# RENSSELAER Fresh Water Institute AT LAKE GEORGE

FRESH WATER IRON-MANGANESE NODULES IN LAKE GEORGE, NEW YORK

By

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# Fresh Water Iron-Manganese Nodules in Lake George, New York

## ABSTRACT

Lake George, New York, is the site of a new discovery of iron-manganese nodules. These nodules occur at a water depth between 21 and 36 m along a stretch of lake extending for about 5 mi north and south of the Narrows, a constricted island-dotted area which separates the north and south Lake George basins. Nodules occur on or within the uppermost 5 cm of a varved glacial clay. Some areas are solidly floored with a carpet of nodules in areas where active currents keep the nodules exposed. The nodules form around nuclei which consist of clay and less commonly of spore capsules, detrital particles, or bark. By their shape we recognize three types of nodules: spherical, discoidal, and lumps.

On X-ray examination all nodules show small goethite peaks; in one nodule the manganese mineral birnessite was identified. Manganese and part of the iron appears to be in X-ray amorphous ferromanganese compounds. The Lake George nodules are enriched in iron with respect to marine nodules but are lower in manganese. They have a higher trace element concentration than nodules from other known freshwater lake occurrences, but a lower concentration than marine nodules.

## INTRODUCTION

Lake George, New York, is the site of a new discovery of iron-manganese nodules reported here for the first time. This study is concerned with the distribution, mineralogy, and geochemical composition of these nodules and presents some observations on their genesis. Moreover, we compare these nodules with those from other lakes as well as within those from the marine environment to focus on similarities and differences between the various reported iron-manganese nodule occurrences. Within recent years marine manganese nodules have become the subject of a growing literature (*see* bibliographies *in* Arrhenius, 1963; Mero, 1965; Manheim, 1965). Yet, surprisingly, in North America the discovery of fresh water nodules in Green Bay (Lake Michigan), Wisconsin, created a stir of excitement in the mid-1960s, although fresh water iron-manganese nodules have been known for well over a century. Despite the expectation that some day marine manganese nodules may become a source of manganese-iron ore, no single occurrence has so far met this expectation. Yet fresh water iron-manganese nodules in Swedish lakes were mined for a long time; in 1860 they yielded approximately 10,000 to 12,000 tons per yr. In fact, after removal the nodules were not depleted but grew again during the following years and were fully replenished in 30 to 50 yr cycles. Many references, summarized by Naumann (1930), Ljungreen (1953, 1955), and Gorham and Swaine (1965) attest to the abundance of iron-manganese nodules in European lakes and rivers. In Canada and the United States, fresh water iron-manganese nodules have been reported by Moore (1910), Kindle (1932, 1936), Twenhofel and McKelvey (1941), Gillette (1961), Beals (1966), Rossmann and Callender (1968, 1969), Harriss and Troup (1969), Johnson (1969), and Dean (1969).

The major differences between fresh water and marine nodules lie in a lower Mn/Fe ratio and a lower concentration of trace elements in fresh water than in marine nodules (Price, 1967). Fresh water nodules would better deserve the name iron-manganese nodules, whereas those from the marine environment are more appropriately called manganese nodules.

## SAMPLING AND LABORATORY PROCEDURES

Surface sediment samples from the Lake George floor were recovered in this study with

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an Eckman dredge. All samples were taken on a grid pattern normal to the long axis of the lake with stations at .5 mi intervals and traverses 1 mi apart (Fig. 1). Some additional samples were taken between the traverses. In the laboratory ashore all samples were dried in an oven at 60°C. Some size frequency distribution studies were carried out by routine analytical techniques (sieving, settling, pipetting). X-ray

