

GEOCHEMISTRY OF FERROMANGANESE CRUSTS, MANGANESE CARBONATE CRUSTS, AND ASSOCIATED FERROMANGANESE NODULES FROM GREEN BAY, LAKE MICHIGAN

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ABSTRACT

The differential solubility of ferromanganese oxides can lead to stratigraphic separation of iron and manganese. Results of chemical analysis of a sequence of ferromanganese nodules overlying iron-rich crusts in northern Green Bay show that selective ion transport is important in concentrating manganese and associated trace elements near the oxygenated water-sediment interface.

Manganese carbonate, which cements ferromanganese nodules, occurs in dark-gray silty sands that are located adjacent to the organic-rich muds of southern Green Bay. These muds contain an average of approximately 3.5 ppm ($6 \times 10^{-5} M$) interstitial Mn and 2.8 meq/l carbonate alkalinity. Thermodynamic calculation shows that interstitial water approaches equilibrium with $MnCO_3$ in the upper 10 cm of sediment. This carbonate has a composition— $(Mn_{73}Ca_{22}Fe_5)CO_3$, and has been identified as rhodochrosite.

INTRODUCTION

Marine manganese nodules are now recognized as an economic, exploitable resource of manganese and the major accessory metals cobalt, nickel, and copper. Considerable financial investment has already been expended in mapping potential deposits, developing mining and chemical separation methods, and conducting *in situ* pilot plant operations. In view of this situation, it is most important to understand the geochemical processes that control regional variations in nodule chemical composition. Such variation will be one of the most important factors in determining which deposits constitute an economically exploitable ore body.

Most current theories concerning the origin of marine ferromanganese nodules rely on one of several mechanisms to account for chemical composition; metals are derived from the reaction of sea water with sub-marine volcanics (Bonatti and Nayudu, 1965), diagenetic mobilization of metals within the sedimentary column (Lynn and Bonatti, 1965), or direct precipitation of metals from sea water overlying the ocean floor (Goldberg, 1954; Goldberg and Arrhenius, 1958). Regional variation in nodule composition can result from variation in one source mechanism (i.e., regional differences in the type of volcanism), or from the combination of several mechanisms which may influence nodule composition in slowly-versus-rapidly accreting deposits (e.g., direct precipitation versus diagenetic mobilization). Price and Calvert (1970) have suggested that regional variations in nodule composition reflect the broad pattern of sedimentation in the Pacific Ocean.

While Green Bay, Lake Michigan is not an ocean basin, it does possess some similar attributes. The range of nodule-associated sediment types (sands, muds, biogenetic organic matter) is similar, and Green Bay interstitial water chemistry (particularly Fe and Mn) shows striking similarities to profiles from the Pacific and Arctic Oceans (Bischoff and Ku, 1970; Bischoff and Sayles, 1972; Li et al., 1969). The range in Fe/Mn ratios of Green Bay nodules varies from shallow marine to deep ocean values, and Green Bay nodules contain the Fe and Mn minerals (goethite, todorokite, birnessite) so often attributed to marine

nodules (Tooms et al., 1969). Green Bay exhibits a sediment-trap effect similar to the Pacific Ocean in that the northeast part of the Bay is isolated from major sediment inputs (Figure 1) much like the

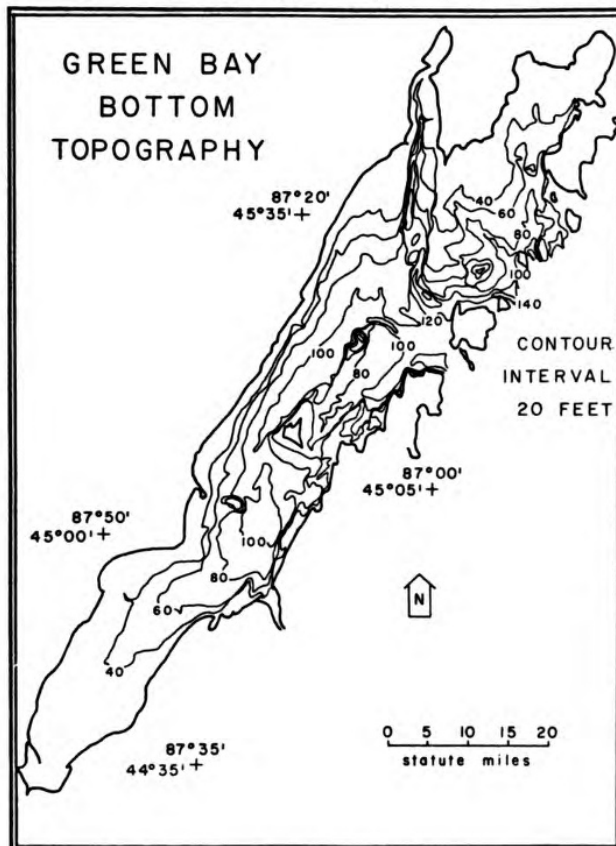


Figure 1. Bathymetry of Green Bay, Lake Michigan (from Moore and Meyer, 1969).

vast area of the central Pacific Ocean.

With the exception of Co, Cu, and Ni, the minor, and trace element content of Green Bay and Lake Michigan nodules is similar to marine nodules (Table 1). In addition, Green Bay nodules have much higher Ba contents which reflect the presence of psilomelane, a Ba-rich manganese dioxide characteristic of some manganese ore deposits. The effects of sulfate upon nodule chemistry can be evaluated by comparing Green Bay with oceanic nodule occurrences because the low sulfate content of freshwater precludes a solubility control for Ba (Church and Wolgemuth, 1972) or a diagenetic control for Fe, in the form of FeS_2 (Cheney and Vredenburg, 1968), so commonly cited for the marine environment.

Therefore, the many similarities between Green

Bay, Lake Michigan nodules and shallow- to deep-water marine nodules, in combination with the less complicated sedimentary and geochemical nature of the fresh water occurrence, make the study of Green Bay, Lake Michigan ferromanganese nodules a potentially important contribution to the understanding of processes affecting the chemical composition of marine nodules.

TABLE 1

COMPARISON OF AVERAGE LAKE MICHIGAN AND OCEANIC ELEMENTAL CONCENTRATIONS IN FERROMANGANESE NODULES (wt.%)

Element	Green Bay	Deep-Sea ^a
As	0.0475	0.0500 ^b
Ba	0.956	0.250 ^c
Cd	0.0012	0.0010
Co	0.0134	0.28
Cu	0.0032	0.40
Fe	19.8	11.7
Mn	8.9	19.0
Mo	0.0033	0.038
Ni	0.0358	0.58
Org. C	0.83	0.10
Pb	0.0100	0.10
Sr	0.0162	0.0850
An	0.0405	0.04-0.40

^a Manheim (1965)

^b Sevast 'yanov (1967), Black Sea

^c Arrhenius (1963)

COLLECTION OF SAMPLES

Samples for this study were collected during August 1971 and June 1972 using the University of Michigan's Research Vessels INLAND SEAS and MYSIS. Ferromanganese nodules, crusts, and associated sediments were obtained with a Ponar dredge, Benthos gravity corer, or an airlift (underwater vacuum cleaner). Nodules were separated from most of the bulk sediment by passing the material through 2.0, 1.0, and 0.5 mm (sieve opening) sieves. The separated nodules were stored in plastic bags.

Benthos gravity cores (8 cm diameter) were extruded in an upright position and 1- to 2-cm slices were placed in linear polyethylene bottles using a plastic spatula. A detailed stratigraphic description was made of the cores as they were sampled. Subsequently the core samples were frozen and freeze-dried at the laboratory in Ann Arbor. Ponar samples containing a well-preserved stratigraphic record of ferromanganese nodules and crusts were sectioned in the sampling bucket in order to obtain representative samples of these important ferromanganese segregations. All subsampling of Ponar grabs was done using plastic utensils, and samples were placed in plastic bags.

All samples were transported in plastic containers to the laboratory where core samples were freeze-dried and nodules/crusts were oven-dried at 60°C for up to 72 hours. Ferromanganese nodules and crusts were hand-picked to separate the nodule/crust material from each other and from any other sedimentary particles.

ANALYSIS OF SAMPLES

The dried, concentrated nodule/crust samples were ground in an agate mortar to pass through a 200-mesh nylon sieve. Sediment samples were ground to a 200-mesh powder using a Spex Mixer-Mill equipped with a tungsten-carbide mill and ball. Sample powders were extracted with 10% hydrochloric acid and several additions of 30% hydrogen peroxide over a period of 2 days. The insoluble residue (mainly silicates in the form of quartz, feldspar, and clays) was separated from the soluble material by centrifugation and decantation. This residue was then collected on preweighted filter paper in order to determine the amount of insoluble residue. The soluble portions were made up to volume in 50-ml volumetric flasks and stored in polyethylene bottles.

