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PAPER 70-69

NOTES ON LACUSTRINE MANGANESE-IRON CONCRETIONS

(Report and 6 figures)

J. Terasmae

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J. Terasmae

DEPARTMENT OF ENERGY, MINES AND RESOURCES

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ABSTRACT

Manganese-iron concretions, and other types of Mn-Fe precipitate, have been found in many small lakes in Ontario and Nova Scotia, and also in Lakes Michigan and Ontario. These deposits may contain up to 40 per cent (by weight) of iron and 35 per cent of manganese, in addition to small amounts of other elements (Zn, Ni, Co, Pb and Cu). The estimated abundance of these deposits indicates that they may have a mineral resource potential. The formation of the lacustrine Mn-Fe precipitates is not clearly understood, but appears to be related to geochemical processes through acid leaching in the watershed areas (caused by surface water rich in humic matter) and transport by groundwater to sites of precipitation in lakes where higher pH levels and oxidizing conditions prevail.

NOTES ON LACUSTRINE MANGANESE-IRON CONCRETIONS

INTRODUCTION

In 1964, button-shaped concretions were discovered in a shallow bay of Mosque Lake, Ontario, and submitted for identification to the Geological Survey of Canada. Chemical analysis indicated that these were manganese-iron concretions and further study was instigated to investigate the geological and limnological conditions related to this accumulation of concretions. This seems to have been the first reported occurrence of this particular type of manganese-iron concretions from Canadian lakes. However, many years ago, Honeyman (1881) and E.M. Kindle (1932, 1935 and 1936) reported manganese deposits from several Nova Scotia lakes and Loughborough Lake in Ontario, a few miles north of Kingston. A. La Rocque has reported manganiferous concretions from Big Trout Lake and Cedar Lake in Algonquin Park, Ontario (*in* Kindle, 1936). Extensive studies of manganese-iron lake and bog ores have been made in Europe and the U.S.S.R. (Ljunggren, 1953, 1955; Perfilev *et al.*, 1965), and much attention has been given to manganese-iron accumulations in the marine environment (Manheim, 1965).

After some 30 years since the first reports on manganese-iron concretions in Canadian lakes were made, there is renewed interest in these deposits as a number of additional occurrences have been discovered owing to increased activity in the field of limnological research. In 1965 Beals and Trost reported on a study of six Nova Scotia lakes with regard to the biochemistry of manganese concretions. Beals (1966) described concretions from Lake Charlotte, Nova Scotia, similar to those found in Mosque Lake, Ontario. In 1967 the writer reported on the Mosque Lake concretions at the Geological Association of Canada meeting. Rossmann and Callender (1968) discovered the presence of manganese concretions in Lake Michigan in 1967, and Callender (1968) reported on further studies of these deposits. Troup (1969) reported on the chemistry and internal structure of these concretions.

The recent studies have provided new information about the occurrence, composition and probable mode of formation of the lacustrine manganese-iron concretions. It appears very likely that many more discoveries of such concretions will be made in Canadian lakes as limnological research expands. If these concretions are found in sufficiently large quantities, they may provide another mineral resource which can be utilized when the need arises. The concretions studied can contain up to 40 per cent (by weight) of iron and 35 per cent of manganese, and several other elements (Zn, Ni, Co, Pb, and Cu) in small amounts.