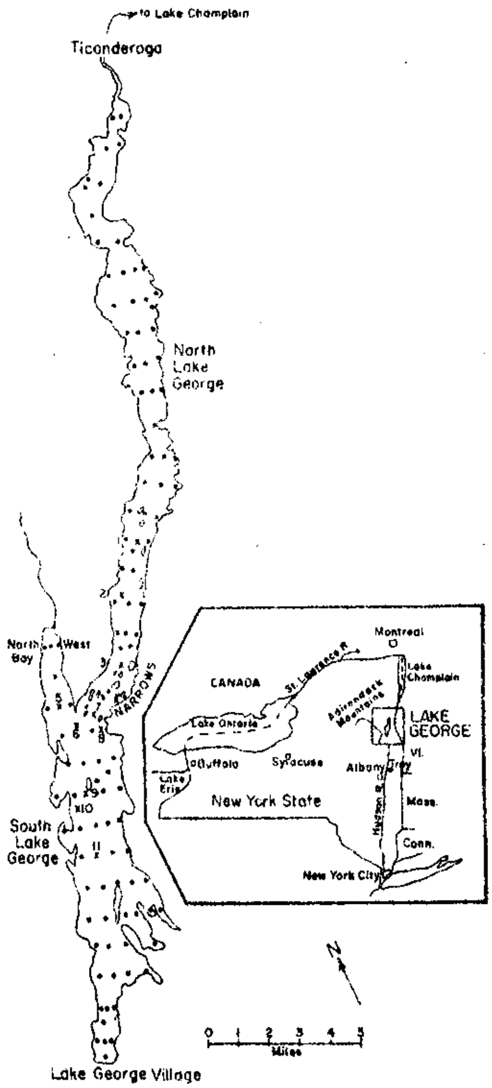


**Figure 1. Index map of Lake George, New York, showing sampling stations and manganese nodule occurrences, with inset map of New York State. X marks nodule occurrences. The numbered stations correspond to sample numbers in Table 1.**

diffraction analysis with a General Electric XRD-5 instrument equipped with a $CuK_{\alpha}$ tube and nickel-filtered radiation was used to identify the mineralogy of sediments and nodules.

The samples for chemical analysis were dried at 105°C. The results were expressed as percent of the total dried sample. Several iron-manganese nodules from each station were ground up together. Hence, each analysis represents an average for several nodules from each station. The concentration of iron and manganese in the nodules was determined by optical emission spectroscopy. Copper, cobalt, nickel and zinc were determined with a Perkin-Elmer 303 atomic-absorption spectrophotometer. The density of nodules was determined with a Jolly Balance using carbon tetrachloride as a liquid.

In the chemical analysis of sediments each analysis represents the uppermost 5 cm below the water-sediment interface. All investigated trace elements were determined with a Perkin-Elmer 303 atomic-absorption spectrophotometer.

## LAKE BASIN MORPHOLOGY, GEOLOGY AND SEDIMENTS

Lake George is located in the eastern Adirondack Mountains of New York State (Fig. 1). The lake is 32 mi long and varies in width from 1 to 3 mi. The surface area is 44 sq mi. There are about 109 mi of shoreline with many small bays. The maximum depth of the lake is 195 ft. The mean lake level height is 319 ft. The lake drains at its northern end into Lake Champlain via Ticonderoga Creek (Lake Champlain level is about 92 ft). There is only one major source of surface water, discharging into Northwest Bay. The lake is divided into two parts, North Lake George and South Lake George.

According to Newland and Vaughan (1942), Lake George occupies a graben surrounded mostly by Precambrian metamorphic, plutonic, and igneous bedrock, for example, gneisses and schists, syenite, granite and gabbro. At a few places along the shore in the south basin are outcrops of the Cambrian Potsdam sandstone and Little Falls dolomite.

The lake bed is covered with a silty clay or clayey mud with a high organic content. The surface coloration of the sediments is usually dark gray to black. Preliminary investigation for organic carbon shows values between 0.15 percent at the beach to 7.46 percent in the middle of the southern basin. Tough, greasy glacial clays of brown coloration occur locally on the lake bottom. Sandy sediments are mainly restricted to the shallow parts in the southern basin where the Potsdam sandstone crops out, and to zones close to shore. The distribution, mineralogy, trace element configuration and contents of organic carbon of the sediments will be more fully described by Schoettle and Friedman (in prep.).

