm.	Ni ppm.	Cu ppm.	Zn ppm.	Hg ppm.	Pb ppm.
Grand Lake, N.S.	Max	20.9	35.9	212	373	16	1,944	64	29
Average 41 concretions	Min	14.2	31.7	183	215	10	1,340	34	13
Results this study	Av	16.6	33.0	196	296	14	1,665	47	26
Ship Harbour Lake, N.S.	Max	20.0	28.3	230	149	9	536	67	28
Average 19 concretions	Min	11.7	25.5	212	107	6	467	14	10
Results this study	Av	16.7	26.6	221	112	7	475	26	27
Mosque Lake, Ontario	Max								
Average 17 concretions	Min								
Results this study	Av	40.2	15.7	135	95	10	250	30	24
English Lake District Crusts	Max	22.1	13.2	60	40	20	2,000		
Gorham et. al., 1965	Min	11.1	8.0	20	10	tr	300		
	Av	15.2	11.1	40	20	10	1,100		
Nova Scotia Concretions	Max	15.6	22.8						
Kindle, 1933, 1935	Min	11.6	22.3						
	Av	13.6	22.5						
New Hampshire Concretion	Max								
Kindle, 1935	Min								
	Av	26.5	14.5						
Swedish Bog Ores	Max	66.0	37.0						
Ljunggren, 1955	Min	0	0						
	Av	32.5	17.0	230	40				
Swedish Bog Ores	Max								
Manheim, 1965	Min								
	Av	35.6	4.7	80	40	40	50	10	27
Karaluii-Finnish Lake Ores	Max								
Manheim, 1965	Min								
	Av	22.5	14.0	130	40				
Pacific Nodules Average	Max	26.6	77.0	23,000	20,000	16,000	800		3,600
Manard, 1964	Min	2.4	8.2	140	1,600	280	400		200
	Av	14.0	24.2	3,500	9,900	5,300	470		900

Examination of all data with regard to trace element concentrations reveals the following:

(1) The cobalt content of lacustrine concretions is an order of magnitude lower than that of Pacific nodules but varies by as much as a factor of five between lakes.

(2) The nickel content of lacustrine concretions is between one and two orders of magnitude lower than Pacific nodules but varies by up to an order of magnitude between lakes.

(3) The lacustrine concretion copper content is between two and three orders of magnitude lower than that of Pacific nodules and varies by a factor of five between lakes.

(4) The lacustrine concretion zinc content varies from an order of magnitude lower to an order of magnitude greater than that of Pacific nodules. Between lakes the zinc content shows variations of up to two orders of magnitude.

(5) The mercury content of lacustrine concretions varies by a factor of five between lakes.

(6) The lead content of lacustrine concretions is two orders of magnitude lower than Pacific nodules and varies by a factor of three between lakes.

Conclusions:

Electron probe examination of individual concretions reveals a chemical banding across which the Fe/Mn ratio varies greatly, indicating a cyclic mode of deposition of the ferromanganese precipitate.

Bulk chemical analyses show that there is a significant difference in the average Fe/Mn ratio between concretions from different lakes, suggesting that the bulk Fe/Mn ratio for samples within a particular lake is to a large extent determined by the water chemistry of the local watershed. However, the large variations in Fe/Mn ratio both within individual concretions between consecutive Fe-rich or manganese-rich bands and among concretions collected from an individual site, such as Ship Harbour Lake, suggest that other very localized phenomena such as depth of formation may be affecting the Fe/Mn ratio of the ferromanganese precipitates.

Trace element determinations, both in this study and in previous studies, show that all trace elements, with the exception of zinc, are between one and three orders of magnitude lower in lacustrine concretions than in Pacific nodules. Price (1967) has suggested that for marine nodules minor element abundance is a function of the rate of concretion growth. Thus the consistently low trace element content of lacustrine concretions suggests a more rapid growth rate than that of Pacific nodules; however, the significance of this observation cannot be assessed until water chemistry studies have been conducted in the concretion sites.