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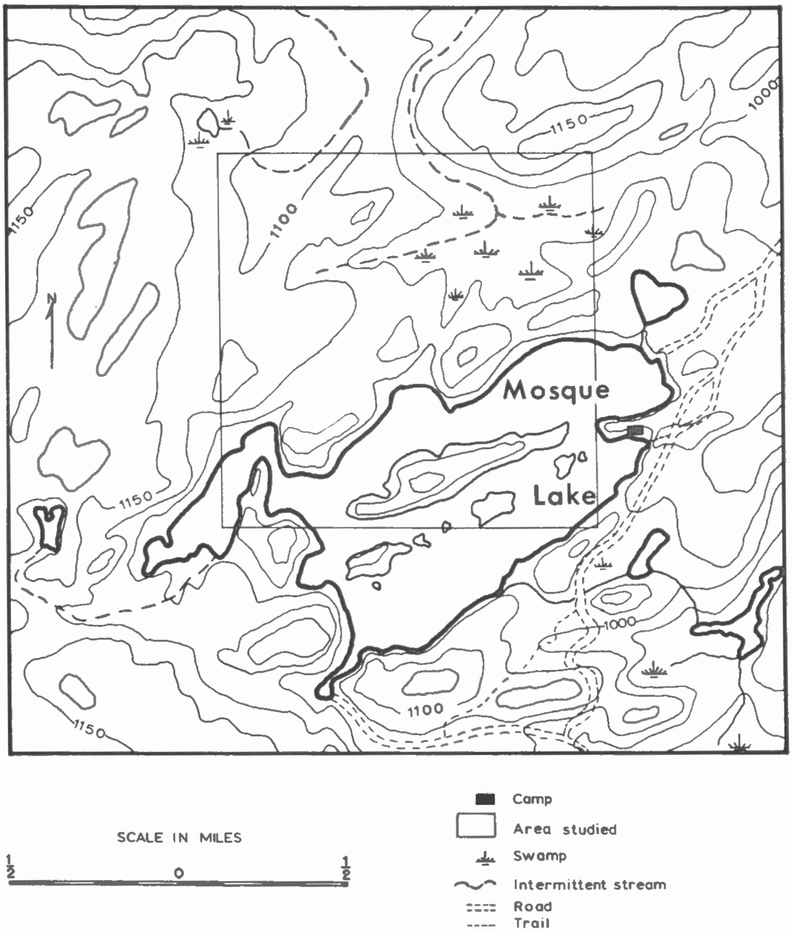


Figure 1. Index map of the study area. Elevations are given in feet above sea level.

The objective of this study is to review the geolimnological conditions under which the manganese-iron concretions have been found, attempt a valuation of the resource potential of these deposits, and provide some guidelines for further prospecting related to manganese-iron concretions in the lacustrine environment.

CONCRETIONS IN MOSQUE LAKE

Mosque Lake is 3.5 miles west of Ompah, which lies about 35 miles south of Renfrew and 55 miles north of Kingston, Ontario. The surrounding area is characterized by a moderately hilly relief of the Canadian Shield, ranging from 100 feet to 400 feet, with maximum elevations of about 1,250 feet above sea level. Mosque Lake is 1,000 feet a.s.l. and lies in a bedrock basin with an irregular shoreline (Fig. 1). A rock ridge divides the lake into a northern and southern basin. The cover of surficial deposits is discontinuous in this area and consists of thin till, sand and gravel with greater accumulations locally. Fine-grained sediments of silt and clay size occur in many depressions and are commonly overlain by organic deposits. The surficial deposits, where studied, have been noncalcareous.

The northern basin of Mosque Lake (Fig. 1) has a maximum depth of 60 to 70 feet and the bottom sediment is a dark brown, fine-grained detritus gyttja. The lake does not differ visibly from any other of the multitude of lakes in this area. However, the bay along the north shore in which the concretions were found (Fig. 2) is different in several respects. About 0.3 mile to the northeast of this bay is a swampy area underlain by previous sediments and from which a valley leads down to the bay. The bay is shallow, has a sand and gravel bottom, and deepens gradually to about 10 feet where the bottom drops off steeply into the deep basin. The sandy bottom of the bay is covered, for the most part, by a thin layer (3-6 inches) of clayey mud with plant detritus. A long beaver dam separates a pond from the lake (Fig. 2), and the water level in the beaver pond may be some 4 feet higher than the lake. However, in dry years such as the fall of 1965, the pond may be dry. Coarse sand with some gravel forms the bottom of the pond and a 4 to 6 inch layer of