## LOCATION OF NODULES

Nodules occur in several places (Fig. 1). They are especially abundant in the Narrows, a constricted island dotted area which separates the north and south Lake George basins, and along a stretch of lake extending for about 5 mi to the north and south of the Narrows. The depth at which nodules occur varies between 21 and 36 m.

## DESCRIPTION OF THE NODULES

In the European literature, particularly that of Sweden, an extensive terminology has developed describing the shapes of fresh water nodules (*see* summary by Naumann, 1930). Terms differentiating between the manifold shapes of nodules include such examples as buckshot ore, bean ore, pea ore, potato ore, cake ore, biscuit ore, and penny ores. An especially manganese-rich variety is known as soot ore (Russerz). In our study these terms were not adopted, instead we used descriptive adjectives. We recognize three different types of nodules on the basis of shape: spherical nodules, discoidal nodules, and lumps.

### Spherical Nodules

These nodules are of dark brown coloration and consist of alternating concentric layers of porous and dense material. Their size varies between <1 mm and 1 cm. They come closest to the pea ore terminology of Naumann (1930). We distinguish two types of spherical nodules: those with a rough porous surface and well developed concentric layers (Fig. 2) and those with a flat smooth surface in which the concentric layering is less well developed. The former have a higher Mn/Fe ratio and are analogous to the soot ores of Naumann (1930). Small nodules of both varieties contain a nucleus which consists of detrital quartz or feldspar particles, of spore capsules or of clay minerals, which are recognized only under crossed nicols in thin section (Fig. 3). In large nodules the nucleus has been obscured or obliterated. In these nodules, the clay minerals of the nucleus were replaced by iron and manganese oxide or, where the nucleus consisted of organic material, the latter became oxidized. Detrital grains as nuclei in the center were observed in only a few examples of large nodules although thin section examination makes it apparent that many grains must have become incorporated in the nodules during growth.

### Discoidal Nodules

These nodules are flat and disk shaped with a thickness ranging from about 2 mm to 1 cm and a diameter of up to 6 cm. Their color is usually brown, somewhat lighter than that of the spherical nodules. Their outermost rim tends to have the darkest brown coloration (Fig. 4). These nodules come closest to the penny ores, biscuit ores, and cake ores of Naumann (1930). Their surface is usually flat and smooth.

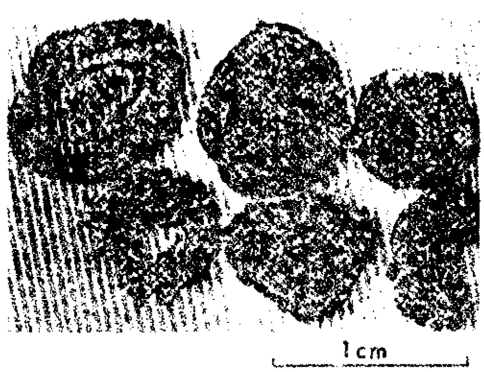


Figure 2. Spherical nodules in thin-section showing well-developed concentric layering.

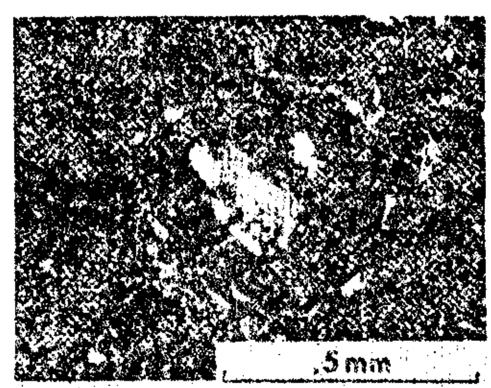


Figure 3. Nodule with clay aggregate as a nucleus (crossed nicols).

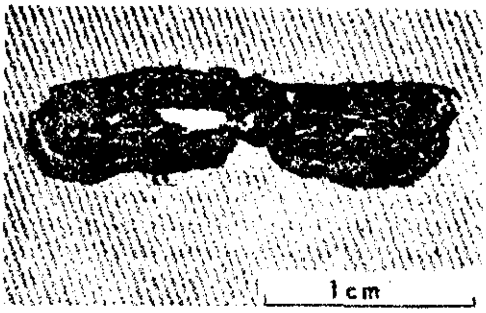


Figure 4. Discoidal nodule in thin section.