CHAPTER VII

DISCUSSIONS

A Model for Concretion Formation:

In the previous literature two mechanisms of lacustrine ferromanganese concretion formation have been proposed. The earliest theory suggested by Kindle (1935) attributes concretion formation to the action of iron and manganese precipitating bacteria. This mechanism is unsatisfactory as it stands since the precipitation of iron and manganese by bacteria is carried out as an energy-providing function (Wolfe, 1964), and thus bacteria can precipitate manganese and iron only when the activities of these elements are already above the equilibrium activities[1] for the environment. Kindle has no explanation for the abnormal activities of these elements. However, the possibility that bacteria act to catalize the precipitation of the ferromanganese oxides should not be ruled out, and it should be pointed

---

[1] The work of Hem (1963) has shown that over the range of pH and Eh conditions found in lacustrine environments the stable oxides of manganese will be MnO_2, Mn_2O_3 and Mn_3O_4, and Garrels and Christ (1965) have shown that over this same range of pH and Eh conditions the only stable iron oxide is Fe_2O_3 (although $Fe(OH)_3$ may form as an intermediate step). Thus throughout the remainder of this paper the above oxides are implied when the equilibrium activities of manganese and iron are discussed.

out that Gorham (1957) has reported the presence of iron precipitating bacteria in Nova Scotia lakes.

The second theory was proposed by Manheim (1965) who suggests that the elements iron and manganese diffuse through the interstitial water of bottom sediments into the oxidizing aquatic environment where they are precipitated around suitable nuclei at the sediment-water interface. Manheim offers a method for increasing activities of manganese and iron above the equilibrium values and initiating precipitation; however, his mechanism does not explain the chemical banding revealed by electron probe studies in the present investigation.

On the basis of the present knowledge of lake processes it is now possible to outline a mechanism for concretion formation which can explain most of the features exhibited by the lacustrine ferromanganese concretions of the present study.

It has been shown by Hem (1963, 1964), Mackereth (1966) and Ruttner (1953) that freshwater lakes act as reservoirs for iron and manganese. During the fall of the year, large quantities of manganese and iron are released from decaying terrestrial plants in the form of organic acid complexes, and are carried by ground water and surface runoff into the oxidizing waters of lakes. Here oxidation results in precipitation of the iron and manganese as $Fe(OH)_3$ and MnO_2 (Hem, 1964).

Ruttner, (1963) has shown that during the winter period the entire lake is oxidizing and thus the $Fe(OH)_3$ and MnO_2 are stored as such on the bottom of the lake. However, during the spring and summer period of lake stratification the hypolimnion waters may become strongly anaerobic, due to the decay of dead organic matter deposited from the epilimnion waters. As a result the $Fe(OH)_3$ and MnO_2 are reduced and the waters of the hypolimnion become heavily enriched in ionic manganese and iron. Mackereth (1966) reports manganese values as high as 30 ppm in the hypolimnion waters of Lake Esthwaite, England, and Ruttner (1963) reports iron concentrations of 18 ppm and manganese concentrations of 9 ppm in the hypolimnial waters of the Krottensee, Salzburg.

Ruttner (1963) has shown that due to the very rapid oxidation rate of iron, its concentration drops almost immediately at the lower boundary of the metalimnion to the equilibrium activity of this zone, while manganese, with a slower rate of oxidation, (Krauskopf, 1956; Hem, 1964) may be present in anomalously high quantities far up into the waters of the metalimnion and epilimnion.

Thus, during the summer period of stratification the upper epilimnion will have near-equilibrium manganese activities, while the lower epilimnion and metalimnion will be supersaturated with respect to this element. At the same time the upper epilimnion will be virtually depleted of iron due to its utilization by plants for the production of chlorophyll; however, the lowermost region of the metalimnion will be supersaturated with respect to iron.

It is thus proposed that during summer, $Fe(OH)_3$ and MnO_2 will precipitate from supersaturated solution in the lower metalimnion, possibly aided by the catalytic activity of bacteria (Ruttner, 1963; Oborn, 1961), while only MnO_2 will be precipitated from supersaturated solution in the upper metalimnion and lower epilimnion. Over deeper portions of the lake the precipitate will fall back into the hypolimnion where the cycle will be repeated. However, in near shore areas the precipitate will come to rest on the bottom within the metalimnion and epilimnion regions. Due to the reducing nature of the bottom sediments the precipitate will be preserved as a pavement over the bottom in only the most tranquil regions of the lake. In all other areas the precipitate dissolves upon burial beneath the sediment-water interface and is only preserved around stable nuclei capable of supporting it in the oxidized form above the reducing substrate. Thus, during the summer, in the lower epilimnion and metalimnion ferromanganese concretions will result from direct precipitation of the manganese and iron from lake water, which is supersaturated with respect to these elements. Since the oxidation rate of iron is much more rapid than that of manganese, precipitation of this element will be greatest near the lowermost boundary of the zone of precipitation and thus the Fe/Mn ratio of the precipitate should increase with depth.