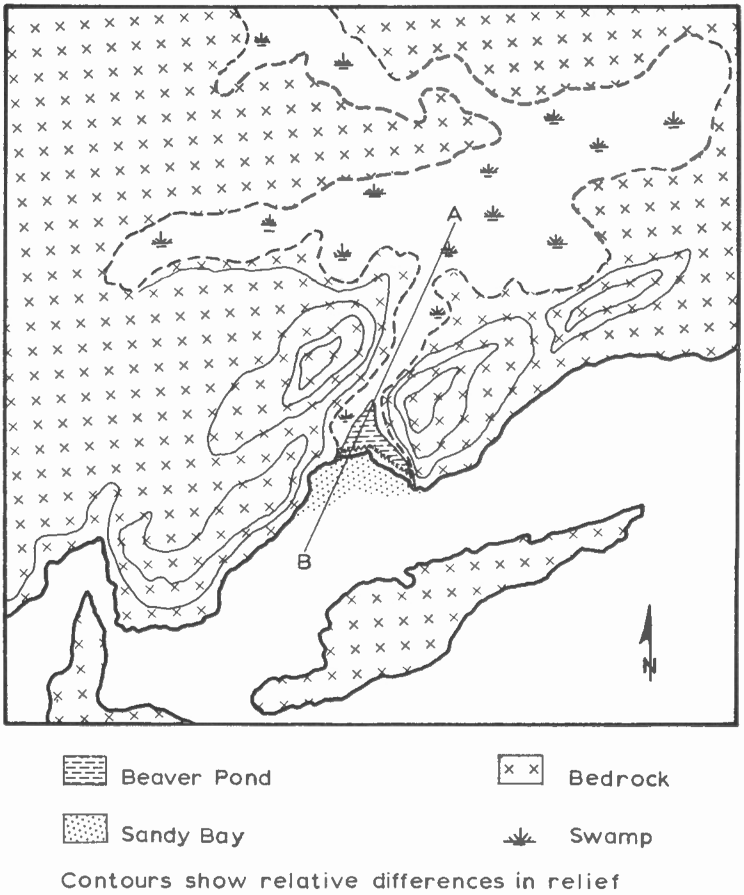


Figure 2. Details of study area. Mn-Fe concretions occur in the sandy bay. A - B indicates location of cross-section shown in Figure 6.

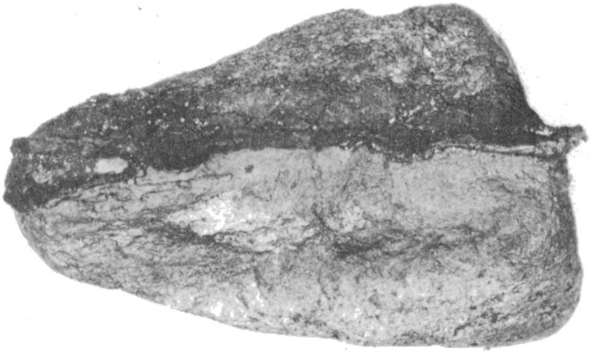


Figure 3. Pebble (longest dimension 3 inches) showing the manganese-iron precipitate 'skirt', or rim. (GSC photo 11-27-54A)

organic detritus has accumulated in it. The water and bottom sediment in the beaver pond are slightly acid and the underlying sand has been reduced to a light grey colour.

Concretions occur at the sediment-water interface in the shallow part of the bay adjacent to the beaver pond, and manganese-iron crust rims, or skirts, were observed on some small stones at this interface (Fig. 3). There was no crust on such pebbles below or above the sediment-water interface. The majority of concretions are flat, round, and about 1 inch in diameter (Fig. 4). They have a slightly convex central part, are composed mostly of sand and occasionally have a small pebble forming the nucleus. This nucleus is surrounded by concentric rings of dark brown and black precipitate. Viewed from the side, the concretions commonly have a constriction at the equatorial plain giving them a pulley shape (Fig. 5). In Mosque Lake the concretions are found mostly on a sand and gravel bottom without a covering mud layer.