These nodules commonly consist of aggregates or crusts which have become hard on the upper surface but are soft both underneath and on the lower surface. Concentric layering has not been recognized. Usually these nodules are made up of encrusted tree bark or larger fragments of clay material or varves.

### Lumps

These nodules have the shape of angular lumps, are devoid of concentric layering, and are of brown color similar to the discoidal nodules. They are mostly fragments of clay material which became hardened on oxidation. The largest samples are about 5 × 5 × 1 cm.

## MINERALOGY

In all nodules studied, small goethite peaks were identified on X-ray examination. The manganese mineral birnessite ($\delta$ $MnO_2$) was recognized in one sample with a particularly high manganese concentration (lines 7.27, 2.44 and 1.41 Å). In others, manganese minerals were not found. The manganese minerals which are common in the marine environment, such as todokorite, ramsdellite, and psilomelane (Buser and Grütter, 1956; Manheim, 1965; and others) are absent, indicating that manganese and part of the iron appear to be present in the form of X-ray amorphous ferromanganese compounds.

The HCl-insoluble fraction of the nodules which averages 24 percent of the bulk weight consists of clay minerals, quartz, or feldspar. These recycled particles became incorporated in the nodules during growth or served as nuclei around which the nodules formed.

The clay minerals found in the sediments underlying the nodules consist of illite and chlorite with minor kaolinite (identified by the method of Andrew and others, 1960), quartz, and feldspar.

## DENSITY

The nodules studied are surprisingly light. The density ranges between 1.86 and 2.57 with an average density of 1.99 g/cm$^3$. They are, therefore, lighter than marine manganese nodules which have an average density of 2.49 g/cm$^3$ (Mero, 1965).

## CHEMICAL COMPOSITION

Table 1 gives the chemical composition (major and some trace elements) of iron-manganese nodules and underlying glacial sediments for seven sampling stations in Lake George. The underlying glacial sediments consist mostly of clay material. This table shows that both the major and the trace elements studied are enriched in the nodules in comparison with the underlying sediments.

## COMPARISONS

The concentration of manganese and iron in Lake George nodules is similar to that of other fresh water lake nodules. Fresh water nodules are enriched in iron with respect to marine nodules but tend to have a lower manganese concentration. Hence, the Mn/Fe ratio is lower in lake nodules than in marine nodules. Exceptions exist as shown by some Canadian fresh water nodules (Fig. 5) which have a higher manganese concentration than marine nodules. The lithology of the bedrock that underlies the lake is likely to have an influence on the iron and manganese concentration.

The average iron and manganese concentration of Lake George nodules falls between that of other fresh water nodules.

Table 2 compares the concentration of manganese, iron, copper, cobalt, nickel, and zinc in the nodules of Lake George with those of three other North American lakes and with average values for Swedish-Finnish lakes and for nodules from the marine environment. With the exception of the Canadian lakes (Grand Lake, Nova Scotia), the iron and manganese concentrations are similar for the nodules of all lakes and quite dissimilar to those of the marine environment. The nodules of the Canadian lakes are unusual in their higher manganese and lower iron concentrations; they are, in fact, closer in composition to marine nodules than to fresh water nodules. The Lake George nodules have a higher concentration of trace elements than those of all other known fresh water lakes, but a lower concentration than marine nodules. The enrichment of trace elements in Lake George nodules is related to

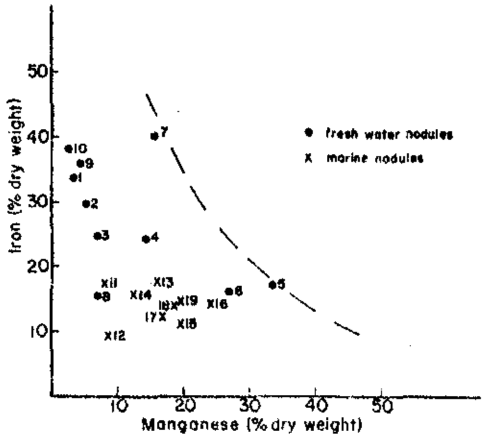


Figure 5. Scatter diagram showing the average concentration of iron and manganese in nodules from various localities, both marine and fresh water.