All ferromanganese nodule and crust samples were analyzed for arsenic, barium, cadmium, calcium, cobalt, chromium, copper, iron, lead, magnesium, manganese, nickel, potassium, strontium, and zinc by atomic absorption spectrophotometry. Sodium was analyzed by flame emission spectrophotometry. Most elements were determined with a Jarrell-Ash MVA spectrophotometer while arsenic, barium, chromium, strontium and sodium were determined using a Perkin-Elmer 403 AA/AE spectrophotometer. Standard machine parameters and sample treatment techniques were used (Jarrell-Ash, 1970; Perkin-Elmer, 1968). All standards were prepared in 10% hydrochloric acid using either commercial (Fisher Scientific Company) or laboratory prepared standards. Interference from high concentrations of iron, manganese, calcium, barium, sodium, and potassium on the atomic absorption of minor and trace elements was found to be negligible with the exception of high concentrations of iron on cobalt, copper, and nickel and high concentrations of calcium and barium on strontium (Rossmann, 1973). While samples for strontium analysis are diluted, those for Co-Cu-Ni are run undiluted and therefore the final results for these metals in high-iron samples must be considered somewhat too high (up to 20% of the mean value).

Final concentrations of metals (weight percent or parts per million total nodule/crust weight) were determined using a computer least squares curve-fitting program that compared the absorption readings of several standards (usually four) with those of samples.

Mineral identifications were performed using X-ray diffraction analysis; either a powder camera with manganese-filtered iron radiation, or glass slide smears with copper radiation and a scintillation counter with pulse energy discrimination and a carbon monochromator.

GEOCHEMISTRY OF GREEN BAY, LAKE MICHIGAN

Because of the many similarities between Green Bay and oceanic ferromanganese nodules, it is clear that a comparative study of the two environments would yield valuable data that could serve to elucidate the critical factors that control marine nodule composition. Scientists at the University of Michigan and the University of Wisconsin (Edward Callender, Carl J. Bowser, Ronald Rossmann) have been conducting geochemical studies on Green Bay since 1967 and a wealth of information now exists. Since the geochemistry of marine ferromanganese nodule localities (Pacific Ocean, Indian Ocean) is known to the oceanographic scientific community, a brief description of the geochemistry of Green Bay, Lake Michigan is presented in order to point out some of the similarities and differences between marine basins and this important fresh-water nodule locality.

Hydrography

Green Bay is approximately 200 km long, 20 km wide, and has a mean depth of 17 m (Figure 1). The

area of the bay is 4200 km² and the volume is 70 km³, approximately one-seventieth the volume of Lake Michigan. The bay can be divided into two distinct areas; a southern and a northern basin, separated from one another by Chamber Island, a large island situated in the middle of the bay (Figure 1). The major river inputs to Green Bay are the Fox River (annual flow of 4 km³/year) and the Menominee River (annual flow of 3 km³/year) which constitute 70% of the total annual river inflow to the bay (10 km³/year, approximately one-third of the total river input to all of Lake Michigan). The Fox River is the major source of domestic and industrial wastes to southern Green Bay (Schraufgael, 1967).

Environmental Characteristics

The southern basin of Green Bay is in an advanced state of tropic evolution. Primary production is seven times higher in southern Green Bay than in northern Green Bay and northern Lake Michigan (Schelske and Callender, 1971). Water transparency (Secchi disc) is substantially lower in southern Green Bay (2 m in the south versus 5.5 m in the north), a condition that reflects greater suspended particulate matter composed chiefly of phytoplankton and detritus.

During observed periods of thermal stratification, dissolved oxygen concentrations in southern Green Bay hypolimnetic waters fall below 30% saturation, while those in northern Green Bay are generally at levels greater than 80% saturation. Southern basin surface waters consistently have higher oxygen saturation levels than northern basin waters, reflecting the increased productivity in the southern waters. Bottom-water pH is lowest in the southern basin during stratification (pH 7.8). With the onset of mixing in the fall and spring, bay water is isothermal and near saturation with oxygen. The orthophosphate content is higher (2.0 µg/l versus <0.5 µg/l) and the nitrate lower (36 µg/l versus 89 µg/l) in the southern Green Bay relative to northern Green Bay, indicating increased nutrient inputs (PO₄) and greater phytoplankton utilization of nitrate (Schelske and Callender, 1971).

Sediments

The southern basin of Green Bay is predominantly underlain by gelatinous dark-gray to black, organic-rich muds and silts (Figure 2) exhibiting redox potentials between +300 and 0 mv. Much of this sediment was derived from Fox River inflow which contains large quantities of suspended material. The northern basin of green bay is underlain by brown, dominantly quartzose, fairly well-sorted, medium to fine sand containing ferromanganese nodules 0.5 to 5 mm in diameter. Redox potentials of these sands are greater than +300 mv, usually in the range of +400 to +500 mv (Figure 3).

The first major deposits of ferromanganese nodules in the Great Lakes were discovered in Green Bay in 1967 (Rossmann and Callender, 1968). Throughout Green Bay the nodules are generally spherical in shape, ranging in size from 0.5 mm to 2 cm in diameter. They are dark brown to black in color when wet and orange-brown to dark gray when dry. Many of the smaller nodules are agglomerates of ferromanganese coated sand grains. Nodule nuclei consist mainly of quartz and feldspar with lesser occurrences of clay, limestone, and wood fragments. Microscopic examination of the nodules reveals a typical concentration structure of alternating iron- and manganese-rich bands. In northern Green Bay, nodules comprise 10 to 80 percent of the associated sands. The nodules and associated sands are generally covered by a light gray-brown flocculent material comprised of silt and organic detritus.

Nodules occur in areas of low to negative sedimentation rates, and in a few localities off the mouths of rivers where they have become buried by

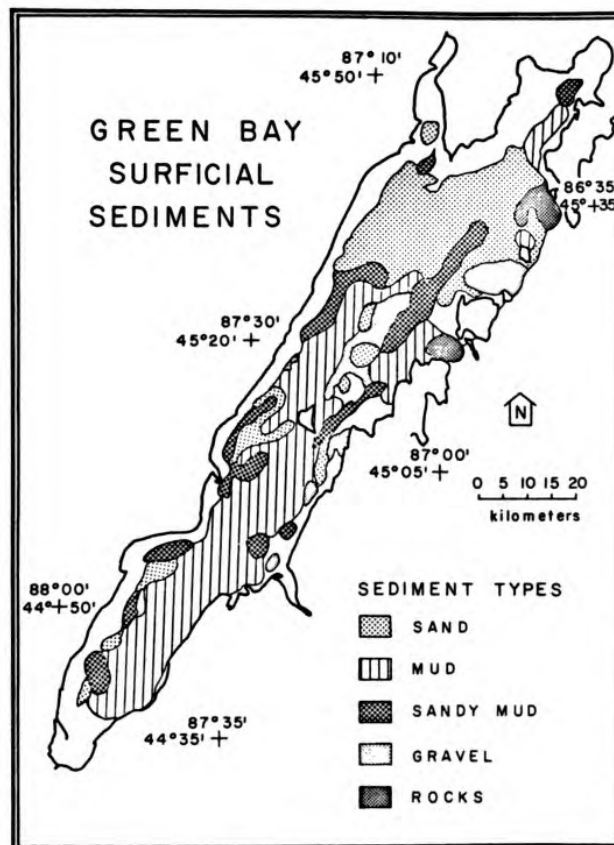


Figure 2. Distribution of surficial sediment types in Green Bay (from Moore and Meyer, 1969).

finer sediment. Generally, only a few centimeters to one-half meter of sand overlies stiff glacial clay that probably predates the Chippewa low lake level of approximately 10,000 years ago (Hough, personal comm.). A minimum accretion rate for ferromanganese nodules in Green Bay is calculated to be 0.5 mm/1000 years using the above date. While sands in northern Green Bay currently exist under low, or even negative, sedimentation rates, the muds of southern Green Bay represent local sedimentation rates up to a maximum of approximately 10 cm/y. This figure was estimated from seismic profiling which shows that up to two meters of sediment accumulated locally in 18 years (Moore and Meyer, 1969). Based on their data, the average sedimentation rate for the southern part of Green Bay has been estimated to be 1 cm/y.

Table 2 shows the average chemical composition of organic-rich muds from southern Green Bay, oxidized sand-silt-clay from northern Green Bay, and ferromanganese nodules from throughout Green Bay. The iron content of the oxidized sediments is only twice that of the organic muds illustrating that iron can occur not only in oxide minerals but also with clay minerals and organic matter. However, manganese is 14 times more concentrated in oxidized than in the aquatic environment. While most other transition metals show a preference for oxidized sediments, Cu and Cr show a preference for dark-gray, organic-rich muds (Table 2).

