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GEOCHEMISTRY OF LAKE MICHIGAN MANGANESE NODULES[1]

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Abstract. Manganese nodules, similar in composition to other freshwater and shallow marine nodules, occur on the sediment surface of Green Bay and northern Lake Michigan. Samples have been analyzed for their iron, manganese, calcium, magnesium, sodium, potassium, inorganic carbon, organic carbon, and total nitrogen content. The nodules average 20% iron and 6% manganese. The trace metal content (copper, zinc, cobalt, and nickel) of the samples is considerably lower than that of marine material.

Interstitial water is one of the major contributors of manganese and iron for the growth of nodules in Lake Michigan. Cores of Green Bay sediment show an inverse relationship between sedimentary and interstitial manganese with the sedimentary manganese increasing to a maximum at or near the sediment-water interface. Sedimentary iron remains fairly constant throughout the length of these cores while interstitial iron decreases slightly toward the sediment-water interface. In addition, lake water may be more than a passive contributor of iron and manganese. There are indications that as much as one-half of the manganese found in lake water is particulate. The source of this material is believed to be the iron deposits of the Canadian Shield that have been subsequently leached of manganese and iron.

INTRODUCTION

This study is part of a general geochemical study of Lake Michigan being conducted by the Great Lakes Research Division of the University of Michigan. The manganese nodule study began in the fall of 1967 following discovery of nodules in Green Bay during that summer (Rossmann and Callender, 1968). During the summer of 1968, extensive sampling of Lake Michigan and Green Bay was carried out from the research vessels MYSIS and INLAND SEAS.

Manganese nodules are a major constituent of the surficial sediments of Green Bay (Figures 1, 1A, and 1B), especially in the north. Southern Green Bay is relatively nodule-free. Nodules at some locations cover as much as 100% of the surface area and are found occasionally to a depth of 0.5 m. In contrast, northern Lake Michigan nodules are much less abundant and have not been found below the sediment surface. Nodules may be more widespread in northern Lake Michigan than they appear in Figures 1, 1A, and 1B because detailed sampling of the area has not been completed.

SAMPLE COLLECTION

Surface sediment and nodules were obtained with a Ponar grab sampler. Short cores (up to 2 m) were collected using a Benthos gravity coring device fitted with a heavy-duty plastic core barrel that could be separated into 20 or 30 cm sections. Station positions were located by resection, or dead reckoning beyond the 20 mi radar range. Eh, pH, and temperature were measured on the upper 5 cm of each core section by inserting glass, platinum, reference electrodes, and a glass thermometer into the wet sediment. The electrodes were connected to a Beckman Model G pH meter. Readings were taken 2 to 3 min after insertion, or when meter

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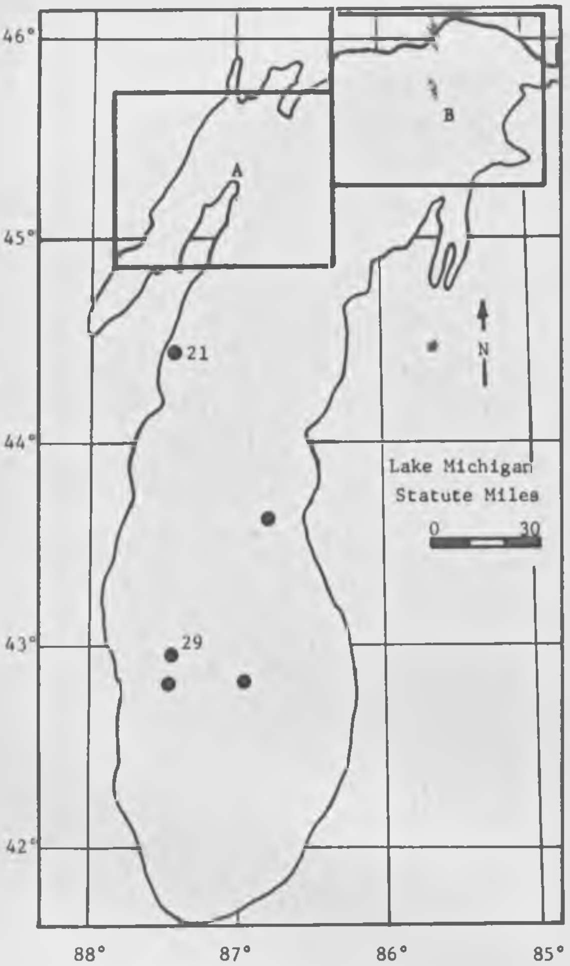