In the upper epilimnion the lake water may be near equilibrium with respect to manganese activity for the pH and Eh of this environment and thus at most only very limited precipitation of MnO_2 will occur. However, Ruttner (1963) has demonstrated that during photosynthesis aquatic plants can increase the pH of their immediate environment due to their utilization of CO_2. Laboratory experiments carried out by Ruttner have revealed that aquatic mosses may raise the pH of their environment to as high as 9 while certain other aquatic plants can produce pH values as high as 11.

It is proposed that in areas of abundant benthonic vegetation, photosynthetic activity establishes a microenvironment in which the pH is increased above that of the surrounding lake water. Therefore, during the period of summer stratification, high in the epilimnion the precipitation of MnO_2 (and $Fe(OH)_3$) may occur at activity values below the equilibrium concentrations for the lake proper. Good evidence that such micro-environments do exist and can influence precipitation in nature has been presented by Ljunggren (1955) who describes the precipitation of a manganese ochre about the rhizoids of the aquatic moss *Marsupella Aquatica*. It is unlikely that much iron will be precipitated in the above fashion during the summer period due to the depletion of iron in the upper waters of the epilimnion by fresh water algae and other aquatic plant life (Oborn, 1960).

During the fall both the iron and manganese content of the surface lake waters will be enriched due to input from the surrounding watershed and transport of these elements to the surface during the fall turnover of the lake. In the oxidizing lake water both elements will be oxidized and precipitated as $Fe(OH)_3$ and MnO_2. This precipitate will accumulate on the bottom where both elements will be remobilized due to the reducing nature of the bottom sediments. The iron rapidly re-oxidizes and is eventually deposited on the nearest nucleus which is capable of supporting it in the oxidized form above the underlying substrate. The manganese oxidizes more slowly and therefore tends to be carried by the turnover process into the deeper portions of the lake where it will be stored during the winter period. Thus during the fall period an iron-rich deposit will be formed in the shallow portions of the lake over the manganese-rich deposits of the spring and summer period.

Rate of Concretion Formation:

Kindle (1935) found concretions in the shallow waters of an artificial lake and concluded, "Many of these manganiferous crusts may therefore represent a growth period not exceeding twenty-five years". In the present investigation both petrographic and electron probe studies have revealed that the concretions display a chemical banding. It has been suggested that this banding is a result of seasonal variations in water chemistry. If it is assumed that one year's growth can produce only two oxide bands, one manganese rich and one iron rich, it is then possible to calculate a hypothetical growth rate for the precipitates.

In Grand Lake samples the distance between the centres of two adjacent similar bands averages 0.1 mm. and in Mosque Lake concretions this distance averages 1.5 mm. Applying the above assumptions indicates that a Grand Lake concretion having an oxide rim one centimeter wide could form in a period of 100 years, whereas in Mosque Lake such a concretion could form in only seven years. Although the growth rate obtained for Grand Lake is quite low, both of the above values are compatible with Kindle's estimate of twenty-five years. This suggests that the initial assumption is valid and if so provides a method for determining concretion age and growth rate.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The results of the present investigation of lacustrine ferromanganese concretions may be summarized as follows.

(1) The ferromanganese portion of lacustrine concretions of the present study occurs only in a narrow zone immediately above the sediment-water interface. On concretions which have been disturbed, that portion of the ferromanganese rim which has been buried beneath the interface has been removed by solution and that portion which has been raised above its original zone of occurrence shows evidence of being removed by abrasion. It is apparent, therefore, that active precipitation of the ferromanganese portion of the concretions of the present study occurs only within a narrow zone immediately above the sediment-water interface.