CONCRETIONS IN OTHER LAKES

Nova Scotia Lakes

Beals and Trost (1965) described seven different types of manganese-iron precipitates in Nova Scotian lakes:

Type 1 - concentric discs
Type 2 - concentric bowls
Type 3 - bun-shaped or nodular
Type 4 - flat, platy crust
Type 5 - rocks with oxide halo (skirt)
Type 6 - nodules
Type 7 - encrustations on rock surface

In Porter's Lake, Type 4 concretions were found with some Type 1 concretions on a sloping clay-covered lake bottom at a depth of 20 feet.

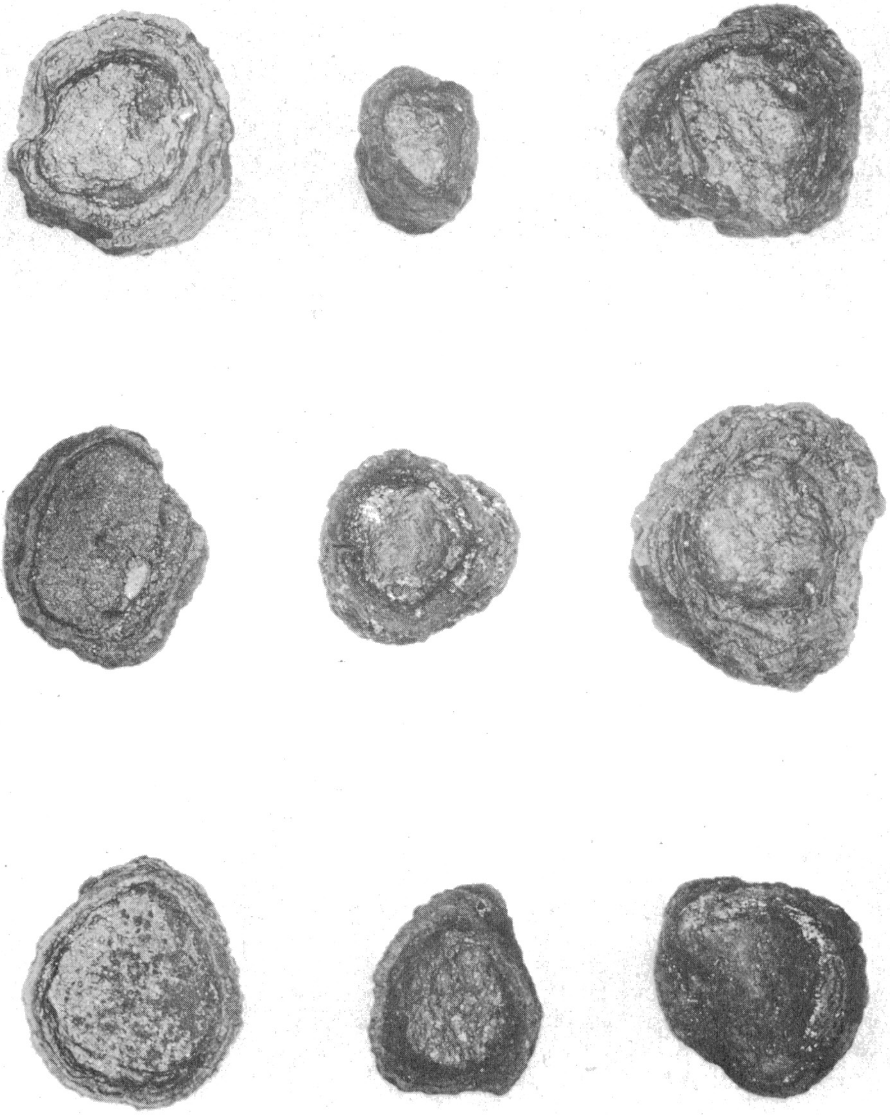
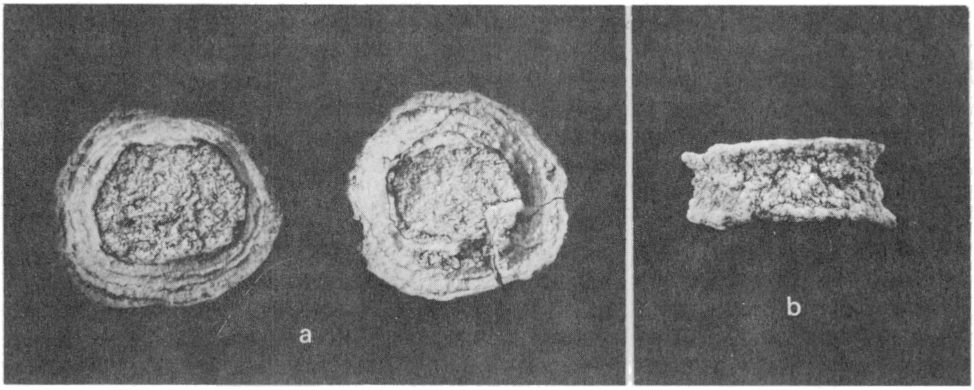