FIG. 1. Occurrences of manganese nodules and manganiferous coated sand grains in Lake Michigan. Numbers refer to station numbers listed in Table 1.

drift was negligible. The short equilibrium time for most readings indicated that the samples were well buffered and "poised". A 5 cm thick portion of sediment from the top of each core section (usually three sections) was placed in a stainless-steel sediment squeezer (Manheim, 1966) and the interstitial fluid expressed into 80 ml pyrex culture tubes. Originally the interstitial fluid was stored in an unpreserved condition but after precipitation of iron hydroxide occurred, the samples were preserved with 1 ml of concentrated HCl. The sediment discs that remained after squeezing were wrapped with Saran wrap and stored for laboratory analysis.

LABORATORY PROCEDURES

Nodules were dried at 90°C for 48 hr and ground to a fine powder. The powdered nodules were used for all chemical and mineralogical analyses.

The total carbon and carbonate carbon contents of the nodules were determined by quantitative dichromate oxidation and by reaction with hydrochloric acid, and measurement of the CO_2 evolved (Maciolek, 1962). The organic carbon content was computed by subtracting the amount of carbonate carbon from the total carbon content. The total nitrogen content was determined by micro-Kjeldahl distillation (Jackson, 1958) of the solution which remained from the total carbon analysis (Maciolek, 1962).

The calcium, magnesium, manganese, iron, and trace metal contents of the nodules were determined on concentrated nitric acid-hydrogen peroxide extracts of powdered nodule samples. Calcium, magnesium, manganese, and iron were determined by atomic absorption spectroscopy using standard addition. Some of the iron contents were also determined colorimetrically using orthophenanthroline to develop the color (Shapiro and Brannock, 1962). Zinc, nickel, copper, and cobalt were determined by atomic absorption using a standard curve. Sodium and potassium were determined using flame emission.

Interstitial water and lake water were both analyzed for iron and manganese by the same colorimetric techniques. Iron was determined on hydrochloric acid extracts using dipyridyl to develop the color (Strickland and Parsons, 1965). Manganese was analyzed using a modification of the leucomalachite green method described by Yuen (1958). Zinc, nickel, and copper in the interstitial water were measured by atomic absorption using a standard curve.