Geochemical Process

Based on extensive studies of Green Bay water/

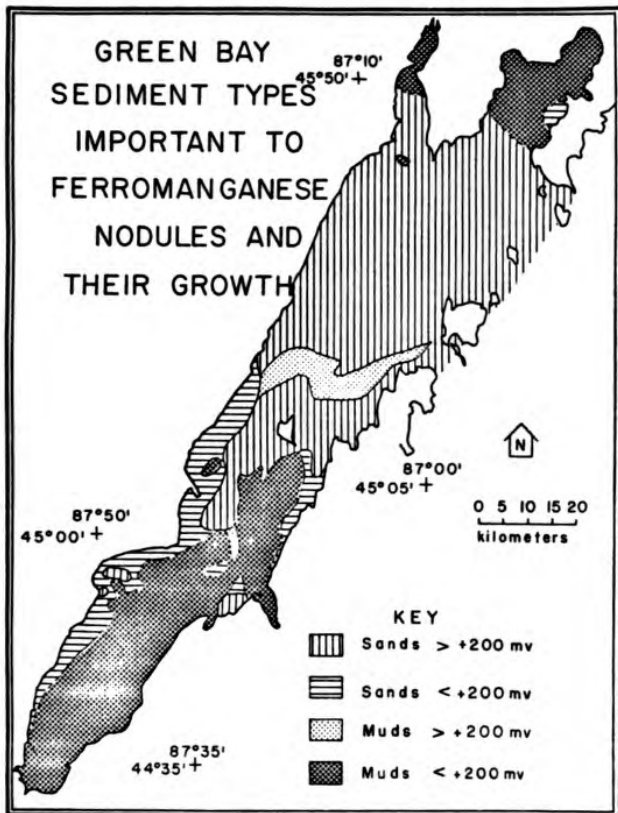


Figure 3. Distribution of surficial sediments important to the occurrence of ferromanganese nodules in Green Bay (from Rossmann, 1973).

sediment geochemistry, the following mechanism for incorporation of trace metals into nodules is proposed (Callender *et al.*, 1973):

- (1) Input of trace metals from rivers as dissolved and particulate matter.
- (2) Precipitation of metals in oxygenated lake water, utilization by living organic matter, or sorption onto particle surfaces.
- (3) Sedimentation and subsequent burial of trace metals and organic matter.
- (4) Sedimentary diagenesis resulting in the resolubilization of some trace elements and the complexation/chelation of others.
- (5) Diffusion and mass transport of metals toward sediment-water interface and subsequent precipitation as iron and manganese oxides (nodules) when interstitial water comes in contact with relatively oxygen-rich lake water.

Trace elements in sediment interstitial fluids can be selectively sorbed by either iron- or manganese-oxide phases. The Fe/Mn oxide ratio of resultant ferromanganese nodules will be a function of the relative inputs of the two metals into the water-sediment interface zone, the redox potential of waters in which precipitation of oxides occur, and the relative precipitation rates of the two oxide phases. Under sufficiently low redox potentials (+100 mv at pH 7), iron is insoluble whereas manganese remains in solution, but at higher E_h values

TABLE 2

CONCENTRATION (PARTS PER MILLION) OF ACID-SOLUBLE TRANSITION METALS IN GREEN BAY SEDIMENT AND FERROMANGANESE NODULES

Element	Dark Muds (S. Green Bay)	Oxidized Sand-Silt-Clay ^a (N. Green Bay)	Ferromanganese Nodules (Green Bay)
No. Samples ()	(23)	(20)	(60)
Iron	100,500	195,600	273,000
Manganese	4,300	62,000	128,000
Arsenic	171	388	578
Barium	331	3,479	12,500
Cobalt	60	93	160
Copper	97	33	41
Chromium	176	90	49
Nickel	85	358	458
Zinc	357	420	460
Organic Carbon ^b	6.5	2.8	0.83
E_h , \pm Mv	+84	+413	---
Fe/Mn	23.4	3.1	2.1

^abulk sediment includes ferromanganese nodules

^bweight percent

(+400 mv at pH 7) both metals are insoluble (Krauskopf, 1957). Normally, oxygenated lake waters would have sufficiently high redox potentials to keep both iron- and manganese-oxide phases insoluble. Solubilization of these phases would also be enhanced by a general lowering of pH that occurs in hypolimnetic waters which are deoxygenated in response to the breakdown of organic matter (Callender *et al.*, 1973).

The trace element content of freshwater nodules is generally lower than nodules from the deep-sea (Table 1). This is due to the faster growth rate of freshwater nodules (Harris and Troup, 1970), ocean/lake water compositional differences, complexation of trace elements in organic-rich source materials (muds), and the fact that freshwater nodules have generally higher iron to manganese ratios. Both iron and manganese oxides occur as discrete phases in nodules and these phases differ in their sorption/desorption characteristics in near neutral waters (Parks, 1965).

The trace element selectivity of iron- and manganese-oxide phases in nodules is confirmed by statistical analysis of electron microprobe and atomic absorption data (Rossmann *et al.*, 1972). Strong correlations are found between As, P and Si with iron and between Ba, Co, Cu, Mo, Ni, Sr, and Zn with manganese (Table 3). Rossmann (1973) believes that the compositional variability of ferromanganese nodules in Green Bay, Lake Michigan, results from their position relative to sources of metals which may be more or less available depending upon the degree of organic complexation or distance from the source.

FERROMANGANESE CRUSTS AND ASSOCIATED NODULES

The location of ferromanganese crusts and associated nodules discussed in this report is shown in Figure 4. Samples from station 71-108 represent an iron-rich crust overlain by ferromanganese nodules and flocculent material. The stratigraphic description of this station is given below:

"Thin layer of gray-brown flocculent material (0.5 mm thick) over 3 cm brown silty medium sand containing 75% of 0.5-2.0 mm nodules, over 0.5-1.0 cm of same but oxidized to orange-brown layer forming patches of crusts."

TABLE 3
CORRELATION COEFFICIENTS FOR GREEN BAY
FERROMANGANESE NODULES

Element	Fe	Mn	Ni	Cu	Co	Ba	Mo	Sr	Mg	Zn	Na	K	Cr
Fe	1.00	0.72	0.64	0.45	0.50	0.39	0.61	0.47	0.14	0.56	0.12	0.17	0.54
Mn		1.00	0.75	0.67	0.84	0.70	0.93	0.84	0.14	0.78	0.26	0.35	0.36
Ni			1.00	0.88	0.71	0.14	0.76	0.43	0.11	0.95	0.18	0.21	0.23
Cu				1.00	0.70	0.06	0.75	0.40	0.22	0.90	0.38	0.33	0.17
Co					1.00	0.65	0.91	0.81	0.13	0.80	0.28	0.45	0.26
Ba						1.00	0.62	0.88	0.07	0.23	0.08	0.30	0.34
Mo							1.00	0.76	0.01	0.84	0.22	0.26	0.20
Sr								1.00	0.24	0.49	0.34	0.42	0.30
Mg									1.00	0.09	0.56	0.71	0.10
Zn										1.00	0.18	0.25	0.22
Na											1.00	0.78	0.09
K												1.00	0.19
Cr													1.00

Samples from this station represent an excellent example of differential precipitation of first iron and then manganese oxides in a vertical sedimentary sequence as first proposed by Krauskopf (1957). Since many trace elements are associated with the manganese oxide phase, this differential oxidation mechanism is one process that can lead to predictable compositional differences in ferromanganese nodules.

Station 71-107 is a little to the west of 71-108 and more directly under the influence of an organic-rich mud source (Figure 3) that is supplying large amounts of iron for nodule growth (Rossman *et al.*, 1972).

"One cm of 0.5-2.0 mm nodules (75%) with brown fine silty sand over 3 mm orange-brown oxidized crust with nodules, over gray-brown clayey fine sand."

Stations 71-19, 72-20, and 72-34 are located off the Oconto River (Figure 4). Here nodules cemented by manganese carbonate are found within muddy sands. A stratigraphic description of a benthos core from station 72-20 is given below:

- 0-1 cm: Olive-gray sandy silt over olive-gray sand with 60% nodules, 2-5 mm diameter.
- 1-2 cm: Olive-gray slightly silty sand with 60% nodules, 1-5 mm diameter.
- 2-3 cm: Mottling with light-brown sand containing 50% nodules, cemented nodules 3 cm diameter.
- 3-4 cm: Mottled olive-gray and light-brown sand with 40% nodules.
- 4-5 cm: Light olive-gray nodules, 1-5 mm diameter, in mottled light and medium dark-brown sand with irregular distribution of cemented nodules.
- 5-6 cm: Carbonate crusts cementing nodules more apparent, otherwise same as 4-5 cm.
- 6-8 cm: Light gray-brown silty sand with 40-50% nodules, 1-6 mm diameter.
- 8-10 cm: Same except at base of interval where nodules are 1 mm diameter.
- 10-12 cm: Grading into olive-gray silty sand with very few nodules, 5 mm diameter.
- 12-14 cm: Mottled dark olive-gray and grayish-green silty fine sand.