1. Lake George, N.Y.
2. Lake Champlain, N.Y. (Johnson, 1969)
3. Lake Michigan (Rossmann and Callender, 1968)
4. Lake Oneida, N.Y. (Dean, 1969)
5. Grand Lake, Nova Scotia (Harriss and Troup, 1969)
6. Ship Harbour Lake, Nova Scotia (Harriss and Troup, 1969)
7. Mosque Lake, Ontario (Harriss and Troup, 1969)
8. English Lakes (Gorham and Swaine, 1965)
9. Swedish Lakes (*from* Manheim, 1965)
10. Karelian-Finnish Lakes (*from* Manheim, 1965)
11. Baltic Sea (*from* Manheim, 1965)
12. White Sea (Gorshkova, 1931, *from* Manheim, 1965)
13. Atlantic Ocean (Mero, 1962)
14. Atlantic Ocean (Mero, 1965)
15. Pacific Ocean (Skornyakova and others, 1962, *from* Manheim, 1965)
16. Pacific Ocean (Mero, 1962)
17. Pacific Ocean (Riley and Sinhaseni, 1958, *from* Manheim, 1965)
18. Pacific Ocean (Goldberg, 1954)
19. Indian Ocean (Mero, 1965)

bedrock lithology surrounding the lake, with its abundance of basic plutonic rocks, including gabbros.

## SEDIMENTS IN WHICH THE NODULES OCCUR

All ferromanganese nodules in Lake George occur on or in the uppermost 5 cm of a diagenetically solidified tough, greasy, varved brown clay. These clays are relict sediments derived from an earlier glacial lake.

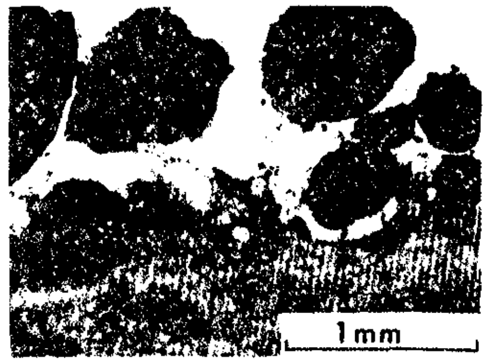


Figure 6. Nodules sitting on surface of lake-bottom clay. Note one detached particle consisting of a clay aggregate.


Figure 7. Nodules in clay near surface of lake floor.

Where nodules are slightly covered with sediment, their size increases upward toward the surface. The largest nodules occur always on or slightly below the surface of the varved clays (Figs. 6 and 7). Some areas of the lake are solidly floored with a carpet of nodules (Fig. 8). Figure 9 shows incipient nodules consisting of fine oxide aggregates about 1.5 cm below the floor of the lake. Figure 10 shows these aggre-