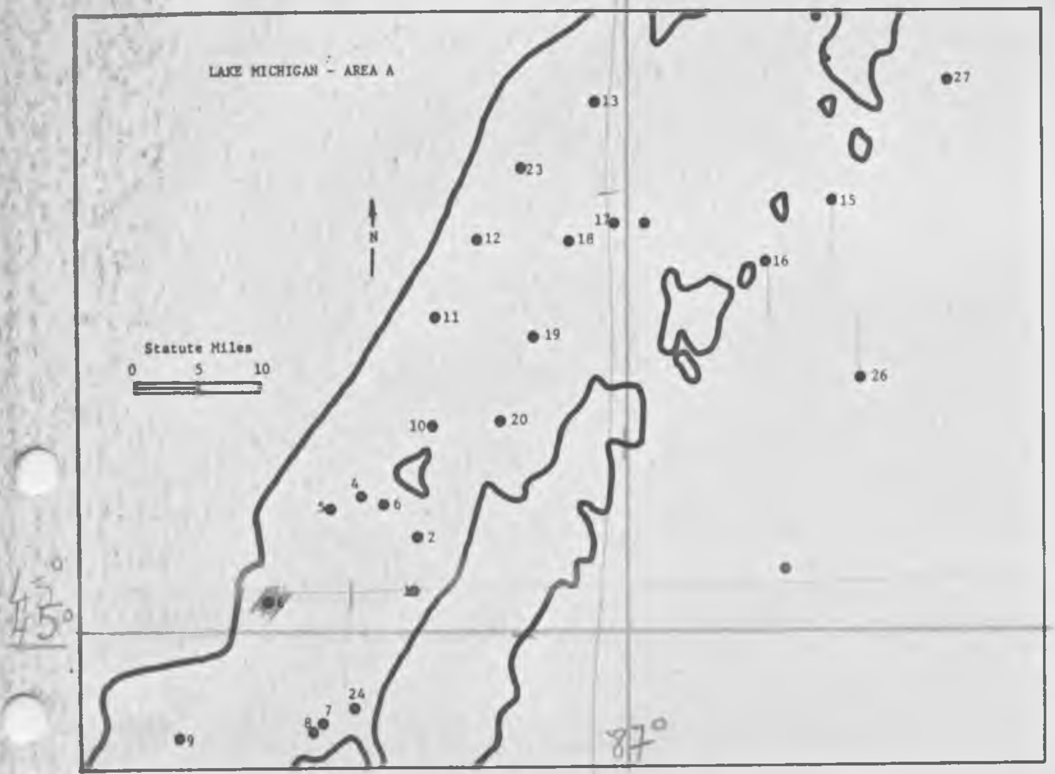

FIG. 1A. Occurrences of manganese nodules and manganiferous crusts in Green Bay. Numbers refer to station numbers listed in Table 1.

Mineralogy of the nodules was examined by X-ray diffraction analysis using a powder pack. Other attempts at phase identification were made by infrared spectroscopy and differential thermal analysis.

CHARACTERISTICS

Lake Michigan-Green Bay nodules are usually spherical and have a feldspar or quartz nucleus. Only those from Station 22 (Fig. 1B) are discoidal. The spherical nodules may or may not have a concretionary structure consisting of alternating brown and black bands (dried sample). The discoidal nodules consist mainly of detrital sand- and silt-sized material cemented by ferro-manganese material. The majority of nodules are 0.5 to 1.0 mm in diameter and occur at water depths of 10 to 65 m (Table 1).

Results of chemical analysis of the nodules are listed in Tables 1 and 2. Constituents of the nodules exhibit the high degree of variability (Stations 3 and 9) expected of lacustrine and shallow-water marine nodules. Comparison of the average composition of Lake Michigan nodules with those of lacustrine and deep ocean nodules (Table 3) reveals that the chemical composition of Lake Michigan nodules lies between these two limits.

Components of the Lake Michigan nodules, like other nodules, are more concentrated than the same components in lake water, interstitial water, and sediments (Table 4). However, Lake Michigan nodules are 5 to 50 times less efficient in