Figure 4. Mosque Lake Mn-Fe concretions showing presence of concentric rings of black and brown precipitate around nuclei of small pebbles or sand. Diameter of largest concretion is about 1.5 inches. (GSC photo 11-27-55)



a. Concentric rings around a sandy nucleus.

b. Side view of the concretion showing pully shape.

Figure 5. Details of a Mn-Fe concretion from Mosque Lake (diameter 1.25 inches). (GSC photos 11-27-54B and C)

In Pace's Lake, which has a rocky shore and steep slopes, Type 5 and Type 7 precipitate were found on boulders and cobbles at a 25-foot depth.

In Chezzetcook Lake, Type 1 and Type 2 concretions (up to 30 centimetres in diameter) were found on a sandy bottom.

In Lake Charlotte, Beals (1966) selected three different environments for a study of concretions and he found that: (1) Type 3 concretions occurred on fine muddy sand which projected through organic mud in a protected cove, at a depth of 15 feet; (2) Type 1 concretions occurred in a shallow bay (water depth 3 to 5 feet); (3) Type 1 and Type 2 concretions occurred within a zone running laterally along a gentle slope. The concretions ranged from 8 centimetres in diameter at the top of the slope (depth - 11 feet) to 14 centimetres diameter at the bottom of the slope (depth - 25 feet). The bottom sediment ranged from a muddy sand at the top of the slope to a smooth clay near the bottom. The upper and lower boundaries of the concretion zone were well defined and sharp. This zone was traced for a distance of 1.5 miles along the lake bottom. Beals noted that there was no significant change in the properties of the water measured (pH, Eh, CO_2, O_2) along a transect crossing the concretion bed. He concluded that, if the chemical, physiochemical and biological properties measured were responsible for the growth of the concretions, a definite variation of some kind would have been detected.

Lake Michigan

Callender (1968) has mapped the distribution of manganese nodules and studied the limnological environment in which these nodules occur. He found that the nodules are most abundant in Green Bay, but occur also in northwestern and northeastern parts of Lake Michigan. In Green Bay the nodules are about 2 millimetres in diameter and consist of aggregates of ferromanganese minerals clustered about a nucleus. The manganese content of nodules averages 10 per cent, and they are found on a sediment surface at depths of 30 to 100 feet. The nodules may cover 30 to 70 per cent of the surface area of a lake bottom, and occur in areas of sandy bottom deposits where the dissolved oxygen is in abundant supply. Nodules are not found on a mud bottom because of a greater sedimentation rate which, according to Callender, results in a chemical environment detrimental to their growth. Further detailed studies of Lake Michigan manganese nodules are being carried on to establish the source of the metals that nourish their growth, and to determine the origin of these manganese deposits.

Kawagama Lake

Concretions in Kawagama Lake, about 8 miles northeast of Dorset, Ontario, were discovered in the eastern part of that lake where they occur on sandy bottom at an estimated depth of 40 to 60 feet. These concretions resembled thick pancakes in shape and size, had an irregular surface, and were dark brown in colour. When dry, the concretions were quite friable. Chemical analysis made by the Geological Survey laboratories indicated that these concretions were composed of goethite. Some elements were present in very small quantities.