In southern Green Bay, ferromanganese nodules and crusts are found in dark olive-gray muddy sands that are usually located adjacent to fine-grained, organic-rich muds (Figure 3). In northern Green Bay, nodules and crusts occur in relatively well-sorted medium-fine sands to a depth of 5 cm. The nodules range from 0.5 mm to 2 cm in diameter and are ovoid to discoid in shape. In some instances the nodules grow together to form a crust (71-98; Figure 4) or are cemented by carbonate (71-19, 72-20, 72-34; Figure 4). Some of the larger nodules consist of a black core and a thin, red rim (70-9, >2 mm diameter; Appendix). Scattered clastic grains occur in the cores and rims.

Composition - Ferromanganese Crusts and Nodules

The chemical composition of ferromanganese crusts and associated nodules are shown in Table 4 and in the Appendix. Because crusts and nodules from station 71-108 present an ideal stratigraphic sequence of iron and manganese oxides that have resulted from differential oxidation (Krauskopf, 1957), the chemical composition of these separated phases is considered in detail (Tables 4 and 5). Stratigraphically, nodules in the flocculent material overlie nodules in medium sand which in turn overlie orange-brown crusts. Nodules were separated into three size fractions which were analyzed in duplicate. The data in Table 4 show that the Fe/Mn ratio decreases with increasing nodule diameter until it falls slightly below 1 for nodules greater than 2 mm in diameter. The manganese content of these larger nodules (20 wt%)

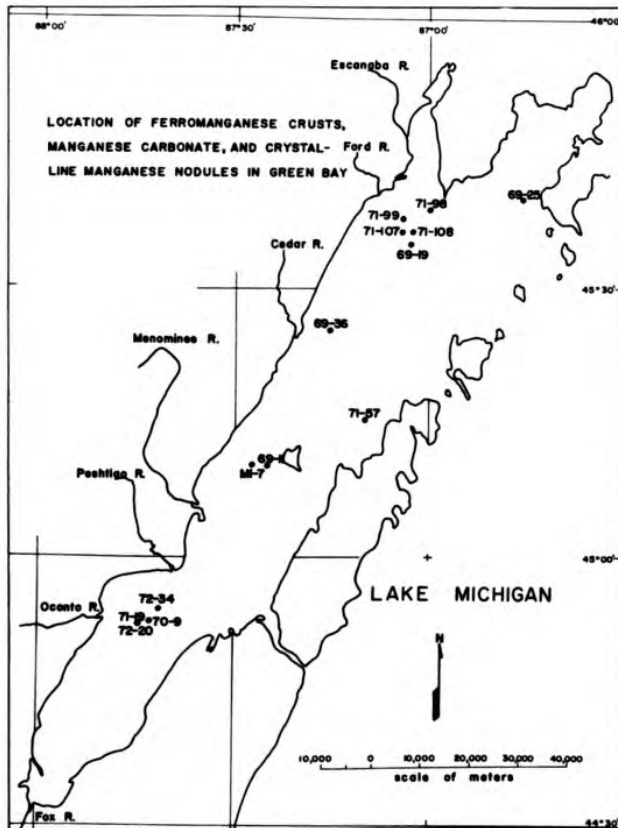


Figure 4. Location of ferromanganese crusts, manganese carbonate, and crystalline manganese nodules discussed in this paper.

TABLE 4
 CHEMICAL COMPOSITION OF FERROMANGANESE CRUSTS AND ASSOCIATED NODULES FROM STATION UM-CB-71-108

	WEIGHT PERCENT										PARTS PER MILLION										% Soluble
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	ZN					
Red Crust	0.9	20.1	0.1	0.7	895.	941.	0.	0.	24.	22.	6.	872.	43.	6.	31.	124.					
	0.13	0.78	0.02	0.21	94.7	513.5	0.0	0.0	0.0	0.0	0.0	288.7	0.0	0.0	3.1	48.9					
Brown Crust	3.6	22.4	0.6	0.8	1342.	579.	0.	0.	92.	36.	6.	1038.	88.	6.	59.	266.					
	1.31	7.82	0.00	0.12	275.2	303.5	0.0	0.0	0.0	14.9	0.0	358.9	0.0	0.0	27.9	120.6					
Nodules 0.5-1 mm diam.	6.7	30.3	0.5	1.2	2110.	166.	715.	12.	83.	54.	14.	583.	135.	79.	130.	444.					
	1.19	5.18	0.00	0.00	650.1	34.0	203.8	0.2	17.5	0.5	5.1	92.2	12.1	3.8	4.0	29.8					
Nodules 1-2 mm diam.	12.1	28.6	1.1	1.4	2007.	149.	657.	16.	156.	25.	18.	664.	226.	91.	175.	555.					
	1.24	5.19	0.10	0.03	163.1	21.0	240.1	6.9	22.3	0.3	2.7	119.9	2.7	29.3	4.0	38.7					
Nodules >2 mm diam.	19.9	18.7	2.5	1.4	2374.	219.	608.	19.	186.	18.	23.	912.	299.	57.	229.	610.					
	1.76	3.45	0.47	0.02	176.2	19.0	356.3	6.0	9.8	2.0	5.0	179.4	16.1	7.0	8.4	4.0					
Nodules (Floc) <0.3 mm diam.	1.3	2.3	0.1	0.9	4539.	682.	0.	7.	12.	34.	62.	2620.	30.	50.	37.	234.					
	0.00	0.12	0.01	0.02	205.3	118.0	0.0	0.0	0.0	1.5	0.0	250.5	10.3	14.6	1.4	80.1					
Nodules (Floc) 0.3-1mm diam.	4.7	22.8	0.5	1.3	1947.	219.	637.	13.	64.	54.	20.	1954.	126.	121.	112.	406.					
	0.28	4.30	0.00	0.18	76.1	4.5	348.1	4.8	7.0	0.0	1.0	940.4	21.5	27.9	5.9	14.8					
Nodules (Floc) >1 mm diam.	19.7	17.1	2.4	1.8	2296.	318.	602.	17.	189.	17.	25.	2013.	322.	76.	256.	693.					
	1.23	3.27	0.59	0.07	226.4	121.5	250.7	2.0	20.8	0.5	5.3	971.7	15.3	16.2	9.5	8.5					

Notes: (1) Concentration in wt. % or ppm total sediment weight
 (2) Analyses for each sample presented as mean (upper) and standard deviation (lower)
 (3) A standard deviation of 0.0 means that there is only one subsample analysis.

is similar to that (19 wt%) of average deep-sea nodules (Table 1). On the other hand, Cu is 200 times less concentrated in the Green Bay nodules while Co and Ni are 15 and 20 times, respectively, less concentrated in the freshwater nodules. The Cu, Co, and Ni contents of Green Bay, Lake Michigan nodules are comparable to similar-sized nodules from Loch Fyne, Scotland (Calvert and Price, 1970). A look at correlation coefficients for the data on crusts and nodules from 71-108 (Table 5) shows that in general most trace elements are strongly associated with the manganese-oxide phase, an observation which is true for Green Bay nodules in general (Table 3). While a strong correlation exists between As and Fe, the correlation between Fe and Cr-Pb is much less pronounced even though all these elements are inversely correlated with Mn. Although Cr and Pb may be associated to some degree with the iron-oxide phase (Calvert and Price, 1970), they may also be associated with detrital silicates that constitute the bulk of insoluble residues in Green Bay nodules.

The very high Ba contents of Green Bay nodules (up to 6 wt%) and the very high degree of correlation of Ba with Mn in these nodules (Tables 3 and 5) must be explained. The manganese mineral psilomelane has been identified in ferromanganese nodules from Green Bay, Lake Michigan (Rossmann, 1973). Structurally, this mineral consists of treble strings of MnO₆ octahedra joined by double strings to form a series of tunnels running in the direction of the b-axis. The tunnels are occupied by a double row of barium ions and water molecules which are crystallographically indistinguishable (Wadsley, 1953). Wadsley (1953) assigned the mineral a formula of (Ba, H₂O)₂Mn₅O₁₀. Although there is a high degree of association between Mn and Ba contents, psilomelane has been identified in Green Bay nodules that are rich in Fe. Nodule sample GB-69-25 listed in the Appendix has a Fe/Mn ratio of 5 and contains psilomelane as well as the iron mineral goethite (Rossmann, personal communication). Considering the relationship between Mn and Ba in Green Bay nodules, this sample appears to have a greater amount of Ba (Figure 5) which may be attributable to the presence of psilomelane.

Composition - Manganese Carbonate Crust

The average chemical composition of manganese carbonate crusts and cement from Green Bay is shown in Table 6. Considering that the carbonate is approximately 75% pure, the crust/cement consists mostly of MnCO₃ (77%) with some CaCO₃ (17%) and minor FeCO₃ (4.5%). Taking into account the variability in chemical composition of four manganese carbonate samples from Green Bay, the composition of the carbonate is calculated to be: (Mn_{72.5} Ca_{22.9} Fe_{4.7})CO₃. The d(211) X-ray diffraction spacing for rhodochrosite is 2.84Å (ASTM 7-268). The measured 211 spacing for carbonate from station 72-34 is 2.86Å which compares favorably with that above.