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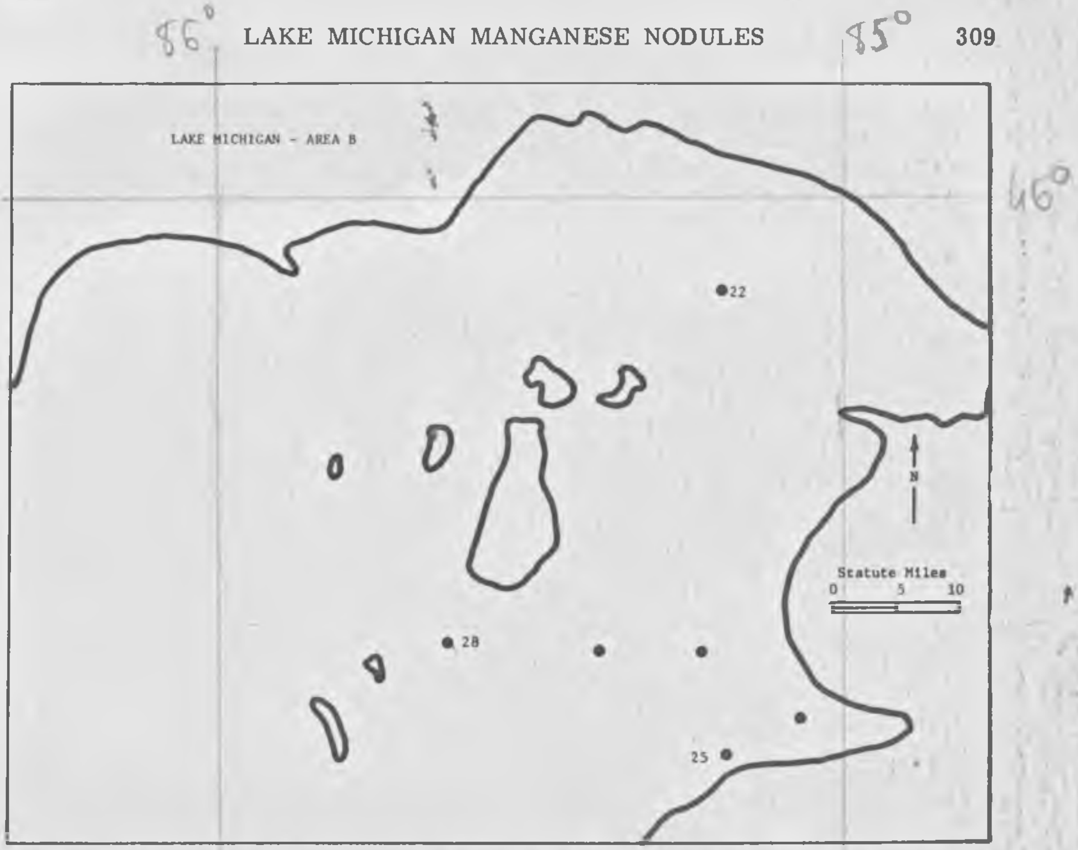

FIG. 1B. Occurrences of manganese nodules in northern Lake Michigan. Numbers refer to station numbers listed in Table 1.

concentrating trace materials than deep ocean nodules. For the components compared (Mn, Cu, Ni, and Zn), the average concentrations in sea water and in lake water are nearly the same (Sverdrup et al. 1942; Manheim, 1965). The concentrations of these elements in Lake Michigan interstitial water are generally higher than those of oceanic interstitial water (Brooks et al. 1968; Presley et al. 1967). Whatever the concentration process, it is believed to be the same for each of the trace metals because of the strong positive relationships that exist between them.

The iron and manganese phases of the nodules appear to be loosely structured hydrated oxides and hydroxides of these metals. The phases are so poorly ordered that X-ray diffraction work has yielded no positive results. Infrared spectroscopy has yielded the expected water and hydroxide peaks. Differential thermal analysis also yielded a water peak. Direct chemical evidence for their hydrated nature is the positive relationship between iron plus manganese plus organic carbon versus loss on ignition at 1000°C minus total carbon (Fig. 2).

ENVIRONMENT OF FORMATION

Though environmental conditions are favorable for the growth of nodules in portions of middle and southern Lake Michigan, few nodules exist in these areas. These conditions are similar to those of northern Lake Michigan and the nodule areas of Green Bay (Table 5). In southern Green Bay where few occurrences of nodules have been found, active sedimentation of silts and muds and occasional

TABLE 1. Lake Michigan manganese nodule chemistry.