(2) In all concretion sites visited in the present study the thickness of the zone of concretion formation corresponds closely with the thickness of a zone of abundant benthonic vegetation, thus suggesting that the vegetation is responsible for the establishment of a micro-environment (possibly having a high pH) in which

oxidation and precipitation of iron and manganese may occur. It should be noted, however, that Beals (1967) has described concretions collected from a depth of 15 feet in Ship Harbour Lake, Nova Scotia, as nodular or bun-shaped, thus suggesting that in deeper water concretion formation results from precipitation of manganese and possibly iron directly from lake water which is supersaturated with respect to these elements.

(3) All concretions of the present study contain a nucleus, which in most cases consists of a pebble or small stone but in some cases consists of a broken fragment of another concretion. This nucleus is probably required in order to support the ferromanganese precipitate above the underlying, reducing substrate where re-solution would rapidly take place.

(4) X-ray diffraction studies reveal the ferromanganese portions of the concretions to be of an amorphous nature. Recent investigations show marine nodules contain only weakly-developed ferromanganese minerals. Thus, the amorphous nature of lacustrine concretions may be a result of a much greater rate of growth.

(5) Electron probe and microscope studies show the concretions to display a concentric chemical banding across which the Fe/Mn ratio shows variations of up to two orders of magnitude. This suggests that concretion

formation is a result of a cyclic process, possibly involving a fluctuation in the Fe/Mn ratio of the overlying lake water.

(6) Bulk chemical analyses show large variations in the Fe/Mn ratio of concretions from similar depth environments in different lakes, indicating that the chemistry of the local watershed has significant influence on concretion chemistry.

(7) With the exception of the occurrence of concretions in a shallow, partially restricted bay in Ship Harbour Lake all concretion formation sites examined were found to occur in areas very close to extremely deep portions of the lakes. This is good circumstantial evidence that ferromanganese concretion development may result from the diffusion of manganese and iron into the oxidizing epilimnion and metalimnion waters from the anaerobic hypolimnion, during summer stratification.

(8) On the basis of the above observations and the present knowledge of lake processes it is suggested that concretion formation is a result of the interaction of the difference in oxidation rates of iron and manganese and the seasonal stratification of lakes. During summer stratification, manganese is carried by eddy diffusion into the oxidizing metalimnion and epilimnion from the manganese and iron rich, anaerobic hypolimnion, resulting

in the deposition of a manganese rich precipitate in these zones. During the fall the surface waters of the lake are enriched in both manganese and iron by surface runoff and lake turnover processes. Due to the rapid oxidation rate of iron an iron-rich precipitate occurs over the manganese-rich summer deposits in the upper portions of the lake, while manganese is transported into the deeper portions of the lake.

(9) It is suggested that the chemical banding displayed by the concretions is the result of a seasonal effect such that one iron-rich band and one manganese-rich band constitute one year's growth. Thus a method whereby concretion age and growth rate may be determined is established. Growth rates calculated in the above fashion vary between lakes from 7 years to 100 years for an increase in concretion width of 1 cm. Such rates of growth are compatible with estimates made by Kindle (1935) and with the consistently low trace element content of lacustrine concretions.

REFERENCES

Adler, I., 1966. X-ray emission spectrography in geology. Elsevier, New York.

Anthony, E. H., and Hayes, F. R., 1964. Lake water and sediment. Vii chemical and optical properties of water in relation to the bacterial counts in the sediments of twenty-five North American lakes. Limnol. Oceanog., 9: 35-41.

Arrhenius, G., Mero, J., and Korkisch, J., 1964. Origin of oceanic manganese minerals. Science, 144 (3615): 170-173.

Barnes, S. S., 1967. The formation of oceanic ferromanganese nodules. Unpublished Ph.D. thesis, University of California, 59 p.

Barnes, S. S., and Dymons, J., 1967. Rates of accumulation of ferromanganese nodules. Nature, 213: 1218-1219.

Beals, H. L., 1966. Manganese-iron concretions in Nova Scotia lakes. Maritime Sediments, 2.

Bonatti, E. and Nayudu, Y. R., 1966. Origin of manganese nodules on the ocean floor. Am. J. Sci., 263: 17-39.

Burns, R. G. and Fuerstenau, D. W., 1966. Electron probe determination of interelement relationships in manganese nodules. Am. Mineralogist, 51: 895-902.