TABLE 1. CHEMICAL COMPOSITION OF LAKE GEORGE, NEW YORK, IRON-MANGANESE NODULES AND UNDERLYING GLACIAL SEDIMENTS

| | Mn % | Fe % | Cu % | Co % | Ni % | Zn % |
|---|---|---|---|---|---|---|
| Nodules | | | | | | |
| 1 | 2.55 | 40.20 | 0.1529 | 0.0350 | 0.0912 | 0.1341 |
| 3 | 2.25 | 30.70 | 0.1433 | 0.0250 | 0.0600 | 0.0734 |
| 6 | 1.50 | 38.00 | 0.2200 | 0.0180 | 0.0590 | 0.1126 |
| 8 | 0.40 | 35.50 | 0.0790 | 0.0090 | 0.0480 | 0.0500 |
| 9 | 16.65 | 18.80 | 0.0939 | 0.0223 | 0.0777 | 0.1192 |
| 10 | 0.40 | 43.70 | 0.1369 | 0.0340 | 0.0775 | 0.1254 |
| 11 | 1.25 | 27.80 | 0.0938 | 0.0109 | 0.0783 | 0.2098 |
| Average | 3.57 | 33.52 | 0.1314 | 0.0220 | 0.0702 | 0.1177 |
| Glacial Sediments | | | | | | |
| 1 | 0.15 | 4.80 | 0.0080 | 0.0100 | 0.0220 | 0.0410 |
| 3 | 0.28 | 4.30 | 0.0220 | 0.0160 | 0.0240 | 0.0284 |
| 9 | 0.30 | 4.50 | 0.0240 | 0.0130 | 0.0220 | 0.0296 |
| 11 | 0.57 | 6.30 | 0.0160 | 0.0150 | 0.0880 | 0.0500 |
| Average | 0.32 | 4.97 | 0.0175 | 0.0135 | 0.0390 | 0.0372 |

The numbers for each sample are station numbers (*see* Fig. 1), hence the glacial sediments designated 11 underlie the iron-manganese nodules designated by the same number.

gates parallel to bedding surfaces in varved clays; these aggregates are believed to have formed on these surfaces when they were exposed.

The nodules were never found associated with modern clayey sediments. Only rarely are the glacial clays which contain the nodules covered by modern sediments, and where covered, this cover consists of a clayey mud <5 mm thick.

## ISOTOPE ANALYSES

### Radiocarbon Date

A radiocarbon date of 3316 ± 475 yrs was calculated by Mobil Research and Development Laboratory, Dallas, Texas (SM 1322). This represents an average age for many nodules which were needed to provide enough material for a radiocarbon date analysis. As this date is an average age for many nodules it does not explain if nodules are forming at the present time. However, this confirms the absence of modern sedimentation in those areas where nodules floor the lake bottom. Active currents have for at least 3300 yrs kept the nodules exposed by sweeping sediment away.

### Stable Carbon Isotopes

Mass spectrographic analysis by Isotopes (a Teledyne Company) gave a $\delta_0(C^{13})_{PDB}$ value

TABLE 2. COMPARISON OF THE CHEMICAL COMPOSITION OF LAKE GEORGE NODULES WITH OTHER LACUSTRINE NODULES AND DEEP OCEAN NODULES

| Weight % | Lake[1] George | Lake[2] Champlain | Lake[3] Michigan | Grand[4] Lake | Swedish L[5] Finnish L | Deep[6] Ocean |
|---|---|---|---|---|---|---|
| Mn | 3.57 | 5.37 | 6.10 | 33.7 | 3.80 | 19.6 |
| Fe | 33.52 | 29.47 | 20.20 | 17.1 | 39.40 | 13.8 |
| Cu | 0.131 | 0.006 | 0.018 | 0.001 | 0.004 | 0.38 |
| Co | 0.022 | 0.023 | 0.020 | 0.020 | 0.010 | 0.30 |
| Ni | 0.070 | n.d. | 0.027 | 0.027 | 0.004 | 0.64 |
| Zn | 0.118 | 0.024 | 0.032 | 0.163 | 0.005 | 0.04–0.40 |

[1] This study (average of seven analyses; *see* Table 1)
[2] Johnson, 1969
[3] Rossmann and Callender, 1969
[4] Harriss and Troup, 1969
[5] Data averaged *from* Manheim (1965)
[6] Data averaged *from* Manheim (1965) and Mero (1965)

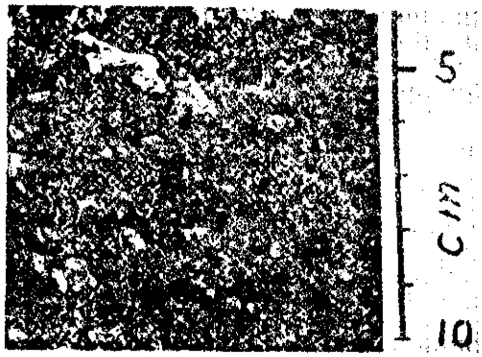


Figure 8. Nodules covering floor of lake.

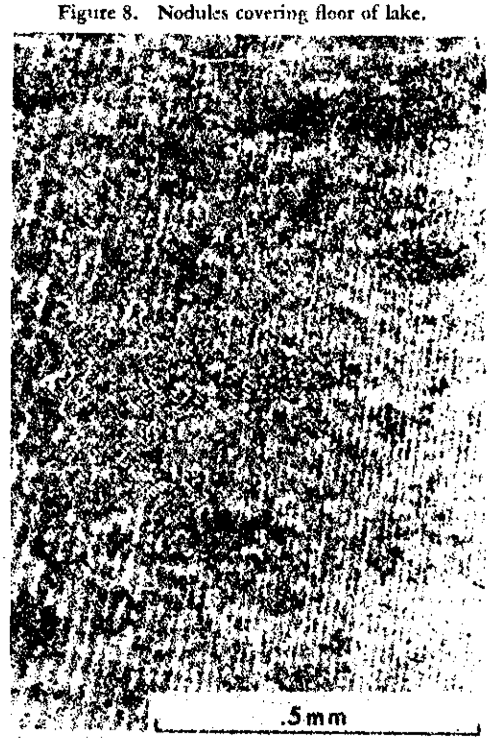


Figure 9. Incipient nodules consisting of fine oxide aggregates about 1.5 cm below lake floor.

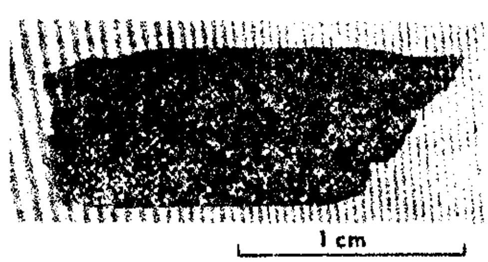


Figure 10. Nodules aligned parallel to bedding surfaces of varved clay.

of −24.1 ‰ for the nodules (Isotopes No. 3 1245 232). This value is in the range for land plants (−22 to −28 ‰), in fact, very close to the mean value for land plants (−25 ‰; Craig, 1953; Wickman, 1952). The carbon in the nodules is mostly derived from local plant matter, such as tree bark and spore capsules. The main reason for making a stable carbon isotope analysis was to find out if bacterially produced methane was involved in forming the nodules. Bacterial fractionation in which methane is formed leads to strongly negative $\delta_0(C^{13})_{PDB}$ values (Rosenfeld and Silverman, 1959). The $\delta_0(C^{13})_{PDB}$ value obtained for the nodules (−24.1 ‰) indicates that bacterial fractionation with methane as a product was not a stage in the history of the nodules.

## ORIGIN

This paper was intended to be descriptive and place on record our discovery. The origin of the nodules will be studied in detail later in connection with pH, Eh, and cation concentration analysis of bottom and interstitial waters. The effect of organic matter and of bacteria will also be taken up at that time.

At this stage we want to outline some of the constraints within which the theory of origin will have to be formulated. These constraints include:

1. Oxidization conditions are necessary on the lake bottom. Reducing conditions would lead to dissolution of the nodules.

2. A low rate of sedimentation is essential so that the nodules are not buried. The fact that the nodules overlie glacial varved clays indicates a low sedimentation rate. Active currents on the floor of the lake keep the nodules exposed and supply manganese containing oxygen-rich waters.

3. Varved clays enclose clay aggregates which have been replaced by oxides and which increase in size toward the surface (incipient nodules). This observation suggests that manganese and iron-enriched pore water is oxidized near the surface, leading to oxide precipitation.

4. The nodules form around nuclei which usually consist of clay and less commonly of spore capsules, detrital particles, or bark. The clay nuclei are broken fragments of hardened oxidized surface crust. We do not know the mechanism responsible for breaking the hardened crusts into fragments but suspect that alternating freezing and thawing (Moore, 1914) during the stage of a lower lake level, or

subaqueously formed shrinkage cracks in the clay (Burst, 1965) may be responsible.

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