Buckshot Lake

In 1968 the writer was informed of concretions in Buckshot Lake north of the Bancroft area, Ontario. These concretions also resembled pancakes in size, were fragile, black in colour, and were arranged like shingles on a roof over a wide area of lake bottom at a depth of 22 to 28 feet. The surface concentric rugosities of the concretions made them resemble an oyster shell.

Further studies of concretions in both Buckshot Lake and Kawagama Lake are in progress.

Loughborough Lake

Kindle (1936) reported soft, black, 'sandy' concretions from Loughborough Lake, north of Kingston, Ontario, at a depth of 105 feet. He gave the composition of this material as follows:

	Per cent
SiO_2	27.51
Al_2O_3	5.41
Fe_2O_3	13.19
FeO	1.14
CaO	5.10
MgO	1.31
H_2O	10.80
MnO_2	32.66
CO_2	2.17

Although the analytical method used is not described by Kindle, it appears that the concretions were composed of iron-manganese precipitate.

Scandinavian Lakes

Concretions similar to those described in this report have been studied rather more extensively in Scandinavia. Ljunggren (1953 and 1955) concluded from his studies of fresh-water manganese-iron deposits in Sweden that the acidity of the waters had a dominating influence on the leaching out of manganese and iron from rocks and also on the transport of these elements by water. Savage (1936) had reached similar conclusions in Canada based on his chemical experiments. He found that peat solution was a good solvent of manganese, because of the free carbonic acid resulting from the decay of organic matter. Although many manganese and iron deposits in Sweden are found in areas dominated by gneiss and granite bedrock, a high percentage of basic rocks does not seem to prevent the formation of such deposits. It appears that cold glacial waters lack any precipitation of iron and manganese oxides. Ljunggren found no correlation between frequency of iron-manganese bog ores and the Mn and Fe content of the waters examined. Apparently, the oxidate crusts are formed where the relatively organic lake and mud deposits are thin or absent above the inorganic sediments. Because of their permeability, sand and gravel bottoms are most favourable for Mn and Fe crust development. Muddy waters with clay particles prevent the enrichment of Fe and Mn oxides since the clay particles can act as protective colloids to the precipitated oxides and hydroxides, according to Ljunggren.

Lake District, England

Gorham and Swaine (1965) concluded from their studies in the Lake District that no geochemical regularities could be established over the whole range of ferromanganese oxidate deposits, and they suggested that the, probably, most rewarding field for future studies would be the detailed analysis of elemental abundance in water, sediments, and associated ferromanganese concretions within small areas.

GEOLIMNOLOGY OF CONCRETIONS

As early as 1918 Aarnio suggested that the iron-manganese concretions were formed by precipitation of iron and manganese from groundwater when it flowed through permeable sand and gravel deposits and entered the lake bottom, where a change in the chemical environment would cause precipitation. This hypothesis would explain the spotty occurrence of concretions on the lake bottom.

Kindle (1935) attributed concretion formation to the action of iron and manganese precipitating bacteria. Many Russian scientists also favour the theory of bacterial action as the cause of the formation of ferromanganese concretions (Perfilev _et al._, 1965).

A number of variations of the two principal hypotheses mentioned above have been proposed by other investigators of this interesting problem.

Both Ljunggren (1953) and Troup (1969) suggested that a combination of organic (bacteria and higher plants) and inorganic factors may be involved in the precipitation of iron-manganese concretions. On the basis of his studies, Ljunggren suggested that the iron precipitate was probably added