Cronan, D. S. and Tooms, J. S., 1966. Geochemistry of manganese nodules from the N.W. Indian Ocean. Deep-Sea Research, 14: 239-249.

Cronan, D. S. and Tooms, J. S., 1967. A microscopic and electron probe investigation of manganese nodules from the northwest Indian Ocean. Deep-Sea Research, 15: 215-223.

Doe, B. R., 1961. X-ray fluorescence determination of iron in sphalerite. Am. Mineral., 46: 1056-1063.

Elster, H. J., 1939. Beobachtungen uber das Verhalten der Schichtgrenzen nebst einigen Bemerkungen uber die Austauschverhaltnisse im Bodersee (Obersee). Arch. Hydrobiol., 35.

Garrels, R. M. and Christ, C. L., 1965. Solutions, minerals, and equilibria. Harper and Row, New York.

Goldberg, E. D., 1954. Marine geochemistry I. Chemical scavengers of the sea. J. of Geol., 62: 249-265.

Gorham, E., 1957. The chemical composition of lake waters in Halifax County, Nova Scotia. Limnol. Oceanog., 2: 12-21.

Gorham, E. and Swaine, D. J., 1965. The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. Limnol. Oceanog., 10: 268-279.

Haughton, D. R., 1967. The electron probe microanalyzer. A mineralogical study of scapolite. Unpublished M.Sc. thesis, McMaster University: 64-72.

Hayes, F. R. and Anthony, E. H., 1958. Lake water and sediment I. Characteristics and water chemistry of some Canadian east coast lakes. Limnol. Oceanog., 3: 299-307.

Hayes, F. R., Reid, B. L. and Cameron, M. L., 1958. Lake water and sediment II. Oxidation-reduction relations at the mud-water interface. Limnol. Oceanog., 3: 308-317.

Hem, J. D., 1960. Chemistry of iron in natural water. U.S. Geol. Survey Water-Supply Paper, 1459-B: 33-55.

Hem, J. D., 1963. Chemistry of manganese in natural water; Chemical equilibria and rates of manganese oxidation. U.S. Geol. Survey Water-Supply Paper, 1667-A: A1-A64.

Hem, J. D., 1964. Deposition and solution of manganese oxides. U.S. Geol. Survey Water-Supply Paper, 1667-B: B1-B42.

Hem, J. D., 1965. Reduction and complexing of manganese by gallic acids. U.S. Geol. Survey Water-Supply Paper, 1667-D: D1-D28.

Honeyman, D., 1881. Nova Scotia Geology (Superficial). Proc. & Trans. N.S. Inst. of Nat. Sci., 5: p. 328.

Keil, K., 1967. The electron microprobe x-ray analyzer and its application in mineralogy. Fortschr. Miner., 44: 4-66.

Kindle, E. M., 1932. Lacustrine concretions of manganese. Am. J. Sci., 24: 496-504.

Kindle, E. M., 1935. Manganese concretions in Nova Scotia lakes. Roy. Soc. Can. Trans. Sect. Iv: 163-180.

Kindle, E. M., 1936. The occurrence of lake-bottom manganiferous deposits in Canadian lakes. Econ. Geol., 31: 755-760.

Krauskopf, K. B., 1957. Separation of manganese from iron in sedimentary processes. Geochim. Cosmochim. Acta, 12: 61-84.

Ljunggren, P., 1953. Some data concerning the formation of manganiferous and ferriferous bog ores. Geol. Foren. Stockholm Forh., 75: 277-298.

Ljunggren, P., 1955a. Chemistry and radioactivity of some Mn and Fe bog ores. Geol. Foren. Stockholm Forh., 77: 33-44.

Ljunggren, P., 1955b. Differential thermal analysis and x-ray examination of Fe and Mn bog ores. Geol. Foren. Stockholm Forh., 77: 135-147.

Loveridge, B. A., et. al., 1960. Determination of Cu, Cr, Pb and Mn in sea water. At. Energy Res. Estab. (Gt. Brit.), Rept., R3323.

Manheim, F. T., 1965. Manganese-iron accumulations in the shallow marine environment. Symp. Marine Geochem., Occ. Publ. 3-1965: 217-276.

Menard, H. W., 1964. Marine geology of the Pacific. McGraw-Hill, New York, 271 p.

Mero, J. L., 1962. Ocean floor manganese nodules. Econ. Geol., 57: 747-767.