The composition of manganese carbonate from Green Bay is compared with similar material from other freshwater and marine environments in Table 7. Most notable is the absence of Mg (less than 0.15 wt%) in the carbonate from Green Bay relative to the marine environment (1.6 wt%; Table 6). Generally, the trace-element content of the manganese carbonate from Green Bay is much lower than that of associated ferromanganese nodules (Table 8). The Ni content of the carbonate cement is comparable to the more manganese-rich nodules from station 71-19 while the Na and K content is somewhat greater in the carbonate. It is apparent that most minor and trace elements so common in the ferromanganese nodules are excluded from substitution in the carbonate lattice.

DISCUSSION

Ferromanganese nodules from Green Bay, Lake Michigan, are similar in composition to nodules from the Baltic Sea (Manheim, 1965; Winterhalter, 1966), the Black Sea (Sevast'yanov and Volkov, 1967), the White

TABLE 6
CHEMICAL COMPOSITION OF MANGANESE CARBONATE CRUSTS FROM GREEN BAY, LAKE MICHIGAN AND LOCH FYNE, SCOTLAND

Element	Green Bay ^a	Loch Fyne ^b
Wt. % Mn	28.6 (5.57)	18.0
" Fe	1.6 (1.29)	1.9
" Ba	0.1 (0.09)	0.1
" Ca	5.3 (5.82)	10.4
" Soluble	84 (4)	75
ppm Mg	1213	15,700
" Na	377 (177)	---
" As	115 (346)	10
" Cd	8 (4)	---
" Co	28 (85)	20
" Cr	8 (16)	---
" Cu	3 (6)	40
" K	1217 (947)	8,700
" Ni	28 (62)	50
" Pb	45 (83)	20
" Sr	24 (11)	425
" Zn	44 (61)	20

^apresented as mean and standard deviation of four (4) samples.

^bCalvert and Price (1970)

TABLE 7
COMPOSITION OF MANGANESE-BEARING CARBONATES IN RECENT SEDIMENTS

Locality	Composition	Source
Baltic Sea	(Mn ₇₀ Ca ₃₀) CO ₃ -(Mn ₆₀ Ca ₃₂ Mg ₈) CO ₃	Manheim (1961)
Baltic Sea	(Mn _{56.8} Ca _{25.5} Mg _{9.7} Fe _{8.0}) CO ₃	Hartmann (1964)
Eastern Marginal Pacific	(Mn ₅₀₋₈₀ Ca ₅₀₋₂₀) CO ₃	Lynn and Bonatti (1965)
Lake Pinnus-Yarvi, Karelia	(Mn _{50.6} Ca _{45.3} Fe _{4.0}) CO ₃ to (Mn _{34.2} Ca _{8.9} Fe _{37.1}) CO ₃	Shterenberg et al. (1966)
Loch Fyne, Scotland	(Mn _{47.7} Ca _{45.1} Mg _{7.2}) CO ₃	Calvert and Price (1970)
Green Bay, Lake Michigan	(Mn ₆₄ Ca ₃₂ Fe ₄) CO ₃ to (Mn ₈₁ Ca ₁₆ Fe ₃) CO ₃	This work

Sea (Gorshkova, 1931) and Lake Ontario (Cronan and Thomas, 1970, 1972). Nodules from these localities have Mn/Fe ratios that are generally less than unity. This is in contrast to shallow-water nodules from Loch Fyne, Scotland (Calvert and Price, 1970) and Jervis Inlet, British Columbia (Grill et al., 1968) which have Mn/Fe ratios that approach 8. Nodules from both these localities contain abundant todorokite, a manganese-oxide mineral that contains abundant elemental impurities which can be accommodated structurally (Fron del et al., 1960; Straczek et al., 1960).

TABLE 8
 CHEMICAL COMPOSITION OF MANGANESE CARBONATE CRUST AND ASSOCIATED NODULES FROM STATION UM-GB-71-19

	WEIGHT PERCENT													PARTS PER MILLION													% Soluble						
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	ZN	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR		CU	K	NI	PB	SR	ZN
Carbonate	31.4	1.1	0.1	2.9	985.	456.	0.	8.	10.0	15.	3.	1553.	51.	18.	18.	72.	31.4	1.1	0.1	2.9	985.	456.	0.	8.	10.0	15.	3.	1553.	51.	18.	18.	72.	81
Crust	0.07	0.13	0.03	1.66	816.3	2.0	0.0	1.7	0.0	0.0	0.0	413.4	28.8	0.0	2.6	1.4	0.07	0.13	0.03	1.66	816.3	2.0	0.0	1.7	0.0	0.0	0.0	413.4	28.8	0.0	2.6	1.4	
Nodules	0.6	2.2	0.0	0.5	997.	593.	819.	0.	6.	19.	3.	2065.	16.	19.	12.	33.	0.6	2.2	0.0	0.5	997.	593.	819.	0.	6.	19.	3.	2065.	16.	19.	12.	33.	12
<0.5 mm diam.	0.14	0.06	0.00	0.10	38.0	192.5	0.0	0.0	0.0	2.9	0.0	848.4	0.0	0.0	2.4	1.5	0.14	0.06	0.00	0.10	38.0	192.5	0.0	0.0	0.0	2.9	0.0	848.4	0.0	0.0	2.4	1.5	
Nodules	6.7	40.1	1.0	2.9	2486.	707.	833.	34.	56.	93.	6.	1323.	274.	374.	106.	371.	6.7	40.1	1.0	2.9	2486.	707.	833.	34.	56.	93.	6.	1323.	274.	374.	106.	371.	86
0.5-1 mm diam.	2.63	1.73	0.61	1.85	56.1	17.0	0.0	0.0	0.0	0.0	0.0	123.9	190.4	0.0	67.3	45.3	2.63	1.73	0.61	1.85	56.1	17.0	0.0	0.0	0.0	0.0	0.0	123.9	190.4	0.0	67.3	45.3	
Nodules	7.0	27.7	1.2	2.4	2152.	348.	0.	14.	57.	36.	6.	871.	74.	37.	148.	359.	7.0	27.7	1.2	2.4	2152.	348.	0.	14.	57.	36.	6.	871.	74.	37.	148.	359.	86
1-2 mm diam.	0.94	5.02	0.01	1.17	23.2	73.0	0.0	7.0	0.0	0.0	0.0	33.0	0.0	0.0	7.8	91.7	0.94	5.02	0.01	1.17	23.2	73.0	0.0	7.0	0.0	0.0	0.0	33.0	0.0	0.0	7.8	91.7	
Nodules	12.8	19.4	2.1	1.1	1968.	385.	0.	10.	60.	18.	3.	921.	69.	52.	259.	389.	12.8	19.4	2.1	1.1	1968.	385.	0.	10.	60.	18.	3.	921.	69.	52.	259.	389.	70
>2 mm diam.	1.55	0.10	0.08	0.00	94.6	50.5	0.0	0.0	0.0	0.0	0.0	135.7	11.2	0.0	17.4	170.3	1.55	0.10	0.08	0.00	94.6	50.5	0.0	0.0	0.0	0.0	0.0	135.7	11.2	0.0	17.4	170.3	

Notes: (1) Concentration in wt. % or ppm total sediment weight
 (2) Analyses for each sample presented as mean (upper) and standard deviation (lower)
 (3) A standard deviation of 0.0 means that there is only one subsample analysis.