Station[1]	Mn	Fe	Ca	Mg	Total Nitrogen	Inorganic Carbon	Organic Carbon	Insoluble	Water loss @ 1000°C	Diameter, mm	Depth, m
1	1.22	29.92	1.07	0.33	0.09	0.14	0.98	31.8	18.2	0.50	28.5
2	2.04	16.22	1.00	0.38	0.18	0.24	1.71	36.0	13.2	0.50	22.0
3	4.88	20.52	1.00	0.38	0.28	0.30	0.41	31.6	15.2	0.07	17.0
3	8.29	17.17	0.86	0.22	0.16	0.52	1.33	44.3	13.1	0.35	17.0
3	16.51	11.53	1.31	0.43	0.25	0.64	0.93	21.0	17.7	0.59	17.0
4	21.68	6.40	2.48	0.40	0.42	0.71	2.11	24.8	21.2	0.50	32.0
5	2.50	23.34	0.64	0.33	0.07	0.16	0.32	43.8	9.8	0.50	13.5
6	0.85	39.45	0.71	0.17	0.09	0.12	0.98	19.3	17.0	1.00	17.0
7(2)	10.24	21.78	2.55	0.92	0.18	0.86	0.49	8.6	12.0	7.00	28.5
8	6.81	6.77	0.79	0.65	0.19	0.30	0.83	53.8	15.4	1.50	18.0
9	4.54	28.55	0.93	0.26	0.09	0.22	1.07	30.7	13.6	1.77	18.0
9	4.54	30.10	1.55	0.18	0.08	0.76	1.25	23.0	16.1	5.00	18.0
10	1.13	35.39	0.84	0.22	0.06	0.16	0.56	21.0	23.2	1.00	14.5
11	15.76	19.90	1.04	0.31	0.23	0.73	1.36	25.2	20.9	0.50	23.0
12	9.68	23.77	1.21	0.19	0.18	0.63	1.00	18.7	21.7	0.50	23.0
13	9.95	25.71	1.00	0.31	0.20	0.57	0.85	18.6	20.6	2.40	35.7
14	1.02	36.91	0.60	0.13	0.03	0.22	0.69	16.5	12.2		11.0
15	2.27	30.64	1.33	0.54	0.08	0.51	1.05	24.8	18.3	1.50	33.0
16	1.93	24.36	1.26	0.44	0.09	0.29	0.76	44.6	14.0	1.00	26.0
17	11.42	25.19	1.64	0.34	0.19	0.39	1.34	16.7	23.7	0.75	19.0
18	4.55	32.16	1.00	0.22	0.20	0.32	1.07	36.9	15.6	0.50	26.0
19	12.98	12.29	1.47	0.35	0.20	0.80	1.38	33.0	16.4	0.50	28.0
20	4.74	10.29	0.77	0.24	0.19	0.28	1.61	58.9	11.3	0.50	32.0
21	3.86	13.80	2.85	0.59	0.44	0.88		51.4	24.2	0.50	35.0
22	2.17	11.78	0.48	0.10	0.02	0.19	0.06	74.8	5.1	30.00	10.0
23	3.42	11.26	0.45	0.10	0.08	0.42	0.37	59.5	8.0	0.50	
24	13.74	15.42	1.50	0.36	0.10	0.71	1.03	21.3	19.8	7.00	23.0
25	2.11	21.67	3.23	0.87	0.06	0.96(?)	0(?)	38.7	15.3	1.00	
26	5.60	20.59	1.84	0.72	0.08					0.50	62.5
27	6.62	16.92	1.35	0.51	0.28					0.50	47.0
28	1.38	21.31	0.37	0.30	0.06	0.12	0.14	73.4	4.5	1.00	35.7
29(3)	0.49	tr.	0.25	0.35	0.01	0.07	0.64	88.5	1.9	0.30	
29	0.35	tr.	0.18	0.32	0.02	0.52	0.17	87.3	3.2	0.15	

[1] Weight percent [2] Manganiferous crust on dolomite [3] Manganiferous coated sand grains

TABLE 2. Lake Michigan manganese nodule trace chemistry.