Mero, J. L., 1965. The mineral resources of the sea. Elsevier Pub. Co., Amsterdam, 312 p.

Morgan, J. J., 1967. Applications and limitations of chemical thermodynamics in natural water systems. Adv. Chem. Series, 67: 1-29.

Morgan, J. J. and Stumm, W., 1964. Colloid-chemical properties of manganese dioxide. Jour. Colloid series, 19: 347-359.

Morgan, J. J. and Stumm, W., 1965. Analytical chemistry of aqueous manganese. Jour. Am. Water Works Ass. 57: 107-119.

Mortimer, C. H., 1942. The exchange of dissolved substances between mud and water in lakes. J. Ecol., 30: 147-201.

Oborn, E. T., 1960. A survey of pertinent biochemical literature; Chemistry of iron in natural water. U.S. Geol. Survey Water-Supply Paper 1459-F: 111-190.

Oborn, E. T., 1964. Intracellular and extracellular concentration of manganese and other elements by aquatic organisms. U.S. Geol. Survey Water Supply Paper 1667-C: C1-C18.

Park, C. F. and MacDiarmid, R. A., 1964. Ore Deposits. Freeman and Co., San Francisco. 475 p.

Pettersson, H., 1959. Manganese and nickel on the ocean floor. Geochim. Cosmochim. Acta, 17: 209-213.

Prescott, G. W., 1951. Algae of the western Great Lakes area. Cranbook Press, Michigan, 949 p.

Price, N. B., 1967. Some geochemical observations on manganese-iron oxide nodules from different depth environments. Marine Geol., 5: 511-538.

Rossmann, R., Callender, E., 1968. Manganese nodules in Lake Michigan. Science, 163 (3858): 1123-1124.

Ruttner, F., 1963. Fundamentals of limnology. Univ. of Toronto Press, Toronto, 295 p.

Sorem, R. K., 1967. Manganese nodules: Nature and significance of internal structure. Econ. Geol., 62: 141-147.

Wasmund, E., 1927. Die stromungen im Bodensee. Int. Rev. 18.

1928. Die stromungen im Bodensee. Int. Rev. 19.

Willis, J. P. and Ahrens, L. H., 1962. Some investigations of the composition of manganese nodules, with particular reference to certain trace elements. Geochim. Cosmochim Acta, 26: 751-764.

Wittry, D. B., 1963. Methods of quantitative electron probe analysis. Adv. X-Ray Anal., 7: 395-418.

Wolfe, R. S., 1964. Iron and manganese bacteria. Principles and applications in aquatic microbiology. John Wiley & Sons: 81-97.

Zapffe, C., 1931. Deposition of manganese. Econ. Geol. 26: 799-832.

APPENDIX

TECHNIQUES FOR SAMPLE PREPARATION AND ANALYSIS

Preparation of Polished Sections:

Samples ¼-inch in thickness were cut from the edge of a ferromanganese concretion using a diamond saw. The surface to be polished was then drawn once or twice very lightly over the cleaned surface of a very sharp file, in order to remove the smeared surface resulting from cutting. The sample was then placed between two anvils in a 3/4-inch stainless steel mould and covered to a depth three times its thickness with powdered leucite. The surface to be polished was placed adjacent to the lower anvil but was separated from it by a thin, approximately 1/32-inch thick, layer of leucite. The mould was then heated to 150°C and held at this temperature for 10 minutes to insure melting of the leucite. The specimen was then placed under 1400 p.s.i. pressure and held at this pressure while it was cooled to 80°C. This produced a leucite mounted specimen with a thin leucite impregnated layer on the surface to be polished. All polishing was restricted to this thin layer since the unimpregnated sample was so soft it was destroyed by the action of the polishing fluids.

Polishing was accomplished with a series of emery papers and diamond-impregnated silk lapping cloths. The final polished surface was produced using diamond paste of less than ¼ micron size. It was found that felt lapping cloth could not be used as the felt produced relief on the sample surface which was unsatisfactory for electron probe work.

X-Ray Fluorescence Preparation and Analysis:

Analyses for the elements Mn and Fe were carried out by x-ray fluorescence methods. The procedure described is similar to the technique used by Barnes (1967) for studies on oceanic ferromanganese nodules.