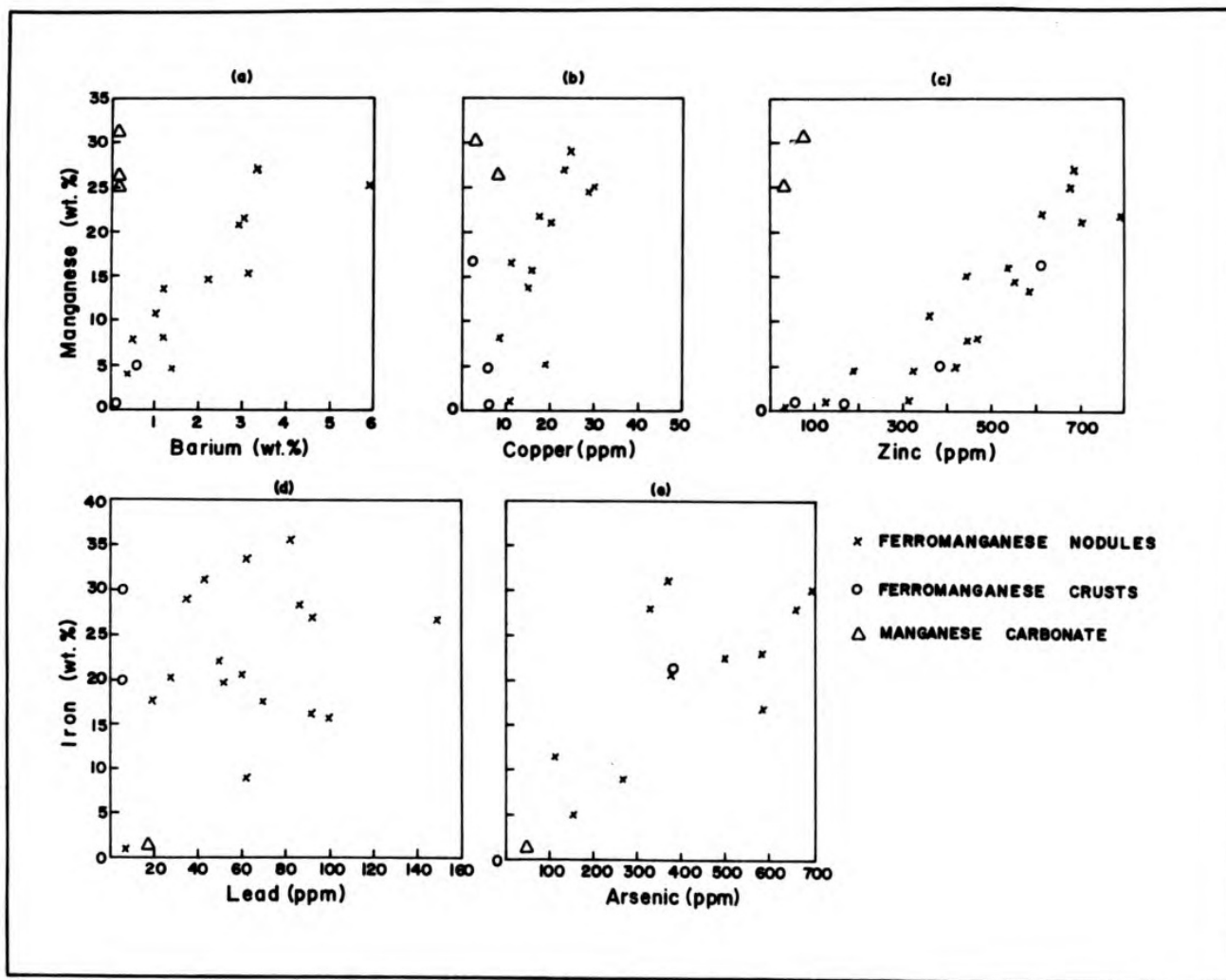


Figure 5. Inter-element relationships between manganese and barium (a), manganese and copper (b), manganese and zinc (c), iron and lead (d), and iron and arsenic (e) in Green Bay ferromanganese nodules, associated nodules, and manganese carbonate. The raw data for these scatter plots are listed in the Appendix.

Many authors have discussed the association of minor elements with manganese and iron phases in deep-sea and shallow marine ferromanganese nodules. Based on bulk chemical (Goldberg, 1954; Riley and Sinhaseni, 1958; Mero, 1962; Willis and Ahrens, 1962; Ahrens et al., 1967; Cronan, 1969) and electron microprobe analyses (Burns and Fuerstenau, 1966; Cronan and Tooms, 1968) of deep-sea nodules, correlations between Mn, Ni, Cu, K, Zn, Mg, Mo, and Ba and between Fe, Co, Pb, Ti, V, Mo, Zr, and Ce have been cited. Mineralogically, deep-sea nodules that contain todorokite have been reported to be enriched in Ni and Cu (Barnes, 1967; Cronan and Tooms, 1967); and those that contain birnessite to be enriched in Co and Pb (Barnes, 1967).

Data on the minor and trace element abundances in nodules from lakes (Ljunggren, 1955; Rossmann et al., 1972; Cronan and Thomas, 1972), the Baltic Sea (Wintertaler, 1966), and Loch Fyne, Scotland (Calvert and Price, 1970) suggest that Ba, Co, Cu, Mo, and Ni

are correlated with Mn, and V and Cr and correlated with Fe. Pb appears to be moderately correlated with Fe (Calvert and Price, 1970), and Zn moderately correlated with Mn (Rossmann et al., 1972; Cronan and Thomas, 1972). Strong correlations exist between Mn and Ba, Co, Cu, Ni, Sr, and Zn and between Fe and As in nodules and iron-rich crusts from station 71-108 (Table 5). These correlations are similar to those calculated for Green Bay nodules in general (Rossmann et al., 1972), and they suggest that the differential solubility of iron and manganese oxides does not affect significantly the partitioning of trace elements among these phases as interstitial fluids become enriched in Mn relative to Fe. However, if data from nodule localities representing different local sources of metals are compared, it is apparent that differences in the chemistry of source material result in significant differences in the minor element composition of nodules (Rossmann, 1973). Of primary importance is the proximity to organic-rich muds which constitute

the most important immediate source of metals for nodule growth. Nodules which occur adjacent to muds have Fe/Mn ratios greater than 10 (extreme northern Green Bay; Figure 6) and lower minor element contents

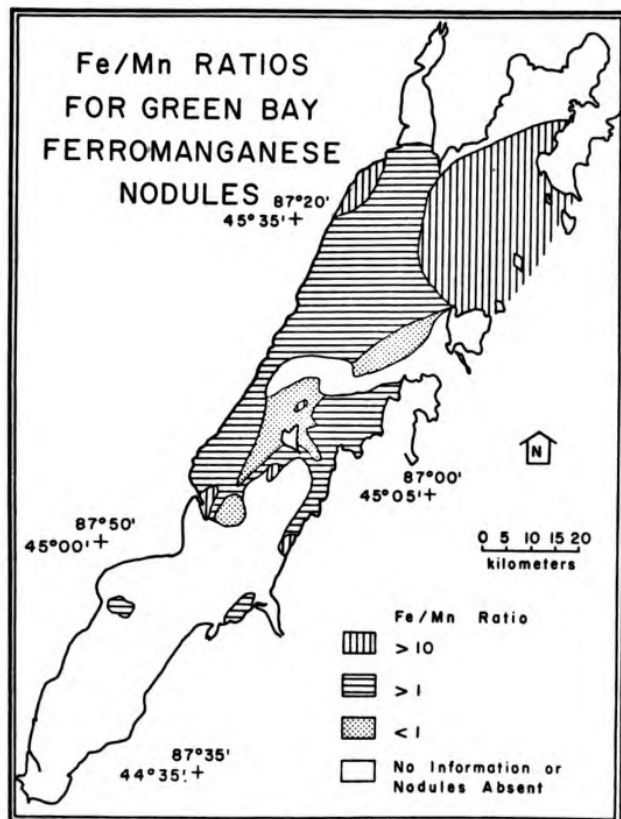


Figure 6. Iron/manganese ratio of ferromanganese nodules from Green Bay, Lake Michigan (from Rossmann, 1973).

compared to nodules which are located farther from muds (central northern Green Bay; Figure 6) and which have Fe/Mn ratios close to unity and greater minor element contents (Rossmann, 1973). Since most of the minor elements found in ferromanganese nodules are associated with the Mn-oxide phase, the Fe/Mn ratio can be used to study the effect of source upon ferromanganese nodule chemistry. Green Bay, Lake Michigan, is an excellent locality for such a study because there are strong differences in the depositional environment as one goes from south to north. Rapidly accumulating organic-rich sediments in the south and extreme north contain interstitial waters enriched in Fe, Mn and certain trace elements which constitute a source of these metals in adjacent oxygenated bottom waters flowing over sand deposits. Trace elements that may be associated with dissolved and particulate organic matter will be less available for adsorption onto an iron- or manganese-oxide surface (Rashid, 1972). In areas where bottom currents and topography have resulted in very slow sediment accumulation, metals occur more probably as free or inorganically-complexed ions which are more readily adsorbed by ferromanganese oxides (Stumm and Morgan, 1970). The distribution of Fe/Mn ratios in ferromanganese nodules from Green Bay reflects this pattern of sedimentation (Figures 1, 3, and 6). Nodules from areas that receive no sediment (north-central Green Bay, Figure 6) or receive soluble and particulate material that is depleted in Fe (east of the Menominee River, Figures 4 and 6) have the lowest Fe/Mn ratios and the highest

minor element contents.

The relatively strong correlation between Fe and As for nodules discussed in this report (Table 5, Figure 5d) is in agreement with that for Green Bay nodules in general (Callender et al., 1973). Sevast'yanov (1967) described the enrichment of As in some Fe-rich nodules from the Black Sea, and Calvert and Price (1970) show a strong correlation between Fe and As in Fe-rich rims of nodules from Loch Fyne, Scotland. Their values of from 500 to 1000 ppm As compare favorably with As values for Green Bay nodules (Callender et al., 1973). Calvert and Price (1970) state that this enrichment probably results from the replacement of arsenate for phosphate ions in an iron phosphate. This implies that arsenate/phosphate is coprecipitated with the iron and not absorbed by hydrous iron oxide. Whichever the mechanism, the association of As and P with Fe in ferromanganese nodules is now well established and deserves a thorough geochemical study. It is interesting to note that the nodules from Loch Fyne occur as Fe rims surrounding Mn cores much the same as Green Bay nodules whose diameter exceeds 2 mm (nodules from station 70-9, Appendix). The origin of these Fe rims probably reflects the recent history of the depositional environment within which the nodules grow and persist. It is possible that these rims represent a dissolution stage (selective leaching of the more soluble Mn oxide) which has been brought about by a change in the sedimentation pattern. Calvert and Price (1970) suggest that the Fe-rich rim surrounding Mn-rich cores in Loch Fyne nodules represents Fe-oxide precipitation under different environmental conditions where there is enrichment of Fe from seawater overlying more oxidized surface sediment.