Station	%Zn	%Ni	%Cu	%Co	%Na	%K
1	0.0163	0.0101	0.0045	0.0252	0.0500	0.0300
2	0.0330	0.0143	0.0072	0.0168	0.0430	0.0430
3	0.0184	0.0174	0.0100	0.0274	0.0650	0.1000
3	0.0185	0.0146	0.0049	0.0268	0.0440	0.0440
3	0.0314	0.0315	0.0058	0.0266	0.0630	0.0920
4	0.0595	0.0571	0.0074	0.0273	0.0590	0.0590
5	0.0109	0.0125	0.0050	0.0125	0.0450	0.0550
6	0.0207	0.0126	0.0066	0.0179	0.0660	0.0250
7	0.0073	0.0122	0.0049	0.0170	0.0340	0.1220
8	0.0176	0.0176	0.0040	0.0125	0.0350	0.1960
9	0.0151	0.0100	0.0038	0.0125	0.0400	0.0350
9	0.0075	0.0125	0.0038	0.0151	0.0200	0.0150
10	0.0153	0.0172	0.0054	0.0099	0.0340	0.0340
11	0.0338	0.0473	0.0050	0.0224	0.0500	0.0700
12	0.0252	0.0272	0.0049	0.0173	0.0400	0.0590
13	0.0378	0.0323	0.0055	0.0224	0.0500	0.0600
14	0.0290	0.0222	0.0054	0.0197	0.0390	0.0150
15	0.0501	0.0200	0.0075	0.0225	0.0650	0.0350
16	0.0256	0.0072	0.0059	0.0197	0.0590	0.1040
17	0.0309	0.0338	0.0053	0.0251	0.0390	0.0340
18	0.0243	0.0151	0.0038	0.0201	0.0450	0.0500
19	0.0456	0.0838	0.0054	0.0249	0.0640	0.0600
20	0.0319	0.0249	0.0050	0.0149	0.0900	0.1050
21	0.0703	0.0474	0.0065	0.0149	0.1660	0.0450
22	0.0068	0.0125	0.0037	0.0200	0.0150	0.0500
23	0.0130	0.0150	0.0037	0.0178	0.0150	0.0150
24	0.0100	0.0200	0.0055	0.0250	0.0140	0.1100
25	0.0182	0.0221	0.0069	0.0123	0.0490	0.0490
26	0.1290	0.0696	0.2180	0.0298	0.0590	0.0590
27	0.1490	0.0902	0.1850	0.0250	0.0900	0.0350
28	0.0081	0.0123	0.0039	0.0123	0.0200	0.0150
29	0.0140	0.0100	0.0040	0.0199	0.0350	0.0150
29	0.0148	0.0099	0.0049	0.0148	0.0390	0.0250

oxygen depletion in the bottom water create an unfavorable environment for nodule growth.

Availability of manganese and iron appears to control the presence or absence of nodules on a lake-wide basis. Table 6 compares various areas of Lake Michigan and Green Bay. Although the relative amounts of manganese and iron (Fe/Mn) in the interstitial water of these areas are nearly the same, the absolute amounts show a significant increase from southern Lake Michigan to Green Bay. This difference is believed to be caused by proximity to the Canadian Shield and tills derived from it.

Lake water appears to be favorable everywhere for nodule growth (Table 4). Eh, pH, sediment type, and possibly dissolved oxygen are those factors that appear to be critical. Preliminary laboratory equilibria experiments of the nodules with lake water indicate that at equilibrium lake water has an Eh of +400 mv or greater. Maximum and minimum Eh and pH values for the sediment and lake water give rise to the stability fields presented in the Eh-pH diagrams of Fig. 3. Iron is stable only in the $Fe(OH)_3$+H_2O state both in sediment and lake water, a fact reflected by the nearly constant average percentages of iron in the lake's surficial and underlying sediments (Table 4). This constant precipitation is also shown by a decrease in interstitial iron near the sediment-water interface. However, iron is so abundant that not all is precipitated until contact with lake water. In the sedimentary environment manganese is stable in the Mn^{+2} state and precipitates as a hydroxide when the interstitial fluid encounters more oxidizing conditions near the sediment surface. Cores have shown an increase in sedimentary manganese near their surfaces.