Sample Preparation:

Concretions were thoroughly brushed to remove all contamination from the surface, and the ferromanganese rim was broken away from the nucleus. This precipitate was crushed to a fine powder by shaking for 15 minutes in a tungsten Spex shatterbox. The crushed sample was dried in an oven at 90°C for a 12-hour period.

Pellets suitable for analysis were prepared by weighing 1.00g of crushed concretion, 0.04g $RbC\ell$, 0.36g La_2O_3, and 1.60g H_3BO_3 into a Spex, model 8003, alumina ball mill with a ½-inch ball. The mixture was shaken in a Spex, model 8000, mill for 50 minutes. A 1.00g sample of this mixture was then placed between two polished anvils in a one-inch stainless steel mould with a 2.00g sample of H_3BO_3 added as backing. This was formed into a pellet by applying a pressure of 20 tons per square inch to the sample in a Spex, model C-30, 30-ton press. In order to check homogeneity, two pellets were made from each mixture.

Ten standard pellets ranging in composition from 5% MnO_2 and 95% Fe_2O_3 to 95% MnO_2 and 5% Fe_2O_3 were prepared in a manner similar to that described above. Mixtures of reagent grade Fe_2O_3 and MnO_2 were substituted for the concretion.

Samples were analyzed in a Philips x-ray unit. Tungsten radiation was used for all analyses and settings were maintained at 34 Kv and 24 mA. Secondary radiation was diffracted by means of a KI crystal. Use of pulse height analysis was found unnecessary since no interference between peaks occurred.

Standard curves were prepared by comparing the relative intensities of the Fe $K\beta_1$ and Mn $K\alpha_1$ peaks. It was found for these particular peaks that the heavy element absorber La_2O_3 virtually eliminated all matrix effects.

Rubidium Chloride was added to the samples in order that Rb could be used as an internal standard. However, standard curves could not be used due to large variations in the intensity of the Rb peak. This was possibly a result of matrix effects which were not eliminated by the La_2O_3.

A standard curve for Mn was constructed at the start of each run by counting for Mn Kα radiation on each of the 10 Mn standards. The various samples were then irradiated and the intensity of the Mn and Fe peaks recorded. After each unknown had been examined the Mn standard closest in composition to the unknown was re-examined. This was done in order that corrections could be made to the graph for instrument drift.

Intensities of Fe and Mn were calculated from the time required for 2×10^5 and 1×10^6 counts respectively. In all cases intensities were computed from the mean of three consecutive counts taken over a given peak.

The percentage of Mn in each sample was calculated from a graph of Fe/Mn - vs - Intensity Fe/ Intensity Mn, constructed from readings obtained on standards at the beginning of each run. Corrections did not have to be made to this graph since the intensity ratio is not affected by machine drift.

TABLE A-1

X-ray fluorescence data obtained for various ferromanganese concretion samples.

Sample No.	Fe $K\beta_1$ Time for $2x10^5$ counts	Mn $K\alpha_1$ Time for $1x10^6$ counts	Fe 50.50 Time for $1x10^4$ counts	Mn 61.80 Time for $1x10^4$ counts
GL-1-W	30.23	27.82	53.36	47.80
GL-1-X	23.35	29.84	48.42	50.42
GL-1-Y	24.75	29.24	51.37	48.55
GL-1-YA	24.77	29.25	52.15	48.29
GL-1-Z	23.98	29.58	47.77	45.66
GL-1-C1	29.70	28.82	48.93	46.48
GL-1-C2	25.90	30.26	59.42	50.73
GL-2-Y	27.52	27.36	58.47	49.39
GL-2-Z	32.06	29.49	57.02	50.92
GL-2-C1	30.75	29.30	53.32	47.19
GL-4-Z	28.60	28.81	51.11	48.30
GL-4-C1	31.02	30.21	53.43	50.01
SH-1-X	39.71	38.68	51.00	52.61
SH-1-Y	22.76	34.78	48.53	50.54
SH-1-Z	29.43	35.22	50.60	44.08
SH-1-C1	27.55	37.59	52.46	46.95
ML-1-Z	10.97	60.98	53.38	55.68
ML-1-C1	11.04	61.66	52.69	59.16
107785	22.73	40.38	46.16	48.59