The formation of manganese carbonate in the gray sandy muds of southern Green Bay is, as in the case of manganese carbonate from Loch Fyne (Calvert and Price, 1970), diagenetic. The carbonate forms after precipitation of ferromanganese nodules since it occurs as a cement surrounding the nodules. The two phases, oxide and carbonate, are not in equilibrium. Environmental conditions near the sediment-water interface in areas of ferromanganese oxide accretion are not conducive to precipitation of a metal carbonate which must derive its carbonate content from interstitial water in contact with decomposing organic matter (Berner, 1966). The manganese carbonate occurrences in southern Green Bay imply a high activity for both Mn^{+2} and CO_3^{-2} in pore waters of the host muddy sands and/or the adjacent organic-rich muds. Interstitial Mn concentrations average approximately 3.5 ppm ($6.3 \times 10^{-5} M$) and carbonate alkalinities 2.8 meq/l. Thermodynamic calculations using interstitial Mn, pH, and alkalinity data result in ion products for $MnCO_3$ that range from 14.3×10^{-11} , for interstitial water at 0-5 cm, to 8.3×10^{-11} for interstitial water at 10-15 cm. Comparison of these values with the thermodynamic solubility product for rhodochrosite ($K_{sp} = 6.3 \times 10^{-11}$ at 25°C and 1 atm) shows that interstitial water is slightly supersaturated with respect to $MnCO_3$. The high carbonate activity probably results from oxidation and fermentation of organic matter (Presley and Kaplan, 1968), and the high manganese activity from reduction of dispersed or nodular ferromanganese oxides which become buried by accumulating sediment (Calvert and Price, 1972). The amount of carbonate produced by degradation of sedimentary organic matter in southern Green Bay may be substantial since the dark gray muds contain up to 6.5% organic carbon by weight. The amount of carbonate alkalinity that can be contributed to interstitial fluids by dissolution of detrital carbonates may be small since the carbonate content of these muds averages less than 5% by weight (Callender, 1969).

Although the origin of manganese carbonate in southern Green Bay is not yet clearly understood,

TABLE 9
 CORRELATION COEFFICIENTS FOR MANGANESE CARBONATE CRUST AND ASSOCIATE FERROMANGANESE NODULES FROM STATION UM-GB-71-19

VARIABLE	MN WT%	FE WT%	BA WT%	CA WT%	MG PPM	NA PPM	CD PPM	CO PPM	CR PPM	CU PPM	K PPM	NI PPM	PB PPM	SR PPM	ZN PPM
MN WT%	1.0000														
FE WT%	-.9331	1.0000													
BA WT%	-.6488	.4234	1.0000												
CA WT%	.2277	.0480	-.8841	1.0000											
MG PPM	-.9793	.9783	.5979	-.1541	1.0000										
NA PPM	-.1818	.5173	-.2686	.5414	.3682	1.0000									
CD PPM	-.6016	.8485	.0000	.4257	.7345	.8855	1.0000								
CO PPM	-.9511	.8181	.8518	-.5133	.9195	.0299	.4239	1.0000							
CR PPM	-.6084	.8527	-.0303	.4630	.7339	.8690	.9978	.4155	1.0000						
CU PPM	-.7572	.8343	0.	.4415	.7539	.3821	.7259	.5195	.7654	1.0000					
K PPM	.6958	-.3914	-.8404	.7078	-.5573	.5580	.1526	-.8113	.1466	-.2469	1.0000				
NI PPM	-.5279	.7944	-.0077	.4025	.6796	.9308	.9908	.3717	.9807	.6261	.2281	1.0000			
PB PPM	-.5011	.7718	.0007	.3800	.6594	.9417	.9813	.3573	.9676	.5799	.2493	.9983	1.0000		
SR PPM	-.5899	.3404	.9951	-.9202	.5252	-.3569	-.0981	.8082	-.1276	-.0663	-.8550	-.1059	-.1059	1.0000	
ZN PPM	-.9494	.8302	.8495	-.5061	.9277	.0723	.4542	.9988	.4434	.5142	-.7842	.4070	.4070	-.1059	1.0000
VARIABLE	MN WT%	FE WT%	BA WT%	CA WT%	MG PPM	NA PPM	CD PPM	CO PPM	CR PPM	CU PPM	K PPM	NI PPM	PB PPM	SR PPM	ZN PPM
PB PPM	1.0000														
SR PPM	-.0969	1.0000													
ZN PPM	.3946	.8028	1.0000												

TABLE 10

CORRELATION COEFFICIENTS FOR MANGANESE CARBONATE CRUSTS FROM GREEN BAY, LAKE MICHIGAN

VARIABLE										
MN WT%	1.0000									
FE WT%	-.8111	1.0000								
BA WT%	-.4880	-.1147	1.0000							
CA WT%	-.9198	.9756	.1063	1.0000						
MG PPM	-.3025	-.3121	.9796	-.0958	1.0000					
NA PPM	.9995	-.7932	-.5140	-.9076	-.3310	1.0000				
K PPM	.7909	-.9994	.1483	-.9676	.3441	.7721	1.0000			
SR PPM	-.9309	.5414	.7731	.7129	.6298	-.9414	-.5126	1.0000		
ZN PPM	.9972	-.7651	-.5519	-.8879	-.3730	.9990	.7428	-.9556	1.0000	
	MN WT%	FE WT%	BA WT%	CA WT%	MG PPM	NA PPM	K PPM	SR PPM	ZN PPM	

the formation of the carbonate occurred after accretion of ferromanganese nodules. The carbonate cements the nodules but there is no evidence of carbonate replacing ferromanganese oxide, such as Calvert and Price (1970) observed in Loch Fyne, Scotland. Rapidly accumulating fine-grained sediment has been deposited over nodule-bearing sands in the vicinity of manganese carbonate localities in southern Green Bay. The change to a less oxidizing, less basic environment where abundant dissolved carbonate is supplied to interstitial water, that surrounds the previously precipitated ferromanganese nodules, results in the precipitation of manganese carbonate from a supersaturated solution of interstitial water.

CONCLUSIONS

The many similarities between ferromanganese nodules from Green Bay, Lake Michigan, and shallow to deep-water marine nodules have been pointed out in this report. The ready accessibility of the freshwater nodules, the simpler geochemical setting of Green Bay (lack of sulfate), and the fact that a wealth of geochemical data now exists on Green Bay, Lake Michigan, serve to emphasize the importance of this freshwater nodule province to the international program studying the origin of marine ferromanganese nodules. Data have been presented which shed light on two mechanisms that affect the chemical composition of ferromanganese nodules. Future studies of the origin of ferromanganese nodules in Green Bay, Lake Michigan should include the following:

- 1) The diagenetic mobilization of transition elements in areas of slowly and rapidly accumulating sediment.
- 2) The effect of organo-metallic complexes on the chemical composition of natural solutions that nourish the growth of ferromanganese nodules.
- 3) Quantitative element-phase associations in ferromanganese nodules originating under different environmental conditions.
- 4) Trace-element partitioning between oxide, carbonate, and sulfide phases in sediments associated with ferromanganese nodules.
- 5) The mechanism of trace-element incorporation into rapidly versus slowly accreting ferromanganese nodules.