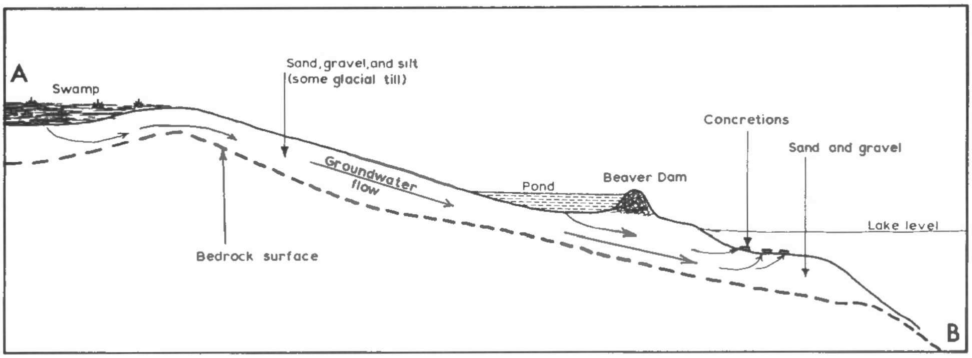


Figure 6. Cross-section A - B of Figure 2 illustrating the postulated groundwater flow hypothesis for the formation of Mn-Fe concretions in Mosque Lake. Broken line indicates assumed bedrock surface.

to the concretions from below and the manganese from above. Harriss and Troup (1969) postulated that, in the case of round concretions comprised of concentric rings of iron and manganese as indicated by electron probe analysis, a pair of oxide bands (one Fe-rich and one Mn-rich) represents the annual growth increment of these ferromanganese concretions. Furthermore, they suggested that, if this assumption was correct, the growth rate of disc-shaped concretions in Nova Scotia lakes was 0.1 millimetre/year and 1.5 millimetre/year for the Mosque Lake concretions.

In spite of the numerous studies made and the corresponding number of hypothesis proposed, there does not seem to be a satisfactory understanding of the formation of manganese-iron concretions in lakes. The explanations offered are applicable in some specific cases but fail to explain other occurrences of similar concretions.

For Mosque Lake concretions the writer proposes the following working hypotheses. As illustrated by Figures 2 and 6, the swamp and bog to the northeast of the bay where concretions are found acts as a groundwater accumulation area collecting surface water from the surrounding bedrock upland. It is postulated (Fig. 6) that the groundwater from the swamp, and also from the beaver pond, flows downslope through the sand and gravel and enters into the lake in the shallow bay. The acid environment coupled with high humic matter content in the swamp and the beaver pond would keep manganese and iron in solution and precipitation of these elements will occur when the groundwater comes into contact with oxidizing lake water, pH above 7, at the bottom of the shallow bay.

Another observation which may support the above hypothesis was made in the shallow bay of Mosque Lake. There appeared to be an absence of dense aquatic bottom vegetation in this bay and the few plants observed were of stunted stature. Other shallow bays of the lake had a dense cover of bottom vegetation. The relatively high manganese content of bottom sediment, owing to upwelling of the manganese-rich groundwater, probably has a toxic effect on bottom vegetation.

Although the groundwater flow hypothesis may explain the presence of manganese-iron concretions in Mosque Lake and other lakes where concretions occur in shallow bays and in near-shore environments the presence of such concretions in deep water is not so readily explained by this hypothesis.

It is hoped that further studies will provide geochemical models which will help to solve the interesting problems related to the occurrence of lacustrine manganese-iron precipitates.

ECONOMIC RESOURCE POTENTIAL

The discovery of manganese-iron concretions or other forms of Fe-Mn precipitate in Lake Michigan, and more recently in Lake Ontario, indicates that such precipitates may be present in the other Great Lakes (Drs. C.F.M. Lewis and P.G. Sly, pers. comm.). Evidently these concretions occur in a large number of small lakes where no prospecting has been undertaken to date. The concentration of these precipitates, at least locally where the studies have been made, is sufficient to suggest a resource potential for these deposits.

It is not possible at this time, because of insufficient data, to estimate a total volume figure for the lacustrine manganese-iron precipitates. However, the easy access to these deposits will minimize exploitation costs and suitable extraction techniques are available (Cruickshank, 1964). Further prospecting clearly seems to be warranted to establish the economic feasibility of utilization of this new mineral resource.

Harriss and Troup (1969) reported the following chemical composition of the concretions from Ontario and Nova Scotia (21 samples analyzed).

	Range	Average
Fe (% by weight)	11.7 - 40.2	18
Mn (% by weight)	15.7 - 35.9	30
Co (ppm)	135 - 230	201
Ni (ppm)	95 - 373	218
Cu (ppm)	6 - 16	10
Zn (ppm)	250 - 1940	1245
Pb (ppm)	10 - 28	24

There is another aspect of these manganese-iron deposits that deserves mention. About 50 years ago Naumann (1922) reported that, in Swedish lakes where ore-scraping had been undertaken, the manganese-iron precipitate formed again in about 50 years and another 'crop' could be harvested. Kindle (1936) estimated the accumulation rate of Fe-Mn precipitate on the basis of the thickness of such deposits formed on human artifacts of approximately known age. It seems probable that a new 'crop' of Fe-Mn precipitate can form in 20 to 30 years after removal of the original deposit and, hence, the manganese-iron concretions and precipitates can be properly classified as a renewable resource.

Assuming that the process of manganese-iron precipitation has occurred over a long period of time (at least several thousand years in the lakes studied) one would expect to find a much thicker deposit of manganese-iron precipitate than actually observed. Ljunggren (1953) suggests two possible explanations for a maximum thickness of the precipitate. The first is that the growth of the ore layer is restricted to the sediment/water interface and cannot occur much above or below that level. The other possibility is that the solutions have arrived at the lake floor through porous bottom sediments, and when the ore layer has grown to a certain thickness, its permeability to the solution is so small that no further precipitation can take place. These are interesting speculations which should be investigated further both in the field and the laboratory. If Ljunggren's suggestions are correct, then the lacustrine manganese-iron deposits can be compared with a forest crop which will reach a certain maturity and will not increase in volume indefinitely. However, when harvested, a new crop will grow again within a known length of time.

GUIDELINES FOR PROSPECTING

The present knowledge of lacustrine manganese-iron precipitates suggests that these deposits can occur in both large and small lakes. The composition of the bedrock and glacial deposits does not seem to have a direct influence on the formation of Fe-Mn precipitates. However, since low pH values of surface and groundwater are required for the transport of Fe and Mn in solution, the 'concretion lakes' are frequently found in areas of acid igneous rocks. The acidity of the surface water also has a dominating influence on the leaching out of Mn and Fe from the rocks, minerals and soils. Relatively high precipitation (rain and snow), the presence of organic deposits (bogs and swamps), and moderate temperatures appear to be other factors contributing to the presence of Mn-Fe precipitates. No precipitation of Fe and Mn was observed in cold glacial waters in Sweden (Ljunggren, 1953). High clay content of both the water and bottom sediment are detrimental to precipitation of iron and manganese.

Because no correlation has been found to exist between the content of Fe and Mn in surface waters and the occurrence of Mn-Fe concretions, an enrichment of iron and manganese must take place before precipitation of these elements can occur. The groundwater flow hypothesis, as suggested for Mosque Lake, would provide such a mechanism for enrichment through a continuous supply of Fe and Mn to the lake bottom. When prospecting for manganese-iron concretions, one might profitably explore situations where groundwater from swampy catchment areas can flow through pervious deposits to a lake and enter the lake bottom through sand and gravel at depths of 3 to 30 feet in small lakes and up to 100 feet in larger lakes.

Although iron and manganese can also be transported to the lakes by streams, the mechanism of precipitation in such cases is rather poorly understood and further studies are eagerly awaited.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Mr. Bill Cheffins, who discovered the concretions in Mosque Lake, Dr. R. Greggs of Queen's University for his information on those in Buckshot Lake, Mr. H.E. Smith, who first found those in Kawagama Lake and many of his colleagues at the Geological Survey who contributed to this study through stimulating discussions and helpful suggestions. Drs. C.F.M. Lewis and P.G. Sly of the Canada Centre for Inland Waters kindly provided information on concretions in Lakes Michigan and Ontario. The assistance in the field by R. J. Mott is gratefully acknowledged.

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