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CHEMICAL COMPOSITION OF FERROMANGANESE CRUSTS AND FERROMANGANESE NODULES FROM GREEN BAY, LAKE MICHIGAN

	WEIGHT PERCENT										PARTS PER MILLION										ZN & Soluble
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	ZN & Soluble					
UM-GB-71-19 Crust	31.3	1.3	0.0	4.5	169.	458.	0.	7.	10.	15.	3.	1139.	22.	18.	16.	74.					
	31.4	1.0	0.1	1.2	1802.	454.	0.	10.	0.	0.	0.	1966.	80.	0.	21.	81.					
UM-GB-71-19 Nodules > 2 mm diam.	14.4	19.5	2.2	1.1	2063.	435.	0.	10.	60.	18.	3.	785.	58.	52.	276.	559.					
	11.3	19.3	2.0	0.0	1874.	334.	0.	0.	0.	0.	0.	1056.	80.	0.	241.	218.					
UM-GB-71-19 Nodules 1-2 mm diam.	7.9	32.7	1.2	1.2	2129.	421.	0.	21.	57.	36.	6.	904.	74.	37.	155.	451.					
	6.0	22.7	1.2	3.6	2175.	275.	0.	7.	0.	0.	0.	838.	0.	0.	140.	267.					
UM-GB-71-19 Nodules 0.5-1 mm diam.	4.1	38.4	0.4	1.1	2542.	724.	0.	34.	56.	93.	6.	1199.	84.	374.	39.	325.					
	9.3	41.9	1.6	4.8	2430.	690.	833.	0.	0.	0.	0.	1447.	464.	0.	173.	416.					
UM-GB-71-19 Nodules > 0.5 mm diam.	0.5	2.2	0.0	0.4	1035.	785.	0.	0.	6.	16.	3.	2914.	16.	19.	15.	35.					
	0.7	2.1	0.0	0.6	959.	400.	819.	0.	0.	21.	0.	1217.	0.	0.	10.	31.					
WEIGHT PERCENT																					
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	ZN & Soluble					
UM-GB-71-57 Crust	1.2	8.7	0.0	5.2	3000.	796.	0.	11.	0.	19.	3.	3672.	37.	62.	73.	59.					
UM-GB-71-57 Nodules 1-2 mm	4.9	26.1	0.5	1.5	120.	916.	0.	21.	107.	60.	9.	2965.	162.	149.	124.	556.					
UM-GB-71-57 Nodules .5-1 mm	3.4	26.7	0.3	1.4	3709.	1165.	0.	21.	109.	74.	6.	3236.	173.	146.	104.	590.					
UM-GB-71-99 Crust	16.4	17.8	0.0	4.6	1610.	371.	264.	11.	55.	12.	3.	675.	48.	19.	65.	616.					
UM-GB-71-99 Nodules > 2 mm	4.0	28.8	0.4	1.4	1810.	485.	257.	5.	53.	14.	6.	1275.	71.	35.	49.	0.					
UM-GB-71-99 Nodules 1-2 mm	2.4	31.0	0.3	0.9	2150.	244.	370.	5.	62.	23.	3.	888.	58.	24.	43.	36.					
UM-GB-71-99 Nodules .5-1 mm	6.5	20.2	0.2	2.6	4105.	616.	0.	0.	63.	42.	5.	1186.	56.	28.	44.	863.					
UM-GB-71-99 Sand .5-1 mm	0.3	1.1	0.0	0.1	360.	975.	0.	0.	2.	5.	1.	125.	0.	7.	3.	104.					
UM-GB-71-107 Crust	1.0	27.1	0.1	0.8	1555.	383.	220.	10.	36.	24.	3.	767.	43.	18.	68.	580.					
UM-GB-71-107 Red Crust	0.4	20.6	0.1	0.7	3143.	255.	381.	8.	20.	17.	5.	2559.	40.	7.	50.	285.					
UM-GB-71-107 Nodules .5-1 mm	1.6	45.1	0.0	1.2	1853.	155.	594.	9.	58.	0.	13.	2839.	109.	120.	72.	564.					
WEIGHT PERCENT																					
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	ZN & Soluble					
UM-GB-71-108 Red Crust	0.8	20.9	0.1	0.5	990.	1454.	0.	0.	24.	22.	6.	583.	43.	6.	34.	173.					
	1.0	19.3	0.2	0.9	801.	427.	0.	0.	0.	0.	0.	1161.	0.	0.	28.	75.					
UM-GB-71-108 Brown Crust	4.9	30.2	0.6	0.9	1617.	882.	0.	0.	92.	21.	6.	679.	88.	6.	86.	386.					
	2.3	14.6	0.0	0.7	1067.	275.	0.	0.	0.	51.	0.	1397.	0.	0.	31.	145.					
UM-GB-71-108 Nodules > 2 mm diam.	21.7	22.1	3.0	1.4	2550.	238.	251.	26.	196.	16.	18.	1091.	283.	50.	221.	614.					
	18.2	15.2	2.1	1.4	2198.	200.	964.	13.	176.	20.	28.	733.	316.	64.	238.	606.					
UM-GB-71-108 Nodules 1-2 mm diam.	13.4	33.8	1.2	1.5	2170.	170.	417.	22.	178.	25.	15.	784.	223.	62.	171.	593.					
	10.9	23.4	1.0	1.4	1844.	128.	897.	9.	133.	26.	21.	545.	229.	121.	179.	516.					
UM-GB-71-108 Nodules 0.5-1 mm diam.	7.9	35.5	0.5	1.2	2760.	200.	511.	12.	100.	54.	9.	675.	123.	83.	126.	474.					
	5.5	25.1	0.0	0.0	1460.	132.	919.	12.	65.	55.	19.	491.	147.	75.	134.	414.					
UM-GB-71-108 Nodules (Floc) > 1 mm diam.	20.9	20.4	2.9	1.7	2070.	439.	351.	19.	210.	17.	20.	2984.	307.	60.	247.	702.					
	18.4	13.9	1.8	1.8	2523.	196.	852.	15.	168.	18.	31.	1041.	337.	92.	265.	685.					

APPENDIX (continued)

	WEIGHT PERCENT					PARTS PER MILLION										Zn % Soluble
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	
UM-GB-71-108 Nodules (Floc) 0.3-1 mm diam.	4.9	27.1	0.0	1.1	2023.	223.	289.	18.	71.	54.	19.	2894.	104.	93.	106.	59
	4.4	18.5	0.5	1.4	1871.	214.	985.	9.	57.	54.	21.	1013.	147.	149.	118.	65
UM-GB-71-108 Nodules (Floc) <0.3 mm diam.	1.3	2.4	0.1	0.9	4744.	564.	0.	7.	12.	35.	62.	2870.	40.	65.	36.	18
	1.3	2.2	0.1	1.0	4333.	800.	0.	0.	0.	32.	0.	2369.	19.	36.	38.	21

	WEIGHT PERCENT					PARTS PER MILLION										Zn % Soluble
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	
UM-GB-72-20 Crust (CO ₃)	25.1	1.5	0.1	9.3	1456.	242.	47.	9.	0.	0.	0.	653.	0.	52.	30.	85
UM-GB-72-20 Nodules	2.1	27.8	0.2	1.7	2469.	275.	0.	0.	0.	0.	0.	910.	159.	0.	54.	72
UM-GB-72-34 Crust (CO ₃)	26.7	2.7	0.1	6.0	1425.	352.	413.	5.	101.	17.	8.	1109.	10.	109.	28.	89
UM-GB-72-34 Nodules	7.5	23.5	0.3	2.0	2246.	820.	153.	19.	138.	20.	20.	1805.	24.	53.	75.	0.
UM-GB-70-9 Nodules >2 mm diam.	15.5	17.5	5.3	0.0	2032.	130.	43.	19.	385.	11.	16.	1109.	25.	70.	298.	44.
	16.4	11.6	0.0	3.0	2841.	220.	106.	7.	59.	6.	35.	0.	730.	0.	0.	85
UM-GB-70-9 Nodules 1-2 mm diam.	1.0	28.1	0.1	1.7	3719.	122.	122.	5.	54.	63.	11.	870.	30.	87.	36.	129.
	0.9	28.1	0.0	1.7	3719.	122.	332.	8.	135.	16.	11.	0.	31.	155.	0.	64
UM-M70-48 Nodules 0.5-1 mm diam.	26.9	4.8	3.3	2.1	4345.	330.	210.	17.	140.	12.	23.	2370.	300.	0.	304.	82
	28.6	4.8	0.0	2.1	4157.	350.	156.	17.	128.	15.	25.	0.	290.	0.	0.	84
UM-M70-49 Nodules 0.5-1 mm diam.	25.1	8.8	6.0	3.5	4660.	505.	273.	14.	130.	14.	30.	2756.	330.	189.	247.	81
	24.5	8.8	0.0	3.7	4661.	410.	158.	4.	53.	63.	29.	0.	320.	0.	0.	82

	WEIGHT PERCENT					PARTS PER MILLION										Zn % Soluble
	MN	FE	BA	CA	MG	NA	AS	CD	CO	CR	CU	K	NI	PB	SR	
M1-7 Nodules	21.0	4.9	3.0	3.4	3919.	710.	264.	21.	131.	19.	0.	3353.	580.	219.	216.	76
M1-7 Nodules	22.5	5.2	0.0	3.4	3986.	120.	517.	7.	105.	25.	0.	0.	570.	0.	0.	70
GB-69-11 Nodules	10.8	5.2	0.0	3.0	2975.	130.	406.	3.	113.	9.	25.	1144.	480.	0.	0.	56
GB-69-19 Nodules	15.2	15.3	3.1	3.1	2571.	710.	-11.	16.	287.	10.	23.	1740.	220.	99.	94.	80
GB-69-25 Nodules	4.4	22.6	1.4	0.9	1728.	130.	501.	6.	110.	26.	21.	571.	69.	90.	106.	81
GB-69-25 Nodules	4.4	22.6	0.0	0.9	1762.	320.	327.	10.	389.	8.	20.	0.	82.	0.	0.	80
IM-69-26 Nodules	16.5	15.9	2.2	3.4	2099.	210.	14.	144.	12.	19.	11.	1133.	30.	92.	